

# ASSESSMENT OF TRACE ELEMENTS IN SURFACE SEDIMENTS FROM HAMMAMET GULF, TUNISIA (MEDITERRANEAN SEA)

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## ملخص

**تقييم عناصر المعادن في الرواسب السطحية من خليج الحمامات (تونس، البحر المتوسط) :** تشكل المعادن الموجودة في الرواسب مصدرا هاما للتلوث البيئي. هذه الدراسة اهتمت بتقييم المعادن الثقيلة في الرواسب السطحية من خليج الحمامات (تونس) وذلك بغية تحديد مستوياتها والتوزيع الجغرافي في علاقة بالتطور العمراني والتنمية الاقتصادية في هذه المنطقة. في اطار هذه الدراسة جلبت العينات من عشرون نقطة منتشرة على كامل الخليج ، بهدف تحليل المعادن فيها باعتماد تقنية الامتصاص الذري . التركيزات المقاسة في الرواسب تتراوح كالتالي: 0,19-1,86 مغ / كغ Cd ، 2,150-47,6 مغ / كغ Pb ، 0,23-1,80 مغ / كغ Hg ، 1,80-30,42 مغ / كغ Cu ، 713-287 مغ / كغ Zn ، 26-3 غ / كغ Fe ، 374-86 مغ / كغ Mn ، 18-11 غ / كغ Mg ، 61-160 غ / كغ Na ، 4-19 غ / كغ K . أظهرت النتائج ارتباطاً هاماً بين Cu و Pb و Zn ، مما يشير إلى أنها ناتجة عن مصادر بشرية وعوامل طبيعية ونفايات أنشطة اقتصادية. يوضح التوزيع الجغرافي للمعادن بخليج الحمامات أن مستوى التلوث بمعندين Zn ، Pb مرتفعة نسبيا في الوسط والجنوب الشرقي للخليج وهو ناتج أساسا عن كثافة الأنشطة البتروكيميائية. مقارنة بتركيزات هذه المعادن في الخليج مماثلة للمستويات المسجلة في مختلف النظم البيئية الأخرى في البحر المتوسط. على ضوء هذه الدراسة يجدر التأكيد على أهمية وضع وتنفيذ برنامج مراقبة مستمرة لمستوى تلوث الخليج بهذه المعادن نظرا لقابلية بلوغها الى مستويات هامة نتيجة التطور الملحوظ للأنشطة الصناعية على ضفاف الخليج.

**كلمات المفاتيح:** التلوث ، خليج الحمامات، الرواسب البحرية، المعادن الثقيلة

## RESUME

**Évaluation des éléments de trace dans les sédiments de surface du golfe du Hammamet (Tunisie, mer Méditerranée) :** Les métaux dans les sédiments constituent une source importante de pollution de l'environnement marin. Les métaux traces et les oligo-éléments dans les sédiments de surface du golfe de Hammamet (Tunisie) ont été évalués afin de déterminer leurs niveaux et leur distribution spatiale en raison de l'urbanisation, du développement économique et touristique de cette région. Vingt stations ont été prospectées et les échantillons de sédiments recueillis ont été analysés par Spectrophotométrie d'Absorption Atomique (SAA). Les fourchettes des concentrations mesurées dans les sédiments étaient les suivantes: 0,19-1,86 mg.kg<sup>-1</sup> pour le cadmium, 47,6-150,2 mg.kg<sup>-1</sup> pour le plomb, 0,23-0,46 mg.kg<sup>-1</sup> pour le mercure, 1,80-30,42 mg.kg<sup>-1</sup> pour le cuivre, 287 -713 mg.kg<sup>-1</sup> pour Zn, 3-26 g.kg<sup>-1</sup> pour Fe, 86-374 mg.kg<sup>-1</sup> pour Mn, 11-18 g.kg<sup>-1</sup> pour Mg, 61-160 g.kg<sup>-1</sup> pour Na, 8-109 g.kg<sup>-1</sup> pour le Ca, 4-19 g.kg<sup>-1</sup> pour K.

Les résultats ont montré une corrélation significative entre Cu, Pb et Zn, indiquant qu'ils y avaient des sources anthropiques et naturelles communes. La distribution spatiale des métaux dans les sédiments du golfe de Hammamet montre que le niveau de métaux dans les parties centrale et sud-est du golfe est relativement élevé pour certains métaux (à savoir le Pb, le Zn). Cette contamination dépend principalement de sources anthropiques et d'activités pétrochimiques. Les concentrations de métaux en traces dans la zone étudiée étaient comparables aux niveaux enregistrés dans différents autres écosystèmes méditerranéens. Une surveillance constante doit être menée car le niveau de métaux lourds peut augmenter avec l'implantation d'industries dans le golfe de Hammamet.

**Mots Clés :** Contaminant, Golfe de Hammamet, Sédiments marins, Métaux traces.

## ABSTRACT

Metals in sediment constitute a significant source of environmental pollution. Trace metals and oligo-elements in surface sediments from Hammamet gulf (Tunisia) were assessed in order to evaluate their levels and spatial distribution due to urbanization, economic and touristic development of this region. Twenty stations were prospected and the collected sediment samples were analyzed by Atomic Absorption Spectrophotometry. The ranges of the measured concentrations in the sediments were as follows: 0.19-1.86 mg.kg<sup>-1</sup> for Cd, 47.6-150.2 mg.kg<sup>-1</sup> for Pb, 0.23-0.46 mg.kg<sup>-1</sup> for Hg, 1.80-30.42 mg.kg<sup>-1</sup> for Cu, 287-713 mgkg<sup>-1</sup> for Zn, 3-26 gkg<sup>-1</sup> for Fe, 86-374 mgkg<sup>-1</sup> for Mn, 11-18 gkg<sup>-1</sup> for Mg, 61-160 g.kg<sup>-1</sup> for Na, 8-109 g.kg<sup>-1</sup> for Ca, 4-19 g.kg<sup>-1</sup> for K. The results showed significant correlation between Cu, Pb and Zn, indicating that they have common anthropogenic

