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Evaluation of the metal contaminations in the surface sediments of the Oubeira lagoon, National park of El Kala, Algeria

Bourhane-Eddine Belabed, Amel Bendjema, Hamid Boudjelida, Larbi Djabri and Mourad Bensouilah

Laboratoire d'Ecobiologie des Milieux Marins et Littoraux, Faculty des Sciences University BADJI Mokhtar, Annaba, Algeria

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ABSTARCT

The anthropic impact activities on the water quality of the Oubeira lagoon, trace elements of the water and sediments were investigated. Sediment samplings points in the Oubeira lagoon were analyzed in order to determine the trace elements of some metals like iron (Fe), copper (Cu), zinc (Zn), chromium (Cr), nickel (Ni), lead (Pb) and cadmium (Cd). The sampling was occurred in two different stations of the lagoon in seasonal manner; and was established by a 4 taking away campaigns of surface sediments, during a year between 2007/2008. The evaluation of the contamination metal level of the sediments was carried out using the application of the index of contamination (I c). The variation space-time of the content in different metals reveals the presence of a contamination dominated by the iron. Therefore, the transposition problem of this contamination towards the embouchures and to its immediate environment remains unclear by considering certain natural phenomena such as the big rains and maregraphic dynamics.

Key words: Oubeira, sediments, metal contamination, index of contamination.

INTRODUCTION

The Mediterranean lagoon, Oubeira, is a sensitive ecosystem and the big space-time variability of its environmental conditions makes it favourable with the position risks caused particularly by the anthropic rejections which contain inorganic pollutants. Among the pollutants there are the heavy metals, which are at the beginning considered as natural elements, essential to the development of the living organisms with very weak concentrations, whereas, a high concentrations, of these elements become toxic [1]. Contrary to many toxic organics, the element traces are not eliminated by a biological way then consequently are prone for a cumulative purpose in the various components of the ecosystem (water, sediment, fauna and flora), [2].

The water quality is a term used to express the suitability of water to sustain various uses or processes [3]. The quality of water may be described in terms of the concentration and state the organic and inorganic material present in the water, together with certain physical characteristics of the water [4]. The composition of surface waters is dependent on natural factors in the drainage basin and varies with seasonal differences in runoff volumes, weather conditions and water levels. Human has also significant effects on water quality. Some of these effects are the polluting activities, such as the domestic, industrial discharge, into the watercourse. The principal reason for monitoring water quality was not only to verify the suitability use but also to control the quality of the aquatic environment if it is affected by a release of contaminants by other human activities or waste treatment operations [5]; [6].

Sediments are one of the possible media in aquatic monitoring and are responsible of nutrient and pollutant transportation in aquatic environment [7]. The choice of the sediments is also justified by the fact that, they reflect the various physicochemical processes having taken place not only in aquatic environment but also on a basin scale and are excellent indicators of the reserve water quality levels to their accumulating capacity [8].

In this survey the index of contamination(IC) was adopted according to the Agency of the Basin Rhône-Méditerranée-Corse (ABRMC) [9] where a space-time follow-up of a seven elements content, iron (Fe), copper (Cu), zinc (Zn), chromium (Cr), nickel (Ni), lead (Pb) and cadmium (Cd) in the surface sediment of the Oubeira lagoon were measured looking forwards to study their impacts on the fauna and flora.

MATERIALS AND METHODS:

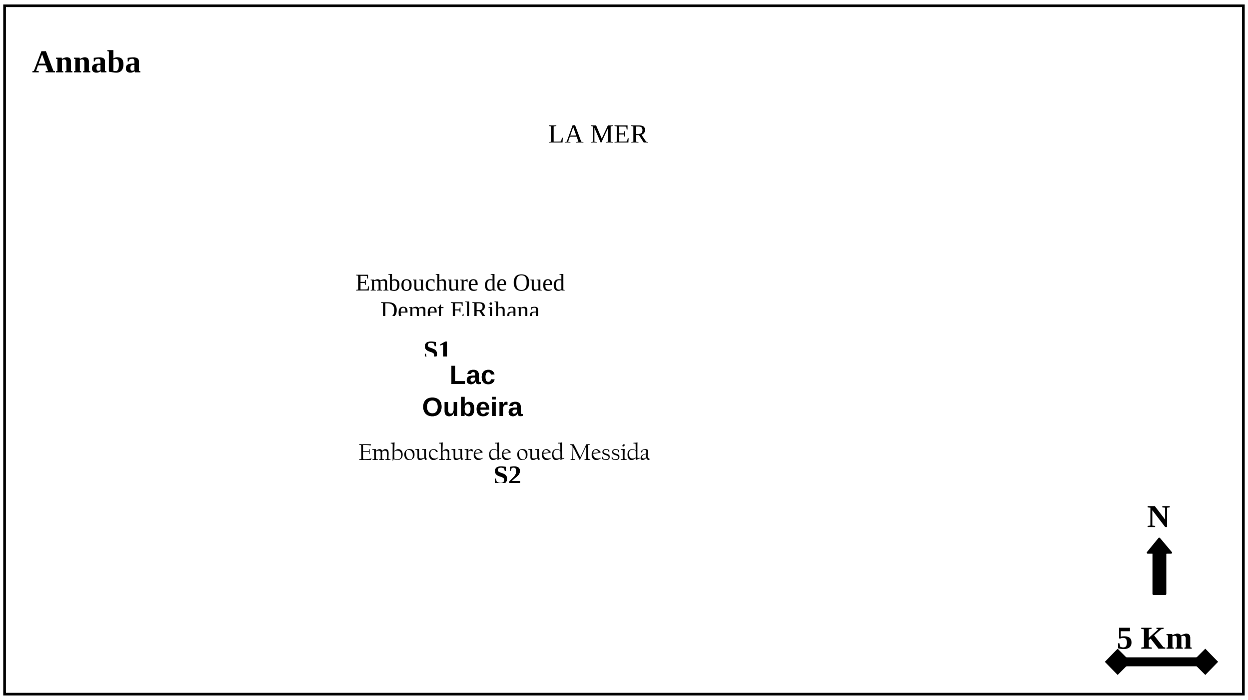

Figure 1: The lake of Oubeira and the localization of the sampling stations (S1& S2). [11].

Presentation of the stations:

The Oubeira lagoon is situated in the extreme North-East of Algeria, 5 km in the south-west of El-Kala and 54 km in the east of Annaba. Its geographical parameters in the middle of the water map are 36° 50' 695 North - 8° 23 ' 272 East (Fig. 1). The Oubeira lagoon is a humid zone of international importance registered on the RAMSAR list and takes an important part from the complex of the humid zones of the National park of El Kala. It is characterized by the permanence of its water level which persists with most dry season. It is an aquatic ecosystem of fresh water of 2200 ha, and less than 6 m of depth which belonging to an exceptional biodiversity. The lagoon is supplied by four important water flaws: the river of Demet Rihana in north, the Boumerchène river in the North-East, the river of dey El Garâa in the east and the Messida river in the South. According to the discovery of the mines deposit of Kef Oum Theboul in 1845, the flaw of Messida river was transformed to drain water of the lake towards the sea, but this mine was abandoned since 1968 [10].

Sampling:
In the lagoon of 0ubeira (fig1.), it was retained 2 stations of sampling: Station 1 (S1) is supplied with the wad of Rihana. It is located at the North-West of the Oubeira lagoon; water is soft and the sediment is muddy. Station 2 (S2) is supplied from the Messida river. It is localised in the South of the lagoon; water is soft and the sediment is composed of slightly mud and sand. Four campaigns were carried out into 2007/2008. The sediment samplings were carried out 6 taking away per season for each station.

Treatment and Analyzes chemical sediments:
The fine sediments are taken by scraping first centimetres on the surface with a plastic shovel. The samples of sediments (300 to 500 g) are collected in polyethylene pots, transported to the laboratory and preserved in a refrigerator at a temperature of 4°C. The analyses (drying, crushing and sifting) were carried out during the following 24 hours [12]. 0.5 g of sediment was added to beaker that contains a mixture of pure acids, HNO3/HF and HCl (1V/1V/2V), then heated at 150°C during 2 hours and evaporated until dry substrate. Mineralized is taken again by successive rinsing with bi-distilled water, filtered on Wattman filter (0,45 mm) and supplemented with a final volume up to 100 ml. The proportioning of lead, cadmium, chromium and copper is carried out by spectrophotometry of atomic absorption with furnace with graphite, that of zinc, nickel and iron by spectrophotometry d' atomic absorption with flame (Perkin Elmer Analyst l00).

