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Bioaccumulation of trace metals by red alga *Corallina elongata* in the coast of Beni Saf, west coast, Algeria

Noria Kada Benabdallah[1], Djamila Harrache[1,*], Alba Mir[2], Miguel de la Guardia[2], Fatima-Zahra Benhachem[1]

[1]Department of chemistry, Faculty of exact sciences, University Djillali LIABES of Sidi Bel Abbes, Algeria
[2]Department of analytical chemistry, University of Valencia, Spain
*Corresponding author's E. mail: djharrache@yahoo.fr

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A B S T R A C T

The aim of present research was to study the accumulation of trace metals s (Cd, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn, Co) by the red alga *Corallina elongata*, collected in four sampling sites located in the Beni saf coast (Algerian west coast), where two of them are characterized by discharges of urban effluents or from port activity, and the two others are seaside resorts. The differences were observed between sampling sites for the presence some heavy metals. Indeed, it appears that the bioaccumulation of Cu, Ni, Cd and Pb by red alga is from continental origin, such as discharges of urban effluents or those derived from port activity. However, the accumulation of Zn, Co, Cr by this alga is not influenced by the surrounding environment, or that the bioavailability of these elements is lower, therefore, it seems that bioaccumulation of these metals by *Corallina elongata* is influenced by other factors. The spatio-temporal variations show that the accumulation of metals Fe, Zn, Cu, Cr, Pb in the red alga is highest in summer. However, the concentration of Co and Cd tend to be accumulated in the alga, in winter. The Fe concentration was a good predictor of Mn, Zn, Cu, Ni,V accumulation in this species of alga. A strong correlation was observed between Fe and Mn, which confirms the big similarity of their biochemical roles, already known in the marine environment. However, Zn inhibits Cd accumulation in red alga. Our study shows that heavy metal accumulation is associated with nature of the metal, degree of contamination of sampling site, physicochemical properties of the marine environment and the season.

Capsule Summary: Accumulation of trace metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn, Co) by the *Corallina elongate* from, Beni saf Coast, Algeria, was evaluated and it was found that heavy metal nature, contamination load, physicochemical properties of the marine environment and season significantly affected the metal uptake by *Corallina elongata* (Red algae).

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INTRODUCTION

In front of the significant increase of urbanization and industrialization in coastal areas, the marine environments are subject to human pressure, especially in terms of pollution. Marine pollution generated by the spill of wastewater and industrial effluents mistreated or sometimes untreated is one of the most widespread forms and the most damaging to all coastal marine ecosystems of the planet (Espinosa et al., 2007). Heavy metals pollution in the marine environments is one of the major problems in environmental toxicology (Kaimoussi et al., 1988). Because of their potential toxicity, persistence, and ability to be accumulated in biota and food chains, these pollutants are found at a toxic concentrations in marine organisms (Neathery and Miller, 1975; Dorn, 1979; Jitar et al., 2013) and they are considered as a serious contaminants of the aquatic environment (Schüürmann and Markert, 1998; Islam and Tanaka, 2004; Ikem and Egiebor, 2005). The transfer of metals from the receiving mid to the organisms depends on the concentrations present in the different sources of contamination and it's influenced by various ecological and physiological factors (Ettajani et al., 2001; Wang, 2001; Mubiana and Blust, 2007). However, traditional physicochemical analyzes only provide punctual information of the mid-state and don't allow measuring the impact of contaminants on different organisms, populations and communities inhabiting a given environment (Kaiser, 2001). In fact, concentrations of potentially toxic substances in seawater are extremely low and vary substantially in space and time and their determination is difficult (Phillips, 1977).
The conditions of the natural environment are altered, for example in the case of contamination by pollutants, some species more sensitive than others, can be affected in several ways reflecting thereby an unsteadiness of the initial conditions for the natural environment. Thus, these biological indicators, according to their ability to characterize the state of an ecosystem subjected to environmental stress, enable to detect or provide serous changes that may occur inside the same ecosystem (Kaiser, 2001 ; Sammarco et al, 2007 ; Daby, 2006 ; Markert et al, 2003). For example, the marine macroalgae are known by their ability to fix and accumulate the polluants naturally present in seawater, as heavy metals, and are extensively used as bioindicators of pollution (Ho, 1987; Haree et al., 1994; Herut et al., 1996). The evaluation of the coastal waters quality is an average to prevent any risk for human health as well as to marine organisms. It identifies the impacts of various potential releases. The aim of this study is to evaluate the degree of the marine environment alteration of the coast of Beni Saf, by bioindicators accumulators of trace metals.

MATERIALS AND METHODS

Presentation of the study area

The study area extends along the bay of Beni Saf, limited to the north by the Mediterranean sea. It's located at 33 km in the east of the city of Ain – Temouchent, at 67 km in the north of Tlemcen, at 80 km in the west of Maghnia. The Algerian coasts are characterized by the presence of coastal meanders and coastal whirlpools of atlantic origin, associated with upwellings wich foster an increase in trophic capacity of environment (Taupier-Letage and Millot, 1988).

The Algerian coast is characterized by its typical climate: hot and dry in summer, mild and relatively humid in winter. As sampling stations, we have chosen four stations (S_1, S_2, S_3, S_4), located on the bay of Beni Saf (figure 1), according to the large gradient of pollution linked to the proximity of algae to effluent discharges, to assess their impact on the receiving marine environment.

The S_1 station (beach of Sidi Boucif): Geographical location of 35° 18'421"N and 001° 22' 746 " O, is located near a manifold of domestic waste water with a flow rate of 9000 m^3/day, discharged by some districts of Beni Saf city.
The S_2 station (Ferphos site): Geographical location of 35° 18' 260"N and 001° 23' 318" O, is located inside the harbor, at the point of discharge of domestic wastewater of Beni Saf city. This site is distant about 800 m from S_1.
The S_3 station (wells range): Geographical location of 35° 18' 067" N and 001° 24' 178" O, represents a seaside area located approximately 1400 m of the S_2 station.
The S_4 station (Rechgoune beach): Geographical location 35° 18' 001"N and 001° 28' 111" O, situated at 8 km from the city of Beni Saf. This site is located at about 500 m from Tafna Oued, which opens into the sea at this range. This station collects all domestic wastewater of Oulhaça and Rechgoune communes, wich are characterized by the presence of agricultural land that can generate pollution outcome of agricultural activity, by leaching.