and natural sources. The spatial distribution of metals in sediments of Hammamet gulf shows that the level of metals in the central and south eastern parts of the gulf is relatively high by some metals (i.e. Pb, Zn). This contamination is depending mainly on anthropogenic sources and petrochemical activities. Concentrations of trace metals in the studied area was comparable to the levels recorded in different other Mediterranean ecosystems. A constant monitoring should be conducted since the level of heavy metals may increase as industries are established in Hammamet Gulf.

**Keywords:** Contaminant, Hammamet Gulf, Marine Sediments, Heavy metals.

## INTRODUCTION

Due to their environmental persistence and biogeochemical cycles and ecological risks, metals are of particular concern worldwide (Liu et al., 2003; Gonzalez-Marcias et al., 2006). Marine sediments have often been regarded as the ultimate reservoir for trace metals in the coastal environment (Sin et al., 2001; Hong Kong, 2006; Petronio et al., 2012). Trace metals are stable and persistent environmental contaminants since they cannot be biodegraded or destroyed. Therefore, they tend to accumulate in the soils and sediments. Excessive levels of metals in sediments affect marine biota and pose risk to human health through the consumption of seafood (Mucha et al., 2003; Zhang et al., 2007). Sediments analysis play a crucial role in assessing the degree of trace metal pollution and the resulting health risk associated with the food chain.

The spatial distribution of trace metals in marine sediments is of major importance in clarifying the pollution history of aquatic systems (Birch et al., 2001; Rubio et al., 2001; Ajibola and Ladipo, 2011; Amano et al., 2011) and assessing the degree of contamination and the resulting impact on the food chain (Baby et al., 2010; Osasona et al., 2011). Thus, sediments are the main repository and source of trace metals in the marine environment and play an important role in the transport and storage of potentially hazardous metals (Guevara et al., 2005; Diaz et al., 2011).

With the rapid industrialization, touristic and economic development in Hammamet region, in addition to run-off during rainy periods, ship and boat traffic, oil transportation, oil spillage and atmospheric fallout, trace metals are continuing to be introduced to estuarine and coastal environment through rivers. When metals enter into the marine environment, most of them will settle down and be incorporated into sediments (O'Connor et al., 2009).

The Gulf of Hammamet is a large gulf situated in northeastern Tunisia and occupied a privilege position (Ben Romdhane et al., 2006) between two basins Occidental and Oriental Mediterranean Sea. Its coast joins Cap RasMaamour (Extreme north of Cap Bon) to Mahdia (Figure 1). It's formed by many sandy beaches separated by rockies points. The mainly important river is OuedHamdoun which diverse water in the Gulf of Hammamet and represents the main source of contamination of this

area. The intense urban, industrial and tourist activities are considered as sources of inorganic, organic and bacterium pollution in the Gulf. However, quantitative studies related to pollution and assessment of metal concentrations in the sediments of the gulf of Hammamet area are very few (Patriata et al., 2003; Mahjoub et al., 2009).

The main objective of this study was to identify the dispersion pathways and repository areas of natural and anthropogenic inputs through a large-scale mapping of the geochemical properties in surficial sediments of the Gulf of Hammamet. The elements investigated are metals and oligo-elements (Cd, Pb, Hg, Cu, Zn, Fe, Mn, Ca, Mg, Na and K); total organic carbon [TOC] and carbonate contents were also considered in order to improve the understanding of geochemical and sedimentological factors that likely control the elemental distributions.

