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# Potentially Toxic Elements Contamination and Ecological Risk Assessment in Surface Sediments of Moulouya Estuary (Northeastern, Morocco)

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**Abstract**

Potentially toxic elements (PTEs) in aquatic ecosystems are a major environmental concern posing serious risks to aquatic life and human health. Understanding their distribution, sources, and effects is crucial for effective environmental management and the protection of biodiversity and natural resources. This study assessed the variability, bioavailability, contamination degree, and ecological risks of PTEs in surface sediments of the Moulouya Estuary. The levels of PTEs were determined using an inductively coupled plasma-optical emission spectrometry (ICP-OES). The mean concentrations of PTEs can be classified in the following order: Zn > Cr > As > Pb >Cu > Cd. The highest values were found in sites (S2, S4, and S5) that receive metals from anthropogenic activities. The mineralogical study showed that the sediment studied is dominated by Ca, which influences the PTEs mobility and makes them bioavailable in the aquatic environment, which means aquatic organisms can easily assimilate them. The PTEs contamination degree was determined by several pollution indices (CF, CD, PLI, EF, Igeo), which indicate that surface sediment shows low to moderate contamination levels. However, the Potential Ecological Risk indicates a moderate to considerable risk in the study area. The multivariate analysis indicates that As, Zn, Cr, Pb, and Cu are derived from anthropogenic activities (urban wastewater, fertilizers, and fishing boats), while Cd could have mixed sources. The results highlight suggest that human activities pose an ecotoxicological risk in the Moulouya Estuary. To minimize these risks and protect the aquatic ecosystem and human health, periodic monitoring and management strategies should be continued. These measures will enable early detection of changes in PTE levels and the implementation of the necessary interventions to reduce their harmful effects.

**Keywords**: Heavy metals; PTE, Bioavailability; Contamination indices, ecological risk; Moulouya.

## 1. Introduction

Aquatic ecosystems have been under threat over the last century due to the degradation of their quality due to rapid economic development [1, 2]. Among the reasons for this degradation is potentially toxic elements (PTEs) contamination, which has become a particular concern because of their persistence, toxicity, and bioaccumulation in the tissues of aquatic organisms [3, 4]. The PTEs can affect the physiological and metabolic activities of organisms, posing a potential risk to the environment and also to human health through transmission and amplification in the food chains [5, 6].

Some metal(oid)s such as Cr, As, Zn, and Cu are essential elements in the metabolism of living organisms, but these elements can be biotoxic above a specific dose. However, Pb and Cd are non-essential elements for biological metabolism and can harm organisms at low concentrations [7].

The sediment may contain PTEs from natural sources because they constitute one of the principal elements of the Earth's crust. Nevertheless, anthropogenic activity (industrial, domestic, and agricultural wastewater) has become a major source of metallic contamination in sediments [8]. Potentially toxic elements are distributed between sediments and the aqueous phase. However, numerous studies have consistently shown that only a small amount of these contaminants remain dissolved in the aqueous phase, and approximately 90 % become trapped in sediments by various processes, including adsorption and co-precipitation [9]. Consequently, the principal Potentially toxic element reservoir is sediment. [10]. However, any change in ecological conditions (temperature, pH, dissolved oxygen, redox potential, and salinity) causes the desorption of PTEs from sediments to the aquatic environment, resulting in secondary water pollution. That will increase potential ecological risks for aquatic organisms and human health [11].

Sediments are frequently employed as an indicator for monitoring the PTE contamination in aquatic ecosystems [12, 13]. However, it has been widely shown that the total concentration of PTEs in sediments cannot accurately reflect the toxicological and ecological risks since only a small fraction assimilated by organisms could be biotoxic. Therefore, heavy metal toxicity depends essentially on the bioavailable fractions.

Estuaries are among the most vulnerable aquatic ecosystems due to intense anthropogenic disturbance and strong land-sea interactions [14]. This area retains contaminants such as potentially toxic elements, which do not rapidly disintegrate in the marine environment. This research examined PTE pollution in surface sediments of the Moulouya River Estuary. The latter is the second longest African river flowing into the Mediterranean Sea, stretching over 500 kilometers, originating from the confluence of the High and Middle Atlas Mountain ranges. Moulouya Estuary is one of the most important wetlands on the Mediterranean coast of Morocco; it represents a site of great biological and ecological interest and has been classified as a RAMSAR site since 2005 [15].

The study area is characterized by a wide diversity of habitats (marine, estuarine, fluvial, palustrine, and lacustrine) and a great variety of endemic flora and fauna. In addition, it supports the local population's livelihoods through tourism and fishing., which makes this coastal area a unique and valuable ecosystem deserving of scientific attention.

In recent decades, wastewater and surface runoff have been discharged into the Moulouya Estuary, seriously affecting the ecosystem and aquatic life through contaminants, including PTEs. Therefore, it is crucial to evaluate the pollution degree in its sediments. The principal aims of the present research were (1) to evaluate the distribution and bioavailability of PTEs in the surface sediments of the Moulouya Estuary, (2) to identify the PTEs sources in sediments, (3) to evaluate the PTE contamination degree using pollution indexes, and (4) to estimate the ecological risks posed by these potentially toxic elements in the Moulouya Estuary.

## 2. Materials and Methods

### 2.1. Study area

The survey area is characterized by various human activities, including agriculture along the Moulouya's banks, fishing (recreational and artisanal), and tourism. The study's sampling locations (Fig. 1) were selected along

the lower reaches of the Moulouya River, considering various elements such as accessibility and proximity to suspected pollution sources. Five stations were selected based on the following criteria:

**(S1)** Located at the Ras Elma bridge, upstream of wastewater discharges from Saidia City. This station serves as a reference point before any potential wastewater discharge.