Various links of the food chain (algae, marine invertebrates) and sediments were used as bioindicators, to characterize marine pollution of the extreme western Algeria coastline. The macroalgae are among the most complex organisms, but the most reliable in studies of pollution by heavy metals due to their fleet rate of accumulation of metal from aqueous solutions (Phillips, 1977). In order to estimate the degree of the environment and living organisms

Table 1: Overall contents in trace metals (µg/g of D.W) accumulated in the alga *Corallina elongata*, in the four sampling stations in the bay of Beni Saf

Station	S_1 Beach of Sidi Boucif			S_2 FERPHOS site			S_3 Wells range			S_4 Rechgoune beach			standards AIEA, 2005
Metals	min	max	average	min	max	average	min	max	average	min	max	average	
Cd	0	0.11	0.041	0	0.19	0.037	0	0.15	0.057	0	0.12	0.038	0.0173
Co	0.02	0.91	0.48	0	0.47	0.20	0	0.62	0.25	0	0.59	0.22	3.33
Cr	1.17	4.51	2.43	0.40	4.07	1.72	0.31	2.81	1.04	0.33	3.01	1.50	4.57
Cu	0	2,62	0.98	0.67	4.82	2.71	0	1.92	0.35	0	0.96	0.12	23.2
Fe	787.9	2608.8	1592.6	419.9	1731.9	919.1	346.5	1936.1	801.8	173.8	1430.9	679.4	497
Mn	19.18	115.81	57.18	13.01	62.35	31.83	12.47	62.90	33.90	7.89	71.80	33.00	67.5
Ni	0	1.45	0.86	0.32	2.79	0.97	0	1.15	0.44	0	1.04	0.55	0.571
Pb	0	2.55	0.94	0	13.31	4.57	0	0	0	0	0	0	0.5
V	2.30	16.05	9.26	0	8.76	2.21	0.76	14.45	7.61	2.25	13.14	6.17	-
Zn	11.65	47.04	25.71	0	93.16	43.53	0	34.15	18.53	0	37.50	18.96	128

alteration, we have chosen, as a trace metals accumulators bioindicators, the *Corallina elongata* red algae, widely available in selected sampling sites.

Collect of algae and biomass preparation

Samples of red algae *Corallina elongata* (see figure 2 (a)) were harvested by hand at the level of the four sites in the bay of Beni Saf, described above stations (S_1, S_2, S_3, S_4). The *Corallina elongata* is calcified red algae, presenting ramifications with articulation (see figure 2 (b)). The collect of the algae was carrying out, at the four stations during the period from january 2011 to may 2012, at a bimonthly quarterly frequency. Once collected, the algae were first rid from debris and their epiphytes adhesive to their thalli then rinsed on site with seawater and retained in polyethylene bags. Once in the laboratory, the algae are rinsed profusely with distilled water. They were then dried at 70 ° C for 48 h and after that finely ground. The obtained powder was retained in hermetically sealed vials in view of mineralization.

Step of mineralization

The algae metallic extraction was carried out by digesting for aliquots fraction of 0.5 g of alga in 8 ml of nitric acid HNO_3 (69%), in teflon bombs, maintained at ambient temperature in an ultrasonic bath for at least 15 minutes. The attack was performed by adding 1 ml of hydrogen peroxide (H_2O_2 at 35%), followed by addition of 1 ml of hydrochloric acid (HCl at 37%), in the ultrasonic bath. Afterward, the solutions are introduced into a microwave oven type (Etho-Sel) according to the Caquis program. After cooling, the digests were diluted to 20ml with water of high purity (doubly ionized 18.2 MΩ.cm), then a second time with a standard solution (25 ppm style): Fluka, Chemika, 84615.The solutions were then stored at low temperature (4 ° C) until analysis. The essay of a series of metallic elements (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn), was carried out using ICP Optical Emission of Spectrometer, Optima 5300 DV Perkin Elmer, available at the University of Valencia, Spain.

RESULTS AND DISCUSSION

Contents of trace metals accumulated in the red alga Corallina elongata

The values of the contents in trace metals (µg /g dry weight (d.w)) characterized in algae samples are illustrated in table 1. In order to evaluate the flow of pollution accumulated in the algae, we have presented in Table 1, the maximum values, minimum and averages of trace metals contents in each sample site.

From these results, it appears that the metals Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn are present in the algae samples but at different levels of contamination, depending on the sampling station and season. Therefore, the interaction between the site and the sampling season significantly affect the contents and the metal accumulation in the red algae. Metals such as Fe, Cu, Zn and Mn are essential because they play an important role in biological systems, but can also produce toxic effects when the intake of metal is excessively high (Türkmen et al., 2005), while Pb, Ni , Cd and Co are a toxic metals, even at traces level. In the case of Fe, the concentrations obtained are very expressive and overstep the standard of IAEA (International Atomic Energy Agency) related to the method of analysis by ICP (International Atomic Energy Agency, 2005), recommended for iron in algae (for 497 µg/g d.w). The highest contents were detected in the samples collected at S_1 station, for a maximum recorded of de 2608, 83 µg/g d.w. The lowest contents in Fe were observed in the samples of red algae at the S_4 station (Rechgoune beach). However, the observed values (maximum and average) in this station remain above the threshold recommended for Fe in algae. The concentrations of Zn recorded in red algae, at all the sites,