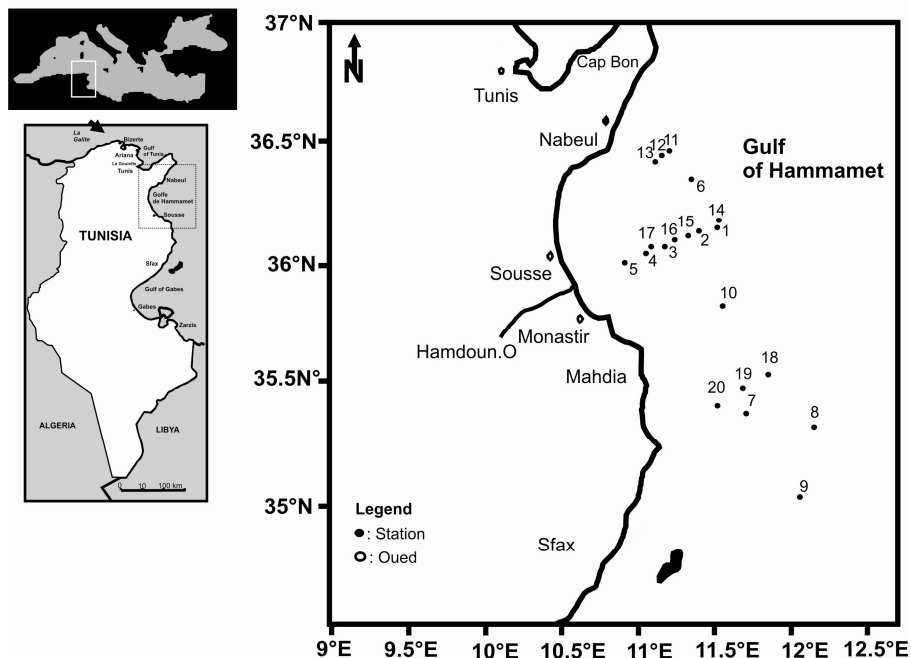
## MATERIALS AND METHODS

Sediment samples from the gulf of Hammamet were collected using a research boat «Hannibal» (vessel of Institut National des Sciences et Techniques de la Mer, Tunisia) during 2008. Sampling stations (n=20) were chosen to provide a good area coverage (Figure 1). Sampling depth ranged from 45 m to 215 m. Surface sediments were collected by a Van Veen grab (surface area is about 0.1 m<sup>2</sup>) whose penetration was typically 10-20 cm. For sampling, we selected only the uppermost of sediment with plastic spoon and transferred to polyethylene bags. Sediments were stored immediately in a freezer (-20 °C) until analysis.

Following freezing, samples were lyophilized and sieved through vibrating stainless sieves with mesh sizes of 2 mm to 63 µm. The fine fraction (<63 µm) was collected and analyzed. This fraction of sediments was used because it contains higher concentrations of mineral elements than the sand fraction. In fact, metals are most often associated with small grains (Morillo et al., 2004) and traditionally, the fine-grained fraction of the sediment has been used to examine metal contamination in sediment. The clay fraction is known to be the most important substrate for metal attachment and metal concentrations tend to increase from sand to silt. Authors reported that metal adsorption capacity was in the order of sand<silt<clay, due to increases in surface areas.

Total Organic Carbon (TOC) and total nitrogen (TN) were determined in these sediment samples by means of a CHNS elemental analyzer. The subsamples for TOC were decarbonated using 1M Hydrochloric acid (HCl) and dried at 60 °C. The total element content in

sediment was determined by digesting the dried samples (0.2 g) with a mixture of concentrated nitric acid (HNO<sub>3</sub>) (5 ml) and fluorhydric acid (HF) (2 ml) in a microwave oven (Milestone model Ethos) at 1.000 W during 20 min



**Figure 1:** Study area and sampling stations in the Gulf of Hammamet (Tunisia).

After digestion samples were diluted with Milli-Q water, 0.8 g of boric acid (H<sub>3</sub>BO<sub>3</sub>) was added. For control quality, Certified Reference Material (CRM) and blanks were included in the set of samples to check the precision and accuracy of the analysis. We used a CRM marine sediment IAEA-405

(International Atomic Energy Agency, Monaco). Analytical results indicate a good agreement between the certified and measured values and metals recovery (95%) being practically complete for most them (Table I).

**Table I:** Mean and standard deviation (mgKg<sup>-1</sup>) of data for reference material (IAEA 405).

| Element   | Certified value | Measured value |
|-----------|-----------------|----------------|
| <b>Cd</b> | 0.73 ± 0.05     | 0.78 ± 0.11    |
| <b>Pb</b> | 74.8 ± 2.2      | 74.59 ± 5.38   |
| <b>Hg</b> | 0.81 ± 0.04     | 0.82 ± 0.07    |
| <b>Cu</b> | 47.7 ± 1.2      | 46.51 ± 6      |
| <b>Zn</b> | 279 ± 7         | 275 ± 20       |
| <b>Fe</b> | 37400 ± 700     | 37045 ± 1645   |
| <b>Mn</b> | 495 ± 11        | 486 ± 65       |
| <b>Mg</b> | 12300 ± 900     | 11552 ± 1557   |
| <b>Ca</b> | 20833 ± 4067    | 23643 ± 5302   |
| <b>Na</b> | 17540 ± 3551    | 20320 ± 4360   |
| <b>K</b>  | 24900 ± 7200    | 23778 ± 3955   |

The concentrations of Cd, Pb and Cu were determined by atomic absorption spectrophotometry (AAS) with graphite furnace with Zeeman correction (Varian 220 Z). Fe, Zn, Mg, Mn, K, Na and Ca were measured by the flame AAS (Varian AA-10) equipped with an air-acetylene flame (acetylene flow 1.5 l min<sup>-1</sup>). For the determination of

total mercury, the technique of cold vapor was used, employing a flow injection vapour generator (VGA-77) system, coupled to a spectrophotometer (Varian AA 10) using a reducing solution of SnCl<sub>2</sub> in HCl. All results were used for the establishment of spatial distribution maps of the elements in surface sediments with the Surfer software package.

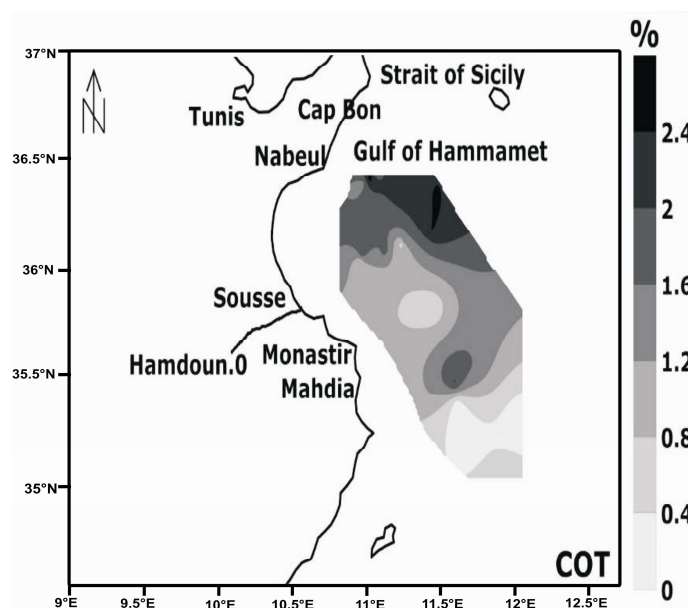
Statistical analysis of data and the Principal Component Analysis (PCA) were used to 20 samples studied in order to understand the distribution modes of the different elements and discriminate the different sources of input. Data reported in this study are calculated as dry weight.