**(S2)** Represent the intersection of the Moulouya River and the effluent from the wastewater treatment plant (WWTP) of Saidia and close to agricultural plots. This station assesses the combined impact of wastewater and agricultural activities on river quality.

**(S3)** Situated downstream of wastewater discharges from WWTP of Saidia. This station helps us to evaluate the river's self-purification ability.

**(S4)** Located at 50m from the Mediterranean Sea, it is characterized by small-scale fishing boats. This station helps us to estimate the impact of the pollutant load drained by the Moulouya River on the quality of the Mediterranean Sea.

**(S5)** Receives treated wastewater from the WWTP via a linear pipe drain (2,117 m). This station allows us to evaluate the impact of treated wastewater on the receiving environment.

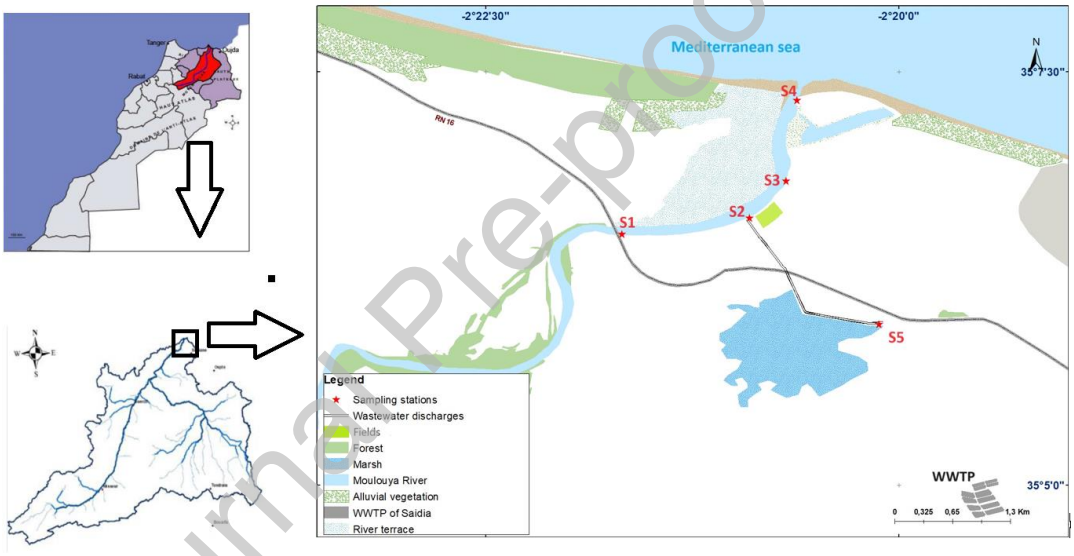


**Fig 1. Study area and sediment sampling sites in the Moulouya Estuary.**

## 2.2. Sample collection and analysis

The sampling process was conducted over a period ranging from February 2022 to October 2022. Twenty samples of surface sediment were collected in triplicate from each studied site at a depth of 5 cm using a plastic scoop. The composite samples are stored in a clean polyethylene box and transported at 4 °C to the laboratory.

Before further treatment, sediment was dried at 80°C for 48h, according to the protocol proposed by Waykar et al. and Wang et al. [16] [17], ground using a manual agate mortar, and sieved to retain fine fractions (63µm) strongly associated with heavy metals and other pollutants [18].

To evaluate the geochemical element, an X-ray spectral method was conducted to determine the mineralogical nature of the sediment. About 1 g of sediment sample was compacted into a sample cell, in which the bottom of it was covered with film (mylar), and then analyzed using Shimadzu X-ray Fluorescence Energy Dispersion Spectroscopy (EDX-7000).

To determine the total extractable metal, 1g of dry sediment sample was digested, according to NF EN ISO 11 885 standards, with aqua regia at 100°C for 2h. After digestion, the samples were diluted with ultrapure water for further analysis.

We employed the Huerta-Diaz & Morse (1990) [19] approach to identify the potentially toxic elements related to the sediment's bioavailable fractions, grouped under SEM (Simultaneously extracted metals). It involves mineralizing 400mg of sediment with a hydrochloric acid solution (1M) at room temperature for 24 hours under continuous agitation.

The sediment extracts (total extractable metal and SEM) were filtered at 0,45µm and analyzed for Pb, Zn, Cu, Cd, Al, Cr, and As using an inductively coupled plasma-optical emission spectrometry ICP-OES, specifically the Horiba Ultima Expert model.

### 2.3. Quality control

The quality of analytical data was ensured using quality control approaches, including applying standard protocols (analysis of replicates, analysis of reagent blanks, calibration, etc.). Certified multielement ICP Standard solution (concentration of 100 mg/L of Ag, Fe, Cr, Na, Ni, Mg, Co, K, Ca, Zn; Cu, Pb, Cd, Mn, Mo, Be, Ba, Sr, Sb, Se, Sn, V, Ti, Tl Al, and As; Carlo Erba reagents) were employed to prepare the calibration standards. The calibration was linear, and $R^2 = 0.9996$. The reagents were all of analytical grade. The ultrapure water was used to make all the dilutions.

### 2.4. Assessment of potentially toxic element contamination

To determine the PTE contamination degree in sediment and to evaluate their risk, various environmental indicators were employed (Contamination Factor (CF), Degree of Contamination (CD), Pollution Load Index (PLI), Enrichment Factor (EF), Geoaccumulation Index (Igeo), Ecological Risk Index (ERI), Potential Ecological Risk Index (PERI). Numerous studies have utilized the average shale values (ASV) or Earth's crust as a reference baseline [20, 21]. In this work, the ASV was employed as a background of PTEs [22].

