Sediment pollution: An assessment of anthropogenic and geogenic trace elements contributions along the central Algerian coast

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1. Introduction

Trace metals in coastal sediment originating from anthropogenic sources are of increasing interest and concern in modern human society. Due to their stability, bioaccumulative nature, persistence, and their various forms of toxicity in the environment (Inal et al., 2018; Gao et al., 2015), metals can affect the quality of the coastal ecosystems and present a considerable risk to the aquatic organisms and human health (Abderrahmani et al., 2021; Guendouzi et al., 2020). Following their release in the catchment areas from various sources, metals are usually transported through the river system to the coastal zone in dissolved form or bound to suspended particles (Benhalima et al., 2022). Historically, trace metals in the coastal areas are predominantly from the continental weathering of rocks and soil materials (Viers et al., 2009). However, an additional fraction of metals discharged from land-based activities, such as mining and various industrial and agricultural activities, may contribute to the contamination of marine sediments (Barron et al., 2022; Belhadj et al., 2017; Sbarbati et al., 2020). To evaluate the potential contamination of sediment, the man-induced accumulation should be distinguished from the natural background values (Esen et al., 2010). Sediment cores from the coastal zone have been shown to be excellent indicators for the investigation of depositional trends, sources and risk of trace metals (Li and Li, 2017). Many researchers have studied geochemistry and the environmental quality of sediment cores in various aquatic ecosystems globally (Barbieri et al., 2018; Gao et al., 2016; Moushmi et al., 2022; Romano et al., 2018; Zhu et al., 2017).

Like many Mediterranean countries, Algeria is facing various environmental challenges in recent years. Among them, the increase in population and their activities in the coastal zone (Khelil et al., 2019). Algeria has a traditional agricultural and oil production-based economy, but with a short history of industrialization and urbanization compared to the developed countries, which makes it a desired area for fieldwork to provide valuable geochemical information on anthropogenic impacts. In fact, Algeria experienced an industrial and agricultural renaissance only in the 1970s after its independence in 1962 and then started an economic recovery after the end of the civil war in 1999,

with rapid agricultural development during the last two decades. Agricultural activity has therefore intensified in response to the rapid increase in population, which has increased by 100 % over the last thirty-five years, from 22 million inhabitants in 1985 to 40.4 million in 2015 (Guendouzi et al., 2020) up to 44 million in 2021. Additionally, the Mediterranean climate that characterized the northern country has led to mass population displacement to coastal towns. As a result, the coastal territory concentrates by itself about 45 % of the population, which represents only 1.9 % of the country's total territory (Chemrouk and Chabbi, 2016). This situation exerts great pressure on the coastal ecosystems adjacent to populated areas (Inal et al., 2018).

Despite these aspects, there were some studies on trace element distribution in the Algerian coastal sediments. These studies have focused on the spatial distribution of trace elements in surficial sediments (Inal et al., 2018; Bachouche et al., 2017; Belhadj et al., 2017; Kouidri et al., 2016); however, trace metal investigations in sediment cores are rarely studied. Hence, the major purposes of this research were (1) to investigate the distribution of trace metals on the central Algerian coast, (2) to analyze the depositional behavior and origin of trace metals through multi-statistical analyses, and (3) to assess the degree of the metal enrichment and the potential sediment toxicity. The results obtained in this work may provide baseline data for the present and future assessment of environmental risks associated with the occurrence of trace metals to implement coastal zone management strategies.

2. Materials and methods

2.1. Study area

Located in the southwestern part of the Mediterranean Sea, Algeria's coastline extends about 1622 km and includes fourteen coastal cities. On the central coast, three towns, namely Algiers, Boumerdes, and Tipasa are exceptional cases of urban expansion areas where land-based and sea activities have intensified in recent years. Most previous studies were limited to Algiers which is

considered the most industrialized in the country. This city hosts the most important industrial zones in the country, among which are the Oued Samar and Baba Ali industrial zones, where factories constantly discharge untreated effluent into Algiers bay via El Harrach river (Fouzia et al., 2013). On the other hand, the inner part of Algiers Bay contains paper and iron factories, chemical and textile industries, desalination plants, metal processing, food and beverage manufacturing, tanneries and oil (Bachouche et al., 2017). Additionally, the port of Algiers which is located in the western part of the bay hosts some of such industries, as well as oil refinery plant and petrochemical factory, which impact the adjacent marine environment (Taieb-Errahmani et al., 2020). The Intensive maritime traffic and urban wastes in the capital are the other factors that influence sediment quality. Unlike Algiers, Tipaza and Boumerdes are regarded as agricultural and tourist zones vocation. In addition to agricultural amendments plants, and fertilizer factories that characterized the areas, several industrial infrastructures have been developed on the coast to meet the growing need for drinking water and energy like seawater desalination plants of Fouka (Tipasa) and thermal power station of cap Djinet (Boumerdes) (Khelil et al., 2019). A recent study reported that the most polluted sediments along the Algerian coastline are located on the central coast (Inal et al., 2018); thus, it is of great interest to evaluate the impact of human activities on this particular marine environment. Furthermore, several rivers are discharged along the central marine coastline (Inal et al., 2018), the most important being El Harrach river entering into Algiers Bay, the Nador river in Bou Ismail Bay, and the Isser river entering Zemmouri Bay (Fig.1). The rivers drain mainly urban and agricultural areas and their hydrological regime is very variable characterized by temporary flows following generally the rainfall contributions (Karahacane et al., 2020). According to meteorological data measured and recorded by the weather station of Dar El Beida (Algiers), mean annual precipitation (P) for the period between 2006 and 2016 came to 644 mm (www.meteo.dz). The precipitation is very irregular in time and space, reflecting heavy rainfall (occasionally reaching 202 mm) over a small number of days during the year (Meddi et al., 2017). This represents the main cause of episodic flash floods which appear

frequently on the central coast (Boutaghane et al., 2020). The knowledge of flash floods is not well documented and studied in Algeria because of the non-availability of Hydrological data in recent years. Nevertheless, the maximum flows (extreme flood flows) recorded for these events before 2011 reached 268, 876 and 1489 m3/s for the Nador, El Harrach and Isser rivers, respectively (Karahacane et al., 2020). During the episodic flash flood, rivers transport unconsolidated soils and reworked anthropogenic materials, which can long-term influence the submarine channels (Orani et al., 2019). Thereafter, most of the sediment discharged in the central coastal sea extends offshore from the mouth of the rivers according to an increasing inshore silt gradient characterized by a succession of fine sand, muddy sand, sandy mud, and pure mud (Bakalem et al., 2009).

2.2. Sampling and sample treatment

The sampling campaign of the sediments cores was carried out in August 2017 onboard the ship "Grine Belkacem". Three sediment cores A, B, and Z were taken from three bays (Bay of Algiers, Bay of Bou-Ismail, and Bay of Zemmouri, respectively) to cover areas likely to be affected by human activities, while a fourth sediment core (S) was taken off Djinet beach (Fig. 1), in an uncontaminated area with the trace metals (Ahmed et al., 2018). Details of the sampling stations are given in Suppl. Tab.1. The four sediment cores were sampled using an Uwitec® gravity sediment corer. Cores were sub-sampled at 1 cm thick intervals for the top 10 cm except for the top interval sliced in two 0.5 cm parts, and then the samples were taken every 2 cm until the bottom. The sliced subsamples (n = 87) were sealed separately in polyethylene bags and stored below 0°C. After their transport to the laboratory, the subsamples were weighed before and after freeze-drying to determine the total water (TW) content.