The validity of the analytical methods is checked by internal control using a reference sample (reference material certified), from a sediment of a Canadian lake (Lake Sediment N°LKSD1) coming from CANMET [13]; [14].

Evaluation of the Index of contamination:
The Index of Contamination (I.C.) represents the relationship between the value guides element traces considered (in reference to the allowed values guides by the Agency of the Rhône-Méditerranée-Corse basin [9] and its content in the studied sediment.

Statistical analysis:
The results were subjected to statistical analysis using the software MINITAB, version 13.31 (Pa State College, the USA).Data were expressed as arithmetic means SEM, and compared to t-Student's test. The level of significance was $p< 0.05$.

RESULTS

Iron contents: The iron proportioned starting from the surface sediment of the Oubeira lagoon shows contents ranging between 8700 and 16900 mg/kg of P.S. (Fig.3), it is however, the station 1 which presents the lowest contents of iron. This metal is present, in the 2 stations, with high and close contents (exceeding 15000 mg/kg P.S.) of spring and festival period; but on the other hand, the lowest contents were recorded in winter and the intermediate contents of autumn; (fig 3). The statistical analyses of the iron in the surface sediment shows a significant differences (p= 0.03 & p=0.003) between the seasons in the station1 and 2 respectively.

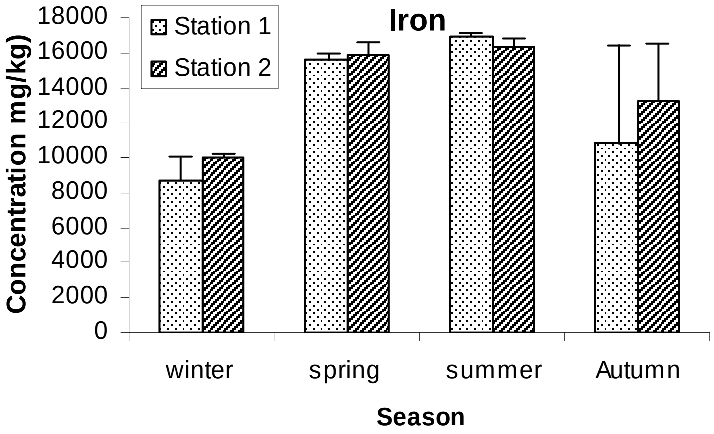

Figure 2: Spatiotemporal distribution of the Iron contents (mg/kg d.w.)in the surface sediment of the Oubeira lagoon.

The evaluation of the Ic for iron in the sediment of the Oubeira lagoon shows a spatiotemporal variations (Table1). The indices of contamination by the iron were found to be ranging between 4.35 and 8.45, in station1, and from 5.02 to 8.15 at the level of station 2. In the two stations the low level of Ic is registered in winter, it is as from spring that the index increases to reach its maximum value in summer. Owing to the fact that the values of the index raised in the Oubeira lagoon lie between 3 and 10, we can regard the sediment of the Oubeira lagoon as a zone polluted by iron.

Table 1: Spatiotemporal variations of the index of contamination by the iron, evaluated in the surface sediment in the Oubeira lagoon

Season	Winter	Spring	Summer	Automn
Iron contents mg/Kg D.W Station 1	8700	15600	16900	10850
Ic (station 1)	**4.34**	**7.8**	**8.45**	**5.42**
Iron contents mg/Kg D.W Station2	10050	15900	16300	13190
Ic (station 2)	**5.02**	**7.95**	**8.15**	**6.59**
The guide value of the Iron= 2000 mg/kg d.w.				

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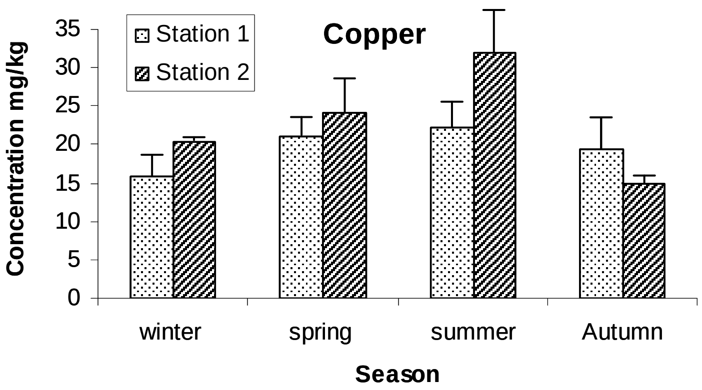

Figure 3: Spatiotemporal distribution of the copper contents (mg/kg d.w.) in the surface sediment of the Oubeira lagoon.

