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Research Article

Assessment of Some Heavy Metals Pollution and Bioavailability in Roadside Soil of Alexandria-Marsa Matruh Highway, Egypt

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To assess the roadside soils contamination with Pb, Cd, and Zn, 34 soil samples were collected along Alexandria-Marsa Matruh highway, Egypt, and analyzed by using the atomic absorption. The contamination with these metals was evaluated by applying index of geoaccumulation (I_{geo}), contamination factor (CF), pollution load index (PLI), the single ecological risk index (E_i), and the potential ecological risk index (PERI). The average concentrations of Pb, Cd, and Zn were 38.2, 2.3, and 43.4 μg/g, respectively. I_{geo} indicates the pollution of soil with Pb and Cd as opposed to Zn. E_i shows that the roadside soils had low risk from Pb and Zn and had considerable to high risk from Cd. Most of the samples (62%) present low PERI risk associated with metal exposure and the rest of the samples (38%) are of moderate PERI. The bioavailable fraction (EDTA-Extract) was 72.5 and 37.5% for Pb and Cd contents, respectively. These results indicate the remarkable effect of vehicular and agricultural activities on Pb and Cd contents in soil.

1. Introduction

Soils are the sink for toxic heavy metals from both natural and a wide range of anthropogenic sources [1, 2]. It may be contaminated by the accumulation of heavy metals through emissions from the industrial activities, land application of fertilizers, pesticides, wastewater irrigation, spillage of petrochemicals, and atmospheric deposition [3, 4]. Vehicular emission has been found to constitute one of the major sources of soil pollution [5, 6]. So, roadside soils often contain high concentrations of heavy metals contamination. These metals are released from fuel burning, wear out of tires, leakage of oils, and corrosion of car metal parts [7]. Vehicle exhaust is considered as first line source of heavy metal pollutants [8]. Simon et al. [9] point to the role of traffic emissions in the pollution of Wien soil by Cu, Pb, and Zn. Increasing levels of soil contamination with heavy metals may be transformed and transported to plant [10] and from plants they pass on to animals and human being [10]. Lead, cadmium, zinc, and nickel are the most metal pollutants from heavy traffic owing to their presence in fuel as antiknock agent [10, 11].

The elevated total metal content in soil cannot predict the bioavailability and toxicity of that metal [12, 13]. Metal availability to plants can be assessed by using selective extraction and chemical speciation [14]. The readily soluble fraction of heavy metals is generally considered to be phytoavailable. The estimation of heavy metal phytoavailability in soils is becoming more important as risk assessment because total metal concentrations may not be the best predictors of metal phytoavailability [15]. Single extraction is the most widely used method for evaluating the phytoavailability of heavy metals in soils. Among single extraction methods, neutral salts, dilute acids, and chelating agents are regarded as the more reliable in predicting the plant availability of metals [16, 17].

The objectives of the present work were to (1) assess the degree of roadside soils contamination by Cd, Pb, and Zn

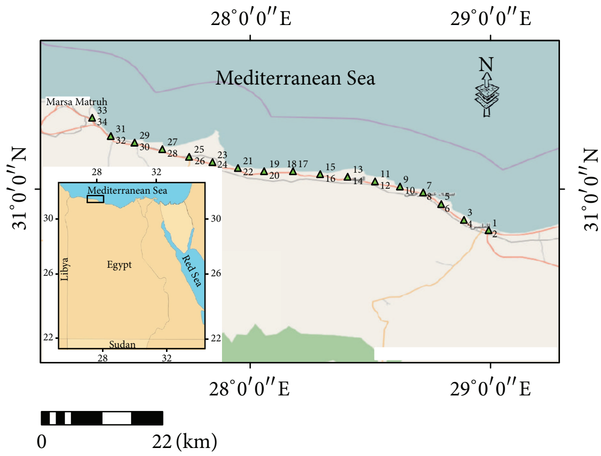

Figure 1: Location map for sampling sites.

using (a) geoaccumulation index (I_{geo}), (b) contamination factor (CF), (c) pollution load index (PLI), and (d) the potential ecological risk index (PERI) and (2) evaluate bioavailable fraction of Cd and Pb in soils. This study supports the hypothesis that traffic emissions and agricultural activity may be one of the major sources of soil pollution with heavy metals.

