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Article

Assessment of Heavy Metal Contamination of Agricultural Soil around Dhaka Export Processing Zone (DEPZ), Bangladesh: Implication of Seasonal Variation and Indices

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Abstract: Intense urbanization, large scale industrialization and unprecedented population growth in the last few decades have been responsible for lowering environmental quality. Soil contamination with metals is a serious concern due to their toxicity and ability to accumulate in the biota. The present work assessed the heavy metal contamination of agricultural soil in the close vicinity of the Dhaka Export Processing Zone (DEPZ) in both dry and wet seasons using different indices *viz*., index of geoaccumulation (I_{geo}), contamination factor (C_f^i), degree of contamination (C_d), modified degree of contamination (mC_d) and pollution load index (PLI). Samples were collected from the surface layer of soil and analyzed by Atomic Absorption Spectrophotometer (AAS). The trend of metals according to average concentration during the dry and wet seasons was As > Fe > Hg > Mn > Zn > Cu > Cr > Ni > Pb > Cd and As > Fe > Mn > Zn > Hg > Cu > Ni > Cr > Pb > Cd, respectively. Because of seasonal rainfall, dilution and other run-off during the wet season, metals from the upper layer of soil were flushed out to some extent and hence all the indices values were lower in this season compared to that of the dry season. I_{geo} results revealed that the study area was strongly and moderately contaminated with As and Hg in the dry and wet seasons respectively. According to C_f^i, soil was classified as moderately contaminated with Zn, Cr, Pb and Ni, considerably contaminated with Cu and highly

contaminated with As and Hg. The general trend of the mean C_f^i was Hg > As > Cu > Zn > Ni > Cr > Pb > Fe > Mn > Cd and As > Hg > Cu > Cd > Zn > Ni >Pb > Fe > Mn in dry and wet seasons, respectively. The mC_f values in the dry and wet seasons were 575.13 and 244.44 respectively indicating an ultra high degree of contamination. The C_d values in both seasons were associated with a very high degree of contamination. PLI results indicated immediate intervention to ameliorate pollution in both seasons. The main sources of metals included effluents from wastewater treatment plants, treated and untreated wastewater from surrounding industrial establishments as well as agricultural activities. Protecting the agricultural soil is a formidable challenge in the study area, which requires modernization of industries, thereby improving the recovery and recycling of wastewater. Indices analysis presented in the present work could serve as a landmark for contemporary research in toxicology.

Keywords: index of geoaccumulation; contamination factor; degree of contamination; pollution load index; heavy metal; zero discharge system ETP; bioaccumulation; Bangladesh

1. Introduction

The role of heavy and trace elements in the soil system is increasingly becoming an issue of global concern at private as well as governmental levels, especially as soil constitutes a crucial component of rural and urban environments [1], and can be considered as a very important "ecological crossroad" in the landscape [2]. Agricultural soil contamination with heavy metals through the repeated use of untreated or poorly treated wastewater from industrial establishments and application of chemical fertilizers and pesticides is one of the most severe ecological problems in Bangladesh. Although some trace elements are essential in plant nutrition, plants growing in the close vicinity of industrial areas display increased concentration of heavy metals, serving in many cases as biomonitors of pollution loads [3]. Vegetables cultivated in soils polluted with toxic and heavy metals take up such metals and accumulate them in their edible and non-edible parts in quantities high enough to cause clinical problems both to animals and human beings consuming these metal-rich plants as there is no good mechanism for their elimination from the human body [4–6]. Toxic metals are known to have serious health implications, including carcinogenesis induced tumor promotion, and hence the growing consciousness about the health risks associated with environmental chemicals has brought a major shift in global concern towards prevention of heavy metal accumulation in soil, water and vegetables [7,8]. Heavy metals and trace elements are also a matter of concern due to their non biodegradable nature and long biological half-lives. Wastewater from industries or other sources carries appreciable amounts of toxic heavy metals such as Cd, Cu, Zn, Cr, Ni, Pb, and Mn in surface soil which create a problem for safe rational utilization of agricultural soil [9–13]. Long-term use of industrial or municipal wastewater in irrigation is known to have a significant contribution to the content of trace and heavy elements such as Cd, Cu, Zn, Cr, Ni, Pb, and Mn in surface soil [12]. As a result, excessive accumulation of trace elements in agricultural soils through wastewater irrigation may not only result in soil contamination but also affect food quality and safety [14–16].

The Dhaka Export Processing Zone (DEPZ) being the 2nd EPZ and the largest industrial belt of Bangladesh at present houses 92 industrial units which are categorically the leading pollution creators. These industrial units include cap/accessories/garments; textile/knitting plastic goods; footwear/leather goods; metal products; electronic goods; paper products; chemicals and fertilizers and miscellaneous products [17,18]. Industrial activities discharge untreated or poorly treated industrial wastewater, effluent and even sludge into the surrounding environment that can decrease soil quality by increasing concentrations of pollutants such as heavy metals, resulting in adverse effects on macrophytes, soil fauna and human health [7,8,19,20]. So it is a nerve-racking issue to find out the present status of toxic and heavy metals in this surface soil, redress the affected subsequent environmental problems and adopt a future mitigation strategy. The present work is aimed at investigating seasonal and spatial variation of the contamination levels of different heavy metals (Fe, As, Mn, Cu, Ni, Pb, Zn, Hg, Cr, Cd) in the agricultural soil around DEPZ using different indices such as the index of geoaccumulation, contamination factor, degree of contamination, and the pollution load index. This approach would help adopt an effective effluent management strategy towards control over enhanced metal levels with recycling of effluents for toxic metal separation and soil remediation and reclamation. The data generated in this work may help to work out an effluent management strategy towards control over effective treatment of the DEPZ discharges in terms of toxic and heavy metal contents.

