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Assessment of trace metals contamination in surficial sediments along Lebanese Coastal Zone

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ABSTRACT

A Characterization and assessment study was conducted for trace metals pollution in surface sediments at six sites including harbors, bays and river input along Lebanese coast (LCZ). A particular attention was given to Tripoli Port in order to identify the main sources of trace metals pollution inside this harbor. Total metals concentrations were compared with those reported for the shale. The results revealed that trace metals (Cd, Pb, Zn, and Cr) contamination was significantly localized at Beirut Port, which is classified as the most highly polluted site. At Tripoli Port site, metals contamination was classified as moderate; it is affected by shipping, ship maintenance activities and sewage outfall. According to the SQGs guideline, the biological adverse effect of Cd, Pb and Zn were expected to occur frequently at Beirut Port. The results obtained would be helpful in developing more effective harbor management strategies to control and monitor the metal discharges.

Some ubiquitous chemicals were found at trace levels have an adverse effect on the aquatic ecosystem and human health if reached toxicity threshold (MacDonald et al., 1996; O'Connor, 2004; Islam and Tanaka, 2004; Lin et al., 2013). Among these chemicals, trace metals are a group of pollutant of high ecological significance (Çevik et al., 2009; Chen et al., 2018) due to their toxicity, wide sources, non-biodegradable properties and accumulative behaviors (Duman et al., 2007; Ruilian et al., 2008; Liang et al., 2011; Lenoble et al., 2013, Vatansever et al., 2017). Indeed, there is a strong and long history of association between metals and human development (Tiller, 1989). Population growth, increasing urbanization, industrialization, and tourism are some of the reasons for the increasing pressure in coastal areas (Clark, 2001; Islam and Tanaka, 2004; Roussiez et al., 2006; Buccolieri et al., 2006) were several studies have been reported that such areas have been greatly contaminated by these pollutants (Buccolieri et al., 2006; Naser, 2013; Wang et al., 2013). Nevertheless, trace metals contamination along coastlines varies with the local economic development, pollution sources and geographical conditions (Pan and Wang, 2012). In Mediterranean Seacoast, sediments have a different geochemical composition where metal concentrations vary according to the area and different anthropogenic inputs from the coastal environment (Stephenson et al., 1998; Buccolieri et al., 2006). A significant amounts of anthropogenic trace metals are released into marine environment (Diop et al., 2012; Memet and Bülent, 2012; Bodin et al., 2013) through land based sources (Islam and Tanaka, 2004; Fu and Wang, 2011) including point sources such as industrial, municipal and domestic effluents, ships discharges, river inputs as well as diffuse sources such as surface runoff, erosion and atmospheric deposition (Solomons and Förstner, 1984; Rivail Da Silva et al., 1996; Karageorgis et al., 2002; Mucha et al., 2003; Islam and Tanaka, 2004; Zahra et al., 2014). > 90% of trace metals load in the aquatic ecosystems have been found to be associated with suspended particulate matter and sediments by particle surface absorption, ion exchange, co-precipitation, and complexation with organic matter (Tessier and Campbell, 1987; Amin et al., 2009; Zheng et al., 2008; Passos et al., 2010). Sediment act as a sink for trace metals (Ruilian et al., 2008) providing a history of pollution pattern (An and Kampbell, 2003; Casas et al., 2003; Singh et al., 2005; USEPA, 2005) and record of anthropogenic pollutants inputs into aquatic ecosystems (Mwamburi, 2003; Santos Bermejo et al., 2003; USEPA, 2004; Lesven et al., 2010) and environmental changes (Shomar et al., 2005). Their bioaccumulation and biomagnification in living organisms and food chains causing the degradation of marine ecosystem (Manahan, 2000; Muhua et al., 2003; Ghrefat and Yusuf, 2006; Khaled et al., 2006; Hosono et al., 2011; Rainbow and Luoma, 2011; Liu et al., 2017). In addition, many trace metals are known to be toxic or carcinogenic to humans causing also a great threat to public health (Islam and Tanaka, 2004; Fu and Wang, 2011). The toxicity of trace metals takes more concern considering the reason that they are not

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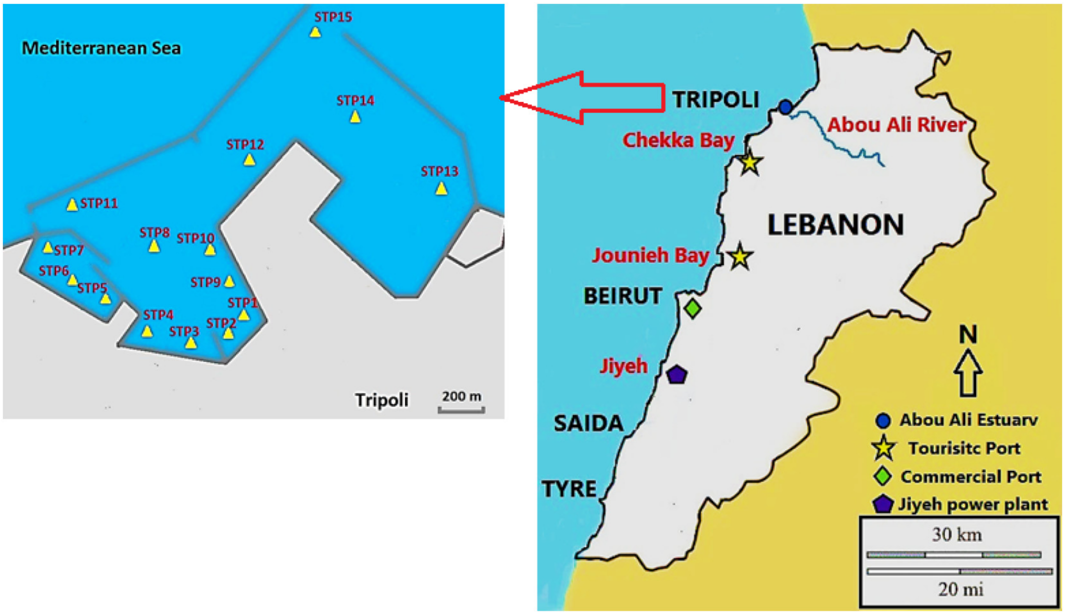