Table 2: Main physicochemical parameters of seawater of the coast of Beni saf

Site	S_1			S_2			S_3			S_4		
Parameters	min	max	average	min	max	average	min	max	average	min	max	average
pH	7,7	8,5	8,11	7 ,6	8,4	7,97	7,9	8,4	8,19	7,9	8,6	8,21
T(°C)	16	28	20,87	16,0	27	20,37	16	27	20,75	15	27	20,62
EC(ms/cm)	53,9	56,7	55,42	54,0	56,3	55,25	54,3	56,4	55,88	50,0	56,7	55,27
Salinity (°/oo)	35,6	37,7	36,77	35,7	37,4	36,62	35,9	37,5	37,1	32,7	37,7	36,65
P_2O_5(mg/l)	0,0039	1,0075	0,16	0,027	0,28	0,13	0,027	0,051	0,045	0,019	0,027	0,042
NO_2^-(µg/l)	1,0	10,55	4,22	1,0	223,59	44,60	0,65	141,66	19,40	0,67	21,33	06,39
Cl^-(g/l)	20,21	20,99	20,60	19,78	20,98	20,51	20,06	21,09	20,75	19,25	21,16	20,63

Table 3: Correlations of trace metal contents accumulated in the alga *Corallina elongata*, to physico chemical parameters (maximum values) relative to the quality of marine water

Parameters	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
pH	-0,522	0,226	0,001	-0,613	0,052	0,379	0,158	-0,438	0,157	-0,534
T(°C)	0,233	0,722	0,540	-0,222	0,446	0,588	0,830	-0,333	0,362	-0,309
EC(ms/cm)	-0,727	-0,167	0,497	-0,587	0,570	0,806	-0,693	-0,490	0,569	0,235
Salinity (°/o o)	-0,777	-0,2002	0,513	-0,631	0,603	0,802	-0,742	-0,548	0,614	0,212
P_2O_5 (mg/l)	0,966	0,966	0,354	0,460	0,433	-0,018	0,812	0,078	-0,522	-0,098
NO_2^-(µg/l)	-0,374	-0,788	-0,769	0,615	-0,598	-0,686	-0,540	0,735	-0,661	0,458
Cl- (g/l)	0,798	-0,963	-0,728	-0,692	-0,482	-0,427	-0,730	-0,699	0,350	-0,937

Table 4: Correlations of trace metal contents accumulated in the alga *Corallina elongata*, to physicochemical parameters (minimum values) relative to the quality of marine water

Parameters	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
pH	0,295	-0,602	-0,829	-0,895	-0,911	-0,752	-0,900	-0,777	0,754	-0,834
T(°C)	0 ,506	0,333	0,439	0,388	0,489	0,522	0,577	0,508	0,105	0,569
EC (ms/cm)	-0,825	-0,998	0,050	0,406	0,374	0,136	-0,478	0,310	-0,639	0,567
Salinity (°/o o)	-0,827	-0,998	0,051	0,413	0,375	0,141	-0,477	0,317	-0,644	0,572
P_2O_5 (mg/l)	-0,354	-0,945	-0,689	0,470	-0,901	-0,687	-0,319	0,164	-0,376	-0,070
NO_2^-(µg/l)	0,577	0,577	0,926	0,934	0,802	0,746	0,978	0,977	0,577	0,404
Cl- (g/l)	0,096	-0,244	0,106	0,085	0,943	-0,063	-0,551	-0,067	-0,649	0,283

stay under the standard established by the IAEA (2005) (ie 128 µg/g d.w) for the accumulation of zinc in the alga. Nevertheless, algae collected at the level of S_2 station are the most enriched in Zn and that for the most of the sampling period.

As for lead Pb, spatiotemporal variations of the contents are indicative and exceed the standards limited by the IAEA (0,574 µg/g) including the S_2 station, where a very high contamination (13.31 ug / g determined in May) was observed in alga collected in the S_2 station. However, no trace of Pb was detected at S_3 and S_4 sites. This could be explained by the fact that S_1 and S_2 sites are located near the collectors draining the effluents, while S_3 and S_4 are seaside resorts.

In addition, these high contents of Pb can be explained, at the level of S_2, by the impact of port activity. Otherwise, the Cu concentrations observed are very low. Almost for all the samples, the highest contents of Cu, was observed at the level of the S_2 station, with a peak of 4,82 µg/g d.w. Samples resulting from several sampling companions at the sites S_1, S_3 and S_4, don't contained any trace of Cu.

It appears that, as in the case of Pb and Zn, the maximum and average values of the concentrations identified in S_2 are higher than those observed in the other sites. This might be related to the discharge of urban effluents at the port and also to the port activity. Otherwise, the maximum values of the Cr contents ranging between 4.07 and 4.51 µg/g

Table 5: Correlation matrices of trace metal contents accumulated in the alga *Corallina elongata*

Metals	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
Cd	1									
Co	0,335	1								
Cr	-0,362	0,120	1							
Cu	-0,134	-0,040	0,245	1						
Fe	-0,244	0,279	0,855	0,236	1					
Mn	-0,278	0,332	0,717	0,003	0,733	1				
Ni	-0,005	0,400	0,458	0,349	0,468	0,411	1			
Pb	-0,241	-0,062	0,156	0,688	0,109	0,022	0,342	1		
V	0,047	0,228	0,367	-0,409	0,324	0,518	-0,006	-0,409	1	
Zn	-0,652	-0,389	0,434	0,728	0,366	0,191	0,141	0,556	-0,257	1

d.w, identified in the algae collected from the stations S_2 and S_1, respectively. The Cr peaks recorded in the *Corallina* red alga are at the limit of the threshold recommended by the IAEA. As for Ni contents, we have identified severe variations during the sampling campaigns. Maximum concentrations observed in Ni, for all the sites, surpass the IAEA standard (0,571 µg/g d.w). However, the highest content of Ni was recorded in the algae gathered at the level of the port (S_2 station). While for the cobalt, the recorded contents aren't critical, with a specified maximum of 0,914 µg/g d.w at the S_1 station.

Conversely, the average contents of Cd were very expressive in the *Corallina elongata* alga collected at the four stations and exceeded the threshold recommended by the IAEA (ie 0,0173 µg/g d.w). In the case of Mn, important fluctuations of the content were observed from one site to another. Although average contents do not exceed the threshold asmissible for the Mn, it wasn't the same for the maximum accumulation recorded at S_1, with a peak of 115,81 µg/g.