2.2.1. Grain size, sulfur and organic matter analyses

Samples for particle sizing were measured at the Laboratory of Science in Industrial Process Engineering (USTHB) using a laser analyzer Mastersizer 2000 (Malvern PANalytical corporation), which is applicable to the grain size ranging from 0.02-2000 µm. Sediment samples were pretreated

with a solution of H_2O_2 (30 %) and distilled water (1:3) and washed to remove salts and organic debris (Romana et al., 2018). Samples were dried at 105° C, gently crushed in an agate mortar, and homogenized by straining through 2-mm nylon sieved. The first stage of analysis was to gradually add a quantity of the sieved sample into a measuring system of the laser analyzer until the obscuration was between 10 and 20%. By circulating the sample in the measuring system using a stirring and sonication device, a detector records the beam diffracted off of the particles in suspension. Each sample was measured under the same conditions: 2800 r min-1 stirring rate, 3 min sonication, and 10%-20% obscuration (Liu et al., 2014). All the analysis steps are described in detail by Ryzak and Bieganowski (2011). The particle size distribution in this work was evaluated as a percentage representation of grain-size fractions according to ISO14688 (2002).

The determination of total sulfur content (%) was carried out at Nuclear Research Centre (DRARIA) using an elementary analyzer TruSpec Micro CHNS (Leco company) which is equipped with a dynamic flux infrared cell for the detection and quantification of the element as SO_2. According to Gazulla et al. (2012), the samples of fine sediment (0.350 g) are placed in cordierite boats, which were introduced in a ceramic furnace and combusted at 1350 °C in a pure oxygen environment (2.4 bar ± 10 %). During this process, the sulfur-bearing compounds broke down and liberated free sulfur, which was oxidized to form SO_2 (Andrade et al. 2009). The method was validated using certified reference materials STSD-1 from Canadian Certified Reference Material Project with 0.18 ± 0.05 % m/m S (Lynch, 1990).

The organic matter (OM) content was determined at the Laboratory of Marine and Coastal Ecosystems (ENSSMAL) by measuring the loss on ignition (LOI) of the sample after calcination in a muffle furnace at 550 °C for 4 h following the method described by Heiri et al., (2001).

2.2.2. Chemical element analyses

Trace and major element concentrations in cores A, B, Z and S (including the background samples) were analyzed at CEREGE (Aix-en-provence, France). The freeze-dried sediment samples were

crushed to powder within an agate mortar, then a quantity of 100 ± 5 mg of this sample was weighed in Teflon micro-wave tubes, and 3 ml of 70 % HCl, 4 ml of 67 % HNO_3, 1 ml of 35 % H_2O_2 and 0.5 ml of 47 % HF (VWR Chemicals, all of trace grade quality) were progressively added into the tubes. The mixtures were digested under high temperature and pressure conditions in a single reaction chamber (SRC) microwave (Milestone UltraWAVE® microwave). A rack of 12 samples is automatically lowered in the reaction chamber, the chamber is sealed and pressurized with an inert gas (N2, 99.5 Linde, pressure 30 bars), then a five-step digestion procedure is applied, microwave energy is auto-regulated to achieve the temperature criteria (step 1 ramp from RT to 120 °C in 15 min, step 2 stay 120 °C during 15 min, step 3 ramp to 220 °C in 15 min, step 4 stay at 220 °C during 20 min and the step 5 cooling to RT, pressure release, rack automatically lifted up). After cooling, the residues of the digestion were diluted with 2 % ultrapure HNO_3 to 50 ml PE tubes and stored at 4 °C. The digested steps used in the present study was described by Inal et al. (2018) and Benhalima et al. (2022), and recommended by the European Centre for Research and Teaching in Environmental Geosciences (CEREGE). Total concentrations of trace metals (Mn, V, Co, Ni, Cr, Cu, Zn, Pb, As, Ag, and Cd) and major elements (Fe, Al and Na) were measured in CEREGE (France) using inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer NexION 300X, USA) and inductively coupled plasma atomic emission spectrometry (ICP-AES, PerkinElmer Optima 4300 DV, USA), respectively.

2.2.3. Quality assurance and quality control

All dilution and preparation of solutions was carried out with Ultrapure water (resistivity N18 MΩ class) obtained from Milli-Q Element system (Millipore, USA). All of the vessels, PE and teflon were soaked in 10 % HNO_3 for at least 24 h and then carefully rinsed with MilliQ water. The calibration curves were established using multi-solution standards CCS4, CCS5, and CCS6 from inorganic ventures (New Jersey, USA) diluted in 2 % HNO3 solution. The internal standards for ICP-MS and ICP-AES were Rh-103 and Y, respectively. Three replicates of each sample were analyzed to control

the precision of measurements, and the results showed that the relative deviations were generally below 5 %, except for cadmium was 2-40 %. All analytical results were presented with their expanded uncertainties (Suppl. Tab. 5): $Ue = k\,uc$ where uc is the combined standard uncertainty and k is a coverage factor (k = 2) as reported in Rasul et al. (2018). The accuracy and precision of ICP-MS and ICP-AES analyses and the possible loss of elements during the digestion steps were checked by the use of Certified Reference Materials CRM020-050, CRM008-050, and CRM 7200 (Suppl. Tab. 2). In all cases, replicate sediment samples were analyzed along with replicates of these reference materials and appropriate blanks at the CEREGE labs (France).

2.3. Risk assessment methods of trace metals contamination

The geologic substrate is generally the main natural source of inorganic chemical species in the ecosystem. However, anthropogenic activities may introduce high amounts of these elements into the coastal zone, making it now sometimes difficult to differentiate natural from anthropogenic components (Belhadj et al., 2017). The common approach used to estimate the anthropogenic impact on sediment chemistry is to compare the metal content of a sediment sample with shale, upper continental crust, and fine-grained sediment (Guo and Yang, 2016). Viers et al. (2009) suggested that the chemical composition of such reference materials used for normalization does not necessarily represent the local geological substratum. For the contamination assessment, considering the mineralogical and physicochemical characteristics of the study area that may imply natural enrichment or depletion for some chemical elements, the use of background levels measured in uncontaminated sediments of the same sampling area was preferred instead of the average crustal composition (Abrahim and Parker, 2008). Numerous studies have used the deep unpolluted levels of the cores to represent the natural geochemical composition of sediments (Guo and Yang, 2016; Morelli et al., 2012; Orani et al., 2019; Romano et al., 2018). Therefore, the average concentrations of metals in the deepest three samples of core S are taken as local background values for the calculation of different pollution assessment indices. The use of core S as background is justified by

the low trace metal concentrations and a very constant trend of almost all elements' profiles along the depth, as shown in supplementary data (Fig. 1S and Tab. 5S).

2.3.1. Enrichment factor (EF)

A very common approach to estimating the anthropogenic impacts on coastal sediment is to calculate a normalized enrichment factor (EF) for metal concentrations above unpolluted sediment levels (Ip et al., 2007; Kouidri et al., 2016). Chester and Stoner (1973) developed the enrichment factor formula, which has been used by many authors (Ahmed et al., 2018; Benhalima et al., 2022; Bing et al., 2016; X. Gao et al., 2015; Guendouzi et al., 2021; Lin et al., 2016; Zhu et al., 2017). The enrichment factor (EF) was calculated for each sub-sample of the sediment core using the following equation:

$$EF = (Element/Fe)_{Sample}/(Element/Fe)_{Background} \quad \text{(Eqt. 1)}$$

Where $(Element/Fe)_{Sample}$ is the ratio of the element concentration in a given sample to Fe, while $(Element/Fe)_{Background}$ is the natural background value of the ratio among the same elements and Fe. Al or Fe are often been used as reference metals (Bachouche et al., 2017) to determine whether the sediment sample was enriched with metals when compared to the natural conditions. Other metals have been proposed for the calculation of EF such as Ca, Ti, Sc and Mn (Salmanighabeshi et al., 2015). In this assessment, iron was taken into account in the EF calculations, the choice of Fe as a reference metal (Eq. 1) will be discussed further later in section 3.4.1.