## RESULTS

The average and range of TOC are  $1.43 \pm 0.75$  and 0.06-2.71%. For TN, a concentration of 0.01% in the

fine particle was found. TOC showed a similar spatial distribution (Figure 2).

The percentage of fine grain size ( $63 \mu\text{m}$ ) in the different stations forming more than 50% of the sediment was found in most stations. The distribution is slightly associated with the areas bathymetry and geomorphology and it's controlled by the physical transport of sediment. The sediments were dominated by sand fractions, extending from the large of Mahdia (>70%).



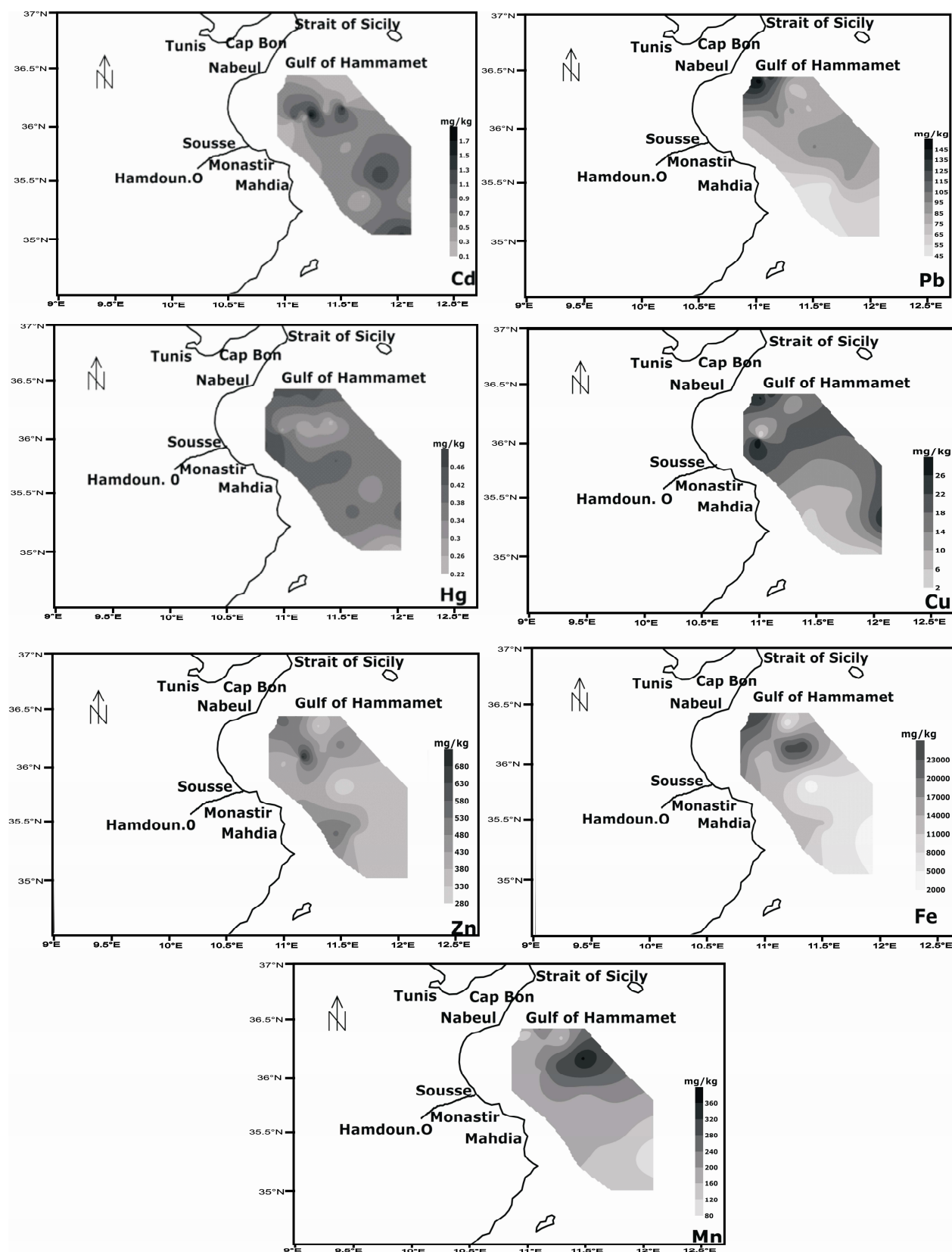
**Figure 2:** Spatial distribution of total organic carbon contents (TOC) (%) in surficial sediments of the Gulf of Hammamet Tunisia (Mediterranean Sea).

The distribution of global mean concentrations of trace metals (Cd, Pb, Hg) and oligo-elements (Mg, Ca, Na, K, Cu, Zn, Fe and Mn) in the surface sediments collected from different stations in the Gulf of Hammamet appear in Figures 3 and 4. Figures 3 and 4 indicate that all elements are subject to a wide variability and heterogeneous spatial distribution, up to  $713 \text{ mg.Kg}^{-1}$  of Zn,  $26100 \text{ mg.Kg}^{-1}$  of Fe,  $30.4 \text{ mg.Kg}^{-1}$  of Cu,  $150.2 \text{ mg.Kg}^{-1}$  of Pb,  $1.86 \text{ mg.Kg}^{-1}$  of Cd and  $374 \text{ mg.Kg}^{-1}$  of Mn.