2. Materials and Methods

2.1. Geological and Hydrological Setting of the Study Area

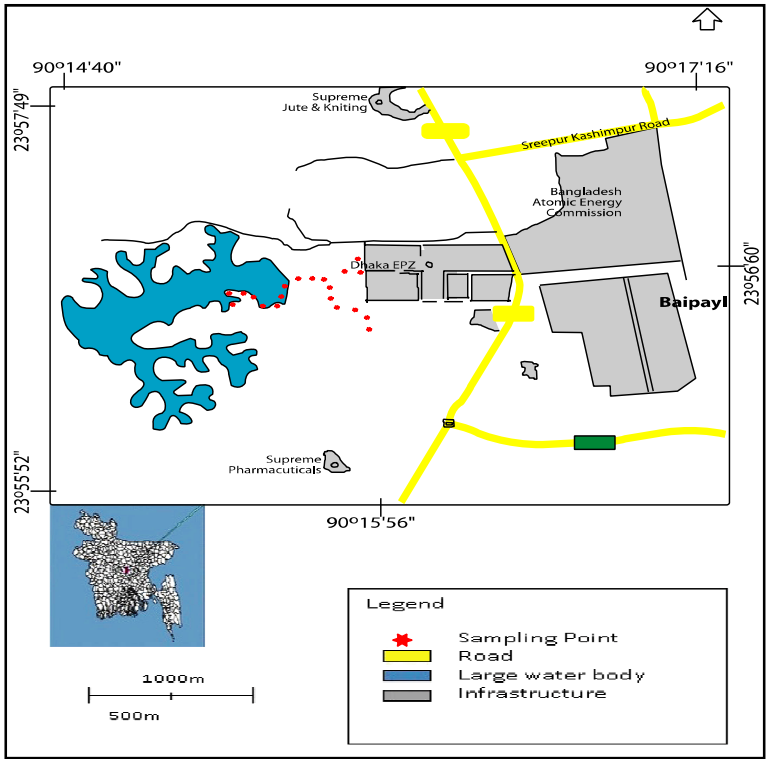
DEPZ, located at about 35 km south-east of Dhaka, the capital city of Bangladesh, was selected as the study area in the present research work. This area belongs to Dhamsona Union under Savar Upazila of Dhaka District. The area is situated at the southwestern fringe of a Pleistocene terrace named the Madhupur Tract, an elevated landscape distinct from the surrounding Fluvio-deltaic plains by the Ganges, Brahmaputra and Meghna River. The major geomorphic units of the area are: the high land, the low lands or floodplains, depressions, swamps, marshes and abandoned channels. Soil of the Modhupur Formation, in general reddish brown in color, contains pre-existing paleosol materials. Hydrology of the study area is governed by rainfall intensity and distribution, permanent or ephemeral water bodies and rivers or canals. The average rainfall distribution pattern in various months shows a distinct conformation with the climatic pattern prevailing, with strong Monsoon influence. The average annual rainfall in dry and wet season in the area is about 25 and 380 mm, respectively. The Bansi-Daleshwari and Turag River comprise the drainage network of the area-Bansi on the west and Turag away on the east.

2.2. Sampling and Analytical Procedure

Agricultural soil samples were collected during February 2010 to April 2011 from the surface layer (15–20 cm) of soil with a stainless steel Ekman Grab Sampler from twenty (20) different locations adjacent to DEPZ (Figure 1) in two different seasons—dry and wet season. The sampler was inspected for possible cross-contamination and cleaned with ambient water for individual sample collection. The difference from one sampling point to another was approximately 100 m. About 250–300 g of the soil

was sampled from the central part of the grab sampler by avoiding contact with the inside materials of the sampler and transferred to a pre-cleaned plastic container. Collected soil samples were air dried for several days over pre-cleaned Pyrex petry dishes. Then 2–3 g dry soil samples were digested in about 15 mL of aqua-regia (HCL:HNO_3 = 3:1) for approximately 4–5 hours using a hotplate maintaining a heating temperature of approximately 110 °C. The samples were next placed in a 100 mL Pyrex glass beaker and diluted with distilled water up to 50 mL. The solution was filtered and the filtrates were analyzed in the Analytical Research Division, BCSIR Laboratories, Dhaka by Atomic Absorption Spectrophotometer (AA-6401 F, Shimadzu, Japan). The working standard solutions for each metal were prepared before every analysis. The analytical procedures were verified with National Institute of Standards and Technology (NIST) traceable certified reference standards. Concentrations of Fe, Mn, Cu, Ni, Zn, Cr and Cd were measured by an air acetylene flame AAS, with As determined by hydride vapor generation AAS, Hg by hydride generation with cold vapor AAS and Pb by graphite furnace AAS.

Figure 1. Map of the study area showing the sampling points.