2.3.2. Pollution load index (PLI)

Another commonly used approach in sediment analysis is the Pollution Load Index (PLI) proposed by Tomlinson et al. (1980) to assess the sediment quality and the degree of trace metal pollution in aquatic ecosystems. It is defined as the n^{th} root of the product of n contamination factors (CF):

$$PLI_{site} = \sqrt[n]{(CF_1 \times CF_2 \times CF_3 \times \dots CF_n)} \quad \text{(Eqt. 2)}$$

Where, CF: contamination factor; and n: number of metals examined.

2.4. Sediment quality guidelines

Numerous sediment quality guidelines (SQGs) have been developed in North America to measure adverse biological effects on aquatic organisms upon exposure to sediment-bound contaminants (Long and MacDonald, 1998). Two sets of SQGs were developed for freshwater and marine ecosystems as non-regulatory benchmarks to facilitate interpretation of chemical data, effect range low/effect range median values (ERL/ERM), and the threshold effect level/probable effect level (TEL/PEL) (Bakan and Özkoç, 2007). ERLs and TELs refer to the concentrations below which harmful effects upon sediment-dwelling fauna would only rarely be expected. In contrast, ERMs and PELs indicate concentrations above which adverse biological effects would always be observed (Long and MacDonald, 1998). However, the concentrations that fall between the ERLs/TELs and ERMs/PELs correspond to a range in which effects on live sediment organisms occasionally occur. Mean sediment quality guideline quotients (Qm-SQG) have been proposed by Long et al. (2006) to estimate the toxicological risks of contaminant mixtures in sediment samples. In this study, mean SQG quotients were determined by dividing the concentrations of metal by their respective SQGs values such as the effects range low (ERM) and probable effect level (PEL), and averaging the obtained quotients for individual chemicals. Qm-SQG can be expressed as:

$$Qm - SQG = \sum_{i=1}^{n} (Mi/SQGi)/n \qquad \text{(Eqt. 3)}$$

Where Mi is the concentration of the i^{th} metal, SQGi is the guideline corresponding to ERL or TEL values for the metal, and n is the number of metals. The probabilities of toxicity in marine sediments increase as chemical concentrations of heavy metals increase relative to empirically derived sediment quality guidelines. According to Long et al. (2000), Sediment with Qm-ERM values less than 0.1, 0.11-0.5, 0.51-1.5, and > 1.50 are predicted to be toxic by 9 %, 21 %, 49 %, and 76 % to sediment-dwelling organisms, respectively, while for Qm-PEL, the values of < 0.1, 0.11-1.5, 1.51-2.3 and > 2.3 corresponds to 8 %, 21 %, 49 % and 73 % likelihood of toxicity in sediments, respectively.

2.5. Statistical analyses of data

Pearson correlation analysis was conducted for each core to establish geochemical associations and behavior of the elements in sediments. A two-tailed Pearson's coefficient was used in correlation analysis. Principal component analysis (PCA) was performed to check the factors that control the geochemical origin of the elements in coastal sediments. PCA was subjected to varimax rotation with the Kaiser normalization method to maximize each factor's component loadings and eliminate invalid components. All variables were tested by Kaiser-Meyer-Olkin and Bartlett tests. Statistical processing of the data was performed using SPSS software 22.0.

3. Results and Discussion

3.1. Variation of sediment properties

The sediment properties, such as organic matter “OM”, total water content “TW”, total sulfur “TS”, and grain size, are key factors affecting the behavior and mobility of metals in marine sediments. The vertical distributions and full data of OM, TW and TS in cores A, B and Z are shown in Fig. 2 and Suppl. Tab. 3, respectively. OM contents were significantly higher in core A located in Algiers Bay, than in the other cores. The contents increased rapidly from the bottom of the core to about 9 cm of depth and presented a wide variability ranging from 9.1 % to 13.3 %. The primary source of OM inputs in Algiers Bay is believed to derive from the allochthonous C fluxes, like domestic and urban effluent in El Harrach river, and represent a severe effect that impacts the ecosystems and sediment-dwelling organism's health (Bakalem et al., 2009; Benhalima et al., 2022; Boudjema et al., 2014). In contrast, significant increases in the top of the cores B and Z (up to 11.7 % and 10.8 %, respectively) were found, suggesting rapid burial of freshly deposited organic carbon following massive inputs from urban and agricultural wastewater discharges. This leads to rapid remineralization of OM near the oxic-suboxic interface (Kristensen et al., 2008). Compared with the evident increasing trend towards the topmost interval of cores B and Z, the OM content in core A exhibited a marked decrease

above 9 cm of depth due to the diversion of El Harrach effluents to the Baraki wastewater treatment plant in 2007 and following the increase in the treatment capacity of the station in 2015. The partially treated effluents discharged from the wastewater plant to El Harrach river have a beneficial effect in total sulfur content which decreased in the topmost interval of core A from 0.9 to 0.25 % (Fig. 2, Suppl. Tab. 3). On the other hand, the TS content was markedly decreased from the bottom until the 4 cm depth in core B, whereas it remained fairly stable along the core Z except for the moderately high peaks observed at 2, 14 and 16 cm of depth (Fig. 2). The high TS contents in cores B and Z probably traduce enrichment by diagenetic processes resulting from the biological sulfate reduction in these depths (Appelo and Postma, 2004).

The cores sampled from the three bays of the central Algerian coast consist of three sediment types (silt, clay, and traces of fine sand). The basic statistics on textural data and mean grain size are listed in Suppl. Tab. 4. Observations reveal that the three fractions vary in the study area. On the whole, the sediments are dominated by silt, which accounts for more than 67 %. This is followed by clay, with an average mass percentage of 20.8 %, while fine sand, is the smallest fraction in sediment with a mean percentage of 2.63 %. These findings indicate that the high supply of fine sediments in the study area was probably due to the lack of substantial river inputs (Ergin and Yörük, 1990) and the increased episodic floods and associated mudflows during the last decades (Taieb Errahmani et al., 2020). The results of texture analysis additionally show that the average grain size followed the order of core A > core B > core Z, ranging from 10.5 µm for core A to 6.75 µm for core Z with a mean value of 9.24 µm (Suppl. Tab. 4), suggesting a relatively stable sedimentary environment at all the sites (Liu et al., 2011). Overall, for all cores percentages of OM, TW, TS and Silt ranged [8.6 - 13.3] %, [32.23 - 50.86] %, [0.15 - 0.9] % and [67.57 - 82.11] %, respectively, and decreased in the following order: core A > core B > core Z. These findings indicate that the central Algerian coast sediments are waterlogged and very fine, rich in total sulfur and organic matter favoring further the accumulation of trace metals, especially in Algiers Bay, which displayed the highest values for sediment properties.

3.2. Trends of major and trace element concentrations in core samples

A statistical summary of chemical analyses on major and trace elements is presented in Table 1 (the complete data are reported as supplementary material) and a graphical representation of elements' depth profiles in the three sediment cores A, B and Z is presented in Fig. 3.

In core A (Algiers Bay), vertical distributions of Fe, Mn, V, Co, Ni, and Pb showed similar patterns and decreased slightly from the bottom to the surface sediment. Conversely, the concentrations of Cd and Zn exhibited somewhat increasing trends up through the layers with obvious fluctuations in the upper section of the core. For Ag, the depth distribution showed overall increasing contents until 8 cm but decreased in the upper Layers. Meanwhile, As and Na contents showed upward trends in the upper 18 cm. Lastly, Cr followed a similar tendency to Cu, and the maximum concentrations of both elements were detected at 12 cm of depth. At this site, the average concentrations Zn, Cu, Cd, Pb, and Ag (162 ± 2.67, 34.8 ± 0.97, 0.29 ± 0.03, 44.4 ± 1.27 and 0.71 ± 0.01 $mg.kg^{-1}$, respectively) are significantly higher than those for the other sites and exceed the background values (Tab. 1). ln fact, the samples collected in Algiers Bay suggest a significant role of Algiers' urban and industrial sites (Chemrouk and Chabbi, 2016). In particular, Zn, Cd, and Ag reach contents in the topmost sediments as high as 180, 0.39, and 0.87 $mg.kg^{-1}$, respectively. The elevated concentrations of metal are also explained by a high input of anthropogenic contaminants from the port of Algiers (Bachouche et al., 2017) and likely from the direct discharge of greywater from ships in the sea area (Ytreberg et al., 2020).