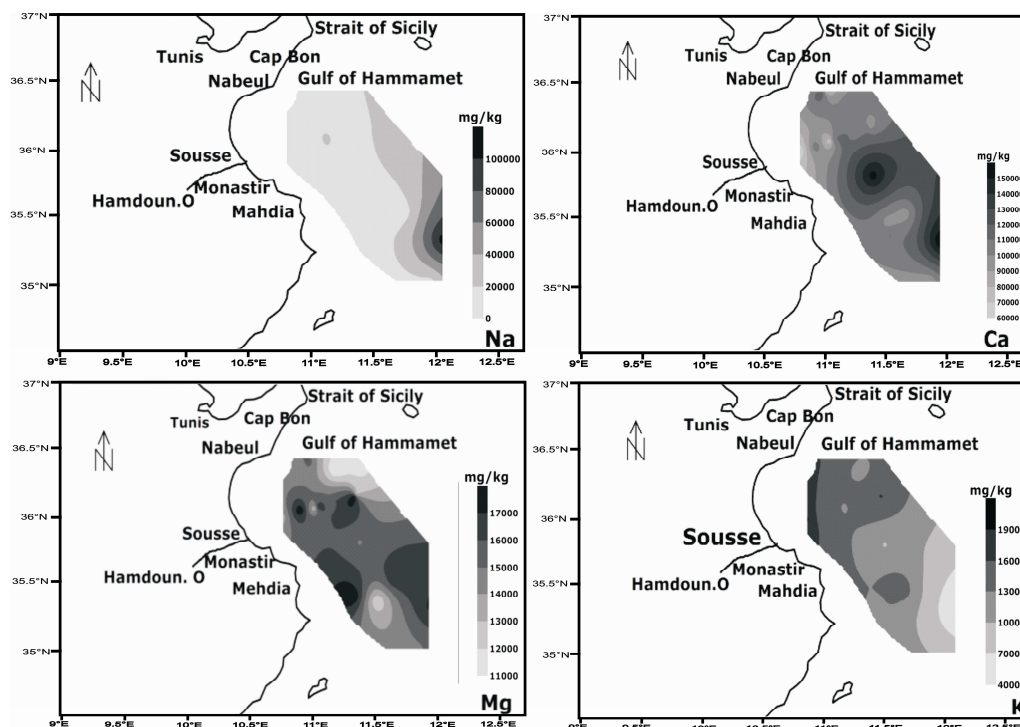
The elements such as Ca, Mg, K and Hg present generally a same repartition in the gulf. Their levels increased specifically in stations 4, 5 and 12; it is scarcely influenced by coastal anthropogenic sources (Oued Hamdoun river). Distribution of Na is

particularly; its concentration increased in the south east of the gulf (Figure 4). The Na concentrations varied from  $7673$  to  $109435 \text{ mg.Kg}^{-1}$  with an average of  $18714 \text{ mg.Kg}^{-1}$ .

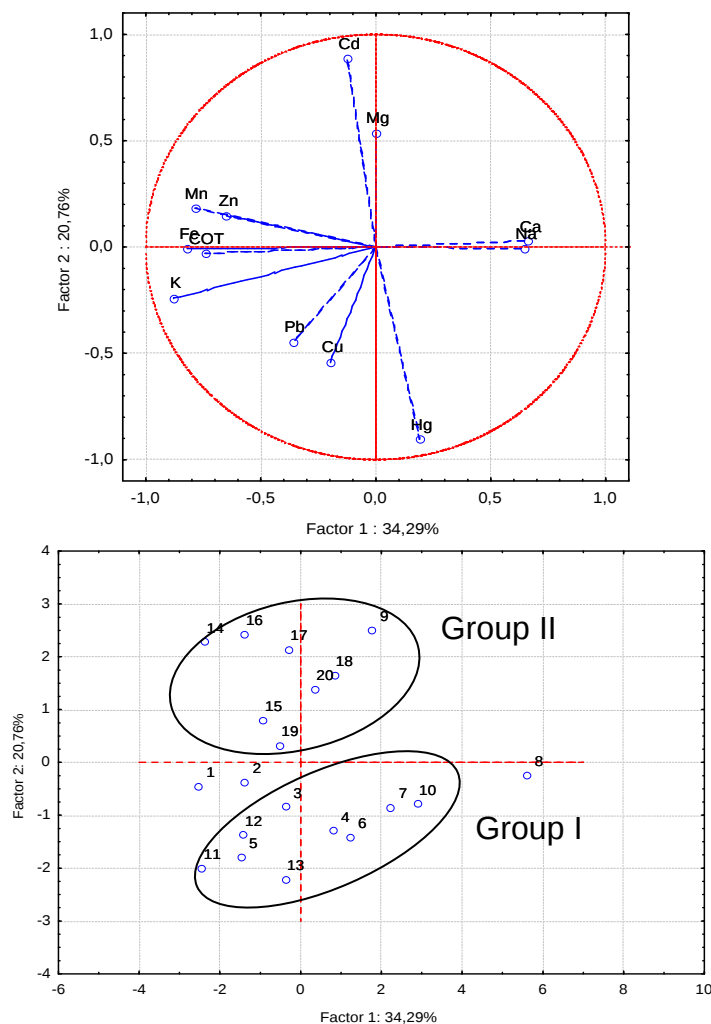
The two principal components analysis (PCA) represented 55.02% of the total variance (Figure 5). Loading of variables on the first two principal components showed that Zn, Mn, Fe, K and TOC accounted for almost 34.3% of the variability. They were the dominant variables on PC1, while Cd, Cu and Pb were the dominant variables on PC2 (Figure 5; Table II). The second factor (PC2) associated with Hg, Pb and Cu negatively and positively with Cd and Mg, accounted for 20.8% of the variance (Table II).



