Article

Assessment of Trace Metals in Sediments from Khnifiss Lagoon (Tarfaya, Morocco)

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Abstract: Surface sediments from Khnifiss lagoon (Morocco) were analyzed to evaluate the contamination degree of the area. Concentrations of V, Cr, Co, Ni, Cu, Zn, As, Cd, Hg, and Pb were determined on samples taken during the summer and the autumn of 2016. On the whole, higher concentrations were found in the summer season. The results revealed the following average concentrations (mg/kg), reported in descending order: Zn (51.7 ± 31.3) > V (38.8 ± 24.7) > Cr (26.6 ± 17.8) > Ni (16.5 ± 5.47) > As (8.50 ± 2.00) > Cu (6.60 ± 3.81) > Pb (6.13 ± 3.46) > Co (3.57 ± 2.09) > Cd (0.16 ± 0.11) > Hg (0.006 ± 0.001). Organic matter showed a positive significant correlation with some trace metals (mainly V, Cr, Co, Zn, Cd, Pb). Three pollution indices were calculated: Enrichment Factor (EF), Index of Geo−accumulation (Igeo), and Pollution Load Index (PLI). Minimal enrichments (for Zn, As, and Cd) were detected at some sampling points. Overall indices showed that the Khnifiss sediments can be classified as not contaminated, and that the trace metals amounts found are ascribable to the geogenic origin. The results of this work can be used as a starting point for further evaluations of trace metals distribution in Moroccan lagoons.

Keywords: Khnifiss Lagoon; trace metals; enrichment factor; sediment geochemistry; contamination assessment

1. Introduction

Coastal lagoons are very important environments, both in ecological and in economic terms, since they provide the habitat for numerous species and are the backbone of various anthropic activities (including food-related ones and tourism) [1,2]. However, the human exploitation of these ecosystems implies a significant potential environmental vulnerability, especially due to their geo-morphological setting (as semi-enclosed area) and their link to terrestrial inputs and continental run-off [3,4]. Indeed, the presence of trace metals in lagoons and coastal zones has been attributed mutually to natural events (volcanism, flash flood, wind transport, erosion) and anthropogenic processes (vehicle emission, industry, urbanization, construction activities, mining activities) [5–8]; for these reasons, lagoon sediments can act both as geogenic source and as a final sink for trace metals in the aquatic ecosystems [9,10]. They can be considered as good geo-indicators of marine environmental quality, since their status can alter benthos and the food chain, thus posing potential ecological risks [11,12]. Therefore, the study of coastal sediments provides useful information on marine pollution [13]. Trace metals are persistent in the environment and

are subject to bioaccumulation (which often causes irreversible adverse effects on animals and humans) [14,15]. In addition, they represent a global-scale environmental issue, since serious problems caused by this category of pollutants are known to exist in many areas of the world (both in developed and developing countries) [16,17]. More than 90% of trace metals load in aquatic systems is associated with suspended particulate matter and sediments [18,19]. The fate and transport of these elements in marine area and lagoons are controlled by a variety of factors such as redox potential, texture, ionic strength, the abundance of adsorbing surfaces, pH, and organic matter content [20,21]. The environmental monitoring helps to develop effective management plans, to improve the strategies for coastal activities, and to distinguish between the anthropogenic and the natural sources of the trace metal enrichments.

Morocco acts as an especially relevant site for the study of coastal ecosystems, since it holds five lagoons: Four facing the Atlantic Ocean (Khnifiss, Sidi Moussa, Oualidia, and Moulay Bousselham lagoons) and one facing the Mediterranean Sea (Marchica Lagoon), covering about 3500 Km of the national coastline. The present study focuses on the most important desert wetland in the Saharan coast of Morocco and of North Africa (RAMSAR site since 1980): The lagoon of Khnifiss. It is a shallow tidal lagoon of open water in an arid environment, where the supply of continental material is strongly limited to aeolian particle inputs; in addition, a coastal upwelling from the Canary Islands induces high biogenic accumulation rates [22]. Although Khnifiss Lagoon is currently protected, information on its sediment's metal concentrations is still lacking. The relevance of Khnifiss Lagoon is further strengthened considering that there is a proposal to use the area as a reference site for the evaluation of trace metal contamination levels, since it is characterized by abundant and various macrobenthic fauna [23], low density of human population (1.07 per/km^2 at Tarfaya Province) [24], and it is far from major cities and industrial activities.

The main objectives of this research are to determine the trace metal contents in the Khnifiss Lagoon, in order to assess the contamination degree of the area; to carry out a preliminary screening that can be used as starting-point for a more detailed activity of geochemical study.

2. Materials and Methods

2.1. Geo−Environmental Setting of the Area

The study area is located in the Province of Tarfaya, between Cap Nachtigal and Cap Juby, in a rural region on the Southwest side of Morocco (27.80–28.05° N, 12.21–12.39° W). It extends for about 20 km, with a maximum of about 5 km width, at Sabkha Tazera [25]. The site is considered one of the most important zones for birds' migrations. Besides, it provides the livelihood of people living in adjacent areas, where most activities are related to fishing and nature tourism.

The lagoon is connected to the Atlantic Ocean through Foum Agoutir at its Northern side. The tidal regime is semidiurnal, and it ranges between a minimum of 1.48 m downstream to a maximum of 2.54 m inside the lagoon. The speed of the tidal current exceeds 91 cm/s at Foum Agoutir. The residence time of the water in the lagoon is 4.4 tidal cycles during neap tides and 1.5 tidal cycles during spring tides [26]. Salinity is between 30‰ and 40‰ in the downstream zone, between 32‰ and 45‰ in the intermediate zone, and between 37‰ and over 45‰ in the upstream zone due to the saltworks at Sebkha Tazera [27]. The phytoplankton community is dominated by diatoms (90%) and dinoflagellates (10%), with Chaetoceros (88.5%) and Amphora (6.7%) being the main exponents of the population [28]. The lagoon has varieties of floral species such as *Zygophyllum geatulum*, *Launaea arborescens*, *Lycium intricatum*, *Cistanche phelypaea*, *Zostera noltii*, and *Spartina maritima* [29]; seaweeds are mainly represented by 24 species (4 Chlorophyceae, 10 Phaeophyceae, and 10 Rhodophyceae) [30]. The air temperature ranges between a minimum of 15.8 ± 2.5 °C to a maximum of 24.0 ± 2.2 °C with an average of 19.9 ± 2.2 °C. The precipitations are classified as extremely rare, with an average of 0.3 ± 0.2 mm daily and 92.6 ± 58.5 mm annually

over the last three decades (1994–2019). The wind speed ranges between 4.47 ± 0.53 m/s to 7.90 ± 0.82 m/s, with an average of 6.13 ± 0.41 m/s.