Fig. 1. Map of studied selected sampling sites along LCZ.

removed from the water and sediments by self-purification (Harikumar and Nasir, 2010). The trace metals immobilized in the sediment becoming bioavailable since they can be released to the overlying water as a result of physicochemical changes either due to natural and/or anthropogenic processes contributing to a permanent source of pollution (Tessier and Campbell, 1987; Lacerda et al., 1992; Sahuquillo et al., 2003; Santana et al., 2007; Gao et al., 2010; Hooda, 2010; Morelli and Gasparon, 2014). The oxidation of anoxic sediments has been reported by numerous studies as the most effective factor capable of mobilizing trace metals adsorbed in sulfide fraction (Morse, 1994; Gagnon et al., 1995; Simpson and Batley, 2003; Massolo et al., 2012; Dhanakumar et al., 2013) and organic phase (Calmano et al., 1993; Hamzeh et al., 2014, 2016). Many mechanisms enhanced sediment oxidation including microbial oxidation of bottom sediments, organic matter degradation, bioturbation (Simpson et al., 1998; Williamson et al., 1999), even tidal currents, erosion, seasonal flooding, wind waves, storm events, ship traffic, remedial dredging (Je et al., 2007), fishing, reclamation and construction activities (Eggleton and Thomas, 2004; Guerra et al., 2009; Hedge et al., 2009) with respect to changes in geochemical gradients (e.g., salinity, turbidity and redox conditions) (Zoumis et al., 2001; Caetano et al., 2002; Masson et al., 2006) can strongly influence the partitioning of metals between the dissolved and particulate phases by increasing the competition between dissolved cations and adsorbed trace metal ions lead to the increase release of these metals (Förstner, 1979; Hamzeh et al., 2014). Thus, their remobilization from contaminated sediment pose also a significant danger towards the aquatic environment (Zoumis et al., 2001; Eggleton and Thomas, 2004; Dean and Scott, 2004). Therefore, the evaluations of ecological risk become a hot topic (Lesven et al., 2009; Mario et al., 2012). Wherefore, sediments qualities are widely used as a tool to understand current water pollution by trace metals and assess their potential ecological risk in coastal ecosystems (Sayadi et al., 2010; Birch et al., 2001; Wang et al., 2005; Bellucci et al., 2002; Solomons and Förstner, 1984; Zonta et al., 1994). In Lebanon, most industrial effluents and domestic sewage outfalls are discharged directly separated or in mixture into the sea or flowing rivers without any treatment. In addition, most dumpsites and landfills are located also on the coast resulting the discharging of leachate and wastes directly into sea and in consequence the release of elevated levels of trace metals and organic pollutants (Stephenson et al., 1998). The assessment of marine sediments contamination by trace metals and organic pollutants especially polycyclic aromatic hydrocarbons (PAHs) has been subjected to several studies indicating the presence of hot pollution levels in sediments near big cities, industrialized coastal zone and river outflows (Stephenson et al., 1998; Nassif, 2004; Abi-Ghanem et al., 2009a, 2009b, 2013). Previous studies show that total PAHs concentrations in sediments are ranged from 243 to 2965 $\mu g \cdot kg^{-1}$ dw at Tripoli Port and ranged from 1.22 to 731.93 $\mu g \cdot kg^{-1}$ dw at Tripoli, Jounieh, Dora, and Tyre indicating low to moderate PAHs concentrations with the predominance of pyrogenic sources (Merhaby et al., 2015; Manneh et al., 2016). And, other studies show that trace metal concentrations were the highest in Tripoli sediments for Pb (104.4 $\mu g \cdot kg^{-1}$ dw) and Cd (0.23 $\mu g \cdot kg^{-1}$ dw) and in Arida for V (270 $\mu g \cdot kg^{-1}$ dw) indicating that Lebanese coast are unpolluted with Cd, moderately to strongly polluted with V at Arida, and extremely polluted with Pb at Tripoli. Also, high Pb concentrations in sediments ranged from 20.78 to 33.15 $\mu g \cdot kg^{-1}$ dw was obtained in Beirut (Abi-Ghanem et al., 2013). Also, they have indicated the need for a continuous and full Lebanese coastal monitoring to detect contamination and to take appropriate preventive measures (Abi-Ghanem, 2008; Fakhri, 2005; Nassif, 2004). Despite these studies, many sites along LCZ remain unexplored in terms of trace-metal contamination. Thus, to have a clear picture of trace metals contamination we focus in our study some trace metals in sediment samples collected from six new sites along Lebanese coastal zone (LCZ) significantly affected by different sources of trace metals discharges in order to investigate their levels, their sources, to quantify and assess the extent of metal pollution by calculating sediment enrichment factor (EF) and geo-accumulation index (I_{geo}) and conduct an ecological risk assessment using sediment quality guidelines (SQG).

The assessment of organic contamination in superficial coastal sediments at some hotspot areas along LCZ was carried out previously by Merhaby et al. (2015). More data about trace metals are needed also to clarify the trend of pollution in these regions. A particular interest was given for the most exposed regions such as ports, bays and estuaries where the accumulation of trace metals is enhanced in enclosed and semi-enclosed areas where the exchange of water with the open sea is limited (Okay et al., 1996; Karageorgis et al., 2002; Pekey et al., 2004). The selected sampling sites are Port of Jiyeh Power Plant, Beirut Port, Jounieh bay, Chekka bay, Abou Ali estuary and Tripoli Port, which extend from the south to the north covering about 110 km of LCZ. Six sampling sites were surveyed in this study. Fig. 1 shows the locations of these sampling sites and Table 1 represents a brief description of their

Table 1
Description of the selected sampling sites along LCZ.