2. Copper contents: The contents of copper measured in the sediment of the Oubeira lagoon vary from 15.95 to 32 mg/kg of dry weight. The highest contents of copper through the year are observed in It is in station 2 with a values of 20.35 to 32 mg/kg of d.w. (fig.3). The presence of the contents of copper is similar in the 2 stations, with minimal contents during winter and maximum contents in summer. These differences between seasons and the two stations were highly significant $p< 0.05$

The evaluation of the Ic by copper in the sediment of the Oubeira lagoon shows a spatiotemporal variations. On the level of station 1 these indices vary between 0.61 and 1.15 and for what station 2, these indices vary 0.78 and 1.23 (table 2). These indices of contamination are higher during the summer with a significant decrease ($p< 0.05$) during the winter. The variation in the indices of contamination in the level of the two stations remain lower than Ic = 3 (table 3) and this makes it possible to regard the sediment of the Oubeira lagoon as a normal zone and of class 1 and to be considered as not polluted.

Table 2: Spatiotemporal variations of the index of contamination by the copper evaluated in the surface sediment in the Oubeira lagoon.

Season	Winter	Spring	Summer	Automn
Copper contents mg/Kg D.W Station 1	16	21	30	19.5
Ic (station 1)	**0.61**	**0.81**	**1.15**	**0.75**
copper contents mg/Kg D.W Station2	20.4	24.2	32	25
Ic (station 2)	**0.78**	**0.93**	**1.23**	**0.96**
The guide value of the copper= 26 mg/kg d.w.				

3. Zinc contents: The zinc contained in the surface sediment of the Oubeira lagoon was evaluated at the concentrations ranging between 70 and 114 mg/kg of d.w. (fig.4). The lowest contents were found in station 2. The zinc contents are significantly ($p< 0.05$) present with seasonal variations in the two stations. The results reveal that the minimal contents are in winter and maximum values in summer, with intermediate values in spring and in autumn (fig.4).

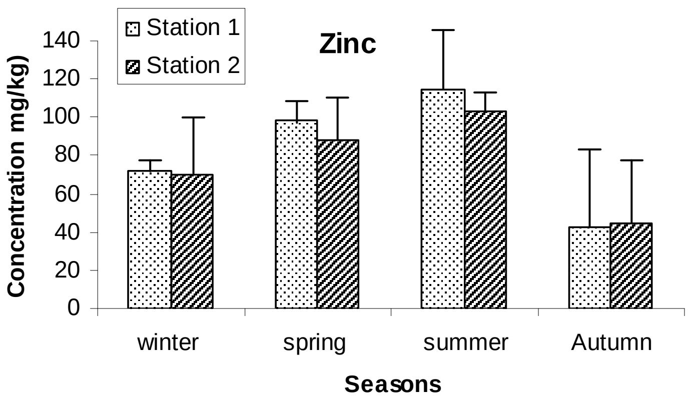

Figure 4: Spatiotemporal distribution of the Zinc contents (mg/kg d.w.) in the surface sediment of the Oubeira lagoon.

The evaluation of the Index o contamination (Ic) by a zinc in the sediment of the Oubeira lagoon shows spatiotemporal variations. This element shows an index of contamination varying from

0.81 to 1.30 for station 1 and from 0.79 to 1.16 for station 2, with a values ranging between 0.81and 1.00 in station 1 (table 3). The differences between values were only significant between seasons ($p< 0.05$). It is noticed that the index of contamination is higher during the summer season, fortunately without causing pollution situation by zinc on the level of the Oubeira lagoon, because there is no significant difference between the values and the guide value of the Zinc (table 3).

Table 3: Spatiotemporal variations of the index of contamination by the Zinc evaluated in the surface sediment in the Oubeira lagoon.

Season	Winter	Spring	Summer	Automn
Zinc contents mg/Kg D.W Station 1	72.1	98.1	114.8	88.4
Ic (station 1)	**0.81**	**1.11**	**1.30**	**1.00**
Zinc contents mg/Kg D.W Station2	70.05	87.6	102.8	85.8
Ic (station 2)	**0.79**	**0.99**	**1.16**	**0.97**
The guide value of the Zinc= 88mg/kg d.w.				