2.3. Index of Geoaccumulation

The index of geoaccumulation (I_{geo}) actually enables the assessment of contamination by comparing the current and pre-industrial concentrations originally used with bottom sediments [21]; it can also be applied to the assessment of soil contamination. The method assesses the degree of metal pollution in terms of seven enrichment classes (Table 1) based on the increasing numerical values of the index. It is computed using the Equation (1) as:

$$I_{geo} = \log_2 \frac{C_n}{1.5B_n} \quad (1)$$

where C_n is the measured concentration of the element in the pelitic sediment fraction (<2 μm) and B_n is the geochemical background value in fossil argillaceous sediment (average shale). The constant 1.5 allows us to analyze natural fluctuations in the content of a given substance in the environment as well as very small anthropogenic influences.

Table 1. Index of geoaccumulation (I_{geo}) for contamination levels in soil [23].

I_{geo} Class	I_{geo} Value	Contamination Level
0	$I_{geo} \leq 0$	Uncontaminated
1	$0 < I_{geo} < 1$	Uncontaminated/moderately contaminated
2	$1 < I_{geo} < 2$	Moderately contaminated
3	$2 < I_{geo} < 3$	Moderately/strongly contaminated
4	$3 < I_{geo} < 4$	Strongly contaminated
5	$4 < I_{geo} < 5$	Strongly/extremely contaminated
6	$5 < I_{geo}$	Extremely contaminated

In the present paper we applied the modified calculation based on the equation given in [22], where C_n denoted the concentration of a given element in the soil tested, while B_n denoted the concentration of elements in the earth's crust [22]. For some elements like As, Hg and Sb the average concentration in the Earth's crust is much higher than the average concentration in the shale accepted by Muller [21] as a reference value. Here the focus is between the concentration obtained and the concentration of elements in the Earth's crust, because soil is a part of the layer of the Earth's crust and its chemical composition is related to that of the crust.

2.4. Contamination Factor and Degree of Contamination

The assessment of soil contamination was also carried out using the contamination factor (C_f^i) and degree of contamination (C_d). The C_f^i is the single element index, the sum of contamination factors for all elements examined represents the C_d of the environment and all four classes are recognized [24]. Table 2 shows the different contamination factor class and level. Equation (2) was used as follows:

$$C_f^i = \frac{C_0^i}{C_n^i} \quad (2)$$

where C_0^i is the mean content of metals from at least five sampling sites and C_n^i is the pre-industrial concentration of the individual metal.

Table 2. Different contamination factor (C_f^i) for soil [24].

C_f^i Value	Contamination Factor level
$C_f^i < 1$	Low contamination factor indicating low contamination
$1 \leqslant C_f^i < 3$	Moderate contamination factor
$3 \leqslant C_f^i < 6$	Considerable contamination factor
$6 \leqslant C_f^i$	Very high contamination factor

The calculated C_d is therefore defined as the sum of the C_f^i for the pollutant species specified by Hakanson [24]. C_d and was assessed using Equation (3).

$$C_d = \sum_{i=1}^{n} C_f^i \quad (3)$$

The C_d is aimed at providing a measure of the degree of overall contamination in surface layers in a particular sampling site. In the present study we applied a modification of the factor as applied by Krzysztof *et al*. [25] that used the concentration of elements in the earth's crust as a reference value, similar to the other factors. The C_d was divided into four groups as given in Table 3.

Table 3. Different degree of contamination (C_d) for soil [24].

C_d Class	Degree of Contamination Level
$C_d < 8$	Low degree of contamination
$8 \leqslant C_d < 16$	Moderate degree of contamination
$16 \leqslant C_d < 32$	Considerable degree of contamination
$32 \geq C_d < 8$	Very high degree of contamination

2.5. Modified Degree of Contamination (mC_d)

Abrahim [26] presented a modified and generalized form of the Hakanson [24] equation for the calculation of the overall degree of contamination at a given sampling or coring site as follows: (a) The modified formula is generalized by defining the degree of contamination (mC_d) as the sum of all the contamination factors (C_f^i) for a given set of estuarine pollutants divided by the number of analyzed pollutants; (b) The mean concentration of a pollutant element is based on the analysis of at least three samples; and (c) The baseline concentrations are determined from standard earth materials The modified equation for a generalized approach to calculating the degree of contamination is given in Equation 4.

$$mC_d = \frac{\sum_{i=1}^{i=n} C_f^i}{n} \quad (4)$$

where n is the number of analyzed elements and and C_f^i is the contamination factor.

Using this generalized formula to calculate the mC_d allows the incorporation of as many metals as the study may analyse with no upper limit. For the classification and description of the mC_d seven gradations are proposed as shown in Table 4.

Table 4. Different modified degree of contamination (mC_d) for soil [26].

mC_d Class	Modified Degree of Contamination Level
$mC_d < 1.5$	Nil to very low degree of contamination
$1.5 \leq mC_d < 2$	Low degree of contamination
$2 \leq mC_d < 4$	Moderate degree of contamination
$4 \leq mC_d < 8$	High degree of contamination
$8 \leq mC_d < 16$	Very high degree of contamination
$16 \leq mC_d < 32$	Extremely high degree of contamination
$mC_d \geq 32$	Ultra high degree of contamination

An intrinsic feature of the mC_d calculation is that it produces an overall average value for a range of pollutants. As with any averaging procedure, care must however be used in evaluating the final results since the effect of significant metal enrichment spikes for individual samples may be hidden within the overall average result.