As for the vanadium, it was detected in all samples of algae, with a maximum of 16,05µg / g detected in the collected algae in S_1 station. According to the obtained results, we can classify the bioaccumulation potential of red alga *Corallina elongata* (according to the values of the average contents) depending on the nature of the metal and the sampling station, as follows:

Station S_1: Fe > Mn > Zn > V > Cr > Cu > Pb > Ni > Co > Cd
Station S_2: Fe > Zn > Mn >Pb > Cu > V > Cr > Ni > Co > Cd
Station S_3: Fe > Mn > Zn > V > Cr > Ni > Cu > Co > Cd > Pb
Station S_4: Fe > Mn > Zn > V > Cr > Ni > Co > Cu > Cd > Pb

This affinity of algae for certain metals is in accordance with that found in other studies showing that macroalgae of temperate regions accumulate a lot of Fe, Zn, Mn and Pb(Aulio, 1983 ; Rajendran et al, 1993 ; Storelli et al, 2001).

Finally, if we refer to the standards established by the IAEA (2005), we can note that the trace metals concentrations in samples of the red alga *Corallina elongata*, reflect a clear contamination by the Fe, Pb, Cd, Mn and the Ni, while the concentrations of Zn, Cu, Co, the Cr still below the values recommended by IAEA. It is possible that the accumulation of the last ones in the alga isn't influenced by the surrounding environment, or the bioavailability of these elements is low. Accordingly, it seems that the bioaccumulation of these metals by *Corallina elongata* is influenced by other factors. Indeed, the authors (Ho, 1990a ; Carlson and Erlandsson, 1991 ; Karez et al., 1994 ; Villares et al., 2002 ; Suzuki et al, 1995 ; Gledhill et al., 1997) have reported that many factors can influence the capacity of the bioavailability of metals in algae. Except the properties of physico-chemical parameters, where the main factors are the pH, salinity, temperature, light, particles and organic material, other factors such as the conditions of water, stage of development and the variation in the growth and the chemical composition of the algae can influence the accumulation model.

Seasonal variation

Stemming from the results given in table 1 and observations that emerge, it appears that concentrations of metals found in *Corallina elongata* are generally quite variable depending on the sites, according to the sampling campaigns (seasons) and the nature of the metal.

Figure 3 illustrates the spatiotemporal variations of metal contents (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn) in the red alga *Corallina elongata*.

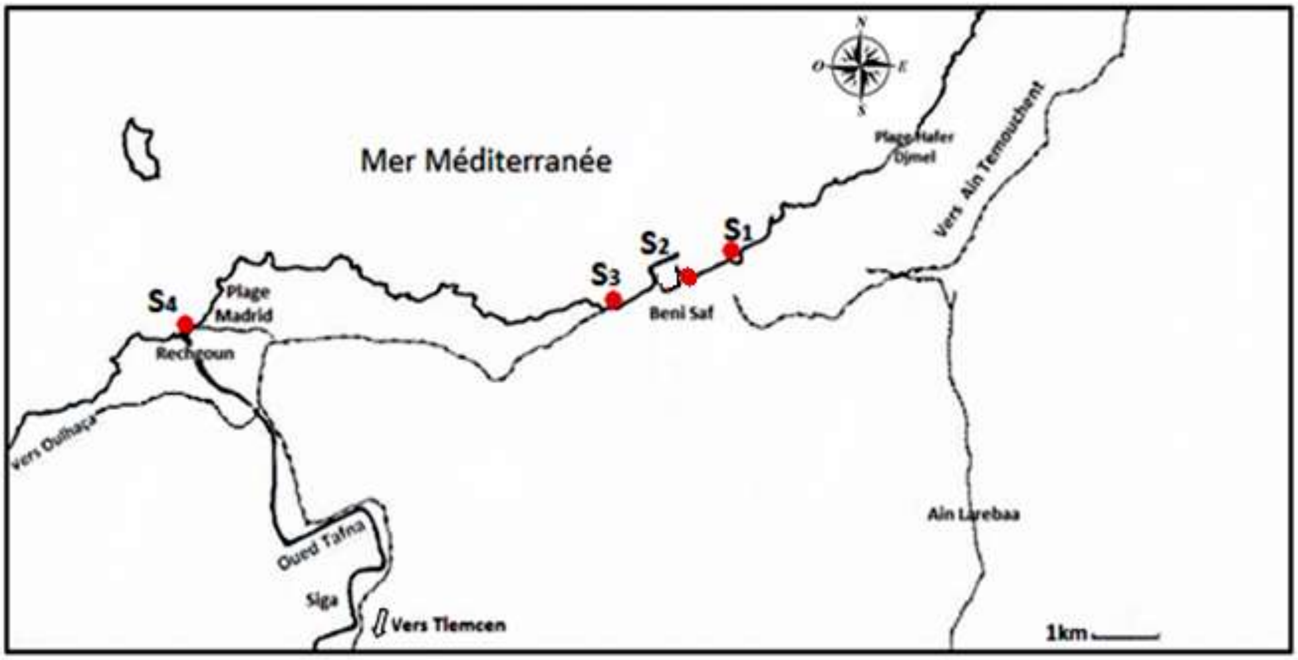


Fig. 1: Localisation of sampling stations of macroalgae *Corallina elongata*, along the bay of Beni Saf

Fig. 2: Samples of red algae *Corallina elongata* collected in the coast of Beni saf. (a) : macroscopic view of the red alga *Corallina elongata* samples ; (b) : enlargement 10x of a sample of the red algae *Corallina elongata*.

The seasonal variation of Fe is important, the station S_1 present the highest level during the sampling period (with the exception of two samples in March 2011 and May 2012). A peak of concentration is observed in July.

The Mn content increases significantly in the summer and reaches a maximum of 115,81 µg/g, recorded at S_1 in July.