The geomorphology of the region is conditioned by the presence of Cretaceous marl or marly-limestone, to which it is over-imposed a harder calcareous-sandstone (Marine Moghrebien) protective slab. From a geological point of view (Figure 1), the study area is located in the North-Eastern side of Tarfaya coastal basin, formed during the Mesozoic and the Cenozoic seaward of the stable West African craton [31]. The main sources of the sediments are the Anti−Atlas in the Est, and the Reguibat dorsal and Mauritanides in the Southern part [32,33].
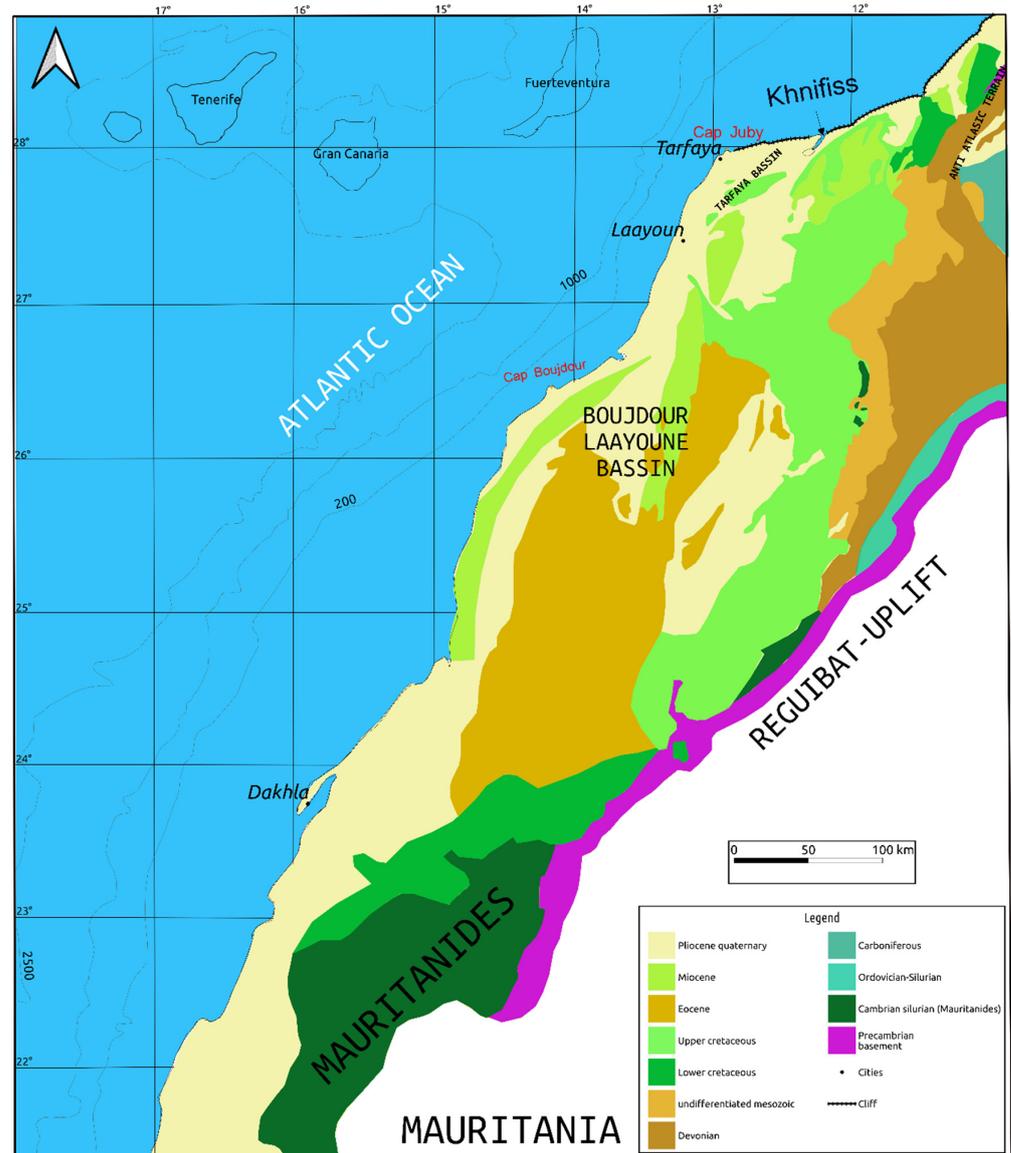
Figure 1. Geological map of the area surrounding the Khnifiss Lagoon (Digitalized from [34]).

2.2. Sediment Sampling and Analysis

Surface sediments were collected in 2016, during two seasons (summer and autumn), at six different stations (S1–S6), for a total of 12 samples, ensuring spatial coverage of the lagoon (Figure 2). The sediments were taken using a stainless steel Van Veen grab sampler, between 0–5 cm depth. The tools were washed with lagoon water before sampling. The sediments were stored in airtight polyethylene bags, labeled, and immediately frozen at −20 °C until further processing. The location of each sample was recorded by a GPS.