4. Nickel contents: Nickel is present in the surface sediment of the Oubeira lagoon at contents ranging between 82 and 128 mg/kg of d.w. in station 1 and between 87and 107 mg/kg of d.w. in station 2 (figure 5). The evolution of the contents during the seasons is similar in both stations, with significant differences ($p< 0.05$) between seasons. The contents are low in spring, and then increase gradually in summer for until reaching the maximum values in autumn period and show a small decrease in winter (fig. 5).

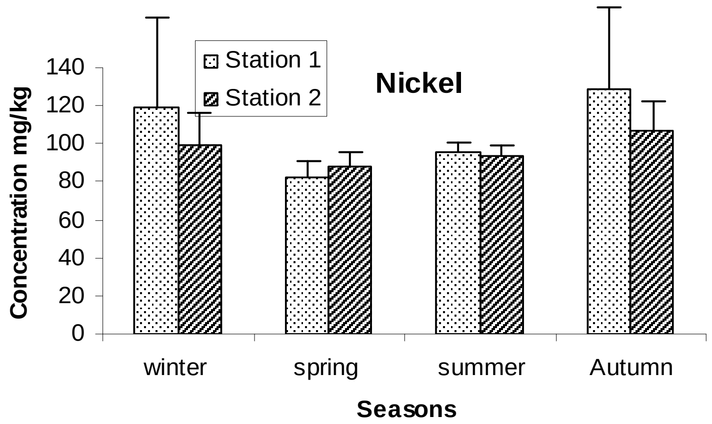

Figure 5: Spatiotemporal distribution of the Nickel contents (mg/kg d.w.) in the surface sediment of the Oubeira lagoon.

The evaluation of the Ic by nickel in the sediment of the Oubeira lagoon shows spatiotemporally variations. The index contamination of this element is varying between 1.84 to 2.85 in station 1 and from 1.95 to 2.38 in station 2 (table 4). The content of the Nickel the level of the indexes of contamination measured on the level of the two stations and throughout different seasons are lower than 3. It makes it possible to conclude with an absence from pollution by nickel on the level from the Oubeira lagoon and to qualify this last like normal zone from classe1.

Table 4: Spatiotemporal variations of the index of contamination by the Nickel evaluated in the surface sediment in the Oubeira lagoon.

Season	Winter	Spring	Summer	Automn
Nickel contents mg/Kg D.W Station 1	119	82.6	96	128
Ic (station 1)	**2.64**	**1.84**	**2.13**	**2.85**
Nickel contents mg/Kg D.W Station2	99.6	87.8	94	107
Ic (station 2)	**2.21**	**1.95**	**2.09**	**2.38**
The guide value of the Nickel= 45mg/kg d.w.				

5. Chromium contents: The chromium contents present in the surface sediment of the Oubeira lagoon vary from 71 to 157 mg/kg of d.w. the lowest contents was measured in station 2 (71.119 mg/kg of d.w.). The chromium contents change in similar way during the seasons in both stations and the differences are significant ($p< 0.05$) between seasons. The contents are low in spring then increase gradually in summer to reach a peak in autumn and then drop slightly in winter (fig. 6).

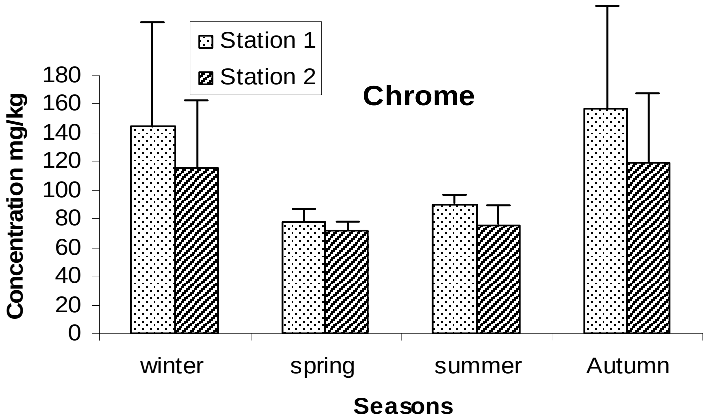

Figure 6: Spatiotemporal distribution of the Chrome contents (mg/kg d.w.) in the surface sediment of the Oubeira lagoon.