The evolution of Zn contents shows seasonal fluctuations, accentuated in the summer. The highest content (93,16 µg/g d.w) was observed at the S_2 station (at the port) in July, while a minimum values that are recorded in the spring at the S_2 station, S_3 and S_4 were nil (0 µg/g d.w).

Seasonal variations in the case of Pb and Cu are similar and pronounced in the whole. A net increase is observed from spring to summer 2011 and a net decrease from summer to spring during the following year. The maximum value measured is 13,31 µg/g of Pb determined in May and 4,82 µg/g of Cu detected in July, observed in alga collected in the S_2 station (at the port).

Besides, an important increase in Ni concentration is observed from the winter to the summer of the first year of sampling, preferentially in the S_1 station, additionally a net decrease is observed, preferably in the S_2 station, in the following period.

In contrast, the seasonal variation of Co and Cd is fluctuating and different from that of the other metals studied. The highest concentrations are not detected in summer.

The biggest enrichment in Cd for the red algae was observed in March, at the S_2 station, while for Co is detected in January, at the S_1 station.

Results show that the accumulation of metals: Fe, Zn, Cu, Cr, Pb, in the *Corallina elongata* alga is higher in summer and decreases in winter. However, the concentrations of Co, Cd tend to be accumulating in the alga, during the winter

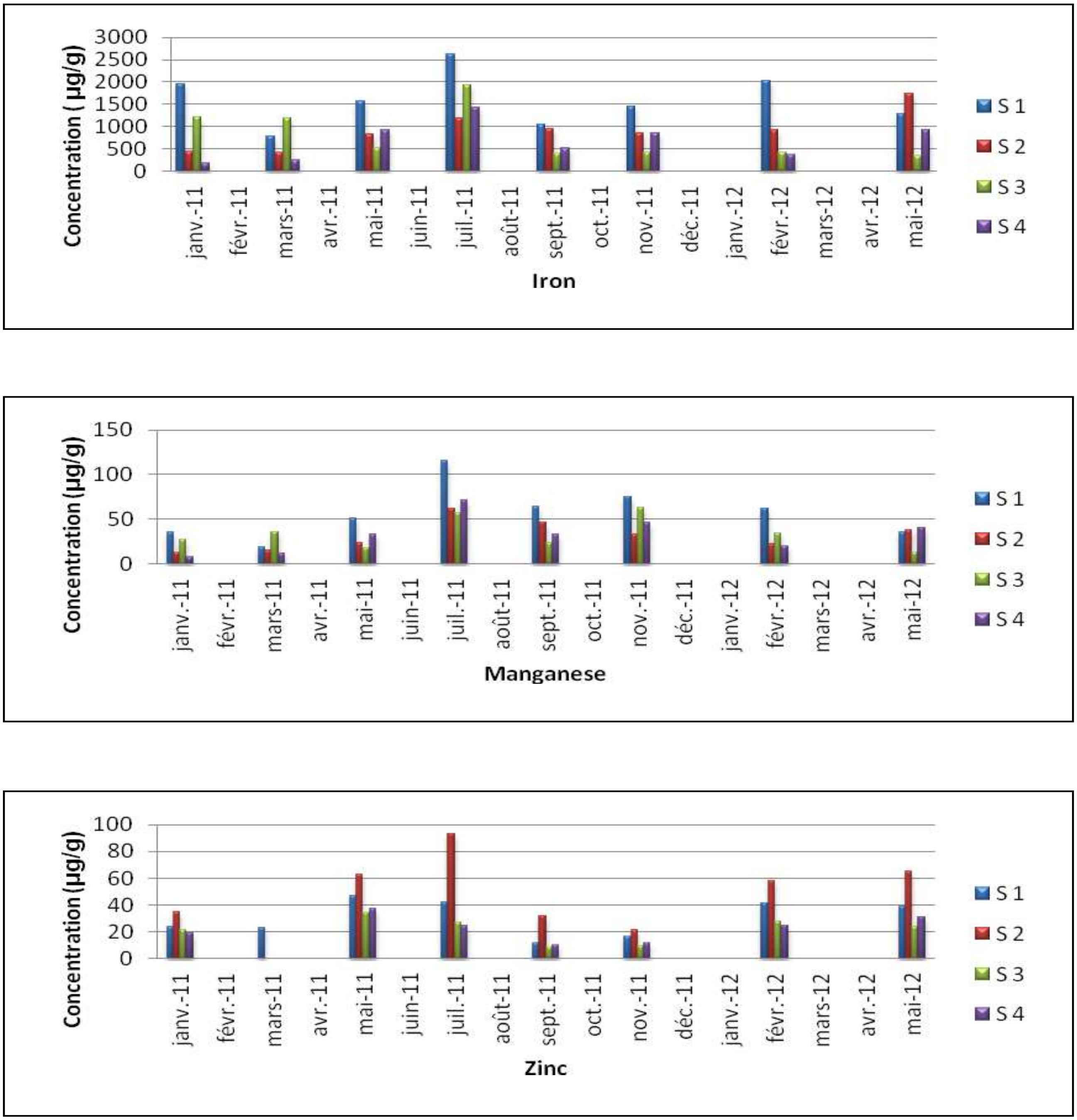


Fig. 3: Monthly variations of trace metal contents (Fe, Mn, Zn, Pb, Cu, Cr, Ni, Co, Cd, As and V), in the red algae *Corallina elongata*