2.6. Pollution Load Index (PLI)

The pollution load index (PLI) was proposed by Tomlinson *et al*. [27] for detecting pollution which permits a comparison of pollution levels between sites and at different times. The PLI was obtained as a concentration factor of each heavy metal with respect to the background value in the soil. In this study, the world average concentrations of the metals studied reported for shale [28] were used as the background for those heavy metals. According to Angula [29], the PLI is able to give an estimate of the metal contamination status and the necessary action that should be taken. A PLI value of ≥100 indicates an immediate intervention to ameliorate pollution; a PLI value of ≥50 indicates a more detailed study is needed to monitor the site, whilst a value of <50 indicates that drastic rectification measures are not needed. The formulas applied are as Equation (5).

$$\mathrm{PLI} = \mathrm{n}\sqrt{\mathrm{cf}_1 \times \mathrm{cf}_2 \times \ldots\ldots\ldots \times \mathrm{cf}_\mathrm{n}} \quad (5)$$

3. Results and Discussion

3.1. Seasonal and Spatial Variation of Heavy Metal Content

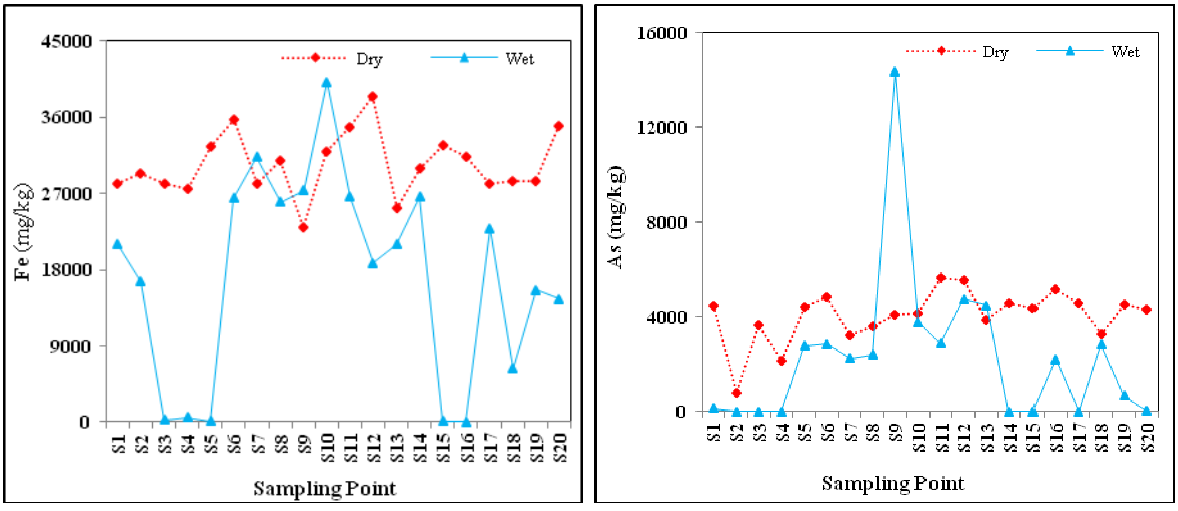
The average concentration of different metals in the agricultural soil of the study area in two seasons is given in Table 5. Average concentration of Fe, As, Mn, Cu, Zn, Cr, Pb, Hg, Ni and Cd in the study area during the dry season was 30,404, 4,073.1, 339, 60, 209, 49.66, 27.6, 486.6, 48.1 and 0.0072 mg/kg, respectively. While average concentration of Fe, As, Mn, Cu, Zn, Cr, Pb, Hg, Ni and Cd in the wet season was 17,103, 2,326.2, 305, 90, 194, 34.2, 23.83, 133.2, 5.5 and 1.04 mg/kg, respectively. So the trend of metals according to mean concentration in the dry season was: As > Fe > Hg > Mn > Zn > Cu > Cr > Ni > Pb > Cd, while in the wet season the trend was: As > Fe > Mn > Zn > Hg > Cu > Ni > Cr > Pb > Cd. The variation of heavy metal concentration in the study area was due to irrigation of land by industrial wastewater and other agronomic practices. The higher standard deviation reveals higher variations in heavy metal distributions from the point source of discharge to the adjacent areas. The low concentration of heavy metals in the soil may be ascribed to its continuous removal by vegetables grown in the designated areas. Among the different metals examined in soil, the concentration of Fe was the maximum and variation in its concentration was several times higher than those reported by Kisku *et al*. [30].

Average concentration of metals during the dry season in the surface layer of the soil is higher than that in the wet season. The highest deposition of Fe (Figure 2) in soil might be due to its long-term use in the production of machine tools, paints, pigments, and alloying in various industries of the study area that may result in contamination of the soil and a change to the soil structure thus making it risky for use in cultivation [31].

Table 5. Different concentrations of metals in the agricultural soil of the study area over two seasons.