Stations	Site	Coordinates	Depth (m)	Description	
1th campaign on December 2013					
Tripoli Port	SPT1	34°27′9.42″N 35°49′35.79″E	8	Old basin	Handling of bulky goods and scraps and Touristic vessels
	SPT3	34°27′5.61″N 35°49′22.72″E	2.5	Old basin	Sewage outfall
	SPT4	34°27′6.09″N 35°49′12.36″E	2.5	Old basin	Ships maintenance (shipyards)
	SPT5	34°27′12.26″N 35°49′5.49″E	1.8	Fishery basin	Fishery basin
	SPT6	34°27′15.66″N 35°48′56.75″E	2	Fishery basin	Fishery basin
	SPT7	34°27′22.85″N 35°48′52.74″E	1.8	Fishery basin	Fishery basin
	SPT8	34°27′20.67″N 35°49′18.24″E	6	Old basin/Fishery basin	Mid of old basin and the entrance of fishery basin
	SPT9	34°27′15.53″N 35°49′31.50″E	8	Old basin	Handling of bulky goods and others.
	SPT11	34°27′29.62″N 35°48′58.36″E	6	Old basin	Before breakwater of old basin
	SPT12	34°27′35.09″N 35°49′35.19″E	15	New basin	Future basin reserved for container trade
	SPT13	34°27′28.96″N 35°50′18.56″E	16	New basin	Near landfill (leachate discharges)
	SPT14	34°27′45.37″N 35°50′0.86″E	16	New basin	Between new basin and landfill
	SPT15	34°28′0.08″N 35°49′49.64″E	16	New basin	Ships entrance
2nd campaign on May 2014					
Port of Jiyeh Power Plant	SPJ1	33°38′53.85″N 35°23′53.50″E	4	Commercial harbor basin	Shipping activities, handling raw materials and petroleum product.
	SPJ2	33°38′53.85″N 35°23′53.50″E	6		
	SPJ3	33°38′53.85″N 35°23′53.50″E	10		
Beirut Port	SPB1	33°54′18″N 35°31′16″E	2	Commercial harbor basin	Handling general cargos and containers, shipping, transportation and fishery activities with the presence of three industrial buildings and sewage outfall.
	SPB2	33°54′18″N 35°31′16″E	3		
	SPB3	33°54′18″N 35°31′16″E	5		
Jounieh bay	SJB1	33° 58′ 59″N 35°38′ 59″ E	4	Touristic beach resort basin (marina)	Touristic activities including swimming, water sports, boating, fishing, and yachting center. Not far from sewage outfall.
	SJB2	33° 58′ 59″N 35°38′ 59″ E	6		
	SJB3	33° 58′ 59″N 35°38′ 59″ E	10		
Chekka bay	SCB1	34°20′4.01″N 35°43′25.75″E	3	Touristic beach resort basin (marina)	Touristic activities including swimming, water sports, boating, fishing, and yachting center. Two cement factories: “Cimenterie Nationale (C.N.)” and “Holcim” located about hundred meters away from this beach and discharge their effluent directly into sea.
	SCB2	34°20′4.01″N 35°43′25.75″E	4		
	SCB3	34°20′4.01″N 35°43′25.75″E	7		
Abou Ali estuary	SAE1	34°27′30.16″N 35°50′29.68″E	3	River outflow, Estuary	Coastal sea receives approximately 369 Mm^3/year freshwater input from Abou Ali River mixed with urban and industrial wastewaters discharged in the river without any treatment and close to Tripoli landfill.
	SAE2	34°27′30.16″N 35°50′29.68″E	6		
	SAE3	34°27′30.16″N 35°50′29.68″E	9		

characteristics.

Two sampling campaigns were performed, the first one was in December 2013 at Tripoli Port where 13 superficial sediment samples (top 5 cm) were collected from different stations into Port basins influenced by various activities (Fig. 1). The second one was in May 2014, at each site three superficial sediments samples (top 5 cm) was collected as following Port of Jiyeh Power Plant, Beirut Port, Jounieh bay, Chekka bay and Abou Ali estuary by a diver using plastic tubes properly prewashed.

Each sample was homogenized before being transferred into prewashed polyethylene (plastic) bags to prevent any oxidation and avoid metal pollution of the samples. After that samples were transported to the laboratory and were frozen at −20 °C for few days then dried at room temperature under the laminar hood until reaching a constant weight. The dried sediments were finely ground to powder manually using an agate mortar. Sediment samples processing were first sieved at 224 μm to remove large particles and homogenize the mixture. In order to reduce the effect of sediment grain size on the variability of the physicochemical measurements, the particles with size < 63 μm were collected and used for the trace metal analysis (Abi-Ghanem et al., 2009a). According to Ouddane (1990) and Lesven et al. (2010), about 200 mg of dry sediment samples and reference materials (HISS-1, and PACS-2) were digested with a mixture of concentrated acids 6 ml HF (40%)/6 ml HCl (37%)/2 ml HNO3 (65%) (3:3:1 v/v/v) in Teflon tubes putted in heating bath at 100 °C for 24 h to mineralized the solid grains. After evaporation, the sample was diluted to a final volume of 20 ml with ultrapure water (Milli-Q). The solutions were then filtered at 0.45 μm to eliminate the carbon residue and stored at 4 °C until analysis (Priadi et al., 2011).