2. Material and Methods

2.1. Study Area. The studied highway is bounded by longitudes 27°19′00″ and 28°59′40″E and latitudes 30°49′00″ and 31°17′40″N (Figure 1). It is considered a vital national and international road connecting Cairo with the coastal Egyptian cities and with Libya. The climate of the study area is unstable characterized by a rainy winter, some storms during spring, and occasional sudden heavy rainfall during autumn. But the summer season is characterized by stable warm and dry climatic conditions [21]. Geologically, the area is covered by sedimentary rocks belonging to the Quaternary and Tertiary. The Tertiary deposits are represented by Marmarica limestone formation. The Quaternary deposits are mainly composed of limestone facies that rest uncomfortably on the Tertiary deposits. The Pleistocene sediments are represented by oolitic limestone, while the Holocene deposits are muddy composed of sand, silt, and clay with abundant carbonate grains [21, 22]. The area has a heavy flora that begins at the coastal zone and extends to the rocky plateau. There are two kinds of flora in this area; the first kind is arks planted with olive, figs, palm tree, and wheat depending on rainfall and wells that are randomly distributed. The second kind is parks of coastal plants and herbs.

2.2. Sampling and Analysis. The soil samples were collected at depths of 0–10 cm using hand driven stainless steel augers. Thirty-four samples (Figure 1) were collected at two distances of 1 and 30 meters from the side of the road. The geographical coordinates of these locations were determined using a Garmin global positioning system (GPS). Soil samples were air-dried, ground, and passed through a 2 mm sieve. Soil pH was measured in 1 : 1 soils to water ratio. Calcium carbonate ($CaCO_3$) was estimated by titrimetric method according to USDA [23]. Organic matter (OM) was determined according to the modified Walkley and Black method [23]. The soil samples were dried at 110°C for 3 hrs, then ground to pass through a 63-mesh sieve, and homogenized for analysis. For the determination of total metal concentration, exactly 1 g of powdered soil sample was digested with aqua regia ($HNO_3 : HCl = 1 : 3$). For available heavy metal content determination, 5 g of soil in 25 mL of 0.05 M Na_2-EDTA, pH 7.0, was shaken for 1 hr [24]. ADAM balance model PW 124 (±0.0001 g) was used for mass measurement. The concentrations of Cd, Pb, and Zn were determined using atomic absorption spectroscopy (Perkin Elmer 400). All measurements were done in three replicates.

2.3. Pollution Assessment. To assess the level of roadside soil pollution with Cd, Pb, and Zn, the index of geoaccumulation (I_{geo}), the contamination factor, the pollution load index (PLI), and the potential ecological risk index (PERI) have been determined.

The index of geoaccumulation (I_{geo}) was calculated using the following equation [25]:

$$I_{geo} = \log_2 \left(\frac{C_m}{1.5 * B_m} \right), \tag{1}$$

where C_m is the measured concentration of the examined metal in the soil samples and B_m is the geochemical background value of the same metal. The background reference in this study is based on the world soil average abundance of metals; Pb = 22, Cd = 0.5, and Zn = 63 μg/g [26]. The constant 1.5 is used for the possible variations of the background data due to the lithogenic effects. Muller [18] has distinguished seven classes of the I_{geo} (Table 1).

To evaluate ecological risk posed by multiple element pollutions, PERI were determined using Hakanson [19] formulas given below:

$$\begin{aligned} \text{PERI} &= \sum E_i, \\ E_i &= T_i * \text{CF}_i, \\ \text{CF}_i &= \frac{C_m}{B_m}, \end{aligned} \tag{2}$$

where E_i is the single ecological risk index, T_i is the toxic-response factor for a given metal (e.g., Cd = 30, Pb = 5, and Zn = 1) [18], and CF_i is the contamination factor for the same metal. The classes of each index were given in Table 1.