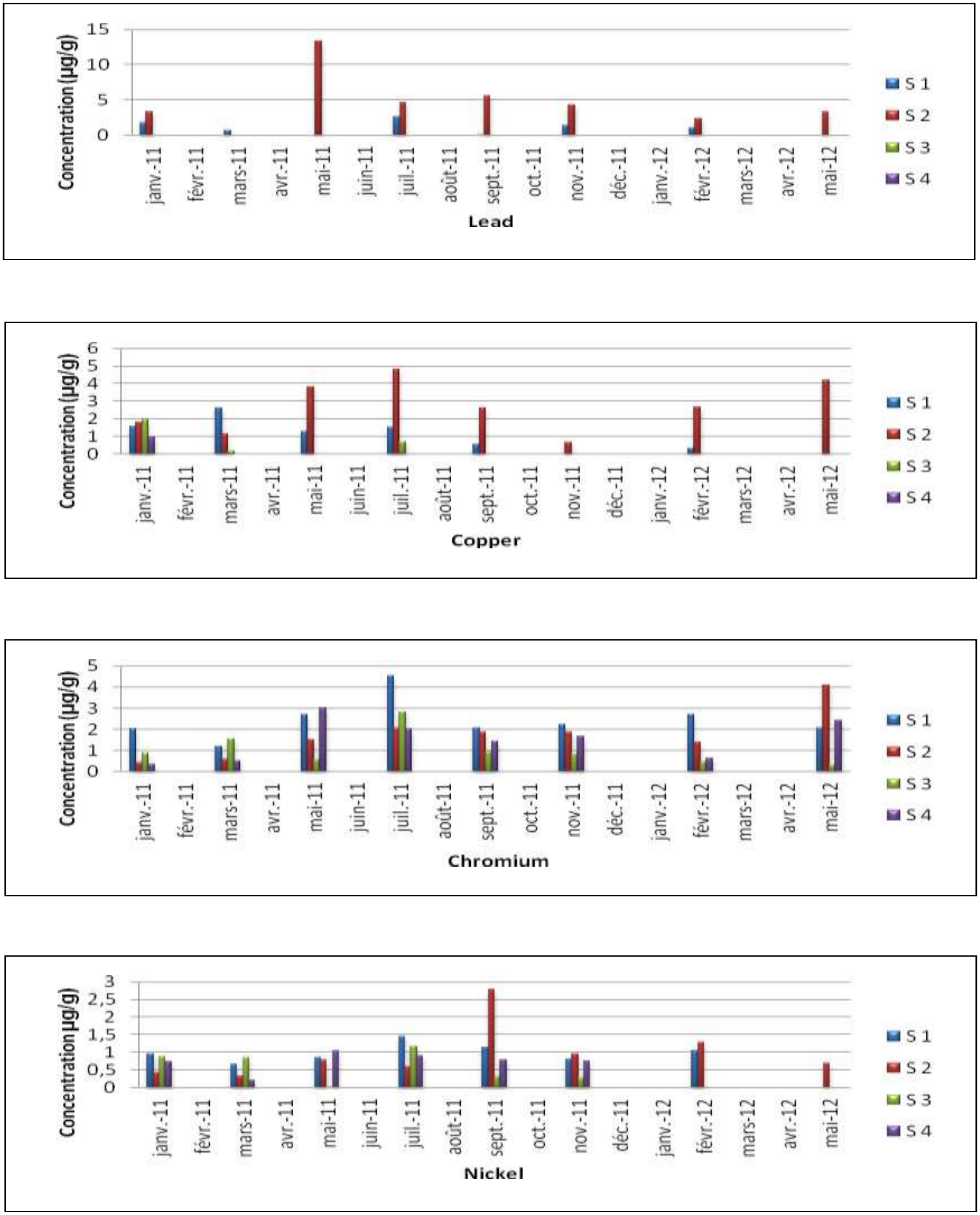
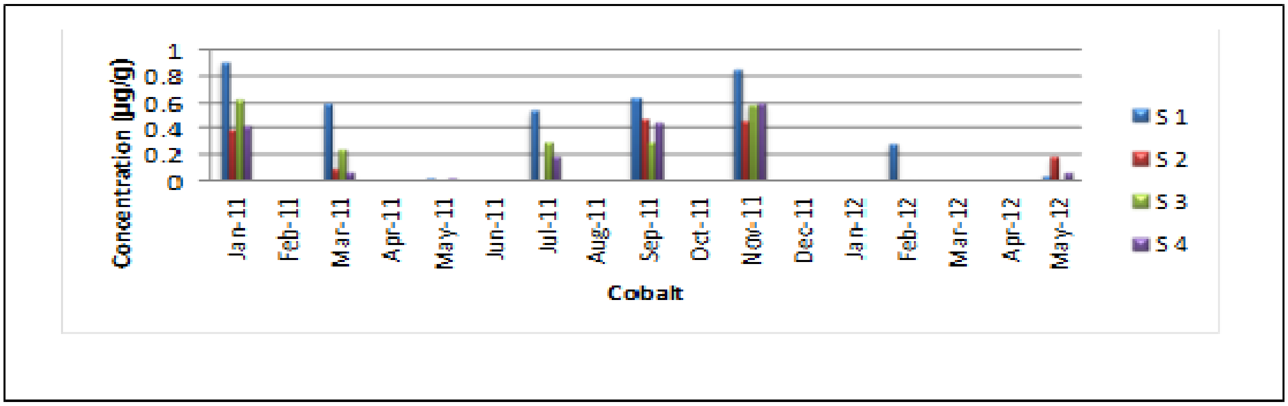
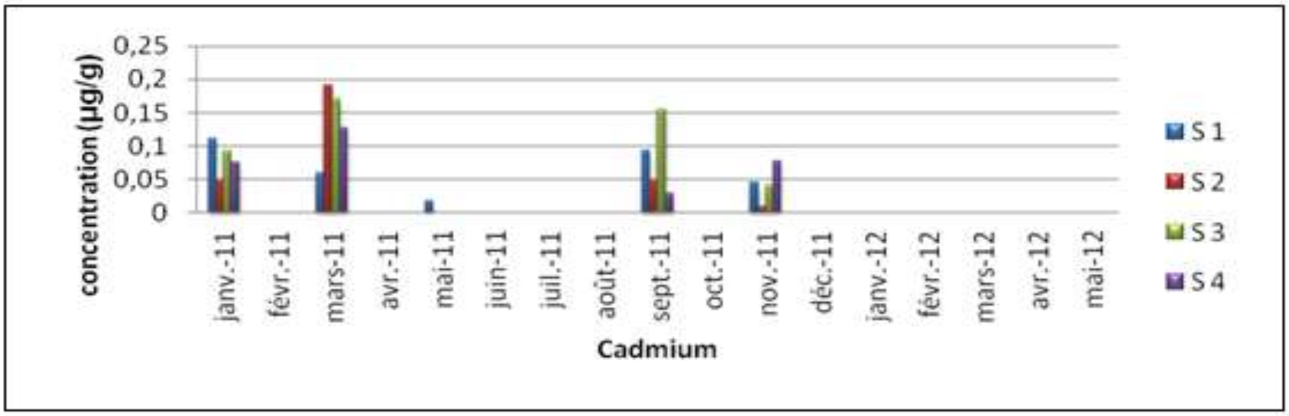