In order to determine trace metals associated with the bioavailable fractions of sediment samples, which are considered as reactive fractions, we used the method of Huerta-Diaz and Morse (1990). About 200 mg of sediment was attacked during 24 h with 20 mL of 1 M HCl (Baker, 37%) at room temperature with continuous agitation. After leaching, the solution was also filtered and stored at 4 °C until analysis. The sediment samples were analyzed for 9 trace metals (As, Cd, Co, Cr, Mo, Ni, Pb, V, and Zn). The individual concentrations of trace elements in the extracts were measured in samples using inductively coupled plasma atomic emission spectrometry (ICP-AES, Varian, Vista-PRO axial view) and Inductively Coupled Plasma Masse Spectroscopy (ICP-MS, Thermo Electron Corporation, Element X7 Series).

1. Quality control and quality assurance

All chemical reagents were ultrapure and analytical grade. All solutions were prepared using ultrapure water. Ultrapure water (Milli-Q) with 18.2 MΩ cm^{-1} resistivity was produced by Millipore apparatus system. All the bottles, glassware, tubes, and filtration equipment were systematically washed with nitric acid (10%) and then rinsed several times with Milli-Q water prior to use. Reagents Blanks were included in each batch of analysis. Total heavy metal concentrations were expressed in μg/g dry sediments. Certified reference materials from the National Research Council of Canada (H2SS-1, and PACS-2) were used as standard reference material to validate the accuracy and precision of the analytical method. Mixed standard solution often trace metals were used to prepare standards solutions (0.5, 1, 5, 50 & 100 mg/L) and individual standards solution for P (1000 mg/L), Ca (1000 mg/L) and S (100 mg/L) was also used to obtain an accurate result by ICP-AES (Varian, Vista-PRO axial view). ICP-MS was used for the lower concentrations determination (< 10 μg/l). The recoveries of trace metals in standard materials with known concentrations were between 95% and 105%, which in general can be considered satisfactory.

The highest trace metals concentrations were detected for the samples collected close to Beirut Port (Figs. 2 & 3). Table 2 summarized the individual mean concentration for each trace metals analyses in sediments of all sampling stations (SAE, SPB, SPJ, SCB, SJB, and SPT).

Referring to the concentrations of the Average shale reported by Turekian and Wedepohl (1961), we found that the concentrations of Cd in sediments exceeded the background value for all samples collected along LCZ and Tripoli Port. Whereas the concentrations of Zinc exceeded the background value at SAE, SPB, SJB, and at SPT for the following stations; STP 1, 3, 4, 5, 6, 7, 9 & 11. Pb concentrations were found above the shale value at SPB and at SPT for the stations STP 1, 3, 4, 5, 6, 7, 9 & 11 (Fig. 2), while Cr and Co exceeded the background values only at SPB and SJB, respectively (Fig. 3). Suggesting that the sediment samples collected along LCZ were polluted with Cd, Zn, Pb, Cr and Co and LCZ is mainly affected by the harbor, touristic activities and rivers inputs. At Tripoli Port, the results indicate that the sediment pollution by these trace metals may be due to the berthing of old and non-antifouling vessels, fishing activities and shipyards that can cause the release of trace metals from paints, batteries and other equipment, and handling activities of some bulky goods including fertilizers, pesticides, coal and scrap metal waste with the presence of sewage outfall and leachate released from Tripoli landfill. The results show that Beirut Port is significantly polluted with Zn and Pb with mean concentrations reach about 965.6 and 443.3 μg/g d.w., respectively (Table 2), and the comparison between these two main commercial Ports in Lebanon shows that Beirut Port is the most polluted site.

The bioavailability is an important topic that should be taken into consideration during the characterization of trace metals pollution in sediments particularly in semi-enclosed basins where we have a very intensive maritime transport leading to the oxidation of anoxic sediments, then the remobilization of trace metals pollutants. It was determined after calculating the percentage of the labile fraction of each trace metals using the following Eq. (1):

$$\%\text{Labile Fraction} = \frac{\text{Ci (AT)} - \text{Ci (AP)}}{\text{Ci (AP)}} \times 100 \qquad (1)$$

where Ci (AT) is the concentration of individual trace metal in sediments samples obtained after the total attack and Ci (AP) is the concentration of individual trace metals obtained after a partial attack. Table 3 shows the percentages of labile fraction of each studied trace metals at each station. The percentage of the labile fraction of almost all trace metals in sediments of the studies stations is up to 50% except for Pb, which was found to be the less labile trace metal. Some exceptions were observed for Zn at SPB, which are the dominant trace metals but the less labile (25%) at this site. At SPT, the Zn, Co, and Cd are also less labile with a percentage about 30%, 32% and 37%, respectively. And, at SPJ the Mo exhibit low bioavailability characteristic with percentage around 34%. These results represent the heterogeneity of the studied sediments. In Mediterranean Seacoast, sediments have a different geochemical composition where metal concentration varies according to the area and anthropogenic inputs (Stephenson et al., 1998; Buccolieri et al., 2006). Therefore, we suggest that the ongoing activities such as the reclamation activities which was occurred along LCZ particularly in Ports and dredging activities which occurred every three or five years at harbor basins influence this geochemical composition of sediments at these sites (was a very coarsely grained/rock-like sediment) thus leading to these results. On other hand, we suggest also that these trace metals immobilized in the bottom sediment at commercial, and industrial ports (SPB, SPT and SPJ) becoming bioavailable due to the permanent remobilization of these trace metals enhanced by many mechanisms particularly the intensive maritime, remedial dredging (Je et al., 2007), fishing, reclamation and construction activities (Eggleton and Thomas, 2004; Guerra et al., 2009; Hedge et al., 2009) which occurred frequently at selected sites contributing to a permanent source of pollution (Tessier and Campbell, 1987; Lacerda et al., 1992; Sahuquillo et al., 2003; Santana et al., 2007; Gao et al., 2010; Hooda, 2010; Morelli and Gasparon, 2014) and strongly influencing the partitioning of trace metals between the dissolved and particulate phases leading to increase their released to the overlying water (Förstner, 1979; Hamzeh et al., 2014), where the need to study the concentrations of these trace metals