In core B (Bou Ismail Bay), concentrations of Fe, Al, V, Co, Ni, Cr, Cu, Zn, Cd, Ag, and Pb uniformly decreased from the bottom to the top of the core and the maximum concentrations of these elements were observed at the bottom sediment layers (Fig. 3). The high loads of these elements were probably caused by the increase in total sulfur contents in the bottom sediments (Fig. 2, 3). This suggests the precipitation of metal sulfide under anoxic conditions (Komada et al., 2016). In contrast, Mn, As, and Na increased significantly and reached the maximum in recently deposited sediments. The presence

of the Mn peak value (315 $mg.kg^{-1}$) at the top of the core in correspondence with the high organic matter content (Fig. 2, 3, Suppl. Tab. 3) could be due to an upward movement of secondary oxidants under the influence of the early diagenesis process. However, this point cannot be confirmed here because of the lack of the analyses of the oxidation-reduction index in the pore water of sediments.

In core Z (Zemmouri Bay), the depth profiles of Fe, Mn, Co, Cu, Zn, Ag, and Pb showed similar trends, and the concentrations were all lower at the bottom section of the core and higher at the surface. The minimum concentrations of these elements were observed at 9 cm of depth except for Ag and Pb and then demonstrated an increasing trend toward the top. As and Na showed increasing trends from the bottom, while Cd, V, Cr and Ni did not follow an increasing tendency and remain relatively stable. In detail, the concentrations of Fe and Mn showed high variability with depth, and increased distinctly upwards from 9 cm of depth ranging from 30 to 43 $g.kg^{-1}$ and 191 to 314 $mg.kg^{-1}$, respectively. These high levels in the top layers are due either to the changes in the terrigenous inputs (Orani et al., 2019), or represent a surface diagenetic enrichment (Janaki-Raman et al., 2007). Moreover, some trace metals such as Co, Cu, Zn, Ag, Pb, and As showed increasing concentrations in surface layers (up to 13.1, 24.3, 130, 0.31, 32.6 and 18.5 $mg.kg^{-1}$, respectively), suggesting increasing metal loads probably from anthropogenic origin unless the distribution of such metals are affected by post-depositional diagenetic processes. However, the average concentrations of most elements are close to the natural background values (Table 1) and relatively low with respect to those found in Algiers Bay sediments where the influence of anthropogenic activities can be easily recognized.

Overall, all cores A, B, and Z showed maximum arsenic concentrations (up to 20.1, 21, and 18 $mg.kg^{-1}$, respectively) in upper sediments (Table 1, Figure 3), which is in good agreement with the results obtained by Inal et al. (2018) for arsenic (21.3 $mg.kg^{-1}$) in surface sediments of the central Algerian coast. Since arsenic serves usually as a marker of agricultural runoff (Bai et al., 2012; Sun et al., 2012), the increasing trends of arsenic toward the top layers of the three sediment cores (Fig. 3)

indicate the increasing use of arsenic compounds as fertilizer, manure, and agrochemicals in agricultural fields (Mao et al., 2020). The results additionally show that the Fe was the most abundant element in all the cores, with concentrations ranging from 29.9 to 45.7 $g.kg^{-1}$ and were far higher than the Al concentrations, which varied between 3.6 and 21.9 $g.kg^{-1}$. This abundance is a result of an additional supply of iron-rich secondary phases from the aeolian dust of the Algerian Sahara (Hassani et al., 2019) in addition to the terrigenous source in semi-arid environments with low runoff (Viers et al., 2009). The elevated level of Fe in such an environment can highly influence trace metal levels in coastal sediment (Janaki-Raman et al., 2007). Therefore, the depth profiles of most trace metals in the study area showed similar patterns to Fe (Fig. 3) due probably to the low-level inputs that characterize the Algerian rivers.

3.3. Geochemical behavior and sources of trace metals

3.3.1. Correlation analysis

In order to strengthen the interpretation of the results and highlight the common patterns and geochemical behavior of the elements, a Pearson's correlation test was performed for each sediment core (Tab. 2). The grain size distribution of sediment particles was not included in this analysis since fine silty clays are dominant in all the cores. In core A, some trace metals like Pb, V, Co, Ni, Cr, and Cu present significant positive correlations ($p < 0.01$) to one another and to Fe, Mn, and Al (except Co with Al), indicating that they were bound to Fe, Mn, and Al oxyhydroxides. As already mentioned, Zn and Cd had similar distributions along the core A, and Pearson's correlation confirms a high relationship between both elements ($p < 0.01$; $r^2 = 0.72$). Additionally, Ag was positively correlated with Zn and Cd ($p < 0.05$; $r^2 = 0.47$), but no positive correlations were obtained for Ag with the major elements or other trace elements, which indicates the anthropogenic source of Ag and a different origin from the other metals. The relationship between organic matter contents and chemical elements was analyzed by Pearson's correlation (Tab. 2); thus, positive correlations are observed between OM and Zn, Cd, and Ag metals ($0.55 < r^2 < 0.66$), which suggests that organic matter acted as a sink or

source for these metals in sediment (Komada et al., 2016; Martínez-Santos et al., 2015). Finally, Na and As were significantly correlated with each other ($p < 0.01$; $r^2 = 0.79$) and with TW ($p < 0.01$) suggesting mobility of both elements in the sediments. However, Arsenic showed no positive correlation with the other elements, indicating that the anthropogenic signal of As were relatively high in Algiers Bay.

In core B, trace metals like Pb, V, Cr, Co, Ni, Cu, Zn, Cd, and Ag showed very significant correlations with Fe ($0.63 < r^2 < 0.97$; $p < 0.01$) and to a lesser extent with Al (Tab. 2), implying that they were more adsorbed by Fe oxyhydroxides than Al. Furthermore, the concentrations of these trace metals (as well as those of Fe and Al) showed an excess when compared to the high TS content and low OM in deep layers of core B (Fig. 2, 3). These findings indicate the precipitation of metalliferous sulfide (Fu and Wang, 2011) following SO_4^{2-} reduction and the formation of H_2S under an anoxic reduced environment (Hong et al., 2020). On the other hand, Mn was positively correlated to OM and TW ($p < 0.01$). Apparently, the early diagenetic process played a major role in the vertical distribution of Mn indicating a peak in the upper layer. The high Mn values at the surface level are attributed to the supply of dissolved Mn^{2+} from the reduced sediment layer which oxidized to Mn^{4+} at the surface (Pattan et al., 2019). As and Na additionally exhibited strong positive correlations to Mn, OM, and TW ($p < 0.01$) and also a significant positive correlation with each other ($r^2 = 0.84$). The increase in As contents in surface sediment of the core suggests the presence of recent anthropogenic input of this element under reducing conditions and its sorption onto the newly formed Mn oxyhydroxides in the sedimentary water column (Ontiveros-Cuadras et al., 2021).

