

Evaluation of heavy metal pollution risk in surface sediment of the South Lagoon of Tunis by a sequential extraction procedure

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Summary: In this study, the total concentrations and chemical forms of heavy metals (Fe, Zn, Pb, Cu, Cr, Cd, and Ni) in surface sediments of the South Lagoon of Tunis located in northeast Tunisia were investigated. Multiple geochemical indices were applied to assess the potential environmental risks. The South Lagoon is a valuable regional resource for fisheries, tourism and aquaculture. Total metal concentrations exhibited significant spatial variation attributed to the principal water circulation direction (east to west). The chemical speciation of Fe, Cr and Ni shows that they were mostly related to the residual fraction (Fe 34.8%, Cr 37.4% and Ni 37.9%), while Pb, Zn, Cu, and Cd were mostly related to the non-residual fraction (labile fraction Pb 89.4%, Zn 26.1%, Cu 71.8% and Cd 84.3%). Pb, Zn, Cu and Cr are of high potential bioavailability. The highest pollution was found on the west side of the lagoon according to the calculated global contamination factors. Besides, individual contamination factors, Pb followed by Zn and Cu, posed the highest risk of contamination. This study shows that, even after dredging, the persistence of low concentrations of some contaminants may cause environmental problems in certain physico-chemical conditions.

Keywords: heavy metal speciation; environmental risks; sediment pollution index; Mediterranean lagoon.

Evaluación del riesgo de contaminación por metales pesados en sedimentos superficiales de la Laguna Sur de Túnez mediante un procedimiento de extracción secuencial

Resumen: En este estudio, se investigaron las concentraciones totales y las formas químicas de los metales pesados (Fe, Zn, Pb, Cu, Cr, Cd y Ni) en los sedimentos superficiales de la Laguna Sur de Túnez, ubicada en el noreste de Túnez. Se aplicaron múltiples índices geoquímicos para evaluar los riesgos ambientales potenciales. La Laguna Sur es un valioso recurso regional para la pesca, el turismo y la acuicultura. Las concentraciones totales de metales exhibieron una variación espacial significativa, atribuida a la dirección principal de circulación del agua (Este a Oeste). La especiación química de Fe, Cr y Ni muestra que están esencialmente relacionados con la fracción residual (Fe: 34,8%, Cr: 37,4% y Ni: 37,9%), mientras que Pb, Zn, Cu y Cd se encontraron mayoritariamente en la fracción no residual. –fracción residual (fracción lábil Pb: 89,4%, Zn: 26,1%, Cu: 71,8% y Cd: 84,3%). Estos elementos (Pb, Zn, Cu y Cr) tienen un alto potencial de biodisponibilidad. La mayor contaminación se encontró en el lado oeste de la laguna, según los factores de contaminación global calculados. Además, los factores de contaminación individuales, Pb seguido de Zn y Cu, presentaron el mayor riesgo de contaminación. Este estudio muestra que, incluso después de la operación de dragado, la persistencia de bajas concentraciones de algunos contaminantes puede causar problemas ambientales en determinadas condiciones físico-químicas.

Palabras clave: especiación de metales pesados; riesgos ambientales; índice de contaminación por sedimentos; laguna mediterránea.

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INTRODUCTION

Coastal lagoons are inland water bodies connected to the open sea by one or more inlets. They serve as buffer zones for various fluxes (sediments, nutrients, heavy metals, etc.) coming from the adjacent hinterland drainage to the marine environment (Levin et al. 2001, Elliott and Quintino 2007, Pérez-Ruzafa et al. 2007, 2011). Natural factors such as wind, tide and variation of terrestrial discharges into the lagoon and anthropogenic factors such as pollution and land-use changes can affect the lagoon with relative importance of physical characteristics (geometry, number of inlets, width and depth) (Kjerfve 1986). Indeed, coastal lagoons are highly sensitive and can be described as vulnerable ecosystems.

In aquatic environments, metallic trace elements are slightly soluble in water. They are rapidly sequestered in sediments and can thus create a high risk for the environment. (Förstner and Wittmann 1981). Polluted sediment can also negatively affect the environment by releasing its contaminants. Hence, evaluating the sediment quantity and quality is an essential aspect of lagoon management.

During the last few decades, Mediterranean coastal lagoons have been subjected to increasing demographic pressure, high industrial concentration and intense tourist activity (Suthar et al. 2009), which has considerably increased the pollutant supply and caused disruptions in the functioning of coastal ecosystems (Prange and Dennison 2000, Radenac et al. 2001). The coastal ecosystems stress response affects the quality of water and sediment and also the faunal and the floral community (Wilkinson et al. 2007).

The lagoon of Tunis, on the Mediterranean Sea, is near to the capital, its most populated city. In 1885, the lagoon was artificially divided into two basins: The North Lagoon and the South Lagoon of Tunis. Both areas are severely polluted by anthropogenic discharges (Zaouali et al. 1983, Ben Charrada 1992, Ben Souissi 2002). Major industrial activities together with the expansion of its population have affected the quality of this ecosystem, which has been considered one of the most polluted lagoons of the Tunisian coast (Zaouali 1977, Caumette 1985). To resolve this environmental problem, both basins required restoration works. The success of the restoration project of the North Lagoon (carried out in 1988) led the Tunisian authorities to undertake a cleansing project in the South Lagoon, which is the subject of our study, (April 1998 - July 2001). The objectives of the restoration work were i) to improve water circulation; ii) to avoid water stagnation by deepening the lagoon (dredging the bottom sediments and filling nearly 580 ha of land, thus reducing the surface of the water to 720 ha); iii) to construct one-way tide gates; iv) to pump seawater into the lagoon; and v) to widen the channels of Rades and Tunis (SPLT-STUDI/SO-GREAH, 1998, Jouini et al. 2005, Abidi et al. 2019). The restoration work improved the hydrodynamic conditions, thus enhancing the biological setting.