At the laboratory, the sediments were defrosted by keeping them at room temperature for about 24 h, then dried in an oven at 40 °C (it has been proved by Gilli et al. [35] that samples drying at 40 °C does not cause evaporation losses of Hg). The samples were at last crushed using a mortar grinder, homogenized, stored inside polyethylene bags until the chemical analyses were carried out.
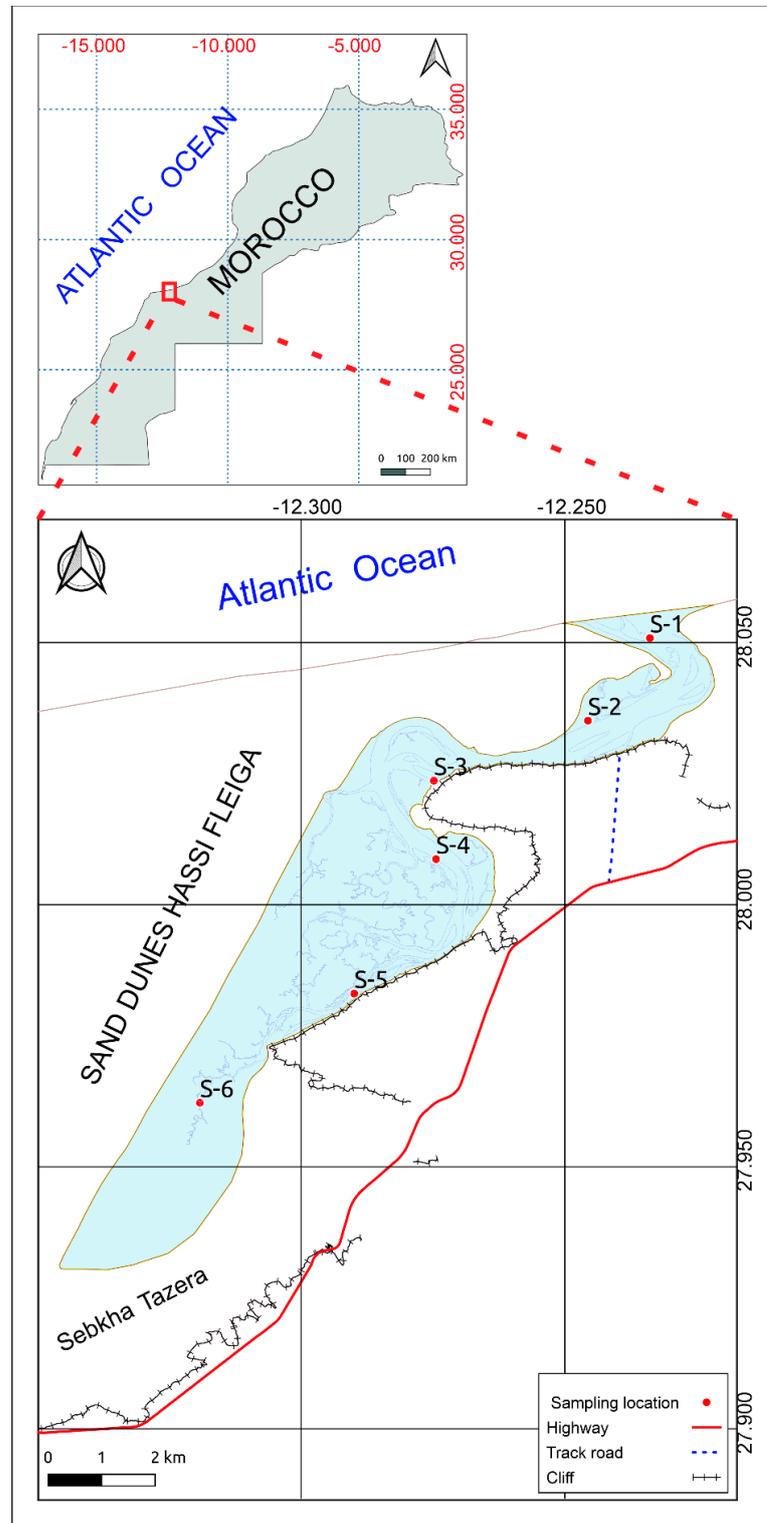
Figure 2. Map of the sampling locations at Khnifiss Lagoon.

The determinations of trace metals (except Hg) were accomplished using a microwave-assisted acid dissolution procedure, according to EPA method 3052, followed by the chemical analyses performed by: (i) An ICP-MS instrument (Perkin Elmer ELAN 6100) for the quantification of V, Cr, Co, Ni, Cu, Zn, As, Cd, and Pb (according to EPA method 6020 b); (ii) an ICP−OES instrument (Perkin Elmer Optima−2000 DV) for Al (according to EPA method 6010 d). All the reagents were of analytical grade. The analysis of Hg was carried out by the automated mercury analyzer FKV AMA-254; the advantage of this device is that Hg is directly determined on the dry sample and the acid dissolution step is not required [36]. Precision and accuracy were verified using marine sediment reference certified materials (PACS-3 and MESS-4; National Research Council Canada, NRCC): The recoveries of Al, V, Cr, Co, Ni, Cu, Zn, As, Cd, Hg, and Pb in MESS−4 ranged from 84.0 to 118.5%; the recoveries of Al, V, Cr, Co, Ni, Cu, Zn, As, Cd, and Pb in PACS−3 ranged from 88.1 to 100.5%. For all the elements, the quantitation limits were: V, Co, As, Pb = 0.05 mg/kg; Cd = 0.03 mg/kg; Cr = 0.5 mg/kg; Ni, Cu = 0.3 mg/kg; Zn = 1.0 mg/kg; Hg = 0.005 mg/kg; Al = 50 mg/kg.

Organic matter (OM), which in sea sediments originates from marine and terrestrial sources, was determined by Loss−On−Ignition procedure (LOI) [37]. About 4 g of each sediment were weighed and transferred in a porcelain crucible. The samples were heated at 105 °C for 24 h to remove the moisture content and the new weight was determined; then, the samples were kept in a muffle furnace at 550 °C for 4 h and weighed again. Lastly, the organic matter was calculated according to Equation (1):

$$LOI = \frac{\left(Weight_{105\,°C} - Weight_{550\,°C}\right)}{\left(Weight_{105\,°C}\right)} \times 100 \qquad (1)$$

The calcium carbonate content ($CaCO_3$) was measured by volumetric calcimetry, using a Bernard calcimeter [38,39]. Grain size measurement was determined using both dry and wet separation techniques [40–42]: The samples were pre-treated with H_2O_2 and washed with bi−distilled water to remove organic matter and chlorides, then oven-dried at 40 °C for 24 h; the coarse fraction was isolated by sieving, while the fine fraction (<63 μm) was ultrasonically dispersed using 0.5~10% sodium hexametaphosphate ($NaPO_3$)$_6$ for 24 h and analyzed by a particle size analyzer (Micromeritics, SediGraph).

2.3. Pollution Indices

To assess the levels of trace metal contamination and the possible anthropogenic impact on the sediments, three of the most used pollution indices were applied [43,44]: Enrichment Factor (EF), Index of geo-accumulation (Igeo), and Pollution Load Index (PLI). The calculations of the indices require the use of reference values from a background matrix, and the Shale data proposed by Turekian and Wedepohl [45] were chosen for this study (because local geochemical background values were not available).

The EF is used to evaluate the degree of anthropogenic influence on the occurrence of a metal in the soil/sediment; it is calculated through the ratio of the metal concentration in the sample with respect to the background matrix, using a normalizing element [46]. Several conservative elements have been used for normalization purposes [47–49], but we selected Al since it is generally the major constituent of clay minerals.

The EF for a trace metal is expressed as follow (Equation (2)):

$$EF = \frac{(C_n/C_{Al})Sample}{(C_n/C_{Al})Background} \qquad (2)$$

where C_n and C_{Al} are the concentrations of the trace metal (*n*) and Al.

The Igeo index, originally developed by Muller [50], was used to quantify the metal contamination related both to natural events and/or human activities [51]. It is calculated according to Equation (3):

$$\text{Igeo} = \log_2\left(\frac{C_n}{k \times B_n}\right) \tag{3}$$

where C_n is the concentration of the metal (n) in the sample and B_n is the geochemical background value of the same element [52]. The constant $k = 1.5$ is used as a correction coefficient for natural fluctuations in background values as well as for very small anthropogenic influences [50].