Metals	MAC in Agricultural Soil in China (mg/kg) [34]	Natural Background Soil in China (mg/kg) [34]	Safe Limit of India (mg/kg) [35]	DEPZ area (mg/kg) [37]	Present Study					
					Dry Season			Wet Season		
					Mean (mg/kg)	SD	Range (Min-Max) (mg/kg)	Mean (mg/kg)	SD	Range (Min-Max) (mg/kg)
Fe			75–150	1715.8	30404	37.3	23016.4–38458	17103	12147	13.9–581
As					4073.1	1116	789.24–565.92	2326.2	3274	0–14307
Mn					339	142	149.94–22.77	305	131.6	107–582
Cu	100	35	135–200	39.14	60	16.5	19.92–728.25	90	66.9	20.4–281
Zn	300	100	300–600	115.4	209	193.6	75.33–859.95	194	120.4	0.15–474
Cr	200	90		53.7	49.66	34.7	22.77–170.83	34.2	26.5	0–89.78
Pb	350	35	250–500	49.7	27.6	7.9	9.79–41.08	23.83	11.3	0.511–45
Hg					486.6	229.3	132.7–5016.2	133.2	72.7	0–328.28
Ni	60	40		58.2	48.1	11.3	29–68.2	35.5	10.5	11.65–52
Cd	0.6	20	3–6	11.4	0.0072	0.02	0–0.09	1.04	2.03	0.25–8.8

Figure 2. Seasonal and spatial variation of (**a**) Fe and (**b**) As in the study area.

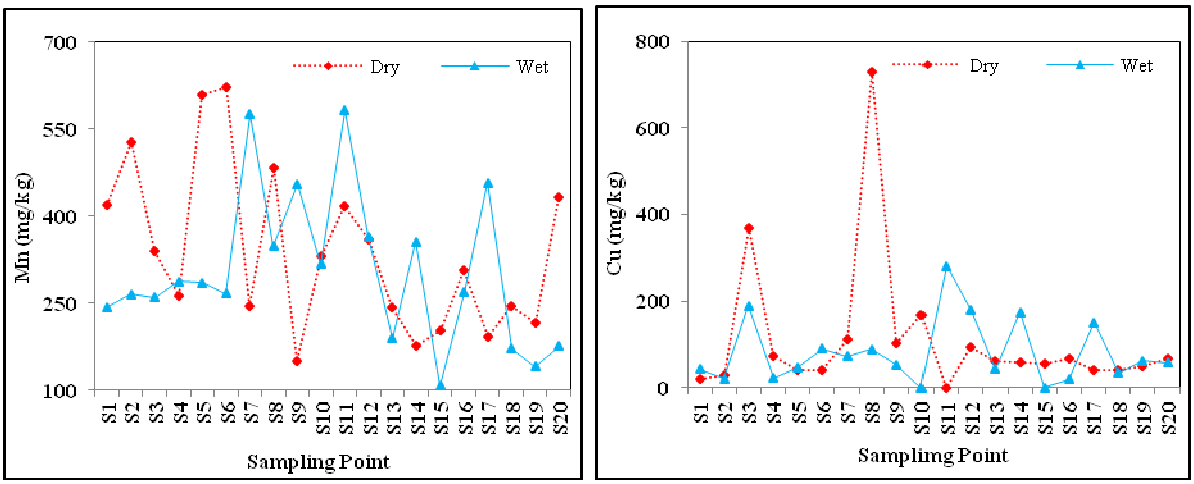


(**a**) (**b**)

High concentrations of As in the soils are due to significant anthropogenicity particularly industrial activities such as the metallurgical and chemical industries and the use of arsenical sprays [32]. Arsenic is a priority toxic element that can cause arsenicosis-related disease and internal cancers, even in trace amounts. The dry season showed about a two times higher concentration of arsenic in the soil than that of the wet season (Figure 2). The mean As content in the soil near industrial areas in Turkey was 9.53 mg/kg ranging from 1.50 to 65.60 mg/kg [32]. Arsenic concentration in uncontaminated Polish soils had a range of 0.9 to 3.4 mg/kg [33].

Mn is one of the commonly found elements in the lithosphere and its concentration in the dry season was about two times higher than in the wet season (Figure 3).

Figure 3. Seasonal and spatial variation of (**a**) Mn and (**b**) Cu in the study area.



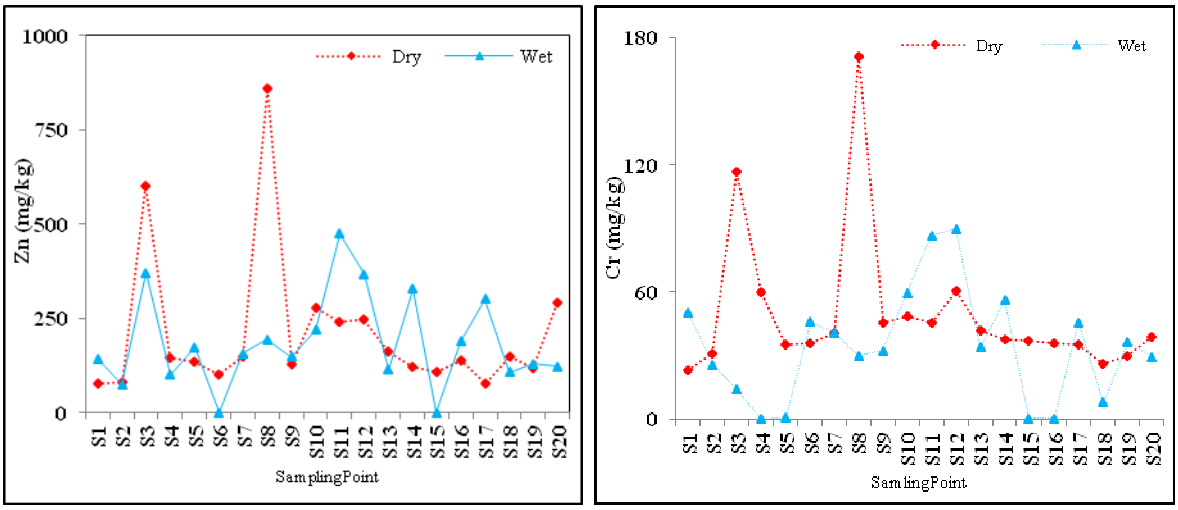
(**a**) (**b**)