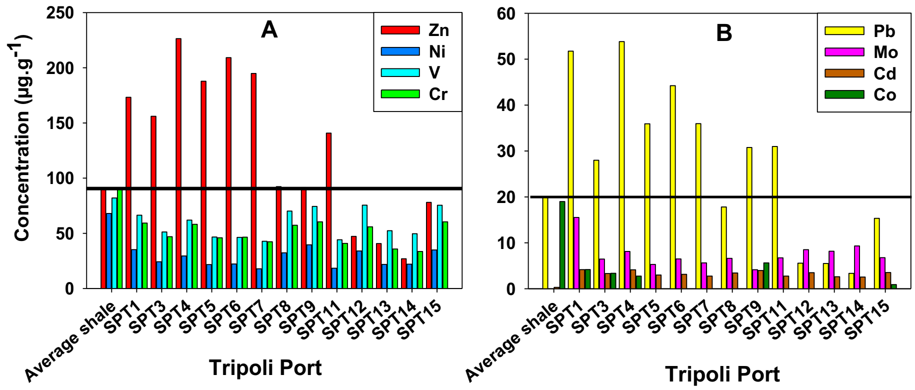

Fig. 2. Concentrations of individual trace metals Concentrations (µg/g d.w.) (**A**: Zn, Ni, V, & Cr) and (**B**: Pb, Mo, Cd, Co) in sediments collected from Tripoli Port compared with the Average shale concentrations.

in the water column and biota in order to have a comprehensive picture of trace metal contamination at these sites.

Multiple evaluation methods were used to evaluate the extent of pollution and the potential ecological risk of trace metal pollutants in sediments of the areas of investigation. In this study, three different methods were used to assess the degree of trace metal contamination and toxicity in sediments.

Sediment Enrichment factor (EF) has widely been used to speculate the origin of a single element by differentiating between their natural and anthropogenic sources (Loska et al., 2004; Sakan et al., 2009; Guo et al., 2010; Choi et al., 2012). In this work, the EF was calculated as follows:

$$EF = \frac{Ci}{CAS} \quad (2)$$

where, Ci is the concentration of individual trace metal in each sediment sample (µg/g d.w.) and C_{AS} is the world average concentration of individual trace metals reported for the shale by Turekian and Wedepohl (1961). Table 4 summarized EF values of studied trace metals obtained at each sampling station and Table 5 represents EF and I_{geo} classes used for sediment quality and pollution extent assessment (Müller, 1981; Ruiz, 2001). Based on EF values, all the sites were categorized into five main classes (Table 5) (Birch and Olmos, 2008). Indeed, EF value $<$ 1, indicate that the metal is entirely from crustal materials or natural processes, while EF values higher than 1, whereas suggesting that the sources are more likely anthropogenic (Buruaem et al., 2012; Diop et al., 2015).

The results show that the EF of Cd varied from moderately severe enrichment to extremely severe enrichment for the all the sampling stations. The extremely severe enrichment was found at SPB and SJB with EF values about 44.90 and 25.10, respectively. Whereas EF of Pb and Zn varied between no enrichment to minor enrichment for the all the sampling stations except at SPB were found as severe enrichment with values reach 22.16 and 10.73, respectively. For, all others trace metals (Cr, V, Li, Ni, and Co) no enrichment was detected except for Cr at SPB where a minor enrichment was observed. Therefore, we suggest that the anthropogenic activities contribute significantly to the coastal sediment pollution with Cd, Pb, Zn and Cr particularly at Beirut Port, Jouniyeh Bay, and Tripoli Port, for STP 1, 4 and 9 indicating the influence of bulky goods handling, shipyards, fishing and touristic activities and sewage outfall input.

Geoaccumulation index (I_{geo}) was also applied as an evaluation method to evaluate and classify the sediment quality of these sampling sites. This index was developed by Müller (1979) as a tool to evaluate the extent of trace metal pollution in sediments and soils (V.K. Singh et al., 2005; Amin et al., 2009; Zahra et al., 2014). I_{geo} was calculated according to Müller and is given in Eq. (3).

$$I_{geo} = \log 2\,(Ci/[1.5]\cdot Bi) \quad (3)$$

where, Ci is the concentration of individual trace metal in each sediment samples (µg/g d.w.) and Bi is the geochemical background value of individual trace metal in the shale by Turekian and Wedepohl (1961) and the factor 1.5 corresponds to possible variations from the baseline due to lithological processes. The overall results of I_{geo} shown in Fig. 4 were interpreted using the I_{geo} classes given in Table 5. The results of I_{geo} revealed that the extent of sediment pollution of all sampling stations was classified as moderately to highly polluted (classes 3 and 4) with Cd except for SPB where the pollution extent was classified as high to very high (Class 5) (Fig. 4). While for Pb the extent of sediments pollution was classified as highly polluted (Class 4) at SPB and as

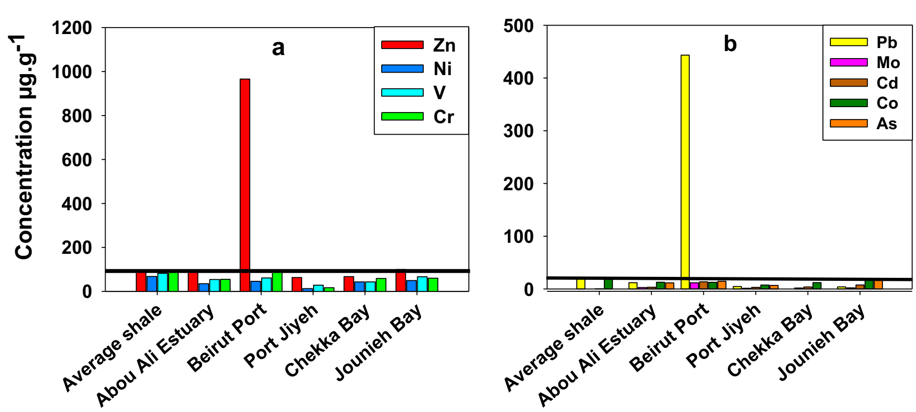

Fig. 3. Concentrations of individual trace metals Concentrations (µg/g d.w.) (**a**: Zn, Ni, V, Cr) and (**b**: Pb, Mo, Cd, Co, As) in sediments collected from five other stations distributed along LCZ compared with the Average shale concentrations.