Studies carried out after the restoration work are few and often fragmented. They have focused essentially on flora and fauna observations (distribution and

composition of communities) (Shili et al. 2002, Ben Souissi et al. 2005, Jouini et al. 2005, El Ati Hellal et al. 2011) or have reported on the state of pollution of the lagoon before the restoration work (Harbridge et al. 1976, Ben Souissi et al. 1999, Ouertani et al. 2006).

In the absence of studies of the sediment geochemical characteristics, we hypothesized that the use of geochemical tools to investigate the environmental disturbance of the surface sediments by means of extracted metals (speciation) could be useful for determining the pollution status of the lagoon after restoration. The information collected on the measurement of heavy metals and their distribution will be used to create a database for future comparison.

In the present study, the geochemical characteristics of surface sediments of the lagoon 14 years after the restoration project were analysed. Heavy metals and sediment nature were assessed and pollution levels were characterized. Using an accurate methodological extraction procedure, we assessed several indices to make the assessment and evaluate the restoration works. Finally, the chemical speciation results were used to evaluate the potential of metal bioavailability and thus sediment toxicity.

MATERIALS AND METHODS

Study area

The South Lagoon of Tunis is the southern basin of the lagoon of Tunis. It is located in the northeast of Tunisia (10°12' to 10°16' E and 36°46' to 36°48' N). After the restoration programme (1998-2001), the lagoon, covering a surface of about 720 ha, has the shape of as an eclipse stretching in a SW-NE direction. It has a regular depth almost equal to 2.1 m, except in some restricted areas on the east side, where it reaches a maximum of 5 m (Abidi et al. 2019).

The lagoon communicates with the Gulf of Tunis through two channels: Channel of Tunis and the Channel of Rades (Fig. 1). The hydrodynamics of the lagoon is mainly controlled by the combination of tide and wind effects (Jouini et al. 2005). Through the variation of the level of water, the tide controls the opening and the closing of the locks. At rising tide, the seawater enters the lagoon via the Channel of Rades, and it comes out through the Channel of Tunis when the tide is down, imposing a mainly east-west water flow circulation.

Owing to its position, the lagoon is considered an outlet for wastewaters from the neighbouring cities. The South Lagoon of Tunis has a drainage watershed of 4000 ha, more than 1500 ha of which consists of industrial areas (food industries, wholesale, etc.) (Jouini et al. 2005). The industrial and domestic waters are discharged to the catchment area (Oued Essalaas and the channel of Ben Arous), from where they are transported to the lagoon. In addition, the lagoon receives water from draining of the urban area of Megrine and the runoff of newly-developed areas after the restoration works (Abidi et al. 2019). The lagoon receives about 5500 m³/day of untreated industrial wastewater enriched with nutrients and heavy metals (Jouini et al. 2005).

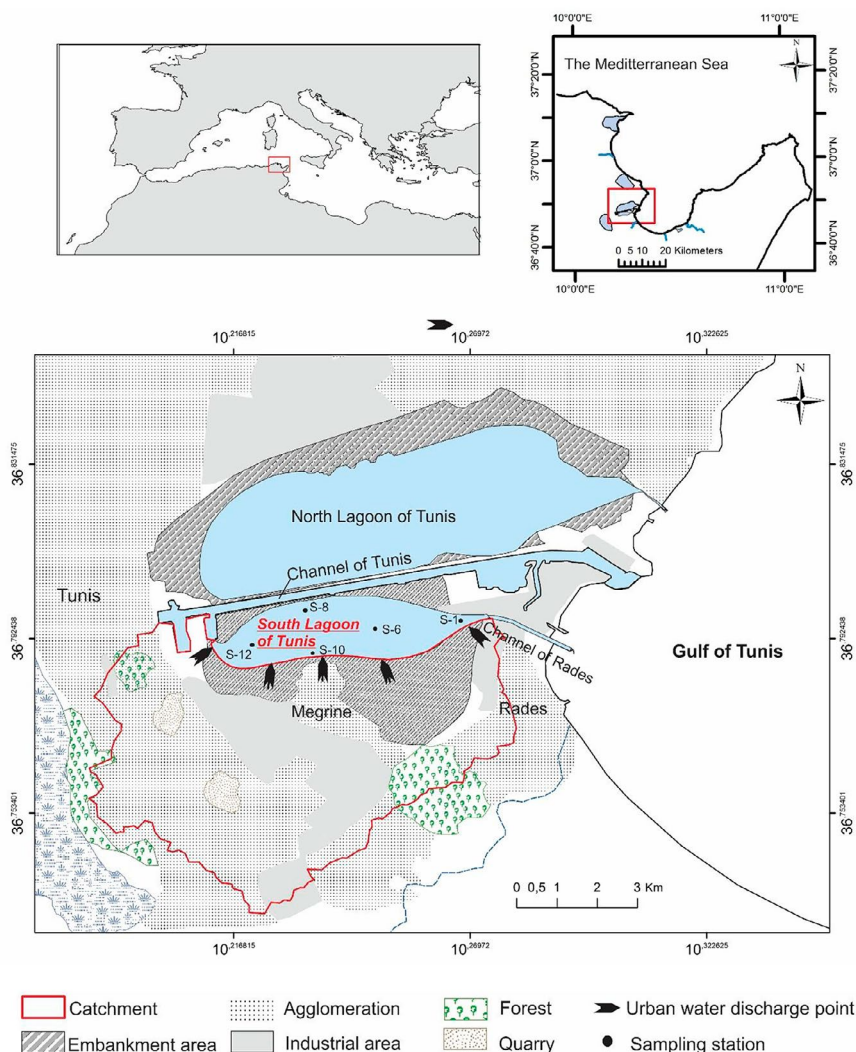


Fig. 1. – Location of the study area and sample stations.

