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Trace Metals in Algae and Sediments from the North-Eastern Tunisian Lagoons

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Abstract The mean concentrations of copper, zinc, plomb, nickel and chrome were determined in algae and sediments collected from three aquatic areas of the Tunisian North-East (Sebkhet Sijoumi and Radès and Bizerte lagoon). The recorded metal levels, ranging (in µg g^{-1}) from 1.58 to 68.56 for macroalgae and from 8.70 to 234.40 for sediment samples, were low in most of the sampling locations and similar to those of sites qualified as «slightly polluted». However, certain locations showed significant differences with the remaining sites indicating some degree of contamination (ANOVA, $p < 0.001$). These locations were found in Sebkhet Radès and Bizerte lagoon for copper, zinc, nickel and chrome metals and in Sebkhet Sijoumi for plomb in algae. The study of the correlation between metal contents in algae and sediments showed highly significant positive values for zinc and plomb ($p < 0.01$). A significant correlation was also noticed for Cr ($p < 0.05$). However, there was no clear relationship between copper and nickel levels in both matrices.

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Tunisia is situated at the eastern portion of the great bulge of North Africa. It is surrounded on the west by Algeria, on the north and east by the Mediterranean Sea, and on the southeast by Libya. Tunisia is at the triple junction of Europe, the Middle East and Africa. Covering a surface of 162,155 km^2, this country has an impressing coastline of 1300 km open on the Mediterranean. Because of the development of its industrial, tourist and agricultural activities, the Tunisian country, especially the north-eastern part is subjected to the contamination of its marine resources by anthropogenic discharges. These activities, together with the expansion of its population may affect the quality of the aquatic environment in the long term.

Due to its high potential of heavy metal accumulation, the *Ulva lactuca* macroalgal specie has been extensively used to monitor environmental contamination in various geographical areas (Storelli et al. 2001; Gaudry et al. 2007). It is able to absorb heavy metals both from water and sediments and to diffuse some of these elements inside its cytoplasmic cells (Davis et al. 2003).

Only few studies have been conducted on the aquatic pollution of the Tunisian littoral, especially in coastal lagoons that are widely distributed in the peri-Mediterranean coasts (Yoshida et al. 2002; Trabelsi and Driss 2005). Investigations concerned in particular the analysis of coastal sediments. In contrast, the biological samples (algae, mussels, etc.) have received comparatively small attention (El Ati-Hellal et al. 2007).

The present work focused on the determination of trace metals in macroalgae tissues (*Ulva lactuca*) and sediments collected from three aquatic areas of the North-Eastern Tunisian country (Sebkhet Sijoumi and Radès and Bizerte lagoon).

Materials and Methods

Sampling was carried out in April 2007 and comprised seven stations located in three aquatic areas from the north-eastern Tunisian country (Fig. 1). The first sampling area is the Bizerte lagoon, which is the second largest lagoon in Tunisia. It's situated in the south-west of the Bizerte city and in the extreme north of the country. The surface area is 128 km^2 and the sea depth is between 3 and 12 m. The lagoon is connected to the Mediterranean Sea through a 7 km long channel. Three stations were sampled. B1 is located at the eastern side of the lagoon, nearby the Menzel Jemil city, where an industrial zone (plastics, textile, ceramics, metallurgy, etc.) and a shellfish farming are found. B2 is situated in the southern part of the lagoon, at proximity of the Menzel Bourguiba landfill, while B3 represents the lagoon central area.

The second sampling area is Sebkhet Radès or the South Lake of Tunis. It is a shallow lake located in the north of Tunisia at the east side of Tunis City. It is separated from the North Lake by the navigation canal and has an average depth of about 2 m. For many years, the sebkha has been used as a disposal area for waste water from Tunis and the adjacent industrial area. Recently, a great project was undertaken for the restoration of the South Lake and its shores in order to stop the pollution which negatively affects the water quality. Two stations were sampled. R1 is situated at the east side of the sebkha, nearby the canal of Radès. R2 is found southward, close to the Megrine industrial zone.