#### 2.4.1. Contamination factor (CF) and degree of contamination (CD)

The CF and the CD are extensively used to evaluate the PTE contamination level of different deposits [23]. The Cf measures the level of contamination caused by an individual metal, whereas the CD measures the contamination degree, including the total CF [24]. These indexes are determined using the following formulas [24]:

**(1)** $CF = \frac{CHM}{CBG}$

**(2)** $CD = \sum_{i=1}^{n} CF$

Where CHM: PTE concentration in sediment, CBG: background concentration of PTE, and n: number of studied PTEs. The CF values were classified according to Hakanson's classification (Table S1).

#### 2.4.2. Pollution Load Index (PLI)

The PLI shows how often the concentration of PTEs in sediment is higher than the typical uncontaminated baseline concentration [25, 26] Considering all potentially toxic elements collectively, the PLI determined each sample's pollution level. The PLI value gives a general indication of metal(oid) toxicity in each sample site [27]. The PLI was calculated using the equation below:

**(3)** $PLI = \sqrt[n]{CF1x\ CF2 \dots CFn}$

Where CF: contamination factor and n: number of PTEs. This empirical index offers a quick, easy method for determining the degree of PTE pollution. If PLI >1, it indicates PTE pollution in sediment; however, if PLI <1, it shows no metallic pollution.

### 2.4.3. Enrichment factor (EF)

The EF were calculated to evaluate whether PTEs are present at elevated levels, compared to Earth's crust values, as a result of anthropogenic contamination [28]. This index is frequently used to analyze anthropogenic impacts on the sediments by normalizing the PTEs to a conservative element, such Al [29]. The EF is determined using the equation shown below:

**(4)** $EF = \frac{\left(\frac{\text{Metal}}{\text{Al}}\right)\text{Sediment (a)}}{\left(\frac{\text{Metal}}{\text{Al}}\right)\text{Background (b)}}$

Where (a) and (b) are the ratio of metal(oid) to Al in the studied sample and background respectively. Sediments are categorized into three categories listed in Table S1 [28].

### 2.4.4. Geoaccumulation index (Igeo)

The degree of potentially toxic element contamination in aquatic ecosystems is generally measured using the geoaccumulation index (Igeo) [30, 31]. The latter represents a quantitative evaluation of the sediment pollution level of each metal(oid). The formula below was used to calculate this index [32].

**(5)** $Igeo = Log_2\left[\frac{\text{Cn}}{1.5(\text{Bn})}\right]$

where Cn: metal(oid) concentration present in studied sediment, and Bn: metal(oid)'s geochemical background concentration (n) [22], the correction factor (1.5) is used to compensate for possible consequences of anthropogenic impacts or alterations in sediments' lithology [14]. Sediments are categorized (Table S1) according to the Muller classification [32].

### 2.4.5. Ecological Risk Index (ERI)

The ERI considers toxicity, variations in background concentrations, and environmental migratory patterns for each specific metal. The ERI is utilized to evaluate the ecological risk of PTEs [33]. According to the following formula, the ERI was determined [24]:

**(6)** $ERI = Tr \times \text{CF}$

Where Cf: contamination factor and Tr: toxic response coefficient. According to Liu, B et al. [14], Tr values are taken: Cd = 30, As = 10, Zn =1, Pb = 5, Cr = 2, Cu = 5. The ERI values are classified according to [24] (Table S1).

### 2.4.6. Potential Ecological Risk Index (PERI)

The expected effect of PTEs on aquatic life was predicted using the PERI [24, 34]. According to ecological sensitivity, the synergy, and the toxicity of each metal(oid), this index indicates the possible ecological risk associated with PTE pollution [35] The formula below was applied to calculate the PERI:

**(7)** $PERI = \sum_{i=1}^{n} ERI$

The classifications of PERI are shown in Table S1 [24].

### 2.5. Sediment quality guidelines (SQGs)

The SQGs can be used to estimate the risk of toxicity to benthic organisms. Examining sediment pollution by comparing contaminant concentration with the related quality standards is useful. The PEC (Probable Effect Concentration) values and the TEC (Threshold Effect Concentration) values suggested by MacDonald et al. [36] appear to be the most appropriate for the protective objective set by the Swiss Federal Law on Water Protection and its implementing ordinance (OEaux) [37]. The TEC (Threshold Effect Concentration) below which negative effects are not observed. The PEC (Probable Effect Concentration) corresponds to a concentration above which a high probability of bad effects is expected.

### 2.6. Statistical analyses

The collected data were subjected to statistical analysis using IBM SPSS software (version 25). The Principal Component Analysis (PCA) and Pearson's correlation were employed to evaluate the relationships between PTEs and to determine the origins of metallic contamination in the surface sediments of the Moulouya Estuary [38]. In addition, the Hierarchical Cluster Analysis (HCA) was applied to show similarities between sampling stations and potentially toxic elements and assess spatial variability.

## 3. Results and discussion

### 3.1. Geochemical element concentrations

The major elements results (Table 1) in surface sediments of Moulouya Estuary are classified in the following order: Ca> Si>Fe>K. The results indicate that Moulouya's surface sediments are rich in Ca, with an average concentration ranging from 42.74 to 60.04%. These results exceed the typical values for the Earth's crust (3.63%). The increased Ca content in the studied sediments is likely due to the petrographic nature of the watershed (dominated by limestone). The Ca abundance can be attributed to bioclastic elements (shellfish debris) [39]. This is followed by Si ranging from 19.52 to 28.011%, Fe (10.67 - 15.61%), and K (1.8 - 4.09%). The average concentrations of Si (S5), Fe (at all stations), and K (S2, S5) exceed those found in the Earth's crust (Table 1). This distribution could be explained by the mineralogical nature of the sediments, marked by the predominance of quartz, chlorites, and micas, which are likely to contain Si, Fe, and K, respectively [39].