**Figure 3:** Spatial distribution of Cd, Pb, Hg, Cu; Zn, Mn and Fe contents ( $\text{mg} \cdot \text{Kg}^{-1}$ ) in the less than 63 µm surficial sediment fraction in the Gulf of Hammamet (Tunisia).



**Figure 4:** Spatial distribution of Na, Mg, Ca and K contents in the less than 63 µm surficial sediment fractions in the Gulf of Hammamet (Tunisia).



**Figure 5:** Principal Component Analysis (PCA) for trace metals and total organic carbon in Hammamet Gulf (Tunisia).

**Table II:** Results of PCA applied to metals and TOC concentrations.

| <b>Variables</b> | <b>PC 1</b> | <b>PC 2</b> |
|------------------|-------------|-------------|
| <b>Cd</b>        | -0.13       | 0.88        |
| <b>Pb</b>        | -0.36       | -0.44       |
| <b>Hg</b>        | 0.19        | -0.90       |
| <b>Cu</b>        | -0.20       | -0.54       |
| <b>Zn</b>        | -0.65       | 0.15        |
| <b>Fe</b>        | -0.82       | 0           |
| <b>Mn</b>        | -0.78       | 0.18        |
| <b>Mg</b>        | 0           | 0.54        |
| <b>Ca</b>        | 0.66        | 0.03        |
| <b>Na</b>        | 0.64        | 0           |
| <b>K</b>         | -0.88       | -0.24       |
| <b>TOC</b>       | -0.74       | -0.02       |

The resultsshowed that the identification clustered two main groups showing an evident difference of heavy metal distribution patterns (Figure 5) resulted from discharges of oil transport boats, gas and petroleum from offshore stations (Tazarka oil platform) in the Northern part of the area.

Group I is formed by nine stations representing a strong evidence of possible impacts of anthropogenic and petrochemical industrial activities rejected by oil off shore platform and OuedHamdoun River (Middle of Hammamet gulf). The second group II contain the

stations in the southern of gulf could be related to anthropogenic activities (maritime traffic), atmospheric contamination and velocity of the current in this area (Figure 5).

Results obtained by Pearson correlation coefficient matrix between the trace elements and TOC, as well as PCA, showed that sediments sampled in the Hammamet gulf presented a significant correlation between the TOC and Fe, Zn Ca and Mn levels and between Hg/Cd; Mg/Cd and Cu/Pb (Table III).

**Table III:** Pearson correlation coefficient matrix between the trace elements and TOC in sediment of Hammamet Gulf (Tunisia).

|            | <b>Fe</b>   | <b>Zn</b>   | <b>Mg</b>   | <b>K</b>     | <b>Ca</b>   | <b>Mn</b>   | <b>Na</b>   | <b>Hg</b>    | <b>Cd</b>   | <b>Cu</b>   | <b>Pb</b>   | <b>TOC</b>  |
|------------|-------------|-------------|-------------|--------------|-------------|-------------|-------------|--------------|-------------|-------------|-------------|-------------|
| <b>Fe</b>  | <b>1.00</b> |             |             |              |             |             |             |              |             |             |             |             |
| <b>Zn</b>  | <b>0.47</b> | <b>1.00</b> |             |              |             |             |             |              |             |             |             |             |
| <b>Mg</b>  | 0.22        | 0.21        | <b>1.00</b> |              |             |             |             |              |             |             |             |             |
| <b>K</b>   | <b>0.67</b> | 0.43        | -0.21       | <b>1.00</b>  |             |             |             |              |             |             |             |             |
| <b>Ca</b>  | -0.43       | -0.24       | 0.26        | <b>-0.69</b> | <b>1.00</b> |             |             |              |             |             |             |             |
| <b>Mn</b>  | <b>0.82</b> | <b>0.45</b> | 0.08        | <b>0.57</b>  | -0.29       | <b>1.00</b> |             |              |             |             |             |             |
| <b>Na</b>  | -0.30       | -0.21       | 0.21        | <b>-0.69</b> | <b>0.60</b> | -0.36       | <b>1.00</b> |              |             |             |             |             |
| <b>Hg</b>  | -0.15       | -0.20       | -0.34       | 0.07         | 0.12        | -0.43       | 0.10        | <b>1.00</b>  |             |             |             |             |
| <b>Cd</b>  | -0.02       | 0.30        | <b>0.48</b> | -0.11        | -0.03       | 0.16        | -0.05       | <b>-0.79</b> | <b>1.00</b> |             |             |             |
| <b>Cu</b>  | 0.38        | 0.24        | 0.09        | 0.18         | 0.16        | 0.26        | 0.32        | 0.38         | -0.37       | <b>1.00</b> |             |             |
| <b>Pb</b>  | 0.17        | 0.38        | -0.02       | 0.25         | -0.06       | 0.13        | -0.20       | 0.32         | -0.12       | <b>0.50</b> | <b>1.00</b> |             |
| <b>TOC</b> | <b>0.51</b> | <b>0.47</b> | -0.04       | <b>0.61</b>  | -0.43       | <b>0.48</b> | -0.41       | -0.00        | 0.14        | 0.04        | 0.28        | <b>1.00</b> |

Concentration of metals are compared to the ERL (Effects Range-Low) and ERM (Effects Range-Median) concentration guidelines derived from the database of Long et al., (1995) to understand the extent of contamination. This database contains measured concentrations and their biological effects of estuarine and marine sediments. ERL define the chemical concentrations below which the probability of toxicity and other effects on benthic biota is minimal. Differently, the ERM value indicates a possible range in which effects would occasionally

occur. Within the interval between the two values negative effects would occur frequently.