The third aquatic area is Sebkhet Sijoumi. This site is located in the South of Tunis city. It is a part of a great hydrologic basin (230 Km^2) extended from Manouba to Sijoumi areas (Fig. 1). The Sebkha receives a great quantity of discharges and wastewater due to the explosion of urbanization during the last years and the implantation of various types of industries (electro-mechanics, textile, plastics, foods, etc.) in the surrounding. Two stations were selected in the sebkha. S1 is located in the east side of the sebkha nearby Bardo agglomeration and S2 is in the southern part, at proximity of Fouchana zone (Fig. 1).

As it is easily recognizable and very abundant in the Mediterranean, the green algae specie *Ulva lactuca* was selected for metal analysis. The collection of the same macroalgal specie at each sampling site was also realized to avoid possible interpretation errors in the comparison of the stations contamination level, due to differences of metal accumulations by various species (Villares et al. 2005). Algae were handpicked in the subtidal zone. The sampling of sediments was realized with a Van Veen Grab.

To obtain a representative sample of each station, five sub-samples of algae and sediments distributed in a 100 m^2 grill were collected at the same sampling points. They were

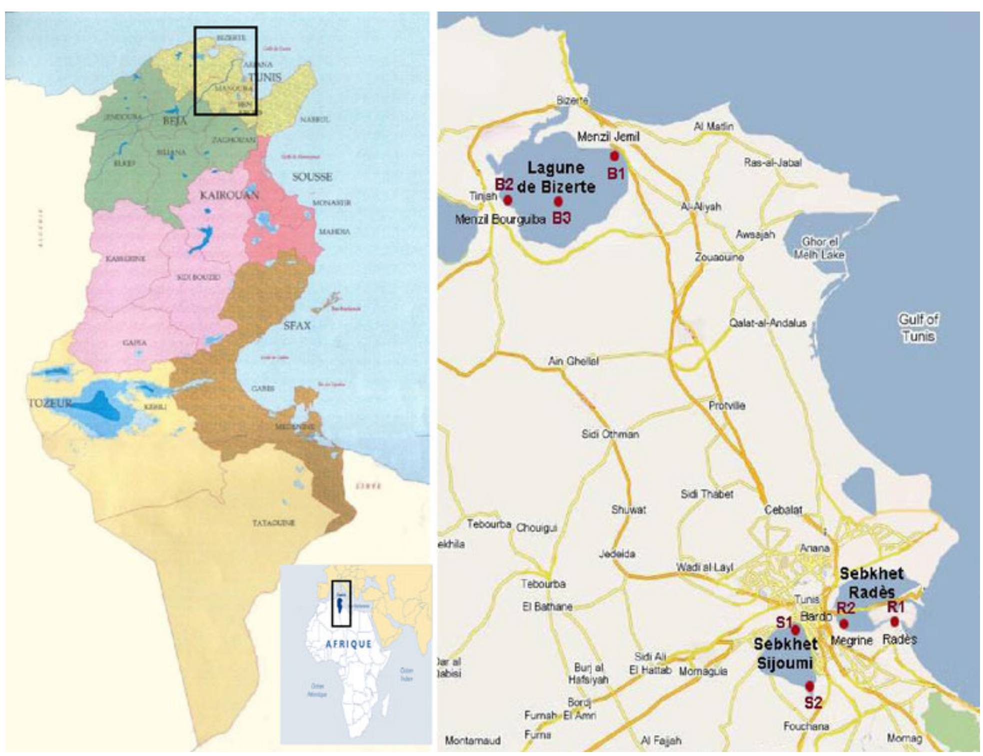

Fig. 1 Sampling stations in the North-Eastern Tunisian lagoons (B1) Menzil Jamil; (B2) Menzil Bourguiba; (B3) Centre of the Bizerte lagoon; (S1) Bardo; (S2) Fouchana; (R1): Canal of Radès; (R2) Megrine

homogenized, transferred to the laboratory in polyethylene bags and stocked at −20°C until analysis.

Samples of algae were initially washed under a jet of tap water and rinsed in metal free double distilled water to eliminate sediments and epiphytic particles. Algae were then dried in oven at 70°C to a constant weight and ground with an agate mortar. In order to perform a homogenous heating of samples, mineralization of algae (∼1 g of dried tissue) was realized in a sandy bath with the mixture HNO_3-H_2O_2 (10:5) (El Ati-Hellal et al. 2007). Reagent blanks were also prepared.