Table 5: Spatiotemporal variations of the index of contamination by the chrome evaluated in the surface sediment in the Oubeira lagoon

Season	Winter	Spring	Summer	Automn
Chrome contents mg/Kg D.W Station 1	115	78.5	90	157
Ic (station 1)	**2.55**	**1.74**	**2.00**	**3.48**
Chrome contents mg/Kg D.W Station2	115.3	71.2	76	119
Ic (station 2)	**2.56**	**1.58**	**1.68**	**2.64**
The guide value of the chrome= 45mg/kg d.w.				

The evaluation of the Ic by chromium in the sediment of the Oubeira lagoon shows important spatiotemporal variations that vary between 1.74 and 3.48 on the level of station 1 and 1.58 to 2.64 on the level of station 2 (Table 5). The highest values of indices are recorded during the autumnal season. These indices being in general lower than 3, we can say that the Oubeira lagoon is a normal zone and of class 1.

6. Lead contents: In the Oubeira lagoon the lead contents measured in the surface sediment are estimated between 13 and 27 mg/kg of d.w. and 17 and28 in station 1 &2 respectively (Fig.7). The lower contents were recorded during the winter period and highest one during summer for both stations. The statistical analyses reveal that the differences in contents between seaons and stations were significant ($p < 0.05$).

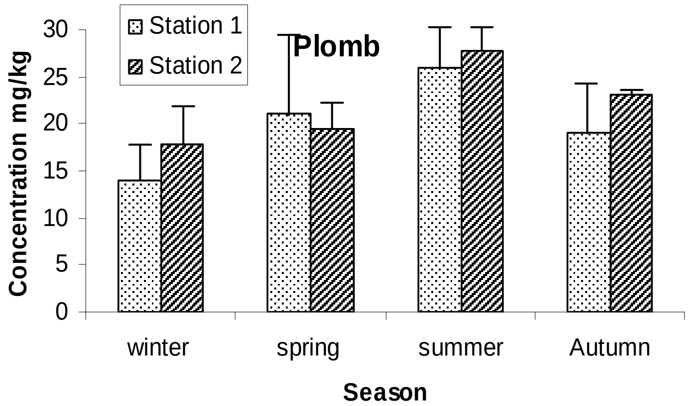

Figure 7: Spatiotemporal distribution of the Lead contents (mg/kg d.w.) in the surface sediment of the Oubeira lagoon.

The evaluation of the Ic by lead in the sediment of the Oubeira lagoon shows important spatiotemporal variations. The index of contamination varies from 0.63 to 1.20 on the level of station 1 and from 0.81 to 1.26 on the level of station 2. In the two stations the Ic low are lower in winter, and increase to reach the maximum value in summer (table 6). The Ic were evaluated to be lower than 3 and it makes it possible to conclude with an absence from pollution by lead on the level from the Oubeira lagoon and to qualify this like is not polluted and belongs to classe1.

Table 6: Spatiotemporal variations of the index of contamination by the Lead evaluated in the surface sediment in the Oubeira lagoon

Season	Winter	Spring	Summer	Automn
Lead contents mg/Kg D.W Station 1	13.9	21	26.6	19.9
Ic (station 1)	**0.63**	**0.95**	**1.20**	**0.86**
Lead contents mg/Kg D.W Station2	17.9	19.5	27.8	23.15
Ic (station 2)	**0.81**	**0.88**	**1.26**	**1.05**
The guide value of the Lead= 22mg/kg d.w.				

7. Cadmium contents: The cadmium contents found in the surface sediment of the Oubeira lagoon vary from one station to another. The contents vary from 0.02 to 0.05 mg/kg of d.w. and 0.03 to 0.04 mg/kg of d.w. in station 1 and 2 respectively (Fig. 8). We note, in addition, that the seasonal contents show significant differences ($p < 0.05$) between the two stations. The results reveal that the highest contents were estimated during summer and autumn period.