Sampling and sample handling

Five surface sediments (–3 cm), S-1, S-6, S-8, S-10 and S-12, were extracted from the lagoon in February 2014. The sample locations are shown in Figure 1. The Eh and pH were immediately measured using portable probes (WTW 82862 Weilheim). Each sample was placed in a plastic bag and stored at 4°C for physical and chemical analysis.

In order to separate the fine fraction, the sediment was wet-sieved with bi-distilled water using a 63 µm nylon mesh. Subsequently, it was, oven-dried at 50°C. The fine fraction (<63 µm) was ground in an agate mortar for further analysis. In order to compensate for the grain size and mineralogical effects on the metal variability in different samples, the method of geochemical normalization was applied (Sakan et al. 2009). All chemical analyses were carried out on the fine fraction.

Total organic carbon (TOC) in the sediment was measured by means of a Perkin-Elmer PE 2400 CHN analyser. The sub-samples for TOC were decarbonized employing

1 M HCl, rinsed with ultra-pure water and dried at 60°C to remove the carbonate fraction (Froelich 1980, Hedges and Stern 1984, Ennouri et al. 2010). A sediment standard supplied by Perkin Elmer (acetanilide, Table 1) was used to calibrate the CHN/S analyser. Calcium carbonate content was assessed by a Bernard calcimeter.

For metallic trace element analysis, 0.5 g of the dried and sieved sediments was placed in a Teflon bomb and digested by adding perchloric (20 mL) and hydrofluoric (10 mL) acid.

The sequential extraction procedure, developed by Tessier et al. (1979), was applied in our experiments. It consists of extractions in the following order with associated chemical reagents and conditions from 1 g of sediment:

1. Exchangeable fraction: 8 mL of $MgCl_2$ (1M) adjusted to pH 7.0 with ammoniac with continuous agitation for 1 hour;

2. Bound to carbonates: 8 mL of NaOAc (1M) adjusted to pH 5.0 with acetic acid with agitation for 6 hours;

3. Bound to Fe and Mn oxides and hydroxides: 20 mL of NH_2OH , HCl (0.04 M) in 25% (HOAc) heated for 6 h at 95°C with occasional agitation;

4. Bound to organic matter: 3 mL of NH_4OAc + 5 mL of 30% H_2O_2 adjusted to $\text{pH}=2$ with HNO_3 . Samples were heated to 85°C for 2 hours with occasional agitation; a second 3 mL of 30% H_2O_2 was added and the samples were heated to 85°C for 3 hours with occasional agitation. After cooling, the samples were diluted to 20 mL and agitated continuously for 30 minutes;

5. Residual fraction: $\text{HF} + \text{HClO}_4$ total digestion.

After each extraction, the separation of the liquid/solid phase was performed by centrifuging the suspension at 3000 rpm for 15 minutes. The supernatant liquid was then separated with a micropipette. The sediment was washed with 10 mL of deionized water and re-centrifuged, while the wash water was discarded. The metal concentrations were determined by flame atomic absorption spectrometry.

Concentrations of metals (Fe, Zn, Pb, Cr, Ni, Cu and Cd) were specified by atomic absorption with flame using the Perkin Elmer Analyst 100 Spectrometer. Calibration standards of AAS were prepared by serial dilution and verified against standard reference materials.

To show the quality, accuracy and repeatability of the extraction, certified-reference sediment samples and blanks were analysed. To validate the analysis results, we mineralized certified sediment (IAEA-405 reference material, trace elements and methyl mercury in estuarine sediment) at predefined concentrations (Table 1).

The correlations of the studied elements were calculated using the XLSTAT (2013) software.

Various indices have been suggested to quantify the degree of metal contamination in sediments and to assess the potential health risk (Müller 1979, Salomons and Förstner 1984, Ioannides 2015). In the present study, the following factors were taken into consideration:

The geoaccumulation index (Igeo) was employed to assess the metal contamination in sediments, compared with a background geochemical reference (Müller 1969). Igeo was calculated applying the following equation:

$$I_{\text{geo}} = \log_2 \left(\frac{C_n}{1.5B_n} \right)$$

where C_n is the measured concentration of the metal (n) in the sample and B_n denotes the geochemical background concentration of the metal (n). The factor 1.5 was utilized to minimize the effect of possible variations in the sediments. Müller (1969) distinguished seven classes of the geoaccumulation index:

- $I_{\text{geo}} \leq 0$: uncontaminated;
- $0 < I_{\text{geo}} \leq 1$: uncontaminated to moderately contaminated;
- $1 < I_{\text{geo}} \leq 2$: moderately contaminated;
- $2 < I_{\text{geo}} \leq 3$: moderately to strongly contaminated;
- $3 < I_{\text{geo}} \leq 4$: strongly contaminated;
- $4 < I_{\text{geo}} \leq 5$: strongly to extremely contaminated;
- $I_{\text{geo}} > 5$: extremely contaminated.

The enrichment factor (EF) is commonly used as a means of identifying and quantifying the anthropogenic impact on sediments for a metal (m). It was calculated according to Salomons and Förstner (1984) as follows:

$$EF = \frac{[C_m/C_r]_{\text{sediment}}}{[C_m/C_r]_{\text{Background}}}$$

where $[C_m/C_r]_{\text{sediment}}$ and $[C_m/C_r]_{\text{Background}}$ are the concentration ratios of element m to the reference element R in the sample and background, respectively. EF values may be interpreted as suggested by Birch and Davies (2003):

- $EF < 1$ indicates no enrichment,
- $1 < EF < 3$ is minor enrichment,
- $3 < EF < 5$ is moderate enrichment,
- $5 < EF < 10$ is moderately severe enrichment,
- $10 < EF < 25$ is severe enrichment,
- $25 < EF < 50$ is very severe enrichment,
- $EF > 50$ is extremely severe enrichment.