### 3.2. Potentially toxic elements in the surface sediment of Moulouya Estuary

The PTEs distribution (Zn, Cd, As, Pb, Cr, and Cu) in the surface sediment of Moulouya Estuary is given in Table 1. Pb and Cr mean values ranged from 10.48 to 15.9 mg/kg and 11.9 to 25.5 mg/kg, respectively. The highest values were recorded in site (S4), which could receive potentially toxic elements from fishing boats since no other human activity is conducted in this region. This assertion is supported by the presence of chrome in antifouling coatings used to protect the boat's hull and metal components from the harsh marine environment [40], as well as the discharge of lead from fishing boats can occur through the use of leaded gasoline, commonly used in marine engines [41, 42]. The mean values of Zn, Cu, and As vary between 33.8- 46 mg/kg, 7.51-17.14 mg/kg, and 11.1-14.8 mg/kg, respectively. The sites (S5) and (S2), exposed to urban effluents from the Saidia WWTP, have higher concentrations of Zn, Cu, and As, most likely originating from wastewater [43, 44]. The average concentration of Cd reveals a minor variation, varying between 0.19- 0.25 mg/kg. The station (S2) shows the maximum value of Cd, which could be attributed to the combined effect of urban effluents and surface runoff receiving potentially toxic elements from phosphate fertilizers (containing high levels of Cd) [45]. The mean concentrations of Zn, Pb,

Cr, and Cu are well below those typical of the Earth's crust, contrary to As and Pb (S4). However, the Cd concentrations are close to Earth's crust values [22].

**Table 1. The average concentrations of PTEs (mg/kg) and major elements (%) in surface sediment samples of Moulouya Estuary.**

| Sites | As | Cr | Zn | Pb | Cd | Cu | Al | Ca | Si | Fe | K | References |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **S1** | 11.15 | 11.93 | 33.84 | 10.48 | 0.23 | 7.51 | 50.23 | 58.72 | 21.02 | 10.67 | 2.58 | This study |
| **S2** | 12.88 | 15.65 | 41.83 | 12.95 | 0.25 | 15.16 | 98.12 | 48.58 | 23.28 | 15.59 | 3.69 | |
| **S3** | 10.91 | 13.00 | 34.05 | 11.94 | 0.20 | 8.59 | 91.92 | 58.08 | 21.04 | 10.80 | 2.45 | |
| **S4** | 13.67 | 25.57 | 37.65 | 15.90 | 0.19 | 12.71 | 111.58 | 60.04 | 19.52 | 13.02 | 1.81 | |
| **S5** | 14.83 | 17.88 | 46.00 | 12.19 | 0.19 | 17.14 | 189.61 | 42.74 | 28.01 | 15.62 | 4.10 | |
| **ASV** | 13 | 90 | 95 | 20 | 0.3 | 45 | 8 | 2.21 | 27.3 | 4.72 | * | [22] |
| **Crust** | 1.8 | 100 | 70 | 13 | 0.2 | 55 | 8.13 | 3.63 | 27.7 | 5 | 2.6 | [22] |

*"*" indicates missing data.*

Total PTEs concentrations in sediment samples from Moulouya Estuary followed the order: Zn > Cr > As > Pb>Cu > Cd. The results are different from the Earth's crust (Cr> Zn> Cu > Pb> As> Cd) and the previous studies carried out in the Moulouya River by Bouzekri et al. et Makhoukh et al., [46, 47] reported that Zn is the most abundant in surface sediment, followed by Pb, Cu, and As.

Compared with previous studies (Table 2), the mean values of Cd and Zn obtained in this research are lower than those found in the Lower Moulouya [48], while the Cu content has increased over the years. This could be explained by the variation over time in geochemical processes, sampling location, sediment composition, weathering, and anthropogenic activities. The results obtained remain lower than the values found in the Upper Moulouya, the Bouregreg River (Morocco), the Tinto River (Spain), the Nile River (Egypt), and the Molopo River (South Africa). This comparison shows that potentially toxic elements do not strongly contaminate the Lower Moulouya.

**Table 2. Potentially toxic element concentrations in studied surface sediment and other Rivers from literature.**

| Locations | As | Cr | Zn | Pb | Cd | Cu | References |
|---|---|---|---|---|---|---|---|
| Moulouya Estuary (range) | 11–14.8 | 12- 5.5 | 33.8- 46 | 10.4- 16.1 | 0.18- 0.25 | 7.5- 7.13 | This study |
| Moulouya Estuary (average) | 12.69 | 16.81 | 38.67 | 12.55 | 0.21 | 12.22 | |
| Moulouya Estuary | * | * | 133 | * | 0.6 | 1.9 | [48] |
| Moulouya River (Upper) | 0.005-31 | * | 59–194 | 47-832 | 0 - 1.91 | 25–32 | [46] |
| Moulouya River (Upper) | * | * | 81 - 949 | 19.2- 710 | 0.18- 0.8 | 12.6-27.8 | [49] |
| Moulouya River (Upper) | 110 - 160 | * | 59- 130 | 97- 11200 | * | 24 - 40 | [50] |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| BouRegreg. Morocco | * | * | 196.69 | 128.05 | 2.9 | 33.48 | [51] |
| Nile Delta, Egypt | * | * | 117 | 31.78 | 0.23 | 32.64 | [52] |
| Tinto River, Spain | * | 11–151 | 68 – 5280 | 17-13400 | 0.13–12 | 22–2700 | [53] |
| Molopo River, South Africa | 1.61 | 92.73 | 110.90 | 17.76 | 0.16 | 53.27 | [54] |