In core Z, Pearson correlation coefficients computed for Fe and Mn showed close relationships to Na, Pb, V, Cr, Co, Ni, Cu, Zn, and As; meanwhile, Al exhibited positive correlations only with Cr and V. The correlation analysis also displayed positive correlations between Fe and OM or Mn and OM ($p < 0.01$) indicating diagenetic modifications and resuspension processes for both elements. In fact, the increased carbon flux can change the redox conditions in sediments overlain by the oxygenated

bottom waters (Pattan et al., 2019) thereby increased the solubility for redox-sensitive metals like Fe and Mn (Charriau et al., 2011). The obtained positive correlations between (Fe-TW), (Mn-TW), and (OM-TW) may support the efficiency of this mechanism (Tab. 2). Similarly, some trace metals such as Pb, Co, and Zn were correlated positively to OM and TW, and significantly to Fe and Mn (Tab. 2), which explains probably their increasing concentrations in the oxic conditions (upper sediment layers) compared to suboxic conditions (Fig. 3). This suggests the remobilization of Pb, Co, and Zn through metal scavenging (Ontiveros-Cuadras et al., 2021). However, no significant correlation was obtained for Cd with major elements, and it only showed positive correlations with V and Cr ($p < 0.01$), indicating that Cd, V, and Cr depositions were affected by the same process in the sediments. Lastly, no statistically significant correlation existed between TS and most elements, which was possibly due to the dissolution of various metals sulfides (Morse and Luther, 1999).

From the simple observation of Pearson correlation results and element variation along the cores, it appears that the vertical distribution of trace metals in cores B and Z has been modified to some extent by diagenetic processes. It is equally clear that core A showed significant changes in some of the analyte concentrations with different metal inputs, most probably of anthropogenic origin given the location of the sampling station.

3.3.2. Principal component analysis (PCA)

To further examine the origin of the elements in the study area, a Principal Component Analysis (PCA) was performed for each sediment core (Tab. 3, Suppl. Fig. 2). PCA has been applied successfully from a correlation matrix including 17 variables (OM %, TS %, TW %, Fe, Mn, Al, Na, V, Cr, Co, Ni, Cu, Zn, Pb, As, Ag, and Cd). The variables used all passed the Kaiser-Meyer-Olkin (KMO > 0.62) and Bartlett ($p < 0.001$) tests, confirming the suitability of the dataset for PCA.

Four principal components (PC) with eigenvalues higher than one were extracted from the variables in sediment core A, which accounted for 88.65 % of the total variance (Tab. 3). The first two

components accounted for 68.82 % of the total variance and reflected the most important information, with PC1 (45.96 % of the variance) characterized by strong loading on Fe, Mn, Pb, V, Cr, Co, Ni, Cu (from 0.72 to 0.98), and PC2 (22.86 %) mainly characterized by high positive loadings of variables such as OM, Zn, Cd, and Ag (from 0.74 to 0.88). PC1, therefore, represents the natural source of sediments such as the weathering of parent rock materials, and PC2 represents the elements (Zn, Cd, and Ag) retained in organic material and, consequently, described the anthropogenic source of sediments. Given that OM origin in Algiers bay sediments was primarily related to direct inputs from El Harrach river (Bakalem et al., 2009), we infer that the major sources of Cd, Zn and Ag in core A were the municipal effluents and surface runoff. PC2 could also be derived from agricultural activities because phosphorus fertilizer has been generally regarded as the main source of Cd and Zn in agricultural areas (Jiao et al., 2015). The third component (PC3) accounted for 14,11 % of the total variance and had strong loading values on As, Na, and TW (PCA coefficients > 0,89) suggesting that PC3 presents the mobile fraction of sediment. Lastly, the fourth component (PC4) accounted for 5.72 % of the total variance and had high loading on TS (0.85). The detected high TS content in core A (Fig. 2) seems to be the consequence of the direct inputs from El Harrach river into Algiers Bay.

For the sediment core B, the dataset used for PCA analyses gave two major components with eigenvalues > 1 and explained 86.43 % of the total variance (Tab. 3). The first component extracted (PC1) explained the most variance (72.29 %) and had high positive loading on Fe, Al, Pb, V, Cr, Co, Ni, Cu, Zn, Cd and Ag. Since Fe and Al are generally derived from weathering and erosion of rocks and soil parent materials (Li and Li, 2017), PC1 was considered the lithogenic source of metals bound in oxihydroxide minerals. Furthermore, PC1 is characterized by the strong association of almost all analytes (except Mn, Na, As) with TS (reducible and/or oxidisable fractions of S), which indicates that they were mainly associated with sulfide fraction. The second component (PC2) accounted for 14.14 % of the total variance and included Mn, Na, As, OM and TW with high loading (from 0.75 to 0.96). Here, the strong positive effect of OM and TW with the Mn suggests that the latter had great

mobility and clearly indicated early diagenetic events in sediments. In light of the results of Pearson correlations and PCA, PC2 is considered to be both the mobile fraction of the sediment and the anthropogenic contaminant associated with the discharge of urban and agricultural wastewater.

PCA performed on core Z gave four significant PCs with eigenvalues > 1, explaining 91.65 % of the total variance (Tab. 3). The principal components PC1, PC2, PC3 and PC4 accounted for 54.21 %, 22.86 %, 10.43 % and 4.15 % of the total variance, respectively. PC1 (54.21 %) is the most important component and was mainly characterized by high positive loadings of variables such as Fe, Mn, Pb, V, Cr, Co, Ni, Cu, and Zn. This indicates that PC1 described the lithogenic source of elements that were principally retained in the crystal lattices of secondary minerals and, consequently, had low mobility (Martínez-Santos et al., 2015). Moreover, some of these variables (Fe, Mn, Pb, Co, and Zn) also had moderate to high positive loadings in PC2, suggesting the partial dissolution and mobility of these elements in the sedimentary water column due to a marked increase of OM content in surficial sediments (Fig. 3) which acts as an electron donor, thus, reducing Fe or Mn oxyhydroxides (Moushmi et al., 2022). This is very well supported by the strong loadings of TW and OM (0.98 and 0.72, respectively) in PC2. A close observation of Tab. 3 results shows that Ag and As had high loadings only on PC2 suggesting they were potentially mobile and bioavailable in sediment. In light of the result of PCA, we infer that PC2 is regarded as an anthropogenic source of OM, As and Ag mainly related to direct input from agricultural wastewater and untreated urban sewage. The third principal component (PC3) consists only of Al, V, Cr and Cd (From 0.64 to 0.78), suggesting that PC3 described the lithogenic source bound in aluminosilicate minerals (Guo and Yang, 2016). However, according to the Pearson correlation analysis, Cd did not show a positive correlation with Al. These results may indicate the anthropogenic origin of Cd in sediments of Zemmouri Bay. With regard to PC4, TS was the only variable with significant positive loading (0.98), indicating that sulfates did not influence the trace metal contents, as was previously stated.

3.4. Assessment of Anthropogenic impact

3.4.1. Enrichment factor (EF)

Like in many developing countries, the Algerian coast suffers deterioration as a result of demographic pressure and untreated discharges from human activities (Abderrahmani et al., 2021; Inal et al., 2018; Guendouzi et al., 2020). According to Chen et al. (2007), EFs with very low values (EF < 1) indicate negligible or none enrichment, EF < 2 represent slight enrichment, 2-5 account moderate enrichment, 5-10 implies moderately severe enrichment, 10-25 shows severe enrichment, 25-50 display very severe enrichment and finally, EF > 50 suggests extremely high enrichment. However, the assessment of trace metal concentrations in the sediment was difficult to interpret because there is no single reference element that exists for normalization. For this purpose, we used Fe as a reference metal to calculate EFs because of the predominance in the study area of Fe-rich secondary phases exclusively of geogenic and eolian origin. Furthermore, it is noteworthy that many authors have used Fe successfully for geochemical normalization (Ahmed et al., 2018; Bachouche et al., 2017; Moushmi et al., 2022; Ranjan et al., 2018).