Table 2
Mean Concentrations (μg/g d.w.) of individual trace metals in sediments collected from six selected sites along LCZ.

Site	Cr	Mn	V	Zn	Mo	Ni	Pb	Cd	Co	As
SAE	54.9 ± 34.5	278.6 ± 55.5	53.9 ± 27.3	95.2 ± 39.0	2.69 ± 1.0	35.1 ± 23.8	11.9 ± 8.5	3.35 ± 2.8	12.7 ± 6.9	11.6 ± 3.3
SPB	94.3 ± 24.1	230.7 ± 50.2	61.1 ± 19.0	965.6 ± 256.6	11.69 ± 1.7	45.7 ± 7.5	443.3 ± 82.6	13.47 ± 3.6	12.6 ± 3.5	14.6 ± 6.1
SPJ	16.9 ± 4.8	286.4 ± 36.7	28.3 ± 8.4	63.2 ± 22.7	1.33 ± 0.3	12.6 ± 3.1	4.6 ± 0.1	3.06 ± 1.2	7.4 ± 1.9	6.7 ± 0.6
SCB	58.6 ± 18.1	207.2 ± 34.9	43.2 ± 9.2	67.2 ± 11.3	1.77 ± 0.4	43.3 ± 12.8	ND	3.77 ± 1.3	12.1 ± 3.1	ND
SJB	60.1 ± 11.0	358.0 ± 59.7	66.6 ± 22.1	99.4 ± 22.4	2.10 ± 0.6	49.3 ± 6.7	3.9 ± 0.7	7.53 ± 3.0	19.8 ± 4.1	18.0 ± 6.0
SPT1	59.3	278.6	66.4	173.2	15.52	35.2	51.7	4.16	4.2	ND
SPT3	46.9	260.4	51.3	156.0	6.46	24.2	27.9	3.32	3.4	ND
SPT4	58.2	302.4	61.9	226.4	8.13	29.5	53.8	4.13	2.7	ND
SPT5	46.0	216.7	46.6	187.7	5.30	21.7	35.9	2.99	ND	ND
SPT6	46.5	219.8	46.3	209.1	6.50	22.2	44.2	3.13	ND	ND
SPT7	42.4	208.9	42.8	194.8	5.63	17.9	35.9	2.76	ND	ND
SPT8	57.3	231.4	70.1	92.3	6.61	32.3	17.8	3.43	ND	ND
SPT9	60.4	363.3	74.4	91.5	4.14	39.6	30.7	3.97	5.62	ND
SPT11	40.9	172.6	44.2	140.8	6.73	18.3	30.9	2.74	ND	ND
SPT12	55.9	246.5	75.6	47.2	8.51	34.0	5.6	3.49	ND	ND
SPT13	35.8	235.5	52.3	40.7	8.17	21.8	5.5	2.62	ND	ND
SPT14	33.6	224.8	49.6	26.9	9.31	22.0	3.4	2.54	ND	ND
SPT15	60.4	247.5	75.4	78.0	6.77	34.9	15.3	3.54	0.91	ND
Mean SPT	49.5 ± 9.6	246.8 ± 47.7	58.2 ± 12.8	128.1 ± 68.8	7.52 ± 2.8	27.2 ± 7.3	27.6 ± 17.0	3.29 ± 0.5	3.36 ± 1.7	ND
Shale[a]	90	850	82[c]	90		68	20	0.3	19	
ERL[b]	81			150		20.9	47	1.2		
ERM[b]	370			410		51.6	218	9.6		

ND: not detected.
ERL: effects range-low.
ERM: effects range-median.
[a] Average shale (Turekian and Wedepohl, 1961).
[b] Long and Morgan (1990), Long et al. (1995, 1998).
[c] Background value determined for Lebanese coastal sediments reported by Abi-Ghanem et al. (2009a, 2009b).

unpolluted to moderately polluted with Pb (Class 1) at SPT for the following samples STP1, STP4, STP 5, STP 6, STP 7, STP 9 & STP 11. And, for Zn also the extent of sediments pollution was classified as moderately to highly polluted (Class 3) at SPB and as unpolluted to moderately polluted (Class 1) at SPT for the following samples STP1, STP 3, STP 4, STP 5, STP 6, STP 7 & STP 11. Above all, the extent of sediment pollution at SPB was classified as highly to very highly, highly and moderately to highly polluted with Cd, Pb, and Zn, respectively. At SPT, the extent of sediment pollution was classified as moderately to highly polluted with Cd and unpolluted to moderately polluted with Pb and Zn, respectively. For all other stations, the extent of sediment pollution was classified as moderately to highly polluted with Cr while for the remaining trace metals (Cr, V, Li, Ni, and Co) the extent of sediments pollution was classified as unpolluted for all sampling stations. A very good agreement was found between the results of EF and I_{geo} evaluation (Table 6).

Table 3
Comparison of Trace metal concentrations (μg/g d.w.) in sediments along LCZ with other regions.