PLI provides an integrated and site wise comparative assessment of cumulative trace metal pollution [53]. This index can be interpreted as an appraisal of the comprehensive trace metal pollution in a given sample. It is calculated using the Equations (4) and (5):

$$\text{PLI} = \sqrt[n]{(\text{CF}_1) \times (\text{CF}_2) \times (\text{CF}_3) \times \ldots \times (\text{CF}_n)} \tag{4}$$

$$\text{CF} = C_{\text{Sample}}/C_{\text{Background}} \tag{5}$$

where CF is the contamination factor, C_{Sample} is the concentration of a selected metal in the sample, and $C_{\text{Background}}$ is the amount of the same element in the background matrix. Each index evaluates the sample quality according to the scores and classes [53–55] reported in Table 1.

Table 1. Scores and classes of Pollution Load index (PLI), Index of geo−accumulation (Igeo), and Enrichment Factor (EF).

PLI [53]	Degree of Contamination	Igeo [54]	Degree of Contamination	EF [55]	Degree of Contamination
<1	Unpolluted	Igeo ≤ 0	Uncontaminated	EF < 2	No enrichment/Depletion to mineral
>1	Polluted	0 < Igeo ≤ 1	Uncontaminated to moderately	2 ≤ EF < 5	Moderate enrichment
		1 < Igeo ≤ 2	Moderately contaminated	5 ≤ EF < 20	Significant enrichment
		2 < Igeo ≤ 3	Moderately to highly contaminated	20 ≤ EF < 40	Very high enrichment
		3 < Igeo ≤ 4	Highly contaminated	EF ≥ 40	Extremely enrichment
		4 < Igeo ≤ 5	Highly to extremely contaminated		
		Igeo > 5	Extremely contaminated		

2.4. Correlation Analysis

The data processing was performed using R statistical software [56]. Mean, maximum, minimum, standard deviation, first quartile, third quartile, and Skewness were calculated. The Shapiro-Wilk test was used to assess the normality of the dataset. Since the data were not normally distributed, the Spearman correlation coefficient was used in order to identify any significant pattern and relationship between the variables.

3. Results and Discussion

3.1. Geochemical Results

The complete dataset and the descriptive statistics are summarized in Table 2. The sediments of the lagoon showed a moderately alkaline pH, which ranged from 7.55 to 8.27, and exhibited spatial differences in the occurrence of trace metals (Figure 3). Stations S–2, S–4, and S–6 revealed higher concentrations compared to other locations, probably due to different grain size distribution; these samples, indeed, may have a larger accumulation of fine grained terrigenous and marine materials as reflected by their higher amounts of Al. In the summer season, station S–4 stands out for the higher concentrations exhibited for all the elements. In autumn, instead, S–6 has higher concentrations of V, Cr, Co, Cu, Zn, As, Hg, and Pb, while S–2 and S–4 had the maximum amounts of Ni and Cd.

The OM in sediments is a key parameter since it is related to the ability to concentrate (either by ion exchange and/or complexation) and release metals in marine and lagoon waters, and it is also a source of nutrients for aquatic fauna [57]. It ranged between 1.50 and 7.56%, with an average of 3.78% (Figure 4). The lowest amounts were observed, in both seasons, at S–1 (Foum Agoutir, inlet of the lagoon), due to high hydrodynamic characteristic

at this station and for the prevalence of sandy texture [26]. Generally, sediments in rough waters are sandy and then exhibit lower metal contents [47]. On the contrary, the maximum amounts of OM, that speed up the adsorption of the metals from the overlying water to bottom sediments, were recorded at station S–2 and S–4 due to the presence of seagrass, which encourages the retention of the fine particles. The relatively higher concentrations observed during the summer season for most of the trace metals may be attributed to the small differences in OM contents, having an average of $3.92 \pm 2.63\%$ compared to the $3.65 \pm 2.28\%$ in autumn. The lower OM in fall may be a consequence of elevated decomposition rates fostered by high levels of dissolved oxygen [27]. However, the lower metal concentrations found during the autumn might be also related to their mobilization from the sediments promoted by the overlying water. The ranges of OM percentages were compared to other Moroccan Lagoons, e.g., Moulay Bousselham Lagoon (1.24–15.74%) [58] and Oualidia lagoon (7.56–15.23%) [59]. The comparison showed that the OM values in the Khnifiss Lagoon sediments are about two times lower than the ones from the other local lagoons. This could justify the low concentration values of trace metals measured in this lagoon. Lefrere et al. [23] achieved the same conclusion using benthic fauna. In addition, the lagoon receives neither freshwater supply from the mainland nor waste discharges, and therefore is characterized only by a continuous renewal of water according to the current tidal trend [26].

The carbonate concentrations varied in a range of 8.25–58.8% and the highest values were registered, in both seasons, in stations S−1 and S−3. These results are reasonably related to the nature of the sediments since the presence of limestone fragments (from shells and snails) causes the rise of carbonate contents. The importance of determining and studying carbonates in marine systems is related to their ability to adsorb metal forming labile species [60].

Overall, the means of the analyzed elements are below the average shale's values [45,61,62] (Table 2) indicating low metal concentrations in the lagoon sediments (Figure 2). The world average shale value represents the background concentration of metals in a collection of several sedimentary rocks derived from argillaceous materials worldwide.

3.2. Contamination Degree Assessment

Pollution indices may help to quantify the level of enrichment of a sediment with trace metals [63]. The EFs calculated on the dataset are reported in Table 3. All the stations showed no enrichments (EF < 2) for V, Cr, Co, Ni, Cu, Hg, and Pb, both concerning the summer and the autumn, thus indicating concentration levels close to the natural background for marine sediments [55]. Moderate enrichments ($2 \leq EF < 5$) were found: For Cd (sample S−4) and Zn (sample S−6) in summer, that can be linked to the upwelling phenomenon of cold water masses on the southern Atlantic coasts of Morocco. Our findings corroborate with results of Idardare et al. [64] using *Nereis diversicolor* as bio−indicator; for As in both the seasons (S−1, S−3, S−5 in summer and S−1, S−3, S−5, S−6 in autumn), that can be attributed to the lithology of this area and especially to the presence of schist rocks [64,65]. On the whole, EF index values showed the following trend in summer As > Zn > Cd > Pb > V > Cr > Ni > Co > Cu > Hg and the following one in autumn As > Cd > Zn > Pb > V > Cr > Ni > Co > Cu > Hg. Nevertheless, according to Atgin et al. [66], EF values less than 5 cannot be considered noteworthy, and a minor enrichment can be related to the effect of the lithology. The Igeo results are summarized in Figure 5, showing that all the sampling stations can be classified as "uncontaminated" for the studied trace metals (Igeo < 0). The PLI values for all the samples ranged from 0.07 to 0.43, with averages of 0.22 and 0.20 in summer and autumn, respectively. The PLI trends were as follow: S−4 > S−2 > S−6 > S−5 > S−3 > S−1 in summer, and S−6 > S−2 > S−4 > S−5 > S−3 > S−1 in autumn (Figure 6). This index supports again the evidence that no appreciable input from anthropogenic sources affects the area (PLI < 1).