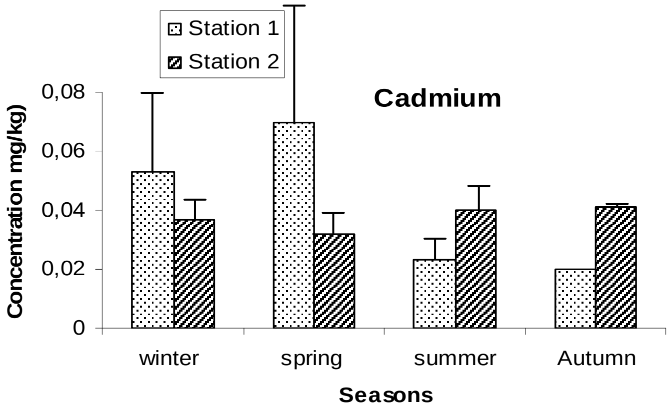

Figure 8: Spatiotemporal distribution of the Cadmium contents (mg/kg d.w.) in the surface sediment of the Oubeira lagoon.

The evaluation of the Ic by cadmium in the sediment of the Oubeira lagoon shows rather variable variations in space and time. The index of contamination varies from 0.03 to 0.12 on the level of station 1 and from 0.05 to 0.07 on the level of station 2. (table7). The values recorded of these indexes of contamination are clearly lower than the normalize values 3. However, the element does not create any pollution, consequently, the Oubeira lagoon zone is considered not polluted by cadmium and its sediment is of classe1.

Table 7: Spatiotemporal variations of the index of contamination by the Cadmium evaluated in the surface sediment in the Oubeira lagoon

Season	Winter	Spring	Summer	Automn
Cadmium contents mg/Kg D.W Station 1	0.05	0.07	0.02	0.02
Ic (station 1)	**0.09**	**0.12**	**0.04**	**0.03**
Cadmium contents mg/Kg D.W Station2	0.04	0.03	0.04	0.04
Ic (station 2)	**0.06**	**0.05**	**0.07**	**0.07**
The guide value of the Cadmium = 0.6mg/kg d.w.				

DISCUSSION

The presence of heavy metals was investigated on the sedimentary fraction lower than 63µm, which represents a sedimentological layer between sand and the mud. An argillaceous mud will easily retain metals in suspension in water; this is not the case for the quartzic fraction (sand) [15]. For each analyzed metal element, the contents generally vary from one station to another. The content increase recorded for the different elements could be related on the sedimentary profiles and the hydrogeology of the lake ecosystems. The bioassay results of the seven heavy metals, from the superficial sediments of the two stations of the Oubeira lagoon, reveal that 6 elements metal traces were present at contents which do not exceed the allowed values guides. Thus, iron contents were higher compared to these metal elements. Indeed, only the metal element, the iron, was present with the indexes of contamination values higher than 3 in both stations. In addition, it was observed that, the contents of these heavy metals are higher in period of low water level (summer) than in period of rising (winter). The highest values, of iron were observed on the level in both stations with 16900 mg/kg in station1 and 16300 mg/kg in station 2. These values represent 8 times more than the values guide allowed. The miner layer, of hydrothermal origin, is made of chalcopyrite, sphalerite and crystal. For the other metals the lowest values are observed on the level of station 2 located at the south of the lagoon. It is however in summer period that the highest contents of iron are noted in the Oubeira lagoon. Such high contents of iron are reported, in Morocco, in the sediment of the lake Fouarat which contains more than 15000 mg/kg d.w. [16]. In Egypt, in the sediment of the Nozha lakes and Mariout which announce more than 57.000 and 25.000 mg/kg of d.w. respectively [17]. These high values of iron are due primarily to erosion during the rains and the emanations of dust steel coming from the steel factory, (Arcelor Mittal, El.Hadjar,Annaba). The presence of a substratum of an acid origin characterizing the grounds of the catchment area of this lagoon, would support more the fixing of heavy metals [18].The highest contents of heavy metals are observed in the sandy sediments located close to the rejections of the rivers which supply the lagoon of water charged with metal and chemical residues [19]. According to [20] and [21], the overtaking of iron can be related on the hydro-dynamical and physico-chemical conditions and especially to the precipitation of iron oxides. This, because during the big rains the flaws create a good oxygenation consequently increase the precipitation of manganese and iron oxides and thus facilitates the formation and the aggregation of the organic and mineral particles. In addition, it is reported that obtaining the substances in colloidal state supports the phenomena of adsorption, complication and precipitation of metals [22]. Other supplement explanation is related to the previous mine activity in the area [10]. The main source of the elements related to the mineralogy of the rich mine in sulphides (pyrite, chalcopyrite and crystal); the presence of this mine would explain the presence of metals Fe, Zn, Cu, Cd, Pb in water and the sediments [23]; [24]; [25]. Concerning the copper and zinc, present a homogeny distribution in the lagoon, and the values do not exceed the values recommended. It was reported that the normal concentration of zinc in the argillaceous sediments is about 80 to 120 mg/kg of d.w, whereas in the sandy rocks still very weak [26]. Thus [27] showed that the higher values of zinc and copper are recorded in the sand-argillaceous sediments located near the rejection sources and their distribution depends on the sediment nature which their content of clay and organic matter plays a determining role. In Tunisia, [28] and [29] found the zinc contents of 100 and 180 mg/kg of d.w. in the lake of Ghar El Mellh and Ichkeul, respectively. In Morocco [16] reported that in the lake of Fouarat the zinc contents equal to 210 mg/kg of d.w. Whereas in Egypt, the zinc contents was evaluated at 106 180 mg/kg of d.w in the Nozha Lake and 94 mg/kg of d.w. in Mariout Lake[17]. The pollution sources of the studied site, by these two heavy metals, would be the mineralogy of the sulphate mine, its layer and its waste. The mine is rich in zinc, chalcopyrite, sphalerite and crystal. The influence of miner waste, noted by the disappearance of the bicarbonates (HCO) which are replaced by hydrogenated protons, generates the acid water, enriched in sulphates (SO) [25] and this explain the presence of a high zinc and copper contents, in the compartments contaminated by the mining activity. In addition, [30] found that copper and zinc are associated to the sandy faces exposed directly to the rejections. The sulphate deteriorations, especially the chalcoperyrite and crystal, can increase sulphates and acidity [31] and would explain their presence remains however related to the miner activity [32], [24] [25].