*"*" indicates missing data.*

### 3.3. Bioavailable potentially toxic element concentrations

The mean concentrations of SEM and the percentages of bioavailable fraction of PTEs in Moulouya's surface sediments are presented in Table 3. The Zn, Pb, As, Cu, and Cr in sediments revealed a high affinity with the sediment's bioavailable fractions; the various PTEs' bioavailability percentages ranged from 32% to 93%. This result indicates that PTEs are highly mobile and bioavailable in the aquatic environment, consequently easily assimilated by organisms. However, Cd was undetectable in the sediment's bioavailable fractions, indicating that it can't be remobilized in the water column.

The high mobility of PTEs in studied sediments could be due to the sediment's salinity and mineralogical nature, dominated by Ca (Table 1), which compete with PTEs for sorption sites [55]. In addition, Du Liang et al., [56] confirmed the impact of salinity and major elements on the bioavailability and mobility of PTEs, especially in surface sediments.

**Table 3. The mean SEM concentrations and bioavailable fraction percentages in Moulouya's Estuary sediments.**

| Sites | As | | Cr | | Zn | | Pb | | Cu | |
|---|---|---|---|---|---|---|---|---|---|---|
| | ***mg/kg*** | ***%*** | ***mg/kg*** | ***%*** | ***mg/kg*** | ***%*** | ***mg/kg*** | ***%*** | ***mg/kg*** | ***%*** |
| **S1** | 10.117 | 91 | 8.795 | 74 | 29.215 | 86 | 8.753 | 84 | 5.975 | 80 |
| **S2** | 11.955 | 93 | 10.623 | 68 | 32.248 | 77 | 9.123 | 76 | 10.412 | 69 |
| **S3** | 9.836 | 90 | 15.764 | 91 | 19.935 | 59 | 8.340 | 70 | 3.857 | 45 |
| **S4** | 12.451 | 91 | 8.184 | 32 | 17.528 | 47 | 11.818 | 73 | 5.872 | 46 |
| **S5** | 11.205 | 80 | 7.549 | 42 | 18.637 | 41 | 8.212 | 67 | 6.938 | 40 |

### 3.4. Assessment of potentially toxic elements pollution risk in sediment

#### 3.4.1. Contamination Factor (CF), Contamination Degree (CD), and Pollution Load Index

The CF is calculated to evaluate the PTE's pollution degree in sediments. According to Hakanson's classification [24], the results of CF indicate low contamination (CF<1) in the Moulouya's Estuary sediment, except As, which shows moderate contamination at sites S4 (1.05) and S5 (1.14) (Fig 2).

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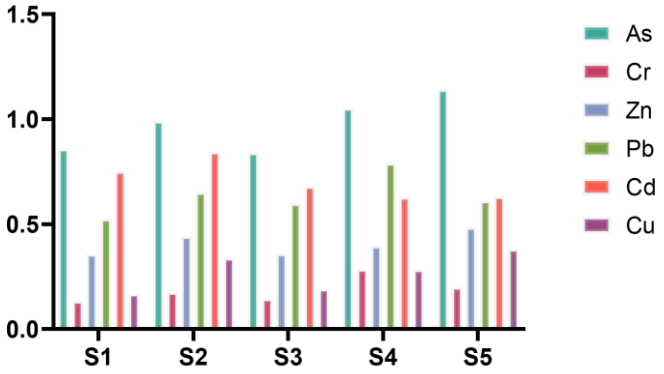


**Fig 2. Variation of Contamination factor (CF) of PTEs in surface sediment of Moulouya Estuary.**

The highest CF was observed in station (S5) for As, Zn, and Cu due to urban wastewater discharges [44], and in station (S4) for Pb and Cr, which receive potentially toxic elements from fishing boats [41]. For Cd, the maximum values were recorded in the station (S2) due to surface runoff from agricultural activities. The CF changes in the following descending order: As> Cd> Pb> Zn > Cu> Cr.

The contamination degree (CD) in sampling sites (Fig 3a) ranged from 2.78 to 3.38, confirming that sediments in the Moulouya Estuary have a low degree of contamination. The sediment exhibits lower contamination degrees because of the limited anthropogenic activities in the Moulouya Estuary, which often serves as a metal contamination source, through industrial or agricultural runoff. Moreover, it could be related to reduced river's flow, heavily influenced by weather conditions, particularly precipitation. During drought periods, the river's discharge decreases significantly, thereby reducing the transport of sediments and metal contaminants from upstream to downstream. In addition, Estuaries are characterized by complex hydrodynamic processes, which can contribute to the dilution of pollutants, thereby reducing the overall level of sediment contamination.

The metallic contamination degree at the sampling stations followed a decreasing order: S5>S2>S4>S3>S1. The PLI in Moulouya estuary sediment is slightly below 1 (Fig 3b), suggesting no pollution in the study area.