Table 2. Geochemical analysis results and descriptive statistics in surface sediments from Khnifiss Lagoon.

	Al %	V mg/kg	Cr mg/kg	Co mg/kg	Ni mg/kg	Cu mg/kg	Zn mg/kg	As mg/kg	Cd mg/kg	Hg mg/kg	Pb mg/kg	pH	OM %	CaCO$_3$ %	Clay %	Silt %	Sand %
S−1	*1.79*	*11. 5*	*7.50*	*1.36*	*12.3*	*2.23*	*15.9*	*6.70*	*0.06*	*<0.005*	*2.89*	*8.20*	*1.80*	*54.5*	*0.03*	*0.80*	*99.2*
S−2	*4.05*	*60.7*	*44.3*	*5.90*	*22.9*	*10.1*	*81.1*	*8.92*	*0.29*	*0.01*	*10.8*	*7.68*	*7.36*	*29.6*	*20.4*	*45.5*	*34.1*
S−3	*1.46*	*17.4*	*12.2*	*1.71*	*13.8*	*2.79*	*22.5*	*6.48*	*0.10*	*<0.005*	*3.44*	*7.89*	*2.25*	*51.9*	*1.80*	*2.80*	*95.4*
S−4	*4.78*	*76.8*	*57.8*	*7.13*	*26.1*	*12.6*	*101*	*11.1*	*0.40*	*0.01*	*12.4*	*7.59*	*7.16*	*13.3*	*22.4*	*58.6*	*19.1*
S−5	*2.10*	*24.6*	*15.4*	*2.40*	*15.0*	*5.77*	*36.6*	*8.57*	*0.09*	*<0.005*	*3.63*	*8.27*	*1.88*	*33.8*	*0.26*	*1.10*	*98.6*
S−6	*2.72*	*61.9*	*35.5*	*4.47*	*13.8*	*8.38*	*81.4*	*8.64*	*0.14*	*<0.005*	*5.71*	*7.82*	*3.07*	*22.4*	*5.54*	*7.82*	*86.6*
S−1	**1.45**	**10.9**	**7.74**	**1.21**	**9.95**	**1.95**	**15.0**	**6.70**	**0.06**	**<0.005**	**2.52**	**8.24**	**1.50**	**58.8**	**0.24**	**0.62**	**99.1**
S−2	**3.47**	**48.0**	**32.8**	**4.80**	**19.0**	**9.50**	**65.9**	**8.33**	**0.24**	**0.01**	**8.85**	**7.55**	**7.56**	**28.4**	**16.3**	**37.4**	**46.3**
S−3	**1.56**	**16.7**	**10.4**	**1.59**	**10.1**	**2.77**	**22.5**	**6.49**	**0.09**	**<0.005**	**3.24**	**7.76**	**2.34**	**45.1**	**0.51**	**2.50**	**97.0**
S−4	**3.41**	**47.1**	**34.5**	**4.36**	**23.0**	**9.71**	**65.4**	**8.87**	**0.23**	**0.01**	**7.17**	**7.93**	**3.93**	**23.8**	**10.3**	**21.4**	**68.3**
S−5	**1.78**	**19.2**	**12.2**	**1.99**	**12.3**	**3.60**	**28.0**	**8.04**	**0.10**	**<0.005**	**3.64**	**7.88**	**1.88**	**32.6**	**0.10**	**0.80**	**99.1**
S−6	**4.04**	**70.8**	**49.1**	**5.88**	**19.8**	**9.77**	**85.0**	**13.2**	**0.18**	**0.01**	**9.29**	**7.72**	**4.68**	**8.25**	**29.4**	**29.3**	**41.3**
Minimum	1.45	10.9	7.50	1.21	9.95	1.95	15.0	6.48	0.06	0.01	2.52	7.55	1.50	8.25	0.03	0.62	19.1
Maximum	4.78	76.8	57.8	7.13	26.1	12.6	101	13.2	0.40	0.01	12.4	8.27	7.56	58.8	29.4	58.6	99.2
Mean	2.72	38.8	26.6	3.57	16.5	6.60	51.7	8.50	0.16	0.01	6.13	7.88	3.78	33.6	8.94	17.4	73.7
St.dev.	1.18	24.7	17.8	2.09	5.47	3.81	31.3	2.00	0.11	0.00	3.46	0.25	2.35	16.1	10.6	20.6	30.4
1 Quartile	1.72	17.3	11.7	1.68	12.3	2.78	22.5	6.70	0.09	0.01	3.39	7.71	1.88	23.5	0.26	1.03	45.1
3 Quartile	3.61	61.0	37.7	5.07	20.6	9.73	81.2	8.88	0.24	0.01	8.96	8.00	5.30	46.8	17.3	31.3	98.8
Ref. data:																	
Average Shale	8	130	90.0	19.0	68.0	45.0	95.0	13.0	0.30	0.40	20.0	-	-	-	-	-	-