According to the local background values determined in this work, the results of the EF's mean and surface values are shown in Fig. 4 and Suppl. Tab. 6, from which it can be found that the enrichment degree of trace metals varies within a narrow range (from 0.95 to 3.36) in all sediment cores. In other words, the EFs for the sediment samples were all classified as deficient or no enrichment to moderate anthropogenic enrichment. The contamination order of these metals in the whole of the study area was Cd > Ag > Pb > As > Zn > Cu > Ni > Cr > V > Co (Fig. 4). In detail, almost all EF values of Ni, Cr, V, and Co on the central coast were very close to or less than 1 demonstrating a crustal origin of these metals in the study area (Suppl. Tab. 6). While the EF values of Zn, Cu, Cd, Pb, As, and Ag were greater than 1 as a whole, and some of them were over 2 or even 3 in surface sediments of core A, indicating moderate contamination by these trace metals in Algiers Bay. The high EF values at sediments of core A can be attributed to direct discharges of contaminants from industrial activities, refineries and oil factories in the inner part of the Algiers port and El Harrach river, which also carries

a significant part of pollution in Algiers Bay (Bachouche et al., 2017). On the other hand, the results showed that some of the EF values of trace metals in surface sediment were higher than in average sediment in cores A and Z, which indicated that anthropogenic trace metals have been recently deposited in sediments during the increasing urbanization in recent years. The EF values of trace metals were plotted against depth profiles, and increasing trends of As EFs profiles were detected in all sediment cores (Suppl. Fig. 3). The profiles of EF were similar to the trends in concentrations of Arsenic (Fig. 3), which reflected the agricultural intensification over the two past decades. For some trace metals, slight to moderate EF values occurred only in some layers of the cores, indicating anthropogenic enrichments of these elements for a certain period.

3.4.2. Pollution load index (PLI)

The PLI introduced by Tomlinson et al. (1980) has been used in the present study to evaluate the sediment's environmental quality and compare the overall metal load in sediments at each site (Fig. 5). Two classes of the PLI value have been identified: When PLI < 1, it means there was no pollution of coastal sediments; otherwise PLI > 1, sediments are moderate to highly polluted. Thus, as metal pollution increases in sediment, the PLI value also increases. The results show that PLI values in deep sediments are lower than at the surface in cores A and Z, indicating recent contamination of some trace metals in Algiers and Zemmouri Bays. The calculated PLI values for all cores followed the decreasing order core A > core B > core Z. The highest PLI value was calculated for core A, indicating that Algiers Bay was moderately polluted by metals where sediment quality might be deteriorated by trace metals especially As, Cd, Pb, Zn, Cu and Ag. Indeed, the Bay of Algiers was previously classified as a hot spot priority in the Mediterranean Sea (UNEP/WHO, 1999). However, the load indices calculated for Bou Ismail and Zemmouri Bays revealed that the metal pollution was relatively low compared to Algiers Bay which showed moderate enrichment for some trace metals mentioned above.

3.5. Application of sediment quality guidelines

The ecological risk of trace metals in the aquatic sediment was evaluated by comparing the concentrations present at the surface of the cores with the respective SQGs (Suppl. Fig. 4). Cd and Ag concentrations were below the TEL values (0.68 $mg.kg^{-1}$ and 0.73 $mg.kg^{-1}$, respectively) and ERL values (1.2 $mg.kg^{-1}$ and 1 $mg.kg^{-1}$, respectively) in all the sediments core, while Zn concentrations were below the TEL value (124 $mg.kg^{-1}$) and ERL value (150 $mg.kg^{-1}$) only in cores B and Z. Moreover, the concentrations of Cu in cores B and Z were also lower than the ERM value (34 $mg.kg^{-1}$) but exhibited higher values than TEL (18.7 $mg.kg^{-1}$). The results also showed that Pb contents in cores A and B exceeded the TEL value of 30.2 $mg.kg^{-1}$. However, none of the sites exceeded the ERL value (46.7 $mg.kg^{-1}$). These findings imply that organisms living within or near sediments are rarely exposed to adverse biological effects. For As, Ni and Cr in the three cores, Zn and Cu in core A, all the concentrations ranged between their respective ERMs and PELs, indicating that biota might be occasionally exposed to toxic effects.

For the toxicity evaluation of combined trace metals, Qm-SQGs calculated based on Ni, Cr, Cu, Zn, Pb, As, Cd and Ag ranged in all cores from 0.21 to 0.26 for m-ERM-Q, and 0.34 to 0.43 for m-PEL-Q (Fig. 5), which coincide with a 21 % probability of being toxic for living species according to the toxicity probabilities of m-ERM and m-PEL quotients (Long et al., 2000). The average Qm-SQG values of the sediment cores ranked as follows: Core A > Core B > Core Z with slightly higher values in the surface sediments of Algiers (Core A) and Zemmouri (Core Z) bays. Although Ni concentrations in the three cores are within the range of natural variability and cannot be related to human impact according to EF values, this metal contributed significantly (more than 30 %) to Qm-SQG in all cores. These results are consistent with those found by Inal et al. (2018) in surface sediments of the central coast, therefore, the authors suggested more monitoring of Ni inputs in the coastal zone as their ecotoxicological levels are doubtful. However, the contents of As fairly exceed its PEL or ERL values (Fig. 4S), which indicate that As presents a higher ecological risk than the other metals for the aquatic species.

4. Conclusion

This study was conducted to determine the effects of natural and anthropogenic processes on depositional trends and risk of trace metals. The results showed that iron was the most abundant element in the study area (up to 45.7 g/kg) because of the predominance of Fe-rich secondary phases of terrestrial and eolian origin. Most trace metals in the three cores showed similar patterns to Fe, and some of Them have been modified to some extent by diagenetic processes, which controlled their distribution in sediments. The local geochemical background was established from the uncontaminated section of the core S located offshore of Cap Djinet and is considered to represent the natural geochemical sediment composition of the central Algerian coast. Thus, the average contents of Zn, Cu, Cd, Pb, and Ag (162 ± 2.67, 34.8 ± 0.97, 0.29 ± 0.03, 44.4 ± 1.27 and 0.71 ± 0.01 mg.kg-1, respectively) exceeded their respective natural background values in the Algiers Bay sediments due to the influence of polluted inputs of El Harrach river and the Algiers port. According to Pearson correlation and PCA analyses, rock weathering acted as the major factor contributing to most trace metal accumulation in all cores, whereas As was bound predominantly in the potentially most mobile fractions of sediment and originated mainly from fertilizer application in the region. The influence of organic matter, total sulfur, and total water content on metals behavior were discussed, and the trace metal availability showed different patterns in the three cores: preferential adsorption of Cd, Zn and Ag to the organic matter in core A; precipitation of Pb, Co, V, Ni, Cr, Zn, Cu, Cd and Ag as metalliferous sulfides in core B and diagenetic enrichment of Pb, Zn and Co in core Z. The enrichment factors (EF) decreased in the order Cd > Ag > Pb > As > Zn > Cu > Ni > Cr > V > Co and showed no significant enrichment and pollution in the entire study area. Regarding to SQGs, all metals had no frequent adverse effects on sediment-living organisms. PLI and Qm-SQG values showed that Algiers Bay was the most polluted area and presented a higher ecological risk than the other sites. This information could be useful for the formation of coastal zone management strategies for the marine environment. The improvement of water and coastal sediment

quality requires the control of agrochemical application in farmland and the implementation of wastewater treatment plants on the river banks.