Location	Cr	Mn	V	Zn	Mo	Ni	Pb	Cd	As	References
Lebanese Coastal sediment	16.9–94.3	207.2–358	28.3–66.6	63.2–965.6	1.33–7.52	12.6–49.3	1.2–443.3	3.29–13.47	0.6–18	(This study)
Lebanese Coastal sediment			22.5–270				6.9–104.4	0.001–0.23		(Abi-Ghanem et al., 2013)
Lebanese Coastal sediment							11–24			(Nassif, 2004)
Kaohsing Harbor Taiwan	0.2–900			52–1369			9.5–470	0.1–6.8		(Chen et al., 2007)
Harbor of Ceuta, Spain	13–381			29–695			10–516		4–42	(Guerra-García and García-Gómez, 2005)
Montevideo harbor, Urguay	79–253			174–491			44–128	< 1.0–1.6		(Muniz et al., 2004)
Elizabeth harbor, South Africa				19–126			9–62			(Fatoki and Mathabatha, 2001)
Ventspils Harbor, Latvia	12–71			17–254			3–44	< 0.1–2		(Müller-Karulis et al., 2003)
12 South Korea harbors	11–401			20–1940			20–599	0.03–15	4–60	(Choi et al., 2012)
Sydney Harbor, Australia	6–298			17–11,300			5–1420	0.2–10	5–48	(McCready et al., 2006)
Port of Barcelona, Spain	45–95			180–300		18–27	85–130	1.4–4		(Guevara-Riba et al., 2004)
Santos Estuary, Brazil	< 5–97.5			6–312		1.3–44.2	< 2–204.8	< 0.5–1.49		(Hortellani et al., 2008)
Santos harbor, Brazil	26.3–42.7			509–1077		10.8–22.2	7.57–16.7	< 0.6		(Buruaem et al., 2012)
Pearl River Delta, China	34.7–1656			62.2–1568.7		28.5–130.7	46–382.8	0.50–8.53	5.77–66.09	(Li et al., 2013)
Taranto Gulf, Ionian Sea, southern Italy	85.9			102.3		53.3	57.8			(Buccolieri et al., 2006)
Abu-Qir Bay, Egypt		233.37	22.66	50.98			8.2	2.93	5.3	(Abdel Ghani et al., 2013)
Eastern Harbour of Alexandria, Egypt		118.76	11.81	92.17			40.57	1.11	7.89	(Abdel Ghani et al., 2013)
Egyption coast		13.5–1384		16.6–166.5			49.9–109.77	3.7–53.41		(El Nemr et al., 2007)
Izmir Bay Turkey				14–412			3.1–119	0.005–0.82		(Kucuksezgin et al., 2011)
Seham Bay, Turkey	118.95	803.63		39.09				2.15		(Çevik et al., 2009)

Table 4
Percentage of labile fraction for the studied trace metals along LCZ.

Site	Cr	V	Zn	Mo	Ni	Pb	Cd	Co	As
SAE	79	69	64	51	69	22	96	61	100
SPB	64	49	25	75	60	16	76	64	92
SPJ	80	81	55	34	78	4	100	84	100
SCB	81	80	73	61	57	–	95	56	–
SJB	81	77	63	48	62	100	96	55	100
SPT	80	70	30	65	69	18	37	32	–

Table 5
Enrichment factor values of studied trace metals obtained at each sampling station.

SITE	Enrichment Factor (EF)								Pollution classification
	Cr	Mn	V	Zn	Ni	Pb	Cd	Co	
SAE	0.61	0.33	0.66	1.06	0.52	0.60	11.17	0.67	WP
SPB	1.05	0.27	0.75	10.73	0.67	22.16	44.90	0.66	HP
SPJ	0.19	0.34	0.34	0.70	0.19	0.23	10.20	0.39	WP
SCB	0.65	0.24	0.53	0.75	0.64	0.00	12.57	0.64	WP
SJB	0.67	0.42	0.81	1.11	0.73	0.20	25.10	1.04	HP
SPT1	0.66	0.33	0.81	1.93	0.52	2.59	13.87	0.22	MP
SPT3	0.52	0.31	0.63	1.73	0.36	1.40	11.07	0.18	WP
SPT4	0.65	0.36	0.76	2.52	0.43	2.69	13.77	0.14	MP
SPT5	0.51	0.25	0.57	2.09	0.32	1.80	9.97		WP
SPT6	0.52	0.26	0.56	2.32	0.33	2.21	10.43		WP
SPT7	0.47	0.25	0.52	2.17	0.26	1.80	9.20		WP
SPT8	0.64	0.27	0.86	1.03	0.48	0.89	11.43		WP
SPT9	0.67	0.43	0.91	1.02	0.58	1.54	13.23	0.29	MP
SPT11	0.45	0.20	0.54	1.56	0.27	1.55	9.13		WP
SPT12	0.62	0.29	0.92	0.52	0.50	0.28	11.63		WP
SPT13	0.40	0.28	0.64	0.45	0.32	0.28	8.73		WP
SPT14	0.37	0.26	0.61	0.30	0.32	0.17	8.47		WP
SPT15	0.67	0.29	0.92	0.87	0.51	0.77	11.80	0.05	WP

WP: weakly polluted MP: moderately polluted HP: highly polluted.

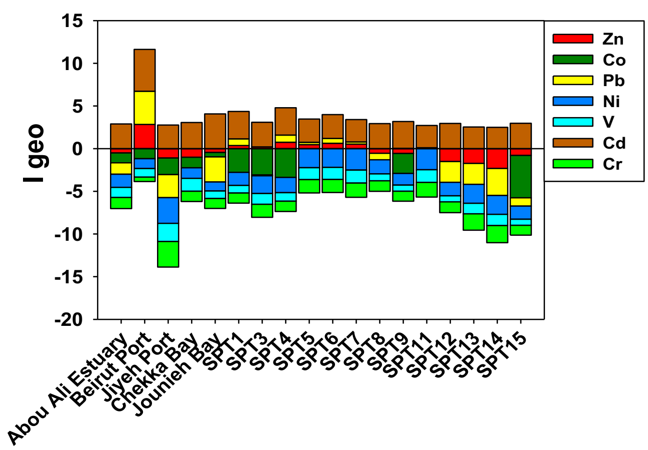

Fig. 4. I_{geo} values of individual trace metals of all sampling sites distributed along LCZ.