The EF, Igeo and C_f for each heavy metal were computed as a function of Fe content, which is a conservative element considered as the detrital fraction of sediment and compared with the amount of Fe in sediments during the preindustrial period. It has been successfully used to normalize metal contaminants in several studies, as revealed by Ioannides (2015).

Table 1. – Measured and certified concentrations of trace metals ($\mu\text{g/g}$) and total organic carbon (%w/w) in the sediment standard reference materials.

Elements	Recovery (%)	LOD ($\mu\text{g/g}$)	LOQ ($\mu\text{g/g}$)	Reference materials	Present study (average)
Fe ($\mu\text{g/g}$)	79.1	1	10	36700 – 38100	29577
Pb ($\mu\text{g/g}$)	102.7	1	10	72.6 – 77.0	76.8
Zn ($\mu\text{g/g}$)	103.0	0.2	2	272 – 286	287.5
Cu ($\mu\text{g/g}$)	86.1	0.4	4	46.5 – 48.9	41.1
Cr ($\mu\text{g/g}$)	104.8	0.2	2	80 – 88	88
Cd ($\mu\text{g/g}$)	124.1	0.1	1	0.68 – 0.78	0.9
Ni ($\mu\text{g/g}$)	105.9	0.2	2	31.1 – 33.9	34.4
TOC (%)	-	-	-	71.09	69.79

LOD: Limit of detection; LOQ: Limit of Quantification

The contamination approximation is defined according to the natural content “background”. To avoid a bad estimation of the pollution indicators, it is necessary to use a local background, i.e. a local geochemical background. In our study, we used a deep sediment (at -8 m), which corresponds to a preindustrial level of the lagoon (Ouertani and Yahyaoui 2019).

Sediment pollution index (SPI): This index is generally used for an overall assessment of sediment quality with respect to heavy metal concentrations along with a proper consideration of the relative metal toxicity. It is the linear sum of the metal enrichment factors. It takes into account metal toxicity weights. The metal toxicity weights are based on the relative toxicity of different metals. Weight 1 was assigned to Cr and Zn, the less toxic metals; 2 to Ni and Cu; 5 to Pb; and 300 to Cd (Rubio et al. 2000, Singh et al. 2002).

The SPI can be expressed as follows (Rubio et al. 2000, Singh et al. 2002):

$$SPI = \frac{\sum(EF_x \times W_x)}{\sum W_t}$$

where EF is the enrichment factor of each metal and W designates the toxicity weight of each metal.

Based on the above calculation, these classes are obtained:

- $0 \leq SPI < 2$ – natural sediments,
- $2 \leq SPI < 5$ – low-polluted sediments,
- $5 \leq SPI < 10$ – moderately-polluted sediments,
- $10 \leq SPI < 20$ – highly-polluted sediments,
- $20 \leq SPI$ – dangerous sediments.

RESULTS

General characteristics of the sediment

Data related to grain size, TOC, CaCO₃, pH and Eh are presented in Table 2. Surface sediments of the South Lagoon varied slightly in texture. The lagoon is mantled in a silty fraction (95%) and a sandy fraction (5%). The restoration project, especially the establishment of two groups of inlets gates of the channel of Rades and Tunis (recalibrated during the restoration management), imposed an east-west water flow direction. This current controls local sediment sorting (Abidi et al. 2019).

The eastern side of the lagoon, near the channel of Rades, has the highest percentage of sand fraction. The central and western sides of the lagoon are covered by fine sand and deposited in relatively calm hydrodynamic conditions. In fact, the sediment dynamics is controlled by the lagoon water currents inducing east-west grain-size sorting.

Eh values varied between -27 and -134 mV, reflecting anoxic conditions in the lagoon sediments. Overall, Eh depended on sediment characteristics such as the percentage of coarse fraction, TOC content and bioturbation (Oueslati et al. 2010). Obviously, the Eh was higher on the eastern side of the lagoon, which can be explained by the diffusion of more oxygenated waters coming from the Gulf of Tunis and by the porosity of the sandy sediments near the channel of Rades. pH values did not change much in the lagoon sediments.

The highest Eh values recorded near the channel of Rades resulted from bioirrigation, waves and currents (Oueslati et al. 2018). Therefore, the east side of the lagoon seems to be more affected by the incoming marine flux from the Gulf.

As shown in Table 2, the calcium carbonate content ranged from 26.91% to 32.55%, showing a decreasing trend from east to west. The highest CaCO₃ content was recorded in the samples with a high coarse fraction. Obviously, the latter was dominated by complete and fragments of shells, suggesting that carbonates in the lagoon have a primarily biogenic origin (Abidi et al. 2019). The concentration of the TOC varied between 1% (0.48 µg/g) and 1.69% (1.84 µg/g), with an increasing trend in the west.

Metal concentrations

The metal concentrations in the lagoon surface sediment and the regional background values are listed in Table 3.

Ranges of metal concentrations in sediments were 38589.3 to 43705.74 µg/g for Fe with an average of 41727.19 µg/g, 125.8 to 188.29 µg/g for Zn with an average of 148.52 µg/g, 69.33 to 147.61 µg/g for Pb with an average of 102.22 µg/g, 22.68 to 28.91 µg/g for Cu with an average of 27.28 µg/g, 89.83 to 118.29 µg/g for Cr with an average of 99.84 µg/g, 1.18 to 1.9 µg/g for Cd with an average of 1.51 µg/g and 53.49 to 86.59 µg/g for Ni with an average of 71.81 µg/g.

Table 2. – Grain size, organic carbon, carbonate content, Eh and pH values in surface sediments from the South Lagoon of Tunis.

Samples	X	Y	Silty fraction (%)	Sandy fraction (%)	pH	Eh (mV)	TOC (%)	CaCO ₃ (%)
S 1	612837.15	4072976.69	98	2	7.07	-27	1	32.4
S 6	610981.91	4072759.73	96	4	7.1	-73	1.56	31.8
S 8	609454.62	4073213.1	85	15	7.28	-134	1.26	32.6
S 10	609601.49	4072159.99	100	0	7.14	-104	1.46	26.9
S 12	608307.42	4072321.31	98	2	7.21	-89	1.69	28.9

Table 3. – Concentrations of heavy metals in the study area.