The average and range of metals concentrations determined in sediment (Table IV) and the classification of sediment samples based on the guideline shown in Table V demonstrated that Zn and Pb were very important. The majority of the sediments may occasionally be associated with the adverse biological effects due to zinc and lead contents in the sediments.

The percentile of Cd is rarely associated with negative biological effects. Cadmium levels at all

stations except 14, 16, 18 and 9 at the large southern part of the studied area were higher than ERL values but were much lower than ERM values. However, copper levels were lower than ERL values. This suggests that the concentration range of this metal in the Hammametgulf sediment would rarely be associated with biological effects. Lead and mercury accumulated in surface layer have an anthropogenic

origin derived from industry, gasoline emissions and atmospheric contamination. Their levels were higher than ERL and lower than ERM (Table V).

If the results obtained in the present work compared with those realised in the Mediterranean Sea (Table VI), it is shown that Hammamet gulf area does not suffer from heavy metals contaminations.

**Table IV:** Average ( $\pm$  standard deviation) and range of metal concentration in the 20 surficial sediment samples of Hammamet gulf (Tunisia)

| Elément   | Moyenne (mgkg <sup>-1</sup> ) | Intervalle(mgkg <sup>-1</sup> ) |
|-----------|-------------------------------|---------------------------------|
| <b>Cd</b> | 0.67 $\pm$ 0.51               | 0.19-1.86                       |
| <b>Pb</b> | 82.8 $\pm$ 26.6               | 47.6-150.2                      |
| <b>Hg</b> | 0.36 $\pm$ 0.07               | 0.23-0.46                       |
| <b>Cu</b> | 15.81 $\pm$ 8.28              | 1.80-30.42                      |
| <b>Zn</b> | 437 $\pm$ 103                 | 287-713                         |
| <b>Fe</b> | 14064 $\pm$ 8009              | 2976-26100                      |
| <b>Mn</b> | 208 $\pm$ 73                  | 86-374                          |
| <b>Mg</b> | 15203 $\pm$ 2090              | 10973-17928                     |
| <b>Ca</b> | 104649 $\pm$ 22998            | 61148-159606                    |
| <b>Na</b> | 18714 $\pm$ 21814             | 7673-109435                     |
| <b>K</b>  | 13331 $\pm$ 3291              | 3958-19402                      |

**Table V:** ERL and ERM guide-line values for trace metals (ppm, dry weight) and percent classification of sediment samples from Hammamet gulf based on the proposed SQGs.

| Metals    | Sediment Guidelines | Quality (mgKg <sup>-1</sup> dw) |       | Percent of samples of Sediment Quality |       | amongst ranges Guidelines |
|-----------|---------------------|---------------------------------|-------|----------------------------------------|-------|---------------------------|
|           | ERL                 | ERM                             | < ERL | > ERL and <ERM                         | > ERM |                           |
| <b>Cd</b> | 1.2                 | 9.6                             | 75    | 25                                     | 0     |                           |
| <b>Pb</b> | 46.7                | 218                             | 0     | 100                                    | 0     |                           |
| <b>Hg</b> | 0.15                | 0.71                            | 0     | 100                                    | 0     |                           |
| <b>Zn</b> | 150                 | 410                             | 0     | 45                                     | 55    |                           |
| <b>Cu</b> | 34                  | 270                             | 100   | 0                                      | 0     |                           |

**Table VI:** Concentration of Cd, Pb, Hg, Cu, Zn, Fe and Mn (mg Kg<sup>-1</sup>) in marine surface sediments of different Mediterranean Gulfs.

| Location                | Cd        | Pb        | Hg        | Cu         | Zn     | Fe          | Mn | Source                 |
|-------------------------|-----------|-----------|-----------|------------|--------|-------------|----|------------------------|
| Gulf of Tunis (Tunisia) | 0.07-0.67 | 18.7-98.8 | 0.09-0.53 | 7.28-89.30 | 75-249 | 25731-47922 |    | Ennouri et al., 2010   |
| Gulf of Gabes (Tunisia) | 0.1-1.3   | 20-120    |           |            |        |             |    | MzoughiandChouba, 2005 |
| Gulf of Lions (France)  | 0.22-0.82 | 20.6-69.7 |           | 9-45.8     | 51-250 | 30000-48000 |    | Roussiez et al., 2006  |

|                            |           |            |             |            |          |             |          |                              |
|----------------------------|-----------|------------|-------------|------------|----------|-------------|----------|------------------------------|
| Ligurian Sea (Italy)       | 0.04-1.13 | 1.2-150    | 0.02-0.47   | 2.3-68     | 13-610   | 4100-49600  |          | Bertolotto et al., 2005      |
| Thermaikos gulf (Greece)   |           | 10-218     |             | 19-165     | 74-358   | 2900-4500   |          | Christophoridis et al., 2009 |
| Gulf of Taranto (Italy)    | -         | 44.7-74.8  | 0.07-0.41   | 42.4-52.3  | 86.8-129 | 27537-36098 | 552-2826 | Buccolieri et al., 2006      |
| Izmit Bay (Turkey)         | 2.5-9.5   | 55.2-172   | -           | 24.5-102.4 | 440-1900 | -           |          | Pekey, 2006                  |
| Gulf of Palermo (Italy)    |           | 11.6-60.2  | 0.025-0.707 | 12.3-38.6  |          |             | 216-379  | Di Leonardo et al., 2009     |
| Gulf of Hammamet (Tunisia) | 0.19-1.86 | 47.6-150.2 | 0.23-0.46   | 1.80-30.42 | 287-713  | 2976-26100  | 86-374   | <b>This study</b>            |