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764 **FIGURE CAPTIONS**

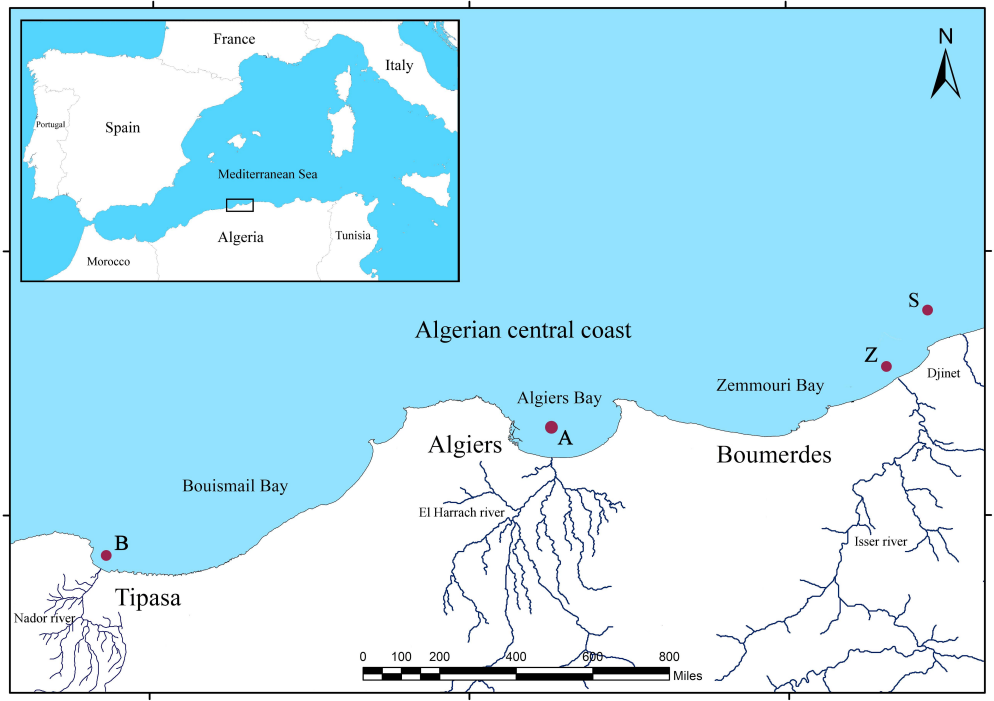
765 **Figure 1.** Map of the study area and locations of sampling sites.

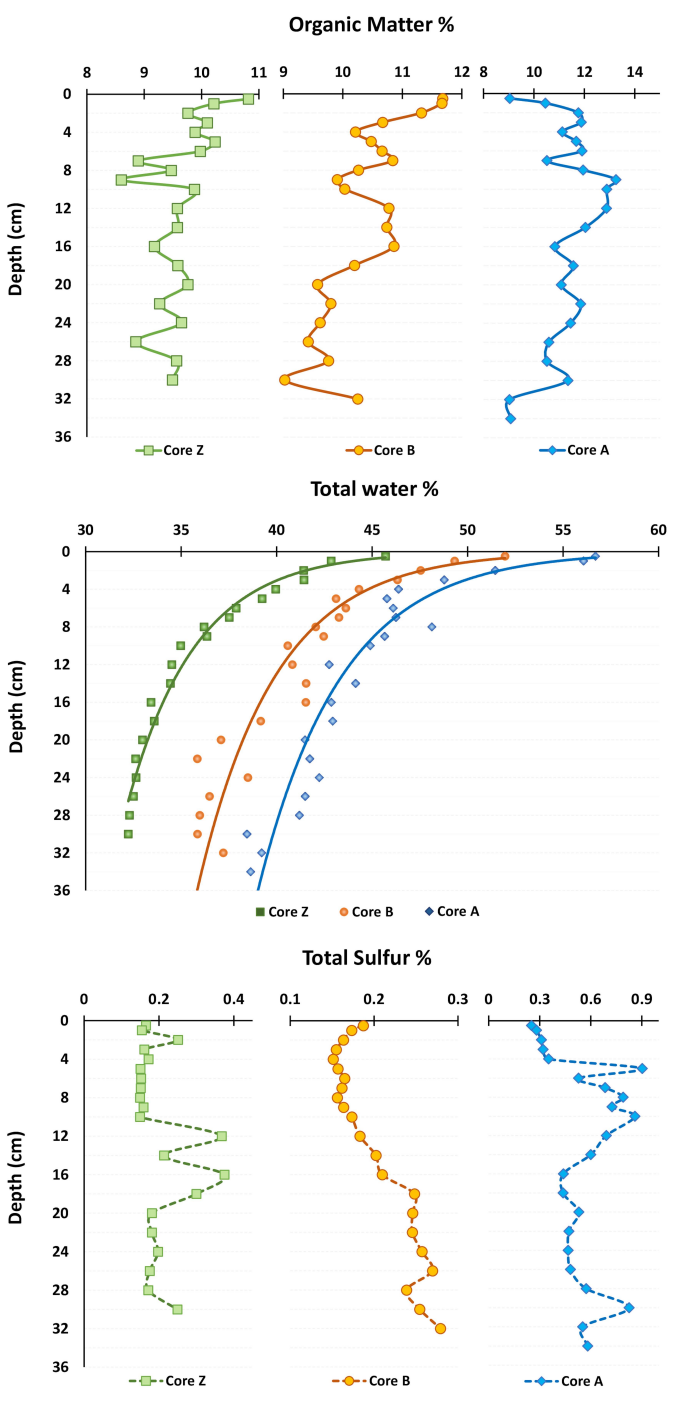
766 **Figure 2.** Vertical distributions of major and trace element concentrations in cores A, B and Z
767 (concentration in $mg.kg^{-1}$ dry weight except for Fe, Al and Na in g/kg).

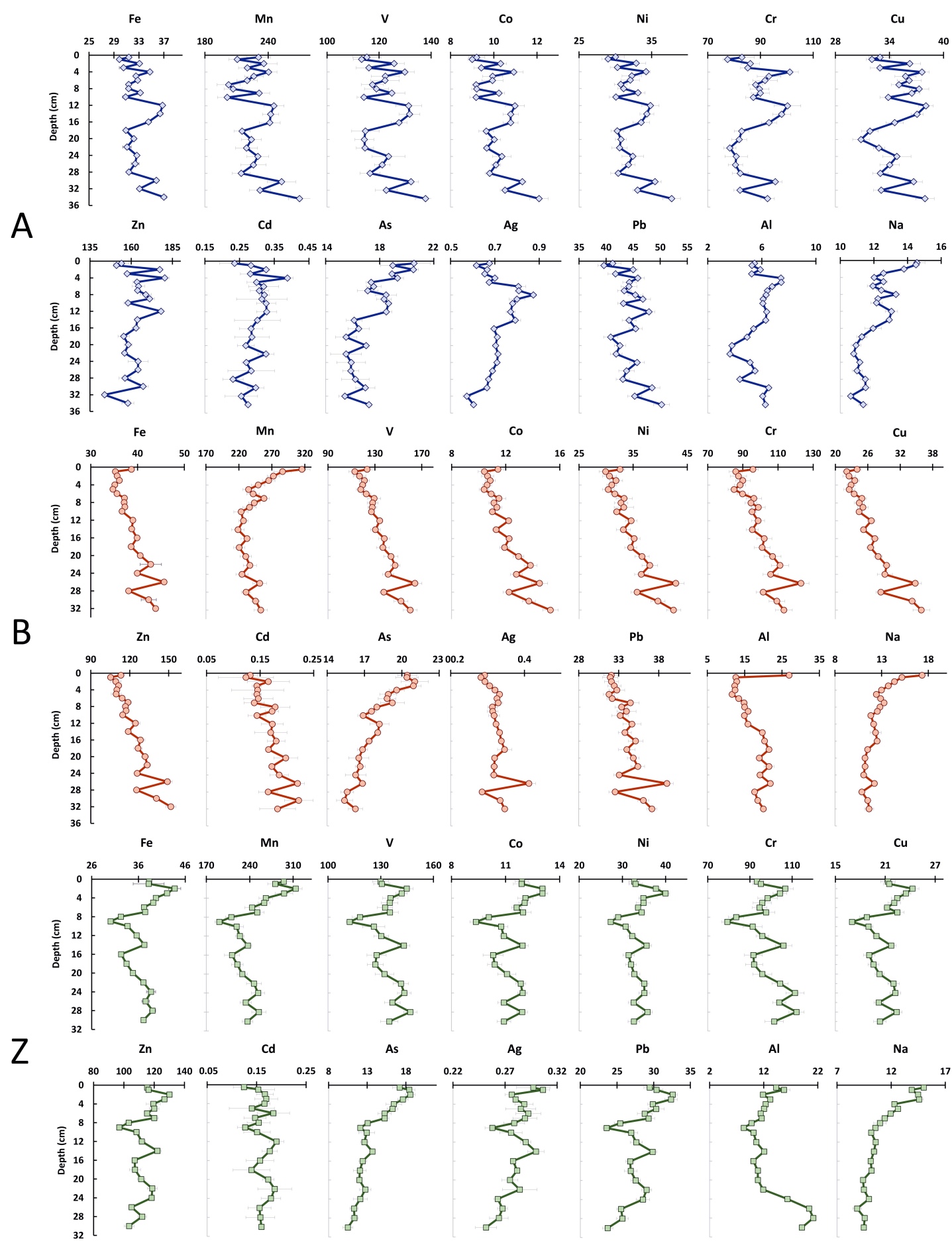
768 **Figure 3.** Vertical variations of organic matter, water and total sulfur contents in the sediment cores
769 A, B and Z of Algerian central coast. The solid lines in (b) represent the exponential curves that has
770 been linked by water content data.