Bold: autumn season; italic: summer season.
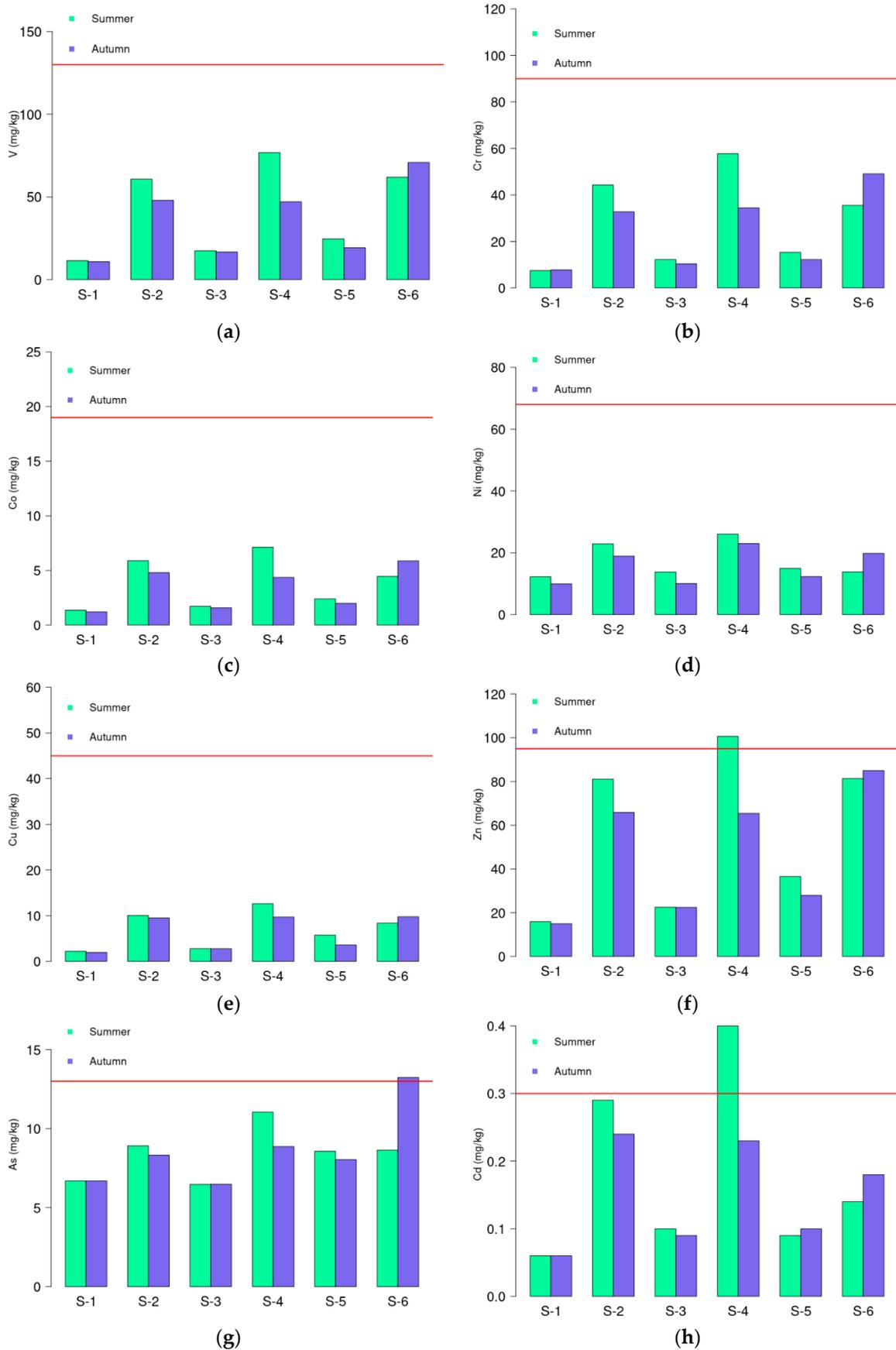
Figure 3. *Cont*.
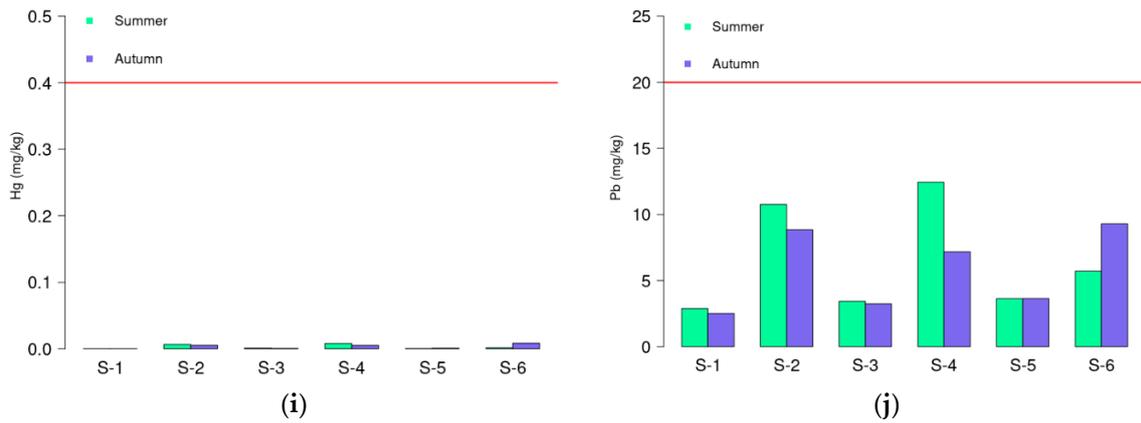
Figure 3. Spatial variations of the investigated metals during summer and autumn of the surface sediments from Khnifiss Lagoon: (**a**) Vanadium; (**b**) Chromium; (**c**) Cobalt; (**d**) Nickel; (**e**) Copper; (**f**) Zinc; (**g**) Arsenic; (**h**) Cadmium; (**i**) Mercury; (**j**) Lead. Horizontal solid red line represents the Average Shale Background value.
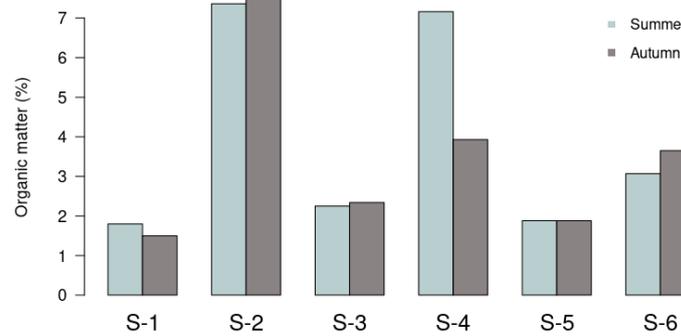
Figure 4. Organic matter (%) distribution in Khnifiss Lagoon during summer and autumn.

Table 3. Enrichment Factor (EF) in the surface sediments from Khnifiss Lagoon.

	V	Cr	Co	Ni	Cu	Zn	As	Cd	Hg	Pb
S−1	*0.39*	*0.37*	*0.32*	*0.81*	*0.22*	*0.75*	*2.30*	*0.86*	*0*	*0.65*
S−2	*0.92*	*0.97*	*0.61*	*0.67*	*0.44*	*1.69*	*1.36*	*1.94*	*0.03*	*1.06*
S−3	*0.73*	*0.74*	*0.49*	*1.11*	*0.34*	*1.30*	*2.73*	*1.73*	*0.01*	*0.94*
S−4	*0.99*	*1.07*	*0.63*	*0.64*	*0.47*	*1.78*	*1.42*	*2.22*	*0.03*	*1.04*
S−5	*0.72*	*0.65*	*0.48*	*0.84*	*0.49*	*1.47*	*2.51*	*1.12*	*0*	*0.69*
S−6	*1.40*	*1.16*	*0.69*	*0.60*	*0.55*	*2.52*	*1.95*	*1.41*	*0.01*	*0.84*
S−1	**0.46**	**0.48**	**0.35**	**0.81**	**0.24**	**0.87**	**2.85**	**1.02**	**0**	**0.70**
S−2	**0.85**	**0.84**	**0.58**	**0.64**	**0.49**	**1.60**	**1.48**	**1.87**	**0.03**	**1.02**
S−3	**0.66**	**0.59**	**0.43**	**0.76**	**0.32**	**1.21**	**2.56**	**1.47**	**0.01**	**0.83**
S−4	**0.85**	**0.90**	**0.54**	**0.79**	**0.51**	**1.61**	**1.60**	**1.84**	**0.03**	**0.84**
S−5	**0.66**	**0.61**	**0.47**	**0.81**	**0.36**	**1.32**	**2.78**	**1.49**	**0.01**	**0.82**
S−6	**1.08**	**1.08**	**0.61**	**0.58**	**0.43**	**1.77**	**2.02**	**1.19**	**0.04**	**0.92**
Average	0.81	0.79	0.52	0.75	0.40	1.49	2.13	1.51	0.02	0.86

Bold: autumn season; italic: summer season.