The evaluation of the contamination indices by copper and zinc shows that the values do not exceed 3, than it characterizes sediment as not contaminated of class 1. The same results were found in Tunisia (lake Ichkeul and the lake Ghar el Mellh) [29]; [28]. The nickel shows a particular distribution; the highest values are recorded on the level of station 1. The pollution, by nickel, of muddy sandy sediment can be explained only by important supply of this metal by the Messida River.

The lead, in summer period, is present in the sediment of the lagoon as on both station 1 and 2 with contents higher than the other seasons. The presence of lead in continental water is done mainly by atmospheric way and the source being still from the automobile fuels. Other probable origins with this high contamination of the lagoon by lead, is the corrosion of old pumps present near this site, especially the mine kef Oum Theboul [24]; under oxidizing conditions that support the presence of this element and the increase of its concentration.

The cadmium contents found in the surface sediments of the Oubeira lagoon show a variable distribution. According to its index of contamination this lagoon is not considered contaminated by the cadmium. These contents are found to be close to those reported from the results of the Tunisian, Morocco and Egypt [28]; [16]; [17] respectively. The presence of cadmium in the sediments of the Oubeira lagoon would have an anthropic origin from the land phosphate fertilizers, and also from the presence of a mine and miner waste containing of sulphides and especially the pyrite [33].

Results obtained, on the level of the sediment matrix of the Oubeira lagoon, reveal that the surface water is the first compartment that being contaminated by heavy metals, then, with time, these metal elements are transferred in the surface sediments. Heavy metals arrived in the water levels are partly metabolized by the watery organizations alive and put in circulation in the food chains. The aquatic environments are very sensitive to the elements traces because of coexistence of two phenomena: bio-accumulation and bio-amplification at the origin of a concentration of the metal elements traces progressively of absorptions by the successive consumers of the food chain (herbivorous water, plankton, fish, carnivorous fish, and man) This metal pollution is, indeed, alarming owing to the fact that it is practically impossible to easily recover these metals once disseminated in nature.

It is concluded that, the elements traces in the surface sediments of the Oubeira lagoon were estimated quantitatively and qualitatively by the use of the index of contamination (IC). This study constitutes an approach by the evaluation of the contributions anthropic of heavy metals. The analysis of the metal load revealed a contamination dominated by the iron; which remains dependent on the polluting load conveyed by the Messida River; of the climatic conditions, the hydrological mode of the water level, and especially of maregraphic dynamics.

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