Cu was distributed uniformly in the wet season, but in the dry some zigzag was found. This metal was about 1.5 times higher in the dry season compared to the wet (Figure 3). There was a sharp variation in average Cu concentration in the dry season at sampling point 8 due to point source contamination. More or less the average concentration of the metal was within the MAC of elements in agricultural soil found in China [34], and within the safe limit of India [35]. Cu content of soils in the Gebze region was between 7.87 and 725 mg/kg with an average of 95.88 mg/kg which was significantly greater than that in uncontaminated soils [32]. In some other works, Cu concentrations lower than in Gebze soils were recorded [33,36].

Zn and Cr are heavy metals and their sources in industrial locations are usually anthropogenic [38]. The main anthropogenic sources of Zn are related to the non-ferric metal industry and agricultural practice [32,33]. Zinc is a very readily mobile element. High doses of Zn show toxic and carcinogenic effects and result in neurologic and hematological complications, hypertension, and kidney and liver function disorders [39].

The Cr content of topsoil is known to increase due to pollution from various sources of which the main ones are attributable to industrial wastes such as Cr pigment and tannery wastes, electroplating sludge, leather manufacturing wastes, and municipal sewage sludge *etc*. Cr behavior in soil is controlled by soil pH and redox potential, while long term exposure to Cr can cause liver and kidney damage [38]. The observed Zn and Cr concentrations in studied soil around DEPZ probably comes from construction materials in the form of alloys for protective coating for iron and steel. These metals are also used in the industries of DEPZ pigment and reducing agents; cotton processing, soldering and welding flux; rubber industry, glass, enamels, plastics, lubricants, cosmetics, pharmaceuticals, agents for burns and ointments [40]. Both metals were unevenly distributed in the study area (Figure 4). Both metals showed higher concentration in a similar study area to Ahmed and Gani [37].

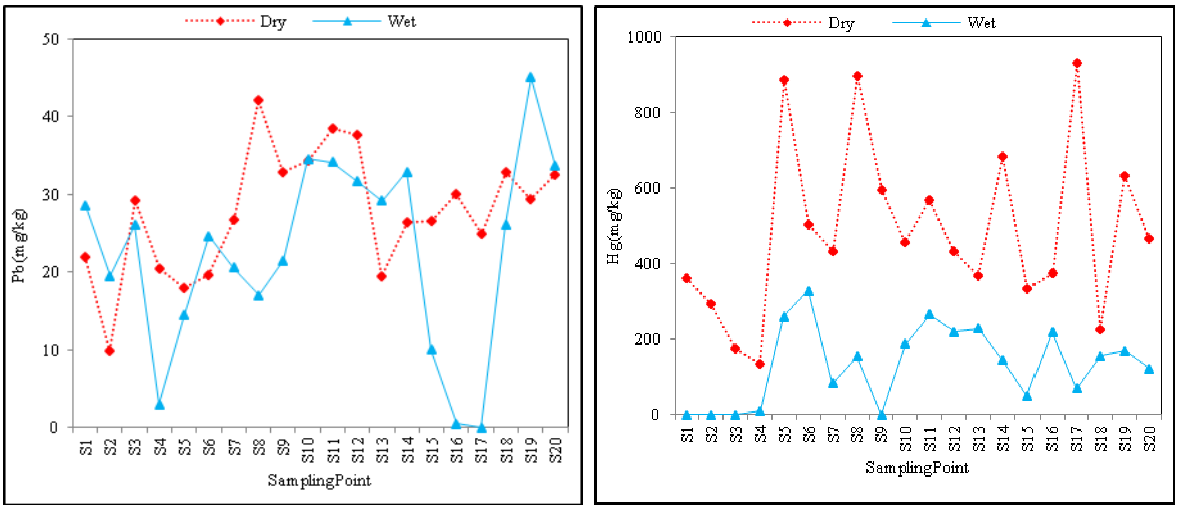
Figure 4. Seasonal and spatial variation of (**a**) Zn and (**b**) Cr in the study area.



(**a**) (**b**)

Pb contamination in soils has been seriously emphasized in recent years since this metal is very toxic for humans and animals [32]. Pb enters human or animal metabolism via the food chain. Pb production and operation facilities without a waste-gas treatment system, battery production and scrap battery recovery facilities, thermal power plants, and iron–steel industries are the other lead sources. Moreover among the heavy metals, Pb is the most immobile element and its content in soil is closely associated with clay minerals, Mn-oxides, Al and Fe hydroxides, and organic material [32]. Although there was point wise variation in concentration of Pb (Figure 5), a very limited average variation was observed over two seasons. Pb concentrations in Gebze soils were between 17.07 and 8,469 mg/kg with an average of 246 mg/kg which is noticeably higher than values reported in the literature [32]. The average Pb concentration in the soils of the Thrace region was recorded as 33 mg/kg [41]. Long term exposure of Pb is risky. Bioaccumulation and bio-magnification can take place. Hence, regular consumption of vegetables from this area by residents could pose a serious neurological health problem from long term Pb exposure.