Metallic trace element ($\mu\text{g/g}$)	Fe	Zn	Pb	Cu	Cr	Cd	Ni
Sample station							
S1	40441.76	139.26	69.33	22.68	89.83	1.29	53.49
S2	38589.3	125.8	98.5	28.3	102.2	1.9	60.8
S3	42988.41	141.33	106.67	28.57	94.29	1.6	79.45
S4	43705.74	147.92	89.0	28.91	94.61	1.18	78.73
S5	42910.74	188.29	147.61	27.94	118.29	1.58	86.59
average	41727.19	148.52	102.22	27.28	99.84	1.51	71.81
Before restoration project (Ben Souissi 2002)	11896.1	183.2	181.1	51.6	137.1	2.0	16.6
Local background values	24926	135.78	42	9	78.84	0.79	20.46

Table 4. – Comparison of the average contents of certain heavy metals in the surface sediments of the South Lagoon of Tunis.

Lagoon	Location	TOC	Fe	Zn	Pb	Cu	Cr	Cd	Ni	Source
Present study	Tunisia	1.4	41727.19	148.52	102.22	27.28	99.84	1.51	71.81	
Ghar el Melh Lagoon	Tunisia (N)	0.7 - 2.4		19.7 - 560.3	37.5 - 139.1	13.9 - 78.2	6.8 - 85.3		13.6 - 31.5	Oueslati et al. 2010
Korba lagoon	Tunisia (NE)	0.5 - 5.2		79 - 214	30 - 135	12 - 48	30 - 99	0 - 8	54 - 101	Bouden et al. 2004
Venice lagoon	Italy	0.4 - 1.1	12646 - 16128	48.3 - 95.7	5.2 - 7.7	4.4 - 21.7	36.6 - 64.9	0.2 - 0.94	0.2 - 15	Rigollet et al. 2004
Thau lagoon	France	0.5 - 1.5	4613 - 8058	23.8 - 51.5	8.2 - 20.9	12.2 - 27.2	13.3 - 38.2	0.21 - 0.47	4.91 - 14.6	Rigollet et al. 2004
the Homa Lagoon	Turkey	1.2 - 4.2	17054 - 30234	46.2 - 91.9	2.43 - 17.2	10.3 - 25.8	83.9 - 129	0.06 - 0.19	58.1 - 108	Uluturhan et al. 2011

Fe concentrations showed no significant variations among sites. The amount of Zn, Cu, Cr and Cd was higher on the eastern side. This increase was more pronounced for Pb and Ni.

The highest metal concentrations were found on the east side of the lagoon as a result of metal-containing wastewater discharges from the urban complex in the watershed. The highest mean values of Zn, Pb, Cr and Ni were found at site S-12, and the highest mean values of Cu were found at site S-10. The sediments from the inner channel of Rades (S-1) had the lowest mean metal concentrations.

To assess the state of contamination of metals in surface sediments in the South Lagoon of Tunis, total mean metal concentrations were compared with those in the North Lagoon of Tunis and those before the restoration project (Table 3). The mean concentrations of total trace metals of our sediments were compared with those of other areas. Unlike the mean concentrations of Ni, which remained high, those of Zn (148.5 $\mu\text{g/g}$), Pb (102.2 $\mu\text{g/g}$), Cu (27.3 $\mu\text{g/g}$), Cr (99.8 $\mu\text{g/g}$) and Cd (1.5 $\mu\text{g/g}$) are lower than those measured before the restoration project, as reported by Ben Souissi et al. (1999). The overall average concentrations of metals in surface

sediments of the lagoon were below or close to the average contents recorded before the restoration project.

The comparison of metal concentrations in the South Lagoon of Tunis with those in other Mediterranean lagoons reveals that the Tunisian lagoons (South Lagoon of Tunis, Ghar el Melh and Korba) (Table 4) have a generally high level of metals because of the rudimentary sanitary network and the overlap of industrial and domestic wastewater discharged into the lagoons. However, the Ni content in the South Lagoon of Tunis is lower than that in the Thau lagoon and the Homa Lagoon. Otherwise, concentrations of TOC are quite similar.

Granulometry, physico-chemical parameters and organic matter content are important factors that influence the geochemical behaviours of heavy metals in sediments. In order to reveal possible associations between these variables, Pearson's correlation was performed. The correlation coefficient matrix is presented in Table 5.

A significant positive correlation was observed for Zn, Pb, Cr, Cu, and Ni (taken in pairs), indicating that these metals are associated with each other and may have similar natural or anthropogenic sources and are

Table 5. – Pearson correlation coefficient matrix for heavy metals and physico-chemical parameters in surface sediments from the South Lagoon of Tunis.

Variables	Silty fraction	Sandy fraction	pH	Eh	TOC	CaCO ₃	Fe	Zn	Pb	Cu	Cr	Cd	Ni
Silty fraction	1	-1	-0.73	0.60	0.24	-0.61	-0.12	0.24	-0.11	-0.25	0.21	-0.38	-0.19
Sandy fraction		1	0.73	-0.60	-0.24	0.61	0.12	-0.24	0.11	0.25	-0.21	0.38	0.19
pH			1	-0.86	0.25	-0.01	0.65	0.41	0.63	0.57	0.29	0.18	0.80
Eh				1	-0.39	0.25	-0.64	-0.16	-0.46	-0.85	-0.14	-0.14	-0.79
TOC					1	-0.56	0.13	0.49	0.78	0.75	0.84	0.45	0.61
CaCO ₃						1	-0.60	-0.52	-0.29	-0.45	-0.34	0.47	-0.58
Fe							1	0.59	0.35	0.37	0.10	-0.57	0.82
Zn								1	0.79	0.14	0.77	-0.17	0.72
Pb									1	0.54	0.92	0.42	0.78
Cu										1	0.39	0.35	0.72
Cr											1	0.44	0.56
Cd												1	-0.05
Ni													1