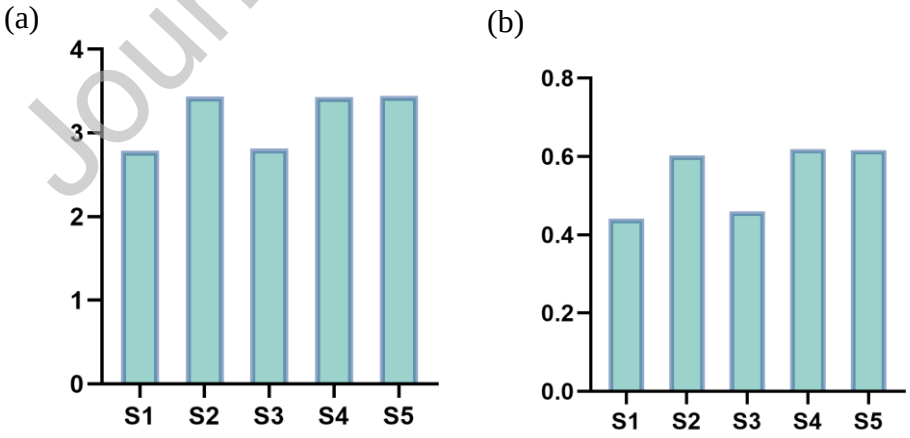


**Fig 3. Contamination Degree (a) and Pollution Load Index (b) variation in surface sediment of Moulouya Estuary.**

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### 3.5. Enrichment Factor (EF)

The EF is largely applied to evaluate the presence of anthropogenic pollutants compared to the natural values [57]. The results (Fig 4) were below 1, indicating low enrichment in the survey area. Overall, the EF results of PTEs in the Moulouya Estuary follow the order As> Cd> Pb> Zn > Cu> Cr.

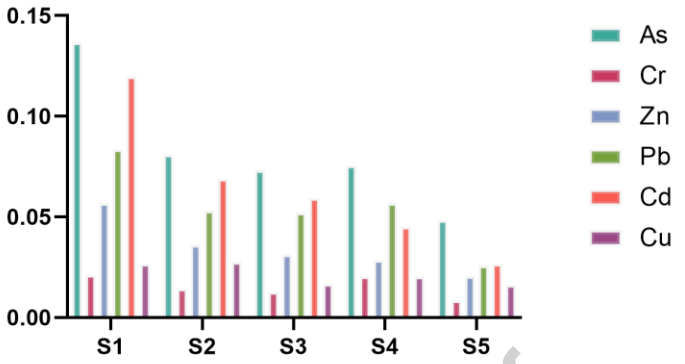



**Fig 4. Spatial variation of enrichment factor (EF) in surface sediment of Moulouya Estuary.**

### 3.5.1. Geoaccumulation Index (Igeo)

The results obtained for Igeo (Fig 5) vary between -0.83 and -0.39 for As, between -3.5 and - 2.4 for Cr, between -2.07 and -1.63 for Zn, between -1.51 and -0.92 for Pb, between -1.25 and -0.83 for Cd, and between -3.16 and -1.97 for Cu. The results obtained are below zero (Igeo < 0), indicating that the sediment in the Moulouya Estuary is uncontaminated. The IgeO values of the studied PTEs decrease in the order below:

As> Cd> Pb> Zn > Cu> Cr.

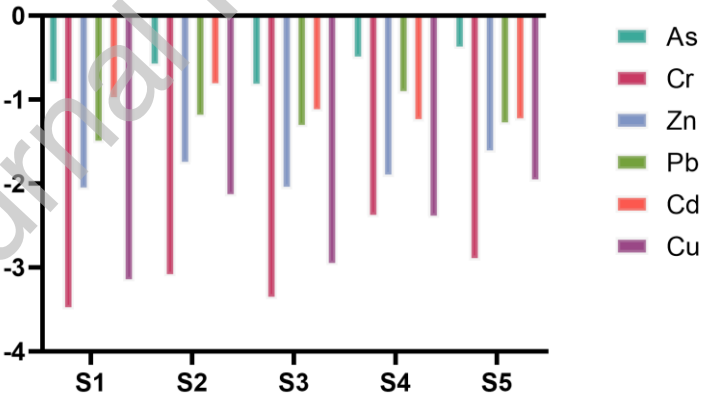



**Fig 5. Spatial variation of Geoaccumulation index in surface sediment of Moulouya Estuary.**

### 3.5.2. Ecological Risk Index (ERI) and Potential Ecological Risk Index (PERI)

The ERI results (Fig 6a) indicate a low risk (ERI<40) for Cd and Cr at all studied sites, for Cu at (S1) and Zn at stations (S1), (S3), and (S4). The ERI indicates a moderate risk (40<ERI<80) for Pb at all stations, for Cu at stations (S2), (S3), (S4), and for Zn at stations (S2) and (S5). In addition, the results show a significant risk (80<ERI<160) for As at all the studied sites and for Cu at the site (S5). The PERI results indicate a moderate

ecological risk (150 <PERI<300) in sites (S1) and (S3) and a considerable ecological risk (300<PERI<600) in stations (S2) (S4) and (S5) (Fig 6b).