Fig. 3: *Continue………*

period. Seasonal variation in concentrations of metals in marine algae was reported in other previous studies (Villares et al, 2002 ; Bryan et Hummerstone, 1973 ; Fuge and James, 1973 ; Rönnberg et al, 1990 ; Catsiki et al, 1991 ; Miramand and Bentley, 1992 ; Kaimoussi et al., 2005 ; Kaimoussi et al., 2004 ; Munda, 1984 ; Struck et al, 1997 ; Wang and Dei,





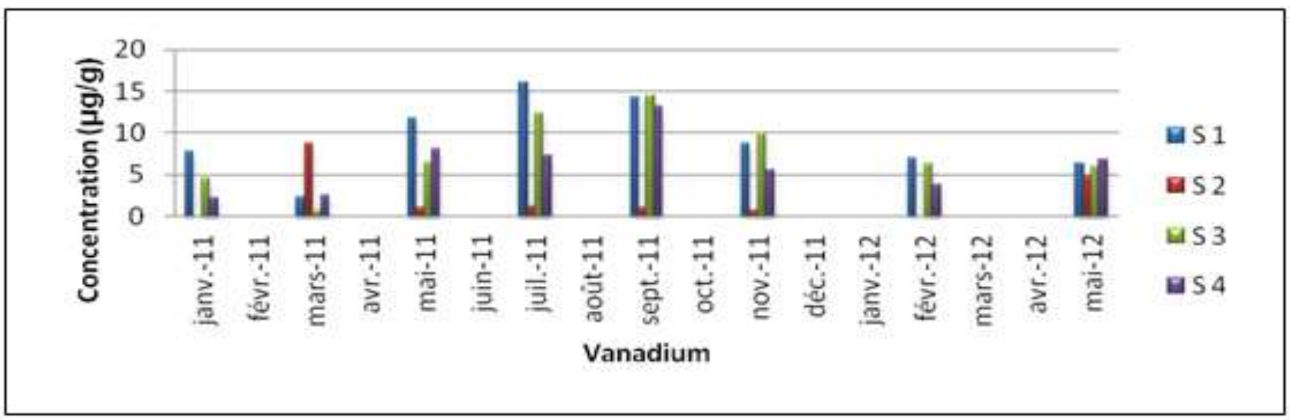


Fig. 3: *Continue…………..*

1999), but at differences observed from a study to another, from the standpoint of the maximum accumulation season of the metal, depending on the type of alga, while other authors have noted the absence of such variation (Young and Langille, 1958 ; Haug et al., 1974 ; Shiber, 1980). Our observations are consistent with those of Kaimoussi works., and al. (2005), where the concentration of five trace metals (Cd, Cu, Fe, Mn and Zn) in the species of Fucus spiralis alga for the city of El Jadida generally increases from winter to summer, according to the sampling site, with the exception of Cd, where the highest concentration was detected in January.

Withal, other previous studies (Villares et al., 2002; Munda, 1984; Struck et al, 1997; Wang and Dei, 1999) have shown that the contents of metals in the aquatic macroalgae are generally low during the warmer months due to the high rate of growth which dilute the accumulated metals. This increase in winter concentrations can be explained by the augmentation of metals concentrations in solution due to the fluvial intake during the winter. In addition, the decrease in salinity produced by these contributions may lead to an increase of metal concentrations in marine organisms.

Role of physicochemical properties of the marine environment on trace metals accumulation

Moreover, we tried to determine the role of environment on the accumulation of metals in the alga. To achieve this, we have first determined the physicochemical parameters, illustrated in table 2, relative to water stations quality in order to correlate them to the accumulated metal contents in the red alga.

Overall, mean values, recorded in the whole period of study, show that the pH is rather basic with a slight variation from one station to another. This alkalinity of the aquatic environment is in support of the accumulation of metals especially the less soluble, in the algae tissues. The highest pH values (8,4-8, 6) were observed only in the summer period.

The temperature of the seawater also varies according to the sampling season. In fact, the values of the superficial marine water temperature vary under the thermal regime of the Mediterranean climate. The identified values range from a low of 15 °C (winter season) and a maximum of 28 °C (summer season). The salinity values vary between 32.7 and 37.7°/oo. The slight fluctuation of the salinity at each station may be due to the effect of the liquid effluent discharge which results a sensitive decrease of the seawater salinity values. Indeed, some values of salinity are well below the specific average of the Mediterranean (for 38.5°/oo) (Lurton, 1988).

The four sampling stations waters are characterized by a very high electrical conductivity included between 50 ms/cm (the minimum observed at S_4) and 56.7 ms/cm (the maximum observed at the level of S_1 and S_4). The average values of chlorides are relatively stable and adjacent 21 g/l. In contrast, nitrite contents are extremely fluctuating during the study period; they oscillate between 0.651 and 223.59 µg/l. It appears a big variability of the concentrations of this nutrient element, depending on the sampling season. The highest contents of 223.59 µg/l and 141.66 µg/l, were recorded in May and November respectively, at the S_2 station (port of Beni Saf) and S_3 (wells beach), respectively. The contents of orthophosphates are, the most often, very variable (from 0.0039 to 1.0075) mg/l. This last content, the most important of the entire series, was recorded in the month of November and March respectively, at the station S_1, located near a collector of urban effluents. This phosphates enrichment observed in the S_1 station, reflects the rejection of suds loaded in detergents contained in urban effluents discharged into the marine environment.