To assess the ecotoxicological risk of sediments contaminated by trace metals we used the sediment quality guidelines developed by Long and Morgan (1990) for marine and estuarine ecosystems. Two guideline values were identified: the effects range-low (ERL) and the effects range-median (ERM). Concentrations < ERL value the biological adverse effect were expected to occur rarely, > ERL and < ERM were expected to occur occasionally and > ERM value were expected to cooccur frequently Long et al. (1995, 1998). The trace metals concentration in sediments were compared with ERL and ERM (Table 2), and the results indicate that the biological adverse effects of Cd in sediments were expected to occur occasionally for 95% of studied stations except for SPB were expected to occur frequently. Whereas the biological adverse effects of Zn were expected to occur rarely for 61% of sampling stations and occasionally for 33% for those collected from Tripoli Port (STP 1, STP 3, STP4, STP 5, STP 6, & STP 7) and frequently at SPB. The adverse effect of Pb was expected to occur rarely for 82% of sampling stations and occasionally for 12% for those collected also from Tripoli Port (STP 1 & STP 4) affected by shipping and maintenance activities and frequently in sediments of SPB. For Cr in sediment, we were expecting the adverse effects to occur rarely for all the studied stations except for SPB, we were expecting it to occur occasionally. For Ni, the effects were expected rarely to 17% of sampling stations and occasionally for 83% while for Cr the adverse effects were expected rarely for 94% of samples and occasionally at SPB (6%). Above all we conclude that the biological adverse effect of Cd, Pb, and Zn were expected to occur frequently at Beirut Port, while Cr and Ni were expected to occur occasionally in this site, whereas at Tripoli Port they were expected to occur occasionally for the samples collected from the corner of old basin, close to the ship maintenance area and sewage outfall.

Table 6
Enrichment factor (EF) and I_{geo} classes used for sediment quality and pollution extent assessment.

EF classes	Sediment quality	I_{geo}	I_{geo} classes	Pollution intensity
EF < 1	No enrichment	< 0	0	Unpolluted
EF < 3	Minor enrichment	0–1	1	Unpolluted to moderately polluted
EF 3–5	Moderate enrichment	1–2	2	Moderately polluted
SEF 5–10	Moderately severe enrichment	2–3	3	Moderately to highly polluted
EF 10–25	Severe enrichment	3–4	4	Highly polluted
EF 25–50	Extremely severe enrichment	4–5	5	Highly to very highly polluted
		5–6	> 5	Very highly polluted

Six strategic sites represent the Lebanese coast from north to south were assessed and investigated for trace metals contamination levels. A particular attention was given to Tripoli Port, which is more accessible for sampling in order to identify the main sources of trace metals in the harbor. We focused in this study on the contamination levels of 9 Trace metals, their bioavailability and their ecological risks in the sediment of the studied sites. The concentrations of five trace metals (Cd, Zn, Pb, Cr, and Co) were found to exceed the background values at four sites; SPB, SPT, SJB, and SAE suggesting that LCZ is mainly influenced by the harbor, fishing and touristic activities and rivers inputs. The percentage of labile fraction of almost all trace metals in sediments of studies stations is up to 50% except for Pb, which were found the less labile trace metals that can be explained by the permanent remobilization of these trace metals at ports strongly influencing their partitioning between the dissolved and particulate phases leading to increase their released into the water column, where the need to study the concentrations of these trace metals in the water column and biota in order to have a comprehensive picture of trace metal pollution at these sites. The results of EF show that the anthropogenic activities contribute significantly to the coastal sediment pollution with severer enrichment for Cd, Pb, Zn, and Cr particularly at Beirut Port, which is classified as a highly polluted site. At Tripoli Port, metal contamination was classified as moderately indicating that the harbor basin was significantly affected by ships berthing, shipyards, handling activities of bulky goods including fertilizers, pesticides, and scrap metal waste and sewage outfall. A very good agreement was found between the results of EF and I_{geo} evaluation. The extent of sediment pollution at SPB was classified as highly to very highly, highly and moderately to highly polluted with Cd, Pb, and Zn, respectively while at SPT was classified as moderately to highly, and highly polluted with Cd and unpolluted to moderately polluted with Pb, and Zn, respectively. For all other stations, the extent of sediment pollution with Cr was classified as moderately to highly while for the remaining trace metals (Mn, V, Li, Ni, and Co) and the extent of sediments pollution was classified as unpolluted for all sampling stations. According to the SQGs, the biological adverse effect of Cd, Pb, and Zn were expected to occur frequently at Beirut Port while Cr and Ni were expected to occur occasionally whereas at Tripoli Port were expected to occur occasionally for the samples collected from the corner of the old basin, close to shipyards and sewage outfall. The reduction of metals concentrations in sediments after remediating actions was insignificant and very expensive (Chen et al., 2007) and the stable organic-metal association in the sediment complicates the engineering remediation of contaminated sediments. The results obtained from this study would be helpful for decision makers in developing more effective harbor management strategies to control and monitor the metals discharges into Tripoli Port basins and detailed study is recommended to Beirut Port in order to take the suitable decisions regards the metal pollution. In general, for metal pollution control we suggest that the proper treatment of industrial and municipal wastewaters is a better strategy to control the coastal sediment pollution by reducing the release of these pollutants from the sources.

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