In addition, each site was evaluated for the extent of metal pollution by applying the pollution load index (PLI) introduced by Tomlinson et al. [20], as follows:

$$\text{PLI} = \left(\text{CF}_1 * \text{CF}_2 * \cdots * \text{CF}_n\right)^{(1/n)}, \tag{3}$$

where n is the number of metals studied. The PLI gives simple comparative means for assessing a site quality. The rank of PLI values is shown in Table 1.

Table 1: Classes of I_{geo}, CF, E_i, PLI, and PERI.

	Value	Soil quality	Reference
I_{geo}	$I_{geo} \leq 0$	Uncontaminated	[18]
	$0 < I_{geo} < 1$	Uncontaminated to moderately contaminated	
	$1 < I_{geo} < 2$	Moderately contaminated	
	$2 < I_{geo} < 3$	Moderately to strongly contaminated	
	$3 < I_{geo} < 4$	Strongly contaminated	
	$4 < I_{geo} < 5$	Strongly to extremely contaminated	
	$I_{geo} > 5$	Extremely contaminated	
CF	CF < 1	Low CF	
	1 ≤ CF < 3	Moderate CF	
	3 ≤ CF < 6	Considerable CF	
	CF ≥ 6	Very high CF	
E_i	$E_i < 40$	Low risk	[19]
	$40 \leq E_i < 80$	Moderate risk	
	$80 \leq E_i < 160$	Considerable risk	
	$160 \leq E_i < 320$	High risk	
	$E_i \geq 320$	Significantly high risk	
PERI	PERI < 150	Low PERI	
	150 ≤ PERI < 300	Moderate PERI	
	300 ≤ PERI < 600	Considerable PERI	
	PERI ≥ 600	Very high PERI	
PLI	PLI > 1	Polluted	[20]
	PLI = 1	Baseline level	
	PLI < 1	Not polluted	

3. Results and Discussion

3.1. pH, $CaCO_3$, Organic Matter, and Heavy Metals Contents in Roadside Soils. Soil properties and concentration of Cd, Pb, and Zn analyzed in the study area are presented in Table 2. The pH values that ranged from 7.3 to 8.7 with 50% of samples have pH between 7.7 and 8.4. It was slightly alkaline to alkaline in nature and did not vary significantly along the selected road. The elevated soil pH in turn enhances metal retention in soil [27]. The $CaCO_3$ content was in a broad range from 25 to 90.5 with 50% of samples that have $CaCO_3$% between 46 and 79.5%. The high $CaCO_3$% comes from Quaternary sediments of the area which are characterized by limestone facies [22]. The organic matter (OM%) contents of the soils are low, less than 2.07% with 75% of samples that have less than 1% OM. The soil close to the road contains high percent of OM compared to the fare soils; this may be the result of the deposition of fuel combustion, wear out of tires, and leakage of oils on soil.

The total lead content ranged from 29.15 to 50.6 μg/g (Table 2) and its level in soil decreased with distance from the road. The high concentration near the road indicates the role of vehicle exhaust as the use of alkyl-lead compounds as antiknock additives in petrol [28]. Unfortunately, these soils contain Pb levels higher than the average concentration of world soil (22 μg/g) [26], also higher than the El-Tabbin industrial area soil of 33.3 μg/g [29]. Shendi et al. [30] found that Pb concentration in Fayoum roadside soils ranges from 22.94 to 38.65 μg/g. The soil Pb/Zn ratio greater than unity (Table 1) indicates the vehicle exhaust role in the soil pollution with Pb [31], while ratio less than unity indicates the role of the local conditions [32]. Lead can be very toxic for human health. For children, it could cause reduction in intellectual quotient, hyperactivity, and hearing loss and for adults increased blood pressure and liver, kidney, and fertility damage [33].