3.3. Correlation Matrix

The Spearman's correlation coefficients for Al, the OM and the studied metals (Al normalized) are presented in Table 4. According to the results, some trace metals (especially V, Cr, Co, Zn, and Pb) show a very good correlation with the OM, Al, clay, and silt, indicating that their distribution in the samples is mainly controlled by the OM and the sediment's fine fraction; moreover, this evidence suggests that the geogenic source of these trace element is still predominant over anthropogenic sources.
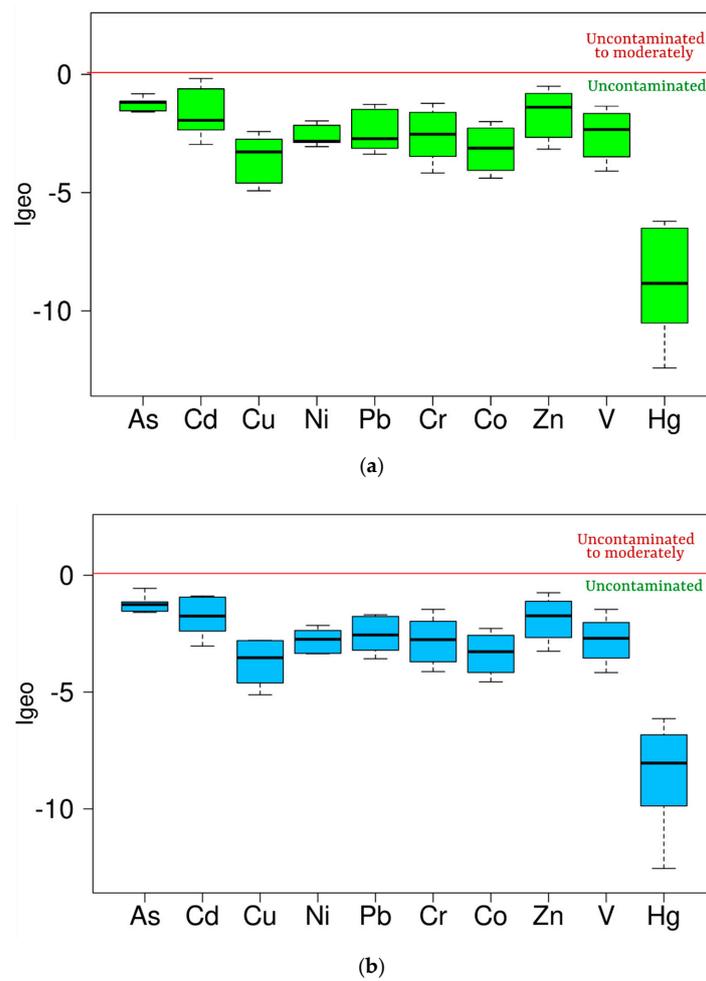
Figure 5. The Index of geo−accumulation (Igeo) of metals in Khnifiss sediments: (**a**) Summer season; (**b**) autumn season.
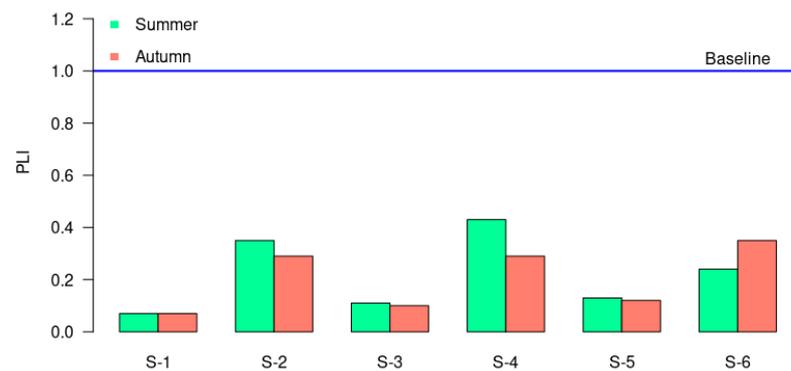
Figure 6. Pollution Load Index (PLI) for all sediments from Khnifiss Lagoon.

3.4. Comparison with Other Studies

The overall results were compared with the data published in a selection of papers focused on lagoon areas of Morocco and other countries around the world (Table 5) [7,58,59,64,67–75]. With the exclusion of the data from Rumisha et al. [68] at Dar es Salam coast (Tanzania), the amounts of trace metals at Khnifiss Lagoon were lower than the ones found in the other sites. Furthermore, a comparison of our results with previous studies in the Khnifiss area reveals that the levels of all trace metals, except for Pb and Zn, are two times lower than those reported by Idardare et al. [64].

Table 4. Spearman's correlation matrix in Khnifiss Lagoon sediments.