On the other hand, the potential influence of the main optimum physicochemical parameters of marine water on the corresponding metal charge can be evaluated using linear correlation matrix illustrated in table 3. In fact, environmental factors may influence the accumulation of metals of various origins, in the algae tissues. The correlations between pH which characterizes the acidity of the environment, and the metal contents are either very low or negative which confirms that the alkaline nature of the aquatic environment is in favor of the accumulation of metals especially the less soluble. As for the temperature of the marine environment, its rise promotes the maximum bioaccumulation of metals such as Fe, Mn, Cr, Ni, Co, Cd and V. Salinity and conductivity are correlated in a similar way for all the metals studied. In fact, considerable positive correlations between salinity/conductivity and Fe, Mn, Cr, V, while positive but weak correlations are observed between the salinity/conductivity and Zn. Important anti-correlations are observed as well as the salinity than the conductivity and Cu, Ni, Co, Cd and Pb.

These anti-correlations between salinity/conductivity and metals Cu, Ni, Cd and Pb, testify to the continental origin of these metals, to the across of urban effluents. Also the nutrients like phosphate and nitrate can affect the accumulation significantly of heavy metal in algae (Sivakumar et al., 2010). Indeed, other positive and highly eloquent correlations are observed between the orthophosphate and Ni, Co and Cd. They are less highly meaningful with Fe, Cu and Cr. These observations are consistent with the works of Wang et al. (2007) who have reported that high concentrations of nutrient elements generally facilitate the biosorption of Ni by algae. Other studies (Wang et al, 2007 ; Yu and Wang, 2004 ; Lee and Wang, 2001) have shown that the increase in the concentrations of phosphates greatly facilitates the absorption of Cd, Zn, Cr and Ni in the algae.

Nitrites are moderately and positively correlated to Zn, Cu but highly correlated with Pb, while they are significantly anti correlated to Cr, Co, Mn and V. The chlorides are very substantially correlated to Cd and averagely to V, whereas they are anti-correlated with all the rest of the metals (Fe, Mn, Zn, Cu, Cr, Ni, Co, Pb). Nevertheless, by correlating the parameters of the marine environment where the values are the lowest, it seems that the reasoning isn't the same for some metals. Table 4 gives the different correlations of minimum values recorded for the main physicochemical parameters of the seawater and the corresponding metal contents. The correlations of the salinity to metals range in the same manner as conductivity, just as in previous correlations. However it is noteworthy that negative correlations of the salinity/conductivity are observed with the metals Ni, Co, Cd, and V. The nitrites provide indicative positive correlations to very cogent, with all the metals studied. A very good correlation is observed between the chlorides and Fe, whereas this correlation becomes either not denoting with Cu, Cr, Cd or negative with Mn, Ni, Co, V and Pb. These findings show that the behavior and the accumulation of metals in the alga *Corallina elongata*, differ according to the medium considered. Besides that, the reply and the survival of a metal depend on the other metals present in the environment in relation with the role that the environmental factors can play. By the way, these interactions, positive or negative, exert a certain influence on the bioavailability of metals, and thence on their bioaccumulation (Ahsanullah et al, 1981). In this context, we have also correlated the metal contents between them, defined in the red algae. Table 5 sums the different correlations.

In the light of this correlation matrix, it appears that the Fe is considerably and positively correlated with Mn (0,733, p<0.0001) and Cr (0,855, p<0.0001) as are Mn and Cr (0,717, p<0.0001), V (0,518, p = 0,00236) and Zn with Pb (0,556, p = 0,0009) and Cu (0,728, p<0.0001), while Zn and Cd is substantially anti-correlated (-0,652 p<0.0001).

These different correlations show that the iron influence the bioaccumulation of other trace elements such as Mn, Zn, Cu, Ni and V but also Cr and Pb (in a slight degree). The Fe-Mn correlation is one of the most expressive of the correlation matrix. Indeed, manganese and iron present a great similarity of biochemical roles in the marine environment. Pb bioaccumulation is influenced by Zn and Cu and that of Zn by Cu. Whereas, negative correlations are observed between Cd and the other metals, except Co and V, and which can be explained by the fact that the metallic elements Fe, Mn, Zn, Pb, Cu, Cr and Ni, particularly Zn, act by inhibiting the accumulation of Cd.

CONCLUSIONS

In the current study, the red alga *Corallina elongata* was used in assessing the degree of metal pollution by the phenomenon of bioaccumulation. The assay carried out using ICP Optical Emission of Spectrometer, of a series of trace metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn) in the red alga collected in four different sites located in the bay of Beni Saf, has proved the presence of all these metals at different concentrations, depending on the nature of the site, the season and the nature of the metals considered. Referring to the standards established by the International Atomic Energy Agency, we have recognized an important enrichment in Fe, Pb, Cd, Mn and Ni in the alga *Corallina elongata*, while concentrations of Zn, Cu, Co, Cr remain below the thresholds recommended by the IAEA. It is possible that the accumulation of Zn, Cu, Co, Cr by this alga is not influenced by the surrounding environment, or that the bioavailability of these elements is lower. Therefore, it seems that bioaccumulation of these metals by *Corallina elongata* is influenced by other factors. The spatio-temporal variations show that the accumulation of metals (Fe, Zn, Cu, Cr, Pb) in the red alga is higher in summer and decreases in winter. However, the concentrations of Co, Cd tend to be accumulated in the alga, in winter.

Alkaline pH, salinity and nutrient elements characterizing the marine environment seem to promote bioaccumulation of some trace metals in the red alga *Corallina elongata*. From different correlations between salinity and metals, it appears that the bioaccumulation of Cu, Ni, Cd and Pb is from continental origin, such as discharges of urban effluents or those derived from port activity. The behavior of each metal, influenced by the role of the other metals, shows that the iron influence the bioaccumulation of the other trace elements such as Mn, Zn, Cu, Ni and V but also that of Cr and Pb, in this species of alga. A strong correlation was observed between Fe and Mn, which confirms the big similarity of their biochemical roles, already known in the marine environment.

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