governed by the same process. This strong correlation between Cu, Pb, Zn, Ni and Cr was also reported in the literature for other urbanized and polluted areas (Ruiz 2001, Spencer 2002, Muniz et al. 2003, Baptista Neto et al. 2006). However, Cd showed a low correlation, proving that it has different metal sources. The strong positive correlations between metals and TOC suggest that Pb, Cu, Cr and Ni contents increase with the rise of the amount of organic matter in the sediments. As demonstrated by Horowitz and Elric 1987, Book and Moore 1988, Stone and Droppo 1996, Murray et al. 1999 and Li et al. 2001, organic matter is an important carrier of metallic trace elements in sediments.

Chemical speciation

In sediments, metallic trace elements exist in several different forms and are associated with a range of components (Cottenie et al. 1979). It is recognized that information about the physico-chemical forms of each element is necessary to understand their environmental behaviour (mobility, pathways and bioavailability) (Bernhard et al. 1986).

In this study, the distributions of different fractions of heavy metals in surface sediments of the South Lagoon of Tunis are presented in Figure 2.

In the sediment of the South Lagoon of Tunis, Fe was almost entirely extracted in the residual phase (more than 90%) followed by the organic matter-sulphide phase. The other phases were negligible or even absent. Chemical speciation of lead revealed its predominant association with the Fe and Mn oxide fractions and to a lesser extent with organic matter and/or sulphides. The residual fraction also played a less important role in lead sorption. More than 40% of Zn was concentrated in the Fe and Mn oxide fraction. From S-1 to S-12, the Zn percentage associated with a residual fraction (F5) decreased slightly at the expense of the organic matter fraction.

The Cu distribution showed a marked association with the organic phase, with contents as high as 65% at S8, at the expense of the carbonate phase and the phase linked to the oxyhydroxide of Fe and Mn. The greatest proportion of Cu was mainly related to the organic matter-sulphide fraction, particularly at S-8, followed by the residual fraction. The exchangeable fraction was relatively negligible. Cr and Ni were combined preferentially with the residual fraction and, to a lesser extent, with organic matter and/or sulphides and Fe/Mn oxides. The other phases (the exchangeable fraction and the fraction linked to carbonates) were negligible. Cd was essentially associated with the Fe/Mn oxy-hydroxides fraction. Cadmium showed a high distribution linked to carbonates in comparison with other metals. Furthermore, the organic matter-sulphide fraction was negligible in comparison with the other fractions (exchangeable fraction, Fe/Mn oxy-hydroxides fraction and residual fraction), except at S-8.

Generally, the highest proportion of extractable metals is found in sediments with a high clay and silt content. Measuring the total content of metals is a fundamental method for sediment quality assessment. However, to further understand the potential mobility, bioavailability and toxicity of heavy metals in sediments, metal fractionation occurring in different geochemical forms is of crucial importance. Trace elements in the different geochemical phases are characterized by different mobility, migration ability and chemical behaviour. Therefore, the sequential extraction procedure was proposed to obtain information about the ways associating metal with sediments (Wang et al. 2015).

Through chemical fractionation, it was possible to determine that metals bound mainly to the residual fraction indicate no environmental risk, and that those predominantly associated with the mobile fractions (exchangeable fraction + carbonates + iron-manganese

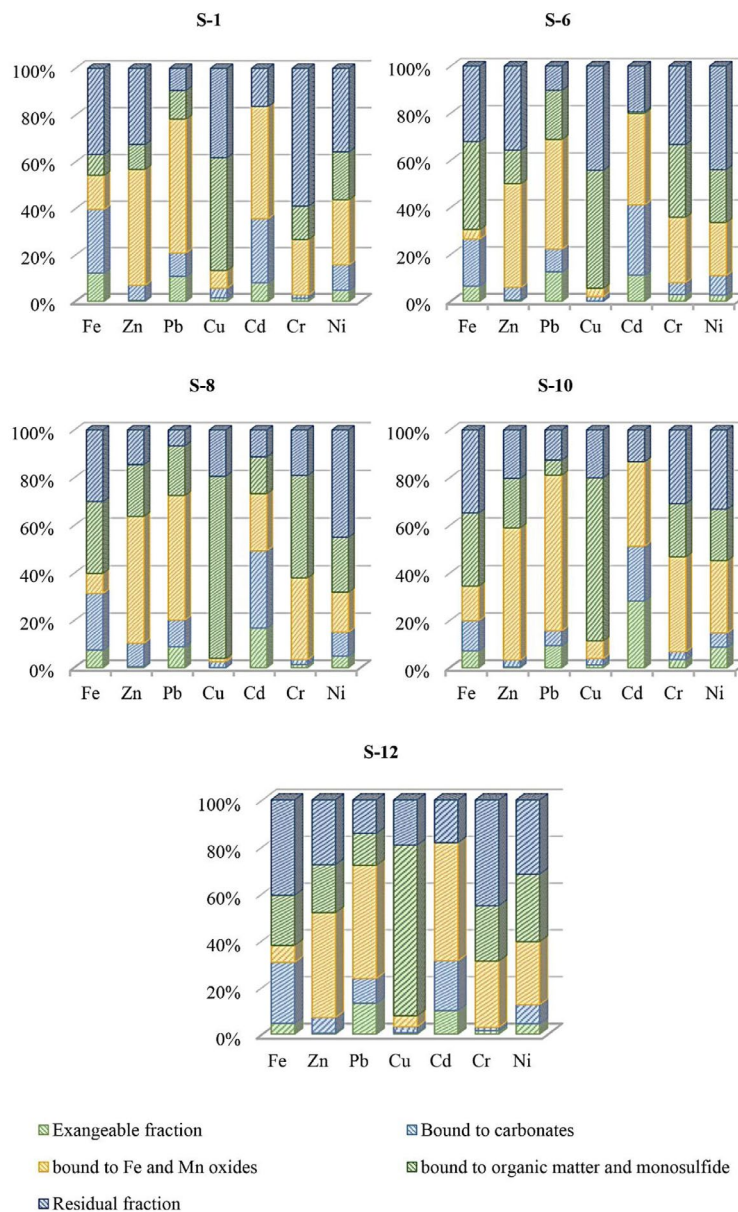


Fig. 2. – The percentage of heavy metals fractionation in surface sediment of the South Lagoon of Tunis.

oxyhydroxides + organic matter-sulphides) show anthropogenic influences.