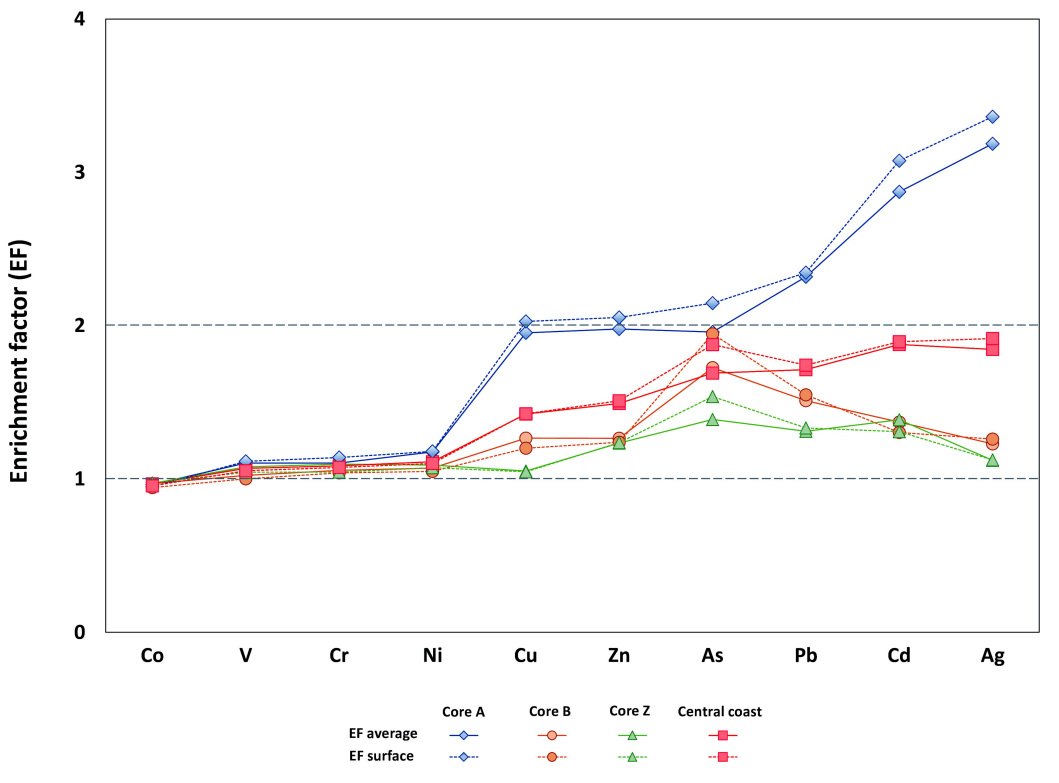
771 **Figure 4.** Enrichment factors calculating for the central coast sediment.

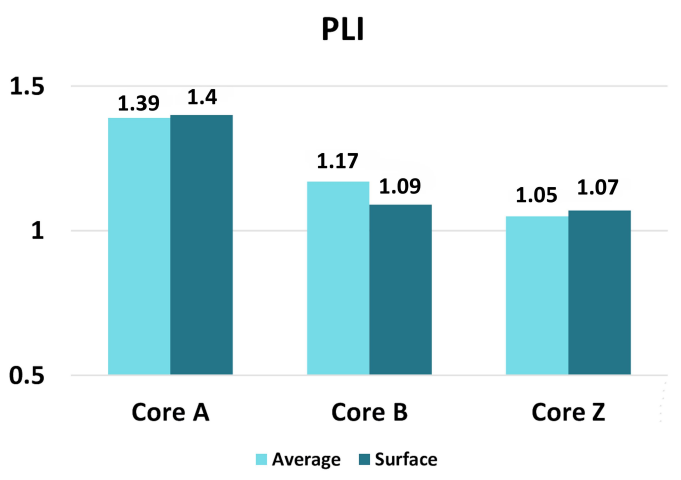
772 **Figure 5.** Results of pollution load index (PLI) and Mean sediment quality guideline quotients (Qm-
773 SQG) according to the method employed by Tomlinson et al. (1980) and Long et al. (2000),
774 respectively.

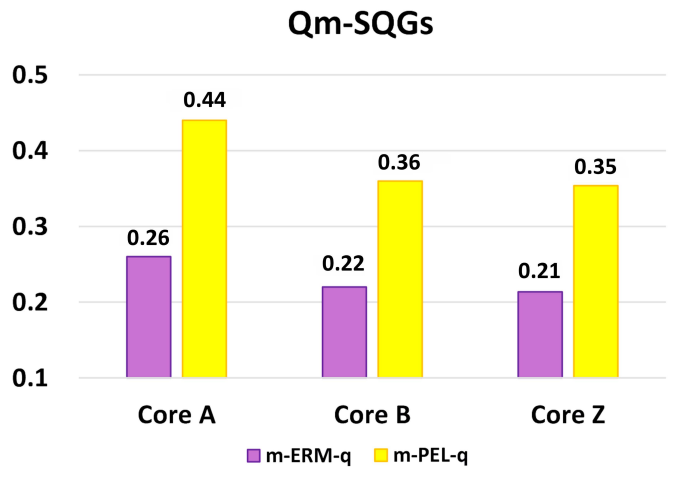

2°30'E
3°0'E
3°30'E
37°0'N
36°40'N
N
France
Italy
Spain
Portugal
Mediterranean Sea
Algeria
Tunisia
Morocco
Algerian central coast
S
Z
Djinet
Zemmouri Bay
Algiers Bay
Algiers
A
Boumerdes
Bouismail Bay
El Harrach river
Isser river
B
Tipasa
Nador river
0 100 200 400 600 800
Miles


Organic Matter %
8
9
10
11
9
10
11
12
8
10
12
14
0
4
8
12
16
20
24
28
32
36
Depth (cm)
Core Z
Core B
Core A
Total water %
30
35
40
45
50
55
60
0
4
8
12
16
20
24
28
32
36
Depth (cm)
Core Z
Core B
Core A
Total Sulfur %
0
0.2
0.4
0.1
0.2
0.3
0
0.3
0.6
0.9
0
4
8
12
16
20
24
28
32
36
Depth (cm)
Core Z
Core B
Core A


A
B
Z
Fe
Mn
V
Co
Ni
Cr
Cu
Zn
Cd
As
Ag
Pb
Al
Na
Depth (cm)


Enrichment factor (EF)
4
3
2
1
0
Co
V
Cr
Ni
Cu
Zn
As
Pb
Cd
Ag
Core A
Core B
Core Z
Central coast
EF average
EF surface


PLI
1.5
1
0.5
1.39
1.4
1.17
1.09
1.05
1.07
Core A
Core B
Core Z
Average
Surface


Qm-SQGs
0.5
0.4
0.3
0.2
0.1
0.26
0.44
0.22
0.36
0.21
0.35
Core A
Core B
Core Z
m-ERM-q
m-PEL-q