Figure 5. Seasonal and spatial variation of (**a**) Pb and (**b**) Hg in the study area.

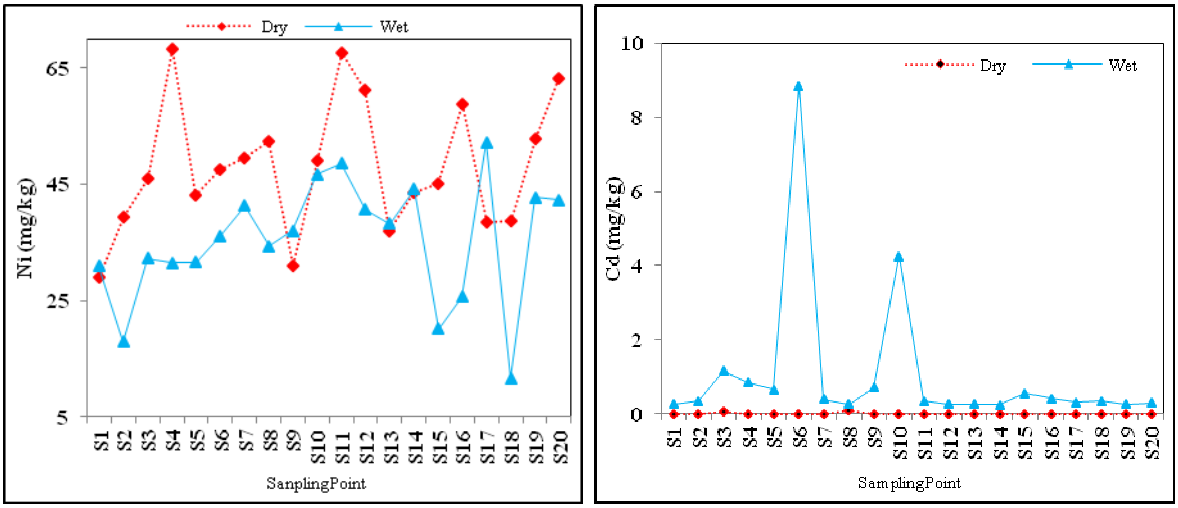


(**a**) (**b**)

Hg is a toxic metal for environmental and human health. Base-metal processing and some chemical industrial activities are the main source for Hg contamination in soils. Mining activities, sewage wastes, and the use of fungicides also result in Hg pollution. The dry season contained about four times higher concentrations of this metal than that of the wet season (Figure 5). Seasonal rainfall may limit the concentration in soil during the wet season. Hg concentration in Gebze soils was between 9 µg/kg and 2,721 µg/kg with an average of 102 µg/kg [32], which is very much lower than present work.

Average concentration of Ni in the dry season was higher than the wet season (Figure 6). Major sources of Ni in the soil are poorly treated wastewater that is discharged from ceramics, steel and alloys and other metal processing industries. Long term exposure of Ni through the food chain may contribute to health problems like skin allergies, dermatitis, rhinitis, nasal sinusitis, lung injury and nasal mucosal injury [38].

Figure 6. Seasonal and spatial variation of (**a**) Ni and (**b**) Cd in the study area.



(**a**) (**b**)

There is a growing environmental concern about Cd being one of the most eco-toxic metals, exhibiting highly adverse effects on soil health, biological activity, plant metabolism, and the health of humans and animals [33]. The comparison of mean concentrations of heavy metals in the soil of the study area with the official Indian standard [35], and the MAC of elements in agricultural soil in China [34] showed that only the concentration of Cd was found to be 3-fold higher than the threshold level of India and 19 times higher than the Chinese standard (Figure 6). Higher concentration of Cd in the wet season may be due to more Cd containing waste water release from DEPZ compared to that of the dry season. The Cd concentrations in Gebze, Turkey soils varied from 0.05 to 176 mg/kg and the average was 4.41 mg/kg [32]. The average Cd concentration in northern Poland soils was 0.80 mg/kg [36] which is significantly lower than that in Gebze soils. Environmental levels are greatly enhanced by industrial operations as Cd is commonly used as a pigment in paint, plastics, ceramics and glass manufacture. Even at very low concentrations chronic exposure to this metal can lead to anemia, anosmia, cardiovascular diseases, renal problems and hypertension [15].

It is commonplace that the concentrations of the studied heavy metals were higher during the dry season, when the rainfall was comparatively low. During the wet season the values were in general low and fall within various standard levels. In the rainy season the pollution was lowest because of heavy rainfall, dilution and other runoff processes. Most of the suspended materials, which were not complexed and precipitated with soil, organic matter and other compounds, were flushed out through the canal into the adjoining vast flood zone. In the dry season rice, grasses and many other types of 'rabi' crops are grown in the contaminated soils which are irrigated with polluted water. Locally produced crops with attractive appearances might have high pollution content of heavy metals. Therefore long term intake of food grown in the area might create serious toxicological effects for the consumers.