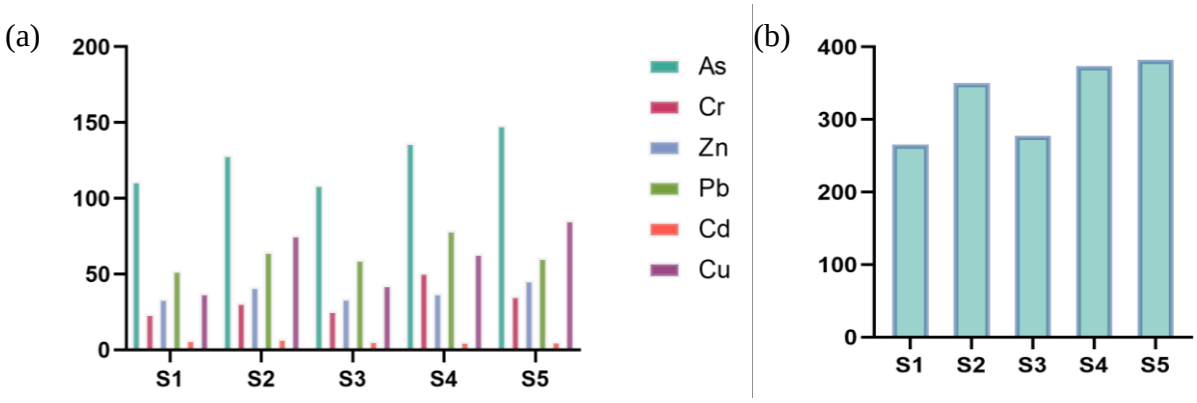



**Fig 6. Ecological risk index (a) and potential ecological risk index (b) variation in surface sediment of Moulouya Estuary.**

### 3.6. Application of sediment quality guidelines (SQGs)

The (SQGs) are essential to estimate the risk of potentially toxic element contamination on benthic organisms. The comparison of PTEs with TEC (Threshold Effect Concentration) and PEC (Probable Effect Concentration) limits is shown in Table 4. The results indicate that Cr, Zn, Pb, Cu, and Cd were below the TEC in all sampling sites (100% of samples), which indicates that the levels of these contaminants are not expected to have harmful effects on the aquatic organisms. However, the As concentration in all samples was between TEC and PEC limits. This indicates that current As levels in Moulouya Estuary sediments can often negatively affect aquatic organisms [36].

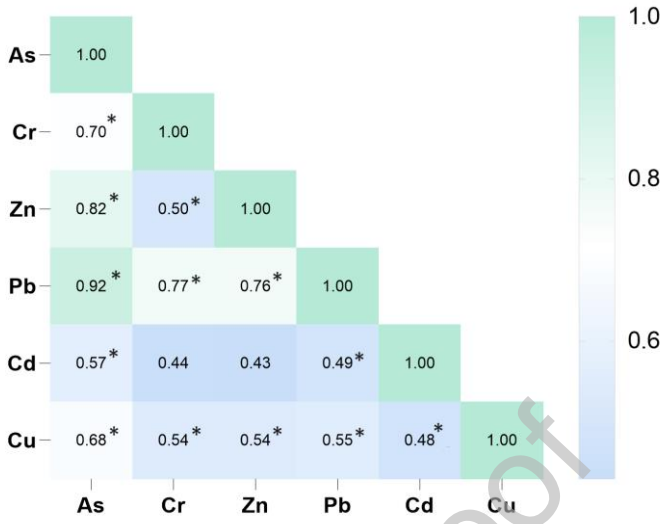
**Table 4. Comparison of PTEs concentrations (mg/kg) in studied sediment with SQGs.**

| Sites | As | Cr | Zn | Pb | Cd | Cu |
|---|---|---|---|---|---|---|
| **S1** | 11.15 | 11.93 | 33.84 | 10.48 | 0.23 | 7.51 |
| **S2** | 12.88 | 15.65 | 41.83 | 13.00 | 0.25 | 15.16 |
| **S3** | 10.91 | 13.00 | 34.05 | 11.94 | 0.20 | 8.59 |
| **S4** | 13.67 | 25.57 | 37.65 | 15.80 | 0.19 | 12.71 |
| **S5** | 14.83 | 17.88 | 46.00 | 12.19 | 0.19 | 17.14 |
| **TEC** | 9.79 | 43.4 | 121 | 35.8 | 0.99 | 31.6 |
| **PEC** | 33 | 111 | 459 | 128 | 4.98 | 149 |
| **Samples< TEC** | 0% | 100% | 100% | 100% | 100% | 100% |
| **TEC<Samples<PEC** | 100% | 0% | 0% | 0% | 0% | %0 |

### 3.7. Statistical analysis

Multivariate statistics were used to estimate the possible sources of potentially toxic element pollution at the Moulouya's Estuary sediment. The result of the correlation analysis between PTEs is shown in Fig 7. The Pearson's correlation coefficient shows that all PTEs had a significant correlation (P<0.05), except for Zn-Cd and Cr-Cd. According to Suresh et al. [58], the high correlation coefficient (0.6) between PTEs indicates that they have similar sources, identical behaviors, and mutual dependence during transport [59]. The As strongly correlates with

Pb, Zn, Cr, and Cu (0.92, 0.82, 0.7, and 0.68, respectively); Pb is also strongly correlated with Cr and Zn with correlation coefficients of 0.77 and 0.76, respectively. This indicates that the PTEs studied could probably have the same source of contamination from anthropogenic activities [60, 61].




** Significant Correlation at 0.05 level*

**Fig 7. Matrix of Pearson's correlation between PTEs in Moulouya Estuary.**

The Principal Component Analysis (PCA) extraction method supported Pearson's correlation result. PTEs in sediment were subdivided into two principal components (Table 5). The PC1 and PC2 are 68.53% and 11.08%, respectively, accounting for an accumulation of 79.62% of total variation. The PC1 has a significant positive loading for As, Pb, Zn, Cr, Cu, and Cd (0.959, 0.920, 0.829, 0.802, 0.758, 0.664 respectively). The results reveal anthropogenic sources for potentially toxic elements could be derived from urban wastewater, fertilizers, and fishing boats. The PC2 has a positive loading for Cd (0.686). The Cd is positively loaded in both PC1 and PC2; this could indicate mixed sources for this element [52].