The observed level of Cd ranged from 1.25 to 3.15 μg/g, which is higher than the global average of Cd content of 0.53 μg/g [26]. It appears that sources of Cd in soils are vehicle exhaust deposition and P-fertilizers in the study area, whereas the Egyptian phosphatic deposits, which are used in super phosphate fertilizers, contain 20 μg/g Cd [34]. The role of agricultural activity appears in the increase of Cd collected from the 30 m distance, agricultural farm lands. Considering the absence of any industry in the sampling sites, the levels of Cd could be due to lubricating oils and the wearing of tires, where Cd in car tires has been found to range from 20 to 90 μg/g [35]. Cadmium is toxic element to humans because it easily moves from soil to food plants through root absorption, and fairly large amounts can accumulate in their tissues without showing stress [36]. Chronic exposure to cadmium can affect the nervous system, liver, cardiovascular system and led to renal failure and death in mammals and humans [37]. Cadmium data from this work is lower than those found in Fayoum roadside soils [30]. The higher concentration of Pb and Cd in the studied samples than those recorded

Table 2: Summary statistics of the analyzed soil samples results.

	pH	$CaCO_3$%	OM%	Pb (μg/g)	Cd (μg/g)	Zn (μg/g)
Mean	8.0	62.4	0.71	38.2	2.27	43.4
Median	8.1	62.0	0.60	37.0	2.25	44.4
Standard deviation	0.4	19.6	0.50	6.2	0.53	13.0
Range	1.4	65.5	2.03	21.5	1.90	40.5
Minimum	7.3	25.0	0.03	29.2	1.25	26.6
Maximum	8.7	90.5	2.07	50.6	3.15	67.1
1st quartile	7.7	46.0	0.4	33.0	2.0	31.5
3rd quartile	8.4	79.5	1.0	42.1	2.7	51.9

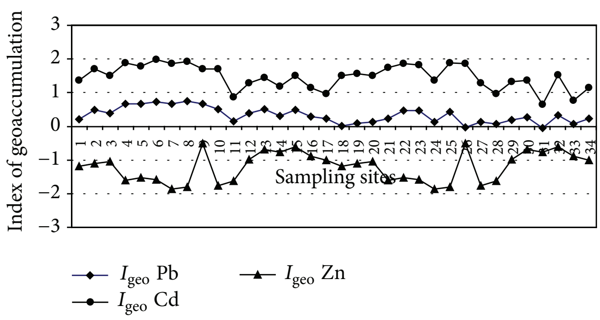

Figure 2: Geoaccumulation index values of Pb, Cd, and Zn in the studied soil samples.

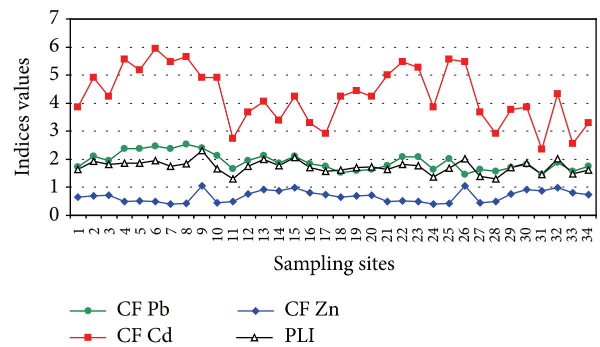

Figure 3: CF values of Pb, Cd, and Zn and PLI in the studied soil samples.

by Ahdy and Khaled [38] in the sediment of the Egyptian Mediterranean coast (Cd 0.721 and Pb 27.85) indicates the anthropogenic source of both metals.

The detected level of Zn ranged between 23.2 and 67.05 μg/g (Table 1). Mean Zn for worldwide soils is calculated as 64 μg/g [26]. Zinc, in the roadside soil close to the highway, exhibited elevated levels of the sampling point studied. The traffic situation in this area of study might be regarded as a source of zinc in the roadside soil. Wear and corrosion of vehicle parts (brakes, tires, radiators, bodies, and engine parts) might also be one of the potential sources of Zn in this area of study. Zinc is used in the process of vulcanization of tires as zinc oxide [39] and as antioxidant in the engine oil. As a result of the tire wear and/or leaks of engine oil and emission of the exhaust fumes, zinc is deposited on the roadside soils [40]. The concentrations of Zn found in the present study are lower than that of roadside soil of Sohag reported by Ibrahim and Omer [41].