## DISCUSSION

The highest concentrations of TOC were found in the north-east part of the gulf, it can be explained by the general current of the Gulf which is dependent of the general Mediterranean current velocities (Sammari et al., 1999). This last divided to the level of the Sicilian Chanel in two branches; a first connects round the north coasts of the Mediterranean Sea while the second branch crosses in the south of the Gulf in a SSE-NNW direction. The passage of this second branch of the general current creates a same zone characterized by sediment relatively sandier than what surrounds it and controls the distribution of the different pollutants. TOC are comparable to those recorded from other region, similar values ours found in the sediments of the Ligurian Sea (Italy) (Bertolotto et al., 2005) and are lower than (0.40-1.17%) those found in Palermo gulf (Di Leonardo et al., 2009).

The levels of Cd, Pb, Cu, Fe, Mn and Zn have a similar spatial evolution characterized by the highest levels in the northern and central area face the Hamdoun River. This implies that the inputs from the Hamdoun River are the main source with anthropogenic pollutions along the coast with regard to the mentioned metals. The elevation of metal levels of Pb, Cd and Cu was found near the north eastern zone, due to boat traffic, semi-submersible oil

and gas platform "Tazarka" (Nabeul offshore) and oil transportation by current in this region.

Ca, Mg, K and Hg present generally a same repartition in the gulf, the level increased specifically in stations 4, 5 and 12; it is scarcely influenced by coastal anthropogenic sources (Hamdoun River). Distribution of Na is particularly the concentration is increase in the south east of the gulf, this variation due to prevailing marine currents in the gulf.

Land-based natural and anthropogenic sources both supply trace metals to the land-locked Mediterranean

Sea (Angelidis et al., 2011). These contaminations imprint is clearly evidenced in most of the Mediterranean near-shore sediments (Miralles et al., 2006; Palanques et al., 2008) where rivers and atmospheric deposition.

The levels of Pb and Zn are maxima in the surface may result either from input of anthropogenically contaminated particles and/or re-deposition of upward fluxes of previously deposited metals released by diagenetic mobilization of Fe and Mn oxides (Abesser and Robinson, 2010). This later process shows a good correlation Zn and Fe with Mn (Table III) in surface sediment layers. The concentrations of metals were controlled by the oxic-anoxic and redox conditions at the bottom (Amano et al., 2011).

Contamination sediment off shore Mediterranean was study a lot and showed well that maritime traffic and atmospheric input plays a key role for the transport of polluted particles to the Mediterranean basin (Angelidis et al., 2011; Mzoughi and Chouba, 2011; Amidio et al., 2014) while river borne anthropogenic metals are mostly stored on continental shelves (Roussiez et al., 2006). Migon (2007) estimated that at least 50% of Cd, Pb and Zn transported to the offshore environment of the Western Mediterranean are of atmospheric origin. However, it is very difficult to assess the importance of atmospheric riverine inputs in the long term because of the limited number of data of trace elements concentrations in the atmosphere and their high temporal variability. The anthropogenic imprint is clearly evidenced in most of the Mediterranean when the petrochemical industry and traffic boats are important in this area.

A comparison of the above mentioned concentrations with the corresponding values of the metals given in different gulfs showed low concentrations compared to those obtained in Naples and Greece gulfs (Bertolotto et al., 2005; Mzoughi and Chouba, 2005; Buccolieri et al., 2006; Pekey, 2006; Roussiez et al., 2006; Christophoridis et al., 2009; Di Leonardo et al.,

2009; Ennouri et al., 2010). An exception has been accorded to Pb and Zn found in the surface sediments of Hammamet gulf which showed higher concentration than those found in Lyon and Palermo gulfs in France and Italia (Bertolotto et al., 2005; Roussiez et al., 2006).

The application of ERL and ERM guidelines for the main toxic metals (Cu, Cd, Pb and Hg) indicated that sediment samples of Hammamet gulf can be characterized as “unpolluted”, while Zn values determined in samples collected in Hammamet gulf centre indicated that sediments were “moderately polluted”. Mn and Fe levels recorded in this study area presented the same values as in Mediterranean sediment.

The results attained in this study should be of considerable value in measuring the impact of future industrial development off shore in the area and anthropogenic atmospheric origin in Mediterranean Sea.

## CONCLUSION

This study enabled the determination of total metals and oligo-elements levels in surface sediments in Hammametgulf and spatial distribution of Cd, Pb, Hg, Cu, Zn, Fe, Mn, Mg, Ca, Na and K. In general, distribution maps showed the highest levels in the northern and central area face to the OuedHamdoun River. Metal levels of Zn and Hg showed a gradual decrease towards the deeper parts of the gulf. The Pbconcentration found near the north eastern zone is due to ship and boats traffic, oil transportation and semi-submersibleoil platform. This phenomenon may also be linked to contamination sources distribution, rivers inputs, water current and atmospheric patterns in Hammamet Gulf.

Statistical study showed that sediments sampled in the Hammamet gulf presented a significant correlation between the TOC and Fe, Zn Ca and Mn and between Hg/Cd; Mg/Cd and Cu/Pb.

The index of sediment quality guide line, indicated that the sediments were classified unpolluted with the exception of Zn that indicated that some sediments were moderately polluted. Compared with Mediterranean gulfs, this work showed low concentrations for maximum metals than those obtained in the north of Mediterranean Sea.

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