	Al	V	Cr	Co	Ni	Cu	Zn	As	Cd	Hg	Pb	pH	OM	CaCO₃	Clay	Silt	Sand
Al	-	*0.66*	*0.66*	*0.66*	*−0.77*	*0.49*	*0.77*	*−0.89*	*0.66*	*−0.83*	*0.60*	*−0.77*	*0.77*	*−0.89*	*0.83*	*0.83*	*−0.83*
V	**1.00**	-	*1.00*	*1.00*	*−0.77*	*0.66*	*0.94*	*−0.54*	*0.66*	*−0.62*	*0.60*	*−0.77*	*0.77*	*−0.89*	*0.83*	*0.83*	*−0.83*
Cr	**0.94**	**0.94**	-	*1.00*	*−0.77*	*0.66*	*0.94*	*−0.54*	*0.66*	*−0.62*	*0.60*	*−0.77*	*0.77*	*−0.89*	*0.83*	*0.83*	*−0.83*
Co	**1.00**	**1.00**	**0.94**	-	*−0.77*	*0.66*	*0.94*	*−0.54*	*0.66*	*−0.62*	*0.60*	*−0.77*	*0.77*	*−0.89*	*0.83*	*0.83*	*−0.83*
Ni	**−0.71**	**−0.71**	**−0.60**	**−0.71**	-	*−0.54*	*−0.83*	*0.77*	*−0.31*	*0.62*	*−0.26*	*0.66*	*−0.54*	*0.77*	*−0.60*	*−0.60*	*0.60*
Cu	**0.77**	**0.77**	**0.83**	**0.77**	**−0.37**	-	*0.83*	*−0.20*	*0.14*	*−0.83*	*0.09*	*−0.14*	*0.31*	*−0.71*	*0.37*	*0.37*	*−0.37*
Zn	**0.94**	**0.94**	**1.00**	**0.94**	**−0.60**	**0.83**	-	*−0.60*	*0.54*	*−0.83*	*0.49*	*−0.66*	*0.71*	*−0.94*	*0.77*	*0.77*	*−0.77*
As	**−0.77**	**−0.77**	**−0.71**	**−0.77**	**0.66**	**−0.89**	**−0.71**	-	*−0.54*	*0.62*	*−0.60*	*0.77*	*−0.77*	*0.66*	*−0.71*	*−0.71*	*0.71*
Cd	**0.24**	**0.24**	**0.24**	**0.24**	**0.00**	**0.72**	**0.24**	**−0.72**	-	*−0.41*	*0.94*	*−0.89*	*0.89*	*−0.71*	*0.94*	*0.94*	*−0.94*
Hg	**−0.88**	**−0.88**	**−0.88**	**−0.88**	**0.68**	**−0.88**	**−0.88**	**0.88**	**−0.41**	-	*−0.41*	*0.41*	*−0.62*	*0.83*	*−0.62*	*−0.62*	*0.62*
Pb	**0.89**	**0.89**	**0.77**	**0.89**	**−0.83**	**0.77**	**0.77**	**−0.94**	**0.48**	**−0.88**	-	*−0.83*	*0.94*	*−0.60*	*0.89*	*0.89*	*−0.89*
pH	**−0.71**	**−0.71**	**−0.49**	**−0.71**	**0.77**	**−0.37**	**−0.49**	**0.66**	**−0.24**	**0.49**	**−0.83**	-	*−0.89*	*0.77*	*−0.94*	*−0.94*	*0.94*
OM	**0.89**	**0.89**	**0.77**	**0.89**	**−0.83**	**0.77**	**0.77**	**−0.94**	**0.48**	**−0.88**	**1.00**	**−0.83**	-	*−0.77*	*0.94*	*0.94*	*−0.94*
CaCO₃	**−0.94**	**−0.94**	**−1.00**	**−0.94**	**0.60**	**−0.83**	**−1.00**	**0.71**	**−0.24**	**0.88**	**−0.77**	**0.49**	**−0.77**	-	*−0.89*	*−0.89*	*0.89*
Clay	**0.83**	**0.83**	**0.77**	**0.83**	**−0.94**	**0.60**	**0.77**	**−0.77**	**0.12**	**−0.88**	**0.89**	**−0.66**	**0.89**	**−0.77**	-	*1.00*	*−1.00*
Silt	**0.89**	**0.89**	**0.77**	**0.89**	**−0.83**	**0.77**	**0.77**	**−0.94**	**0.48**	**−0.88**	**1.00**	**−0.83**	**1.00**	**−0.77**	**0.89**	-	*−1.00*
Sand	**−0.94**	**−0.94**	**−0.89**	**−0.94**	**0.89**	**−0.71**	**−0.89**	**0.83**	**−0.24**	**0.88**	**−0.94**	**0.77**	**−0.94**	**0.89**	**−0.94**	**−0.94**	-

Bold: autumn season; italic: summer season.

Table 5. Metal concentrations (mg/kg), as dry weight, measured for the present study (ranges and mean) and comparison with other lagoon areas around the world.

Country	Location	V	Cr	Co	Ni	Cu	Zn	As	Cd	Hg	Pb	References
Morocco	Khnifiss Lagoon	10.9–76.8 (38.8)	7.50–57.8 (26.6)	1.21–7.13 (3.57)	9.95–26.1 (16.5)	1.95–12.6 (6.60)	15.0–101 (51.7)	6.48–13.2 (8.50)	0.06–0.40 (0.16)	<0.005–0.01 (0.01)	2.52–12.4 (6.13)	This study
	Khnifiss Lagoon	-	62	-	35	17	70	-	0.37	-	6	[64]
	Moulay Bousselham Lagoon	-	19–113	-	11–96	22–311	167–759	-	0.02–0.84	0.02–0.61	6.2–32	[58]
	Oualidia Lagoon	-	52.48	-	-	36.46	227.86	-	-	0.66	54.59	[59]
	Nador Lagoon	85	55	15	26	36	98	14	1	-	52	[67]
	Oualidia Lagoon	76.9	102.4	13.1	15.73	17.7	75.8	10.9	0.66	-	10.1	[72]
Italy	Bagnoli	100	39.8	-	12.6	26.4	287	41.6	0.46	0.35	121	[7]
Tanzania	Dar es Salaam Coast	4.55	4.28	0.76	1.12	0.83	5.75	0.71	0.217	-	1.21	[68]
Puerto Rico	Joyuda Lagoon	-	-	-	-	22	52	18	0.10	0.17	7.6	[69]
	San Jose Lagoon	-	-	-	-	105	531	13.3	1.8	1.9	219	[69]
Iran	Chabahar Bay, Oman Sea	47.21	185.01	8.91	40.51	14.16	37.86	13.22	-	-	12.87	[70]
Saudi Arabia	Al Kharrar Lagoon	-	20.62	4.77	8.67	16	39.71	1.67	0.26	0.01	50.87	[71]
Bangladesh	Sangu River Estuary	-	25.15	-	32.75	29.24	88.97	2.58	-	-	19.58	[73]
Turkey	Çardak Lagoon	43.6	55.6	12.0	57.9	32.9	65.3	18.6	0.2	0.046	18.6	[74]
Australia	Narrabeen Lagoon	-	21	5.0	11	16	103	-	-	-	47	[75]

4. Conclusions

In this study, 10 trace metals (V, Cr, Co, Ni, Cu, Zn, As, Cd, Hg, and Pb) in surface sediments from Khnifiss Lagoon (Morocco) were examined and compared to the values found in the lagoon sediments from other countries and with the literature background data. The results, including correlations and a selection of contamination indices, suggested that the trace element contents in Khnifiss Lagoon are of natural origin and not significantly affected by anthropogenic sources. The current status of the area is also related to the limited access to the ecosystem, denoting a good example of wetland management. Our data represent only a preliminary screening that can be used as a starting point for a more detailed evaluation of the background levels of trace metals in the Moroccan lagoon areas. Further investigations are in progress on the site, including the study of the trace metals temporal trend. Due to the presence of low concentrations of trace metals, periodic monitoring campaigns of the lagoon are required, in order to highlight any possible early-stage contamination event and to limit/reduce any negative effects utilizing the best environmental management practices available.

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