3.2. Assessment of Pollution. The calculated values of single (I_{geo}, CF, and E_i) and integrated (PERI, PLI) contamination indices are summarized in Table 2. The I_{geo} values for Pb (Table 3, Figure 2) indicate that the soil samples are uncontaminated-moderately contaminated except samples 26 and 31 which are considered uncontaminated with Pb. The I_{geo} results indicate the anthropogenic input of Cd into soil where most of samples fall in the moderately contaminated class ($1 < I_{geo} < 2$). Only samples 11, 17, 28, 31, and 33 are considered uncontaminated-moderately contaminated with Cd. The obtained I_{geo} value < 0 revealed that nearly all the samples are uncontaminated with Zn.

The CF values for Zn are low (<1), but it was >1 for Pb and Cd (Figure 3). It was found that 85% of the samples have considerable CF for Cd and the rest is of moderate CF, while all the samples have moderate CF for Pb. The PLI values for all samples are >1 indicting the role of external discrete sources, vehicle exhaust, and agricultural activities, of soil pollution. These results indicate probable environmental pollution especially with hazards Pb and Cd.

The calculated E_i indicated that Pb and Zn have low risk into the local ecosystem (Table 3; Figure 4), while Cd reported the highest E_i ranged from 70.8 to 178.3 (considerable to high risk). The overall potential ecological risk of the observed metals in 62% of the studied soil constitutes low risk to the local ecosystem with PERI < 150. The rest of samples (38%) have moderate PERI. The ecological risk comes mainly from the soil pollution with Cd.

3.3. Bioavailability of Metals. Metal bioavailability is a key factor in risk assessment procedures for contaminated sites [42]. Metal toxicity to plants and transfer to food chain are related to metal bioavailability. In the present study, Pb and Cd have $I_{geo} > 1$ so the bioavailable content of them was estimated. The bioavailable lead content estimated in the roadside soil (Table 4; Figure 5) varies from 13.48 to 45.58 μg/g. The average bioavailable component of Pb observed in study area was 71.6% of the total concentration

Table 3: Summary statistics of I_{geo}, CF, PLI, E_i, and PERI for the determined elements.

Parameter	I_{geo}			CF			PLI	E_i			PERI
	Pb	Cd	Zn	Pb	Cd	Zn		Pb	Cd	Zn	
Mean	0.33	1.5	−1.2	1.91	4.3	0.7	1.7	9.6	128.3	0.7	138.5
Median	0.30	1.5	−1.1	1.85	4.3	0.7	1.7	9.3	127.4	0.7	137.1
Standard deviation	0.23	0.4	0.4	0.31	1	0.2	0.2	1.6	29.9	0.2	30.9
Minimum	−0.04	0.7	−1.9	1.46	2.4	0.4	1.3	7.3	70.8	0.4	78.9
Maximum	0.75	2	−0.5	2.53	5.9	1.1	2.3	12.7	178.3	1.0	191.2
1st quartile	0.14	1.3	−1.6	1.65	3.7	0.5	1.6	8.2	110.4	0.5	119.5
3rd quartile	0.49	1.8	−0.9	2.11	5.1	0.8	1.9	10.5	154.2	0.8	166.1

Table 4: Summary statistics of bioavailable fractions of Pb and Cd and their percent.