**Table 5. Principal component loading of PTEs in studied surface sediment.**

| | PC1 | PC2 |
|---|---|---|
| **As** | 0.959 | -0.102 |
| **Cr** | 0.802 | -0.145 |
| **Zn** | 0.829 | -0.228 |
| **Cd** | 0.664 | 0.686 |
| **Cu** | 0.758 | 0.227 |
| **Pb** | 0.920 | -0.245 |
| **Variance (%)** | 68.537 | 11.087 |
| **Accumulation (%)** | 68.537 | 79.624 |

The HCA was used to show similarities between sampling stations and the studied PTEs and assess spatial variability. The first dendrogram (Fig. 8a) indicates that the sediment sampling stations are clustered into three groups. The first group includes stations (S1) and (S3); they are less contaminated than the other stations. This



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could be explained by the low anthropogenic input (S1) and the river's self-purifying capacity (S3). The second group includes high pollution stations (S2) and (S5), which receive wastewater from Saidia WWTP. The third group includes station (S4), which is relatively polluted due to Pb and Cr concentrations derived from fishing boats.

Similarly, PTEs were grouped into three significant clusters (Fig. 8b), and their distribution is classified according to the metal concentrations. Cluster 1 consists of As, Pb, Cr, and Cu, characterized by similar average concentrations; Cluster 2 includes Cd, present in low concentrations in sediments; and Cluster 3 includes Zn, the most dominant PTE in the studied sediments.

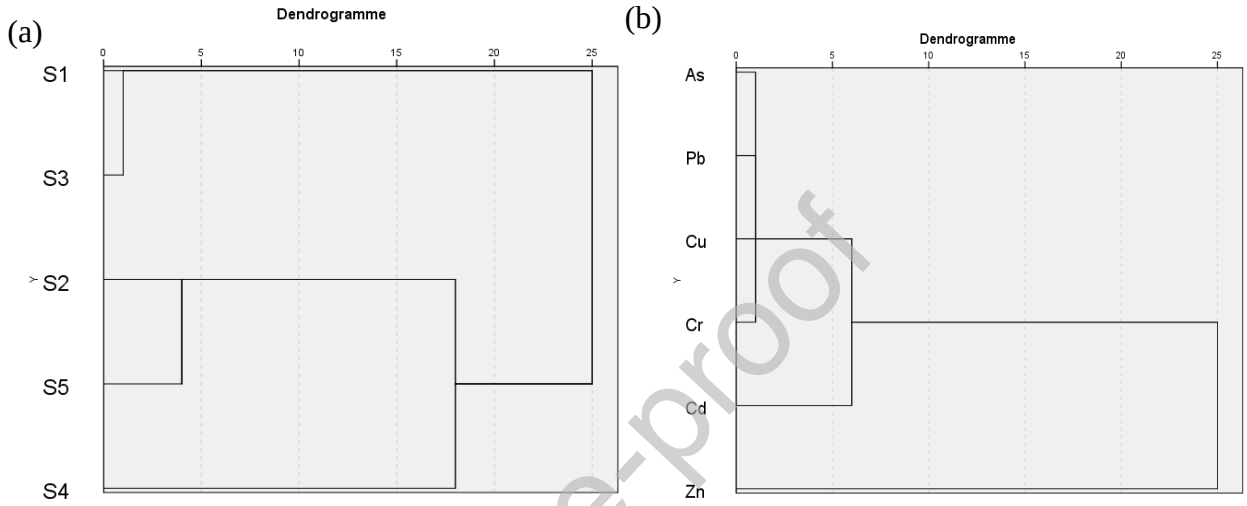


**Fig 8. Cluster dendrogram of sampling sites (a) and potentially toxic element contents (b) in surface sediment samples.**

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**4. Conclusion**

Potentially toxic element concentrations and bioavailability (As, Cr, Pb, Zn, Cu, and Cd) were examined in surface sediments collected from Moulouya Estuary to evaluate the pollution degree using guidelines and multi-indicator methods. The highest values of PTEs were recorded in stations (S2), (S4), and (S5) receiving potentially toxic elements from anthropogenic activities (urban effluents, agriculture, fishing). The bioavailability percentages show a high mobility of PTEs in the water, which means aquatic organisms can easily assimilate them. The average PTE concentrations in sediment followed a descending order: Zn > Cr > As > Pb>Cu > Cd.

The results of PTEs contamination indexes (CF, CD, PLI, EF, And Igeo) demonstrated that the surface sediment in Moulouya Estuary was from low contamination to moderate contamination. However, the ERI indicates a significant risk for As. The latter exceeds the Sediment Quality Guidelines, which indicates that As can often negatively affect the Moulouya Estuary's aquatic organisms. The PERI results showed that the study area had a moderate to considerable ecological risk. The multivariate statistics indicate that As, Zn, Cr, Pb, and Cu were strongly correlated and resulted from anthropogenic activities, whereas Cd may have originated from various sources. Although the level of metallic pollution is currently low in the sediment of the Moulouya Estuary, a long-term monitoring program must be set up to prevent any potential risk to the ecosystem. By collecting initial data, this program can identify normal variations and detect any abnormal increase in PTE levels, it allows us also to capture seasonal variations and better understand the factors that influence PTE dynamics, and it becomes easier to identify potential sources of contamination.

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## CRediT authorship contribution statement

All authors contributed to the conception and design of the study. **Nour-elhouda Basraoui** designed the experiments, collected data, analyzed and interpreted data, wrote the draft, performed the statistical analysis, and reviewed the draft. **Rihab Ben-tahar** helped collect and analyze data and reviewed the draft. **Jean-François Deliège** reviewed the draft, **Bouchra El Guerrouj** supervised the work and reviewed the draft. **Abdelhafid Chafi** supervised the work and reviewed the draft.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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