Before metal analysis, sediments were dried in oven at 70°C for 48 h. Then, they were ground and sieved through a 63 µm screen. Mineralization of sediments was realized in a sandy bath with the mixture HF-HNO_3-$HClO_4$ (10:10:5). Reagent blanks were also prepared.

The metal analysis (Cu, Zn, Pb, Ni and Cr) was performed with a novAA 400 atomic absorption spectrometer (Analytic Jena, Jena, Germany), equipped with a deuterium background corrector. All metals were determined using flame atomic absorption spectrometry, except for Pb, Ni and Cr in algae that were detected with graphite furnace.

The one-way ANOVA (log-transformed data) was done to compare the concentrations of metals in the different sampling sites. A Pearson correlation analysis was carried out to associate the heavy metal contents in algae with those in sediments.

Results and Discussion

Metal concentrations determined in algae and sediments collected from all sampling stations are given in Table 1. As regards macroalgae, metal concentrations were in the order Zn > Pb > Cr > Cu > Ni. The mean Cu concentrations ranged from 2.95 to 7.55 µg g^{-1}, Zn was in the range 26.25–53.42 µg g^{-1}, Pb was 6.36–68.56 µg g^{-1}, Ni varied from 1.58 to 7.92 µg g^{-1}, while Cr ranged between 2.97 and 14.59 µg g^{-1}. Large significant differences ($p < 0.001$) were observed between metal concentrations in all sampling sites (ANOVA). Generally, highest metal levels were found in stations R1, R2, B2 and B3, except for Pb where the most elevated levels were observed in S1 and S2 sites. The station B1 showed the lowest heavy metal concentrations. The differences were significant with the other sites.

Concerning sediment samples, the metal distribution was in the order Zn > Cr > Pb > Cu > Ni. The mean levels of Cu, Zn, Pb, Ni and Cr varied from 11.29 to 35.99, 59.20 to 234.40, 13.06 to 60.52, 10.27 to 25.83 and 8.70 to 61.95 µg g^{-1}, respectively. The statistical analysis of the

Table 1 Metal levels (µg g^{-1}) in macroalgae of the North-Eastern Tunisian lagoons (means ± S.D)

Lagoon or Sebkha	Site	Cu	Zn	Pb	Ni	Cr
Bizerte	B1	2.95 ± 0.04	26.25 ± 0.26	6.36 ± 0.53	2.35 ± 0.03	2.97 ± 0.47
	B2	6.91 ± 0.28	53.42 ± 0.38	33.11 ± 0.39	7.92 ± 0.22	10.25 ± 0.21
	B3	5.50 ± 0.46	32.50 ± 0.57	16.15 ± 0.34	6.64 ± 0.47	13.00 ± 0.23
Radès	R1	7.55 ± 0.33	45.13 ± 0.63	21.90 ± 0.57	3.50 ± 0.24	12.99 ± 0.29
	R2	6.75 ± 0.04	49.22 ± 0.71	15.33 ± 0.44	4.60 ± 0.46	14.59 ± 0.25
Sjoumi	S1	5.38 ± 0.26	39.34 ± 0.30	47.88 ± 1.46	1.58 ± 0.20	6.24 ± 0.17
	S2	5.33 ± 0.15	33.16 ± 0.40	68.56 ± 1.22	1.73 ± 0.04	3.52 ± 0.03

Table 2 Metal levels (µg g^{-1}) in sediments of the North-Eastern Tunisian lagoons (means ± S.D)

Lagoon or Sebkha	Site	Cu	Zn	Pb	Ni	Cr
Bizerte	B1	22.77 ± 0.70	150.2 ± 0.2	15.06 ± 1.10	13.11 ± 0.37	8.70 ± 0.39
	B2	35.99 ± 0.13	234.4 ± 4.7	60.52 ± 0.53	17.92 ± 0.39	55.77 ± 0.30
	B3	19.00 ± 0.74	202,9 ± 2.3	12.60 ± 0.73	10.27 ± 0.07	15.86 ± 0.77
Radès	R1	11.29 ± 0.41	213.7 ± 1.2	13.06 ± 0.50	20.97 ± 0.65	54.54 ± 0.51
	R2	15.77 ± 0.41	231.0 ± 2.3	18.79 ± 0.40	25.83 ± 0.53	61.95 ± 0.39
Sjoumi	S1	25.99 ± 0.24	75.6 ± 1.3	53.97 ± 0.61	10.27 ± 0.24	40.64 ± 0.55
	S2	28.00 ± 0.49	59.2 ± 0.3	41.70 ± 1.51	11.87 ± 0.32	36.87 ± 0.19