The “exchangeable fraction + carbonates fraction” forms the acid-soluble fraction. The first two fractions have the weakest bond to sediments and become, which makes them the most mobile. The higher the metal content is in this fraction, the easier their extraction will be and the more bioavailable they become; hence they involve a high risk to the environment.

Among the studied metals, the relative proportions of metals in the acid-soluble fraction were generally low (Fe 29.7%, Pb 20.6%, Zn 6.7%, Cr 41.8% and Ni 13.8%), except for Cd. The contents of acid-soluble Cd on average (41.8%) were higher than those of other Cd fractions. It is distributed more as iron and manganese oxide forms (reducible forms) and as carbonates. Obviously, metal re-

moval required strong acid conditions; hence their poor association with the carbonate and exchangeable phases. Exchangeable species play a minor role in metal fixation in the lagoon sediments. They are usually related to the adsorbed metals on the sediment surface that can be easily remobilized into the lagoon water.

Fe/Mn oxyhydroxides, or the reducible fraction, was the most abundant fraction. Zn (49.6%), Pb (54%), Cr (31%), Cd (39.3%) and Ni (25%) were largely associated with the Fe/Mn oxyhydroxides (reducible forms). They are excellent trace element scavengers (Jenne 1968, Oakley et al. 1981). However, metal-Fe/Mn oxyhydroxides can be mobilized under anoxic conditions (Tessier and Campbell 1987).

The percentage of Cu bound to the organic matter fraction (the oxidizable fraction) was more higher than

Table. 6 – Calculated values of Igeo index, Enrichment factor and Sediment Pollution Index.

Samples	S 1	S 6	S 8	S 10	S 12	
Igeo	Fe	0.11	0.05	0.20	0.23	0.20
	Pb	0.14	0.64	0.76	0.50	1.23
	Zn	-0.55	-0.69	-0.53	-0.46	-0.11
	Cu	0.75	1.07	1.08	1.10	1.05
	Cr	-0.40	-0.21	-0.33	-0.32	1.50
	Cd	0.36	0.92	0.68	0.24	0.66
	Ni	5.74	5.93	6.31	6.30	6.44
EF	Pb	1.02	1.51	1.47	1.21	2.04
	Zn	0.63	0.60	0.60	0.62	0.81
	Cu	1.55	2.03	1.84	1.83	1.80
	Cr	0.70	0.84	0.69	0.68	0.87
	Cd	1.0	1.55	1.17	0.85	1.16
SPI	Ni	1.61	1.92	2.25	2.19	2.45
		1.65	1.92	2.02	1.90	2.29

that of other metals bound to this fraction, with a range of 31%. According to Li et al. (2001), copper tends to form stable complexes with organic matter.

Under oxidizing conditions, metals present in both natural organic matter (due to complexation) and living organisms (as a result of bioaccumulation of metals) may be remobilized into the aquatic environment. The results obtained show that most of the Ni and Fe in all the sediments was strongly retained in the residual fraction. Their average percentage in this fraction was 37.9% and 34.8%, respectively. These facts indicate that these metals are strongly bound in the crystal lattices of minerals and, consequently, they have relatively low mobility, bioavailability and toxicity (Wang et al. 2015). Copper exists mostly as oxidizable species and also as iron and manganese oxide forms (reducible forms).

Contamination assessment

In order to evaluate sediment pollution in the lagoon, the geo-accumulation index (Igeo) and the EF were calculated using total concentrations of metals (Table 6).

The results of calculating the geo-accumulation index in the sediments of the lagoon show that Zn and Cr did not reflect any pollution, with an Igeo of between -0.69 and -0.11. For Fe, Pb, Cu and Cd, the Igeo indicated slight pollution. The lagoon sediments showed strong Ni pollution. The highest values were recorded west of S-12. The Igeo results show that lagoon sediment pollution by Ni was the most acute, while it was moderate for Cu. The Igeo calculated for Fe, Pb and Cd showed uncontaminated to moderately contaminated sediments, while those calculated for the other metals (Zn and Cr) were uncontaminated. EF values for Zn, Cr, Fe, Cd and Pb ranged from 0 to 2.5, indicating

moderate contamination. However, for Ni and Cu, the sediments of the lagoon were considerably contaminated. The highest EF values characterized C12 sediments. The EF values showed no enrichment of Zn and Cr to minor enrichment of Pb, Cu, Cd and Ni. The highest values were recorded at S12.

The sediment pollution index values demonstrate that the sediments of the lagoon are slightly polluted (SPI <5), except for the S-12 sediments, which have strong indices of sediment pollution.

However, only the mobilizable fractions (i.e. exchangeable species, carbonate bound metals, Fe/Mn oxides species and organic matter-bound metals) in the sediments showed a real potential risk of water contamination caused by lagoon sediment. The remobilization of metals from sediment into the water column is influenced by pH, chemical forms of the trace elements and the physico-chemical characteristics of the

Table. 7 – Classification of individual and global contamination factors (ICF and GCF).