Parameter	Pb		Cd	
	μg/g	%	μg/g	%
Mean	26.8	72.5	0.82	37.5
Median	27.6	73.9	0.76	34.4
Standard deviation	6.5	19.5	0.23	14.7
Range	32.1	57.2	0.98	53.1
Minimum	13.5	41.3	0.50	21.3
Maximum	45.6	98.5	1.48	74.4
1st quartile	22.6	57.0	0.7	26.7
3rd quartile	31.3	91.9	0.2	43.9

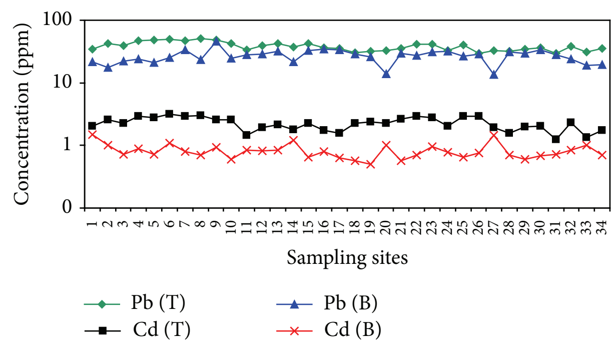

Figure 5: Total (T) and bioavailable (B) fraction of Cd and Pb.

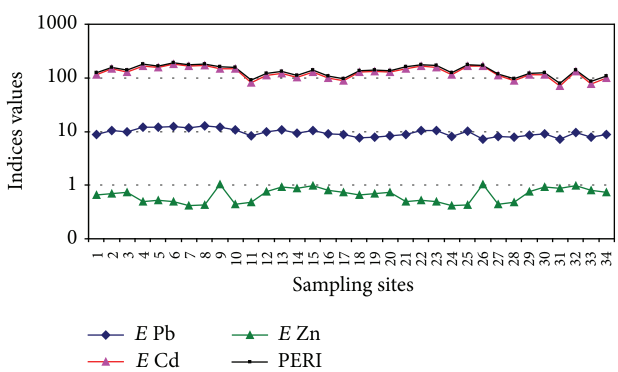

Figure 4: Single ecological risk values of Pb, Cd, and Zn and PERI in the studied soil samples.

of Pb. The observed level of Pb in study area and its higher mobile component could be attributed to automobile exhaust emissions. Rashad et al. [43] recorded the range 1.4–2.5 μg/g with an average of 1.9 μg/g for the available Pb in the Nile Delta soils. A range of 0.46–1.03 μg/g available lead was found for some soils in Assiut [44], while the available fraction of Pb in the surface roadside soil of Fayoum was ranged from 1.59 to 8.05 μg/g [30].

Cadmium available fraction varied between 0.5 and 1.48 μg/g with an average of 0.82 μg/g (Table 4 and Figure 5). The estimated average bioavailable fraction of Cd in study area was 38.7% of the total concentration of Cd. Cadmium in soil may be found in forms that range from sparingly or moderately to highly soluble. This information suggests that cadmium in soils will exhibit a wide range of bioavailability [45]. The observed high concentration in study area could be due to anthropogenic effluents from agricultural activity, spillage of lubricating oils, wear and tear of tires of vehicles, emissions by heavy-duty vehicles that lift oil at the depot, and particles from gasoline combustion. Heavy metals from anthropogenic sources tend to be more mobile than pedogenic or lithogenic ones [46]. Pollution of soils, sediments, and water with Cd causes their incorporation into the food chain, which could result in wide variety of adverse effects in animals and humans, since it is a cumulative contaminant [47, 48]. The DTPA-extractable values of Cd ranged between 0.1 and 0.85 μg/g in the top roadside soil of Fayoum [30], while Ali [49] recorded 0.025 μg/g available (DTPA) Cd in floodplain soil of Sohag.

4. Conclusion

This study provides valuable results about Pb, Cd, and Zn contents along Alexandria-Marsa Matruh highway roadside soils. These soils contain considerable Pb and Cd concentrations in comparison with worldwide soils, while Zn concentrations are below its average worldwide. From the studied samples, the results of I_{geo}, CF, and E_i indicate that the main soil pollutant metal is Cd. The PLI and PERI calculations pointed to the pollution and low to moderate PERI of soils.

Lead (Pb) was observed to have a higher bioavailable fraction than Cd. It appears that the motorway contributes to the soil pollution with Pb and Zn, while agricultural activities contribute to the soil pollution with Cd.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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