results (ANOVA), showed that the station B2 presented the highest levels of Cu, Zn and Pb. However, the R2 site was the most contaminated by Ni and Cr. Differences were significant with the other sites (ANOVA, $p < 0.001$).

Table 2 shows the Pearson correlation coefficients between heavy metal concentrations in macroalgae and sediments. Highly significant correlations were observed for Zn and Pb ($p < 0.001$). A significant correlation was also noticed for Cr ($p < 0.05$).

The recorded metal concentrations in macroalgal tissues were generally low compared to those reported in clearly contaminated areas (Villares et al. 2005; Gaudry et al. 2007) but they sometimes exceed background levels established in clean sites (Campanella et al. 2001; Villares et al. 2002). On the other hand, the statistical analysis by ANOVA tests indicated significant differences between metal contents in the studied locations. This result reflects an anthropogenic contamination in the sites showing higher metal levels.

Villares et al. (2002) calculated background levels of Cu, Zn and Ni in *Ulva* in summer and winter. They found concentrations (in µg g^{-1}) varying between 4.65 and 9.25; 14.3 and 25.1 and between 1.18 and 2.09, respectively for Cu, Zn and Ni. In comparison with our recorded data (Table 1), a low or moderate contamination is observed, except for Ni in B2 and B3 sites, where a considerable contamination is found. As B2 site is located in the Bizerte lagoon southern part submitted to the discharges of an industrial zone and a military arsenal and located near the Menzel Bourguiba′s waste disposal (Fig. 1), B3 is in the central area of the lagoon. Hence, a diffusion phenomenon of the Ni contaminated water from the south to the centre of the lagoon could be considered in this case. Contamination of the Bizerte lagoon by Ni was also observed in a precedent research study and was attributed to the closeness to the industrial zone (Yoshida et al. 2002).

Relatively high Pb levels were recorded in the algae collected from S1 and S2 sites, situated in sebkhet Sijoumi (Table 1). This contamination could be attributed to important industrial discharges on one hand, and to a strong urban development around the sebkha in the last 20 years, on the other hand.

The *Ulva lactuca* Zn and Pb contents calculated in this study are similar to those reported by Sanchiz et al. (2000) in aquatic macrophytes collected from the Spanich Mediterranean coast. According to Sanchiz et al. (2000), these levels are low and similar to those found in uncontaminated areas, except for certain locations where a slight metal contamination is detected. Samecka-Cymerman and Kempers (2004), measured particularly Cu, Zn, Pb, Cr and Ni concentrations in aquatic plants surviving in surface water polluted by copper mining industry, located in the Legnica-Glogow copper district in Southwest Poland. They recorded high metal levels that exceed seriously background values (up to 1,040, 515, 850 and 59 µg g^{-1}, respectively for Cu, Zn, Pb and Ni). Compared to the other metal concentrations, Cr levels were relatively low, as they didn't surpass 2.7 µg g^{-1} in the aquatic plants tissues. Sawidis et al. (2001) calculated Cu, Zn, Pb and Ni concentrations in algae from the Aegean Sea in Greece. Different species of green, red and brown seaweeds were collected, including the green macroalgae *Ulva lactuca* which was selected in the present study. For this specie, the mean reported metal contents varied between 7.0 and 14.5; 16.4 and 88.0 and between 0.02 and 2.8 µg g^{-1}, respectively for Cu, Zn and Pb. In the case of Ni, minimal levels weren′t detected and the highest mean concentration was 52.6 µg g^{-1} (Sawidis et al. 2001). In comparison with our results, the concentrations determined by Sawidis et al. (2001) were higher for all metals, except for Pb where the calculated levels were too low. Contrarily to the other studied metals, Pb is as a purely toxic element and has never been considered as essential to the organism's survival (Saryan and Senz 1994). Therefore, a monitoring for Pb contents, especially in Sebkhet Sijoumi stations is recommended to avoid a considerable contamination of these sites.