ICF	GCF	Risk level
$ICF_m = \sum C_{mb}/Cr$	$GCF = \sum ICF$	
Cmb: concentrations of a metal m in the mobile fractions		
Cr: the concentration of a metal m in the residual fraction		
$ICF < 1$	$GCF < 6$	low
$1 < ICF < 3$	$6 < GCF < 12$	moderate
$3 < ICF < 6$	$12 < GCF < 24$	considerable
$ICF > 6$	$GCF > 24$	high

Table. 8 – Calculated individual and global contamination factors (ICF and GCF) for surface sediment of South Lagoon of Tunis.

Samples	ICF							GCF
	Fe	Pb	Zn	Cu	Cr	Cd	Ni	
S 1	1.7	9.7	2.1	1.6	0.7	5.1	1.8	22.7
S 6	2.1	8.7	1.8	1.3	2.0	4.1	1.3	21.3
S 8	2.3	14.2	5.9	4.2	4.3	7.9	1.2	40.0
S 10	1.9	6.9	3.9	4.0	2.2	6.5	2.0	27.6
S 12	1.5	6.0	2.6	4.2	1.2	4.5	2.2	22.1

water column (Ikem et al. 2003). To estimate the risk of remobilization of metal from the sediment to the water column and to the lagoon biota, the individual contamination factor (ICF) and the global contamination factor (GCF) were calculated as shown by Ikem et al. (2003) and Zhao et al. (2012) (Tables 7 and 8). The factor calculation shows that the lagoon sediments had a high ICF for Pb (ICF: 6–14) and Cd (ICF: 4.1 to 7.9), a moderate ICF for Ni (1.3 to 2), Cu (1.3 to 4.2), Zn (1.8 to 5.9) and Fe (1.5 to 2.3) and a low ICF for Cr (0.7 to 4.3). Surface sediments showed a considerable to high global risk with a GCF varying from 21.3 to 40.

DISCUSSION

In terms of grain size, pH and Eh values, the sediments of the lagoon showed two different sides. The east side consisted of sandy silt rich in shell debris and less anoxic, whereas the western side consisted of anoxic silty sediment and was almost homogenous.

For TOC, the lowest values were recorded on the eastern side of the lagoon. In this sector, these TOC contents are mainly of marine origin. When the organic matter is deposited on the bottom, it undergoes “mixing processes” at the water-sediment interface and microbial degradation. The west sector showed the highest value of TOC. This side of the lagoon is a shallow relatively calm area (Abidi et al. 2019), which facilitates the accumulation of organic matter. Hence, the organic carbon accumulation is partly attributed to the discharge of industrial and urban wastewater on the west side of the lagoon. The values obtained for organic carbon were lower than those given before the restoration project (ranging from 1.90% to 10.39%) (Ouertani et al. 2006). The decrease in organic content can be attributed to dredging.

The distribution of elements is consistent with the prevailing water direction (most often east to west). Furthermore, the lowest values of trace metals measured in the east near to the channel of Rades were probably due to the re-suspension affecting the seabed of the lagoon. Because of the fine size of the sediment particles at the study site (Abidi et al. 2019), it appears that re-suspension affecting the seabed is not ruled out and is even very likely near the channel where the strongest currents are observed (Kochlef 2003).

Comparing the values found in the present study with those of the contents recorded in the sediments of the northern lagoon of Tunis (known as Lac de Tunis),

which also underwent development works in 1981, we noticed that the South Lagoon had higher levels of trace elements arising from the various liquid inflows from the industrial zones installed in the surrounding area (of the South Lagoon).

The study of the distribution of metals in the lagoon sediments showed that Fe, Cu and Ni exist largely in the sedimentary matrix (residual phase) and in the iron and manganese oxide phases (reducible species). The residual phase represents metals embedded in the crystal lattice of the sediment fraction that are not available for remobilization, except under very harsh conditions.

In the lagoon sediments, the metals were mainly bound to the non-residual fraction, suggesting an anthropogenic input. They are mainly accumulated by precipitation and co-precipitation mechanisms with Fe/Mn oxyhydroxides and organic matter (Li et al. 2001).

The calculation of contamination indices reveals that the western sector of the lagoon is contaminated and more polluted. On the other hand, the eastern sediments show metal levels close to natural values. It is clear that zinc and chromium do not involve a risk of contamination. Samples 8 and 12 generally had higher individual and global contamination factors than the other samples. The high trend for sites 1 and 2 may be attributed to the hydrodynamic conditions. The ICF values involve a low risk for Cr, a moderate risk for Ni, Cu, Zn and Fe, and a high risk for Pb and Cd. The GCF involves a considerable to high risk for the surface sediment samples.

CONCLUSION

This study supports the integrative approach as a powerful tool for scientifically diagnosing the pollution status of coastal sediment in a complex environment for management decisions. A variety of tools, guidelines, indices and approaches (sequential extraction, geochemical normalization and multivariate statistical analysis) were employed to evaluate sediment contamination in the South Lagoon of Tunis.

Chemical speciation of surface sediment shows that oxyhydroxides of Fe/Mn and organic matter constitute the main carrier fractions for all metals. However, in the case of Fe and Ni, the residual fraction is the major carrier fraction. Metal speciation analysis also suggested a high levels of non-residual fractions of Pb, Zn, Cu, Cr and Cd. The sediment of the lagoon can generally reflect increasing anthropogenic inputs, because most

anthropogenic metals are loosely bound to mineral or organic matters in sediment in the form of non-residual fractions. This assumption is supported by the ICF results, which clearly show that bioavailability affects especially Pb, Zn and Cd.

Despite the restoration works (dredging and improved marine flushing), the levels of some metals in the surface sediments remain relatively high. Chemical speciation confirms that these elements are weakly sequestered in the sediment and are potentially toxic for lagoon organisms and towards marine in the Gulf of Tunis. Therefore, in view of the continuous pollutant input, the sediment quality should be monitored in the long term to protect the environment of this urban area.

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