Compared to metallic contents of algae from the Tunisian coast, investigated in a precedent research (El Ati-Hellal et al. 2007), the concentrations determined in this study were in the same order of magnitude of those found in the least polluted sites. These sites are situated in the beaches of Sousse and Mahdia cities that showed heavy metal levels varying between 1.3 and 5.6; 27 and 172 and between 2.2 and 13.0 µg g^{-1}, respectively for Cu, Zn and Cr (El Ati-Hellal et al. 2007).

As regards metal concentrations determined in the sediments of the studied locations, their values are comparable to those recorded in "slightly polluted" sites (Sanchiz et al. 2000). Muniz et al. (2004) reported metal levels ranging from 59 to 126; 174 to 425; 46 to 181; 27 to 34 and from 79 to 192 µg g^{-1}, respectively for Cu, Zn, Pb, Ni and Cr, in the sediments of Montevideo Harbour in Uruguay. These increased levels were the consequence of the growth of urbanisation in this region, leading to the introduction of large quantities of discharges originating from fuel combustion, urban sewage, marine traffic and a petroleum refinery. Bosch et al. (2009) calculated metal contents in the sediments of the Ebro river in Spain and found levels ranging (in µg g^{-1}) from 8 to 47; 35 to 127; 11 to 320 and from 7 to 193, respectively for Cu, Zn, Ni and Cr metals. These elevated concentrations were due to the release of high amounts of urban and industrial wastes, especially from a big organochlorine industry that rejects particularly Ni and Cr pollutants. Compared to data relative to other polluted sites, such as those recorded by Guevara-Riba

Table 3 Pearson correlation coefficients between the metal concentrations in algae and sediments

Metals	Cu	Zn	Pb	Ni	Cr
Pearson correlation coefficient *P*	−0.190	0.573**	0.691**	0.265	0.522*

* $p < 0.05$, ** $p < 0.01$

et al. (2003) in Barcelone Harbour (Spain), the concentrations determined in the present study could be considered as low. Ranges of metal contents reported by Guevara-Riba et al. (2003) were from 70.6 to 531; 183 to 1133; 86.3 to 589; 18.3 to 34.3 and from 38.8 to 110 $\mu g\ g^{-1}$, respectively for Cu, Zn, Pb, Ni and Cr.

Yoshida et al. (2002) measured concentrations of potentially toxic elements in bottom sediments of the Bizerte lagoon. They found peak type high concentration sites, nearby the landfill of Menzel Bourguiba and a plateau type very high concentration zone, from the southwestern (Menzel Bourguiba, Tinja and its north) to the west central part of the lagoon. The first type concerned in particular Cu, Zn and Pb metals and the second was observed especially for Ni and Cr (Yoshida et al. 2002). In the present study, among the three selected sites of the Bizerte lagoon (Fig. 1), the B2 station, located in Menzel Bourguiba, presented the highest metal levels. Differences were significant with the other Bizerte lagoon sites ($p < 0.001$). Moreover, the Cu, Zn and Pb mean concentrations determined in B2 site were significantly higher than those recorded in all the remaining stations. This result confirms the relatively high contamination of the Menzel Bourguiba's station found by Yoshida et al. (2002). On the other hand, The R2 site, located in the south lake of Tunis presented the most elevated Ni and Cr levels (Table 2). This contamination is probably due to the urban and industrial complex of Radès and Megrine agglomerations.

The Pearson correlation coefficients calculated between metal concentrations in algae and sediments showed positive significant values for Zn, Pb and Cr (Table 3). This result indicates the potential of *Ulva lactuca* in the biomonitoring of metal pollution in aquatic environments. However, there was no clear relationship between Cu and Ni levels in both matrices. Correlations between metal contents of aquatic plants and sediments were evaluated by many authors (Cardwell et al. 2002; Deng et al. 2004). Generally, studies have shown poor relationships except for Zn which reveals a relatively clear pattern of increasing accumulation in aquatic macrophytes with increasing sediment concentration (Cardwell et al. 2002).

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