3.2. Index of Geoaccumulation

Average I_{geo} and contamination levels of different metals in soil are given in Table 6 while Figure 7 representsthe sampling point wise I_{geo} value in two seasons. I_{geo} is distinctly variable and suggests that soil around the DEPZ ranged from uncontaminated to strongly/extremely contaminated with respect to the analyzed metals. I_{geo} revealed that all the samples examined in both seasons in respect of Fe and Mn fell into class 0—uncontaminated. In the case of As in the dry season, 18 sampling points fell in class 4 and the average I_{geo} was 3.23 indicating strongly contaminated. During the wet season I_{geo} for As belong to moderately/strongly contaminated. This high index is caused mainly by the metallurgical industry; hence its content in the areas affected by industrial activity may be elevated. I_{geo} values for Cu in the dry season ranged from −2.74 to 1.28 with a mean value of 0.31 and most of the samples in both seasons fell into class 1 of uncontaminated to moderately contaminated. I_{geo} of Zn in the dry and wet season was 0.19 and 0.07, respectively and belongs to I_{geo} class 1. In the wet season, Cr showed an uncontaminated state, but uncontaminated/moderately contaminated in the dry season. A similar trend to Cr was also found for Pb, but different for Cd. Ni followed uncontaminated/moderately contaminated index over two seasons. I_{geo} of Hg in the dry season ranged from 2.7 to 3.98 and the value was 0 to 4.85 in the wet season. Figure 8 shows overall statistics of I_{geo} over two seasons.

Table 6. Average I_{geo} and contamination levels of soil in two seasons.

	Dry Season		Wet Season	
	I_{geo} Value	**Contamination Level**	**I_{geo} Value**	**Contamination Level**
Fe	−0.37	Uncontaminated	−1.09	Uncontaminated
As	3.23	Strongly contaminated	2.16	Moderately/strongly contaminated
Mn	0.61	Uncontaminated/moderately contaminated	−0.66	Uncontaminated
Cu	0.31	Uncontaminated/moderately contaminated	0.24	Uncontaminated/moderately contaminated
Zn	0.19	Uncontaminated/moderately contaminated	0.07	Uncontaminated/moderately contaminated
Cr	0.08	Uncontaminated/moderately contaminated	−0.45	Uncontaminated
Pb	0.06	Uncontaminated/moderately contaminated	−0.19	Uncontaminated
Hg	3.08	Strongly contaminated	2.09	Moderately/strongly contaminated
Ni	0.19	Uncontaminated/moderately contaminated	0.05	Uncontaminated/moderately contaminated
Cd	−0.03	Uncontaminated	0.53	Uncontaminated/moderately contaminated

Figure 7. Representation of I_{geo} of metals at different sampling points and seasons.

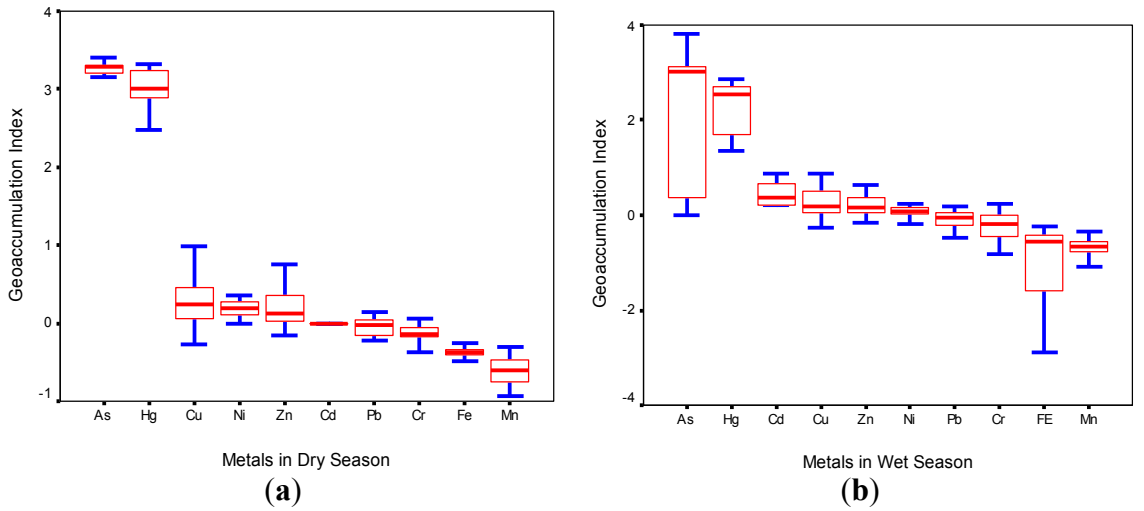
SP	Fe		As		Mn		Cu		Zn		Cr		Pb		Hg		Ni		Cd	
	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W
1								•		•					■			•	•	•
2			■	+											■		•		•	•
3							•	•	•	•	•				■		•	•		•
4			■				•		•		•	•			■		•	•	•	•
5							•	•	•	•						+	•	•	•	•
6							•	•								■	•	•	•	+
7							•	•	•	•						■	•	•	•	•
8				+			+	•	•	•			•			■	•	•		•
9							•	•	•	•			•			■	•	•	•	•
10							•	•	•	•		•	•	•			•	•	•	+
11							•	•	•	•		•	•	•		■	•	•	•	•
12							•	•	•	•		•	•	•	■	■	•	•	•	•
13							•	•	•	•					■	■	•	•	•	•
14							•	•	•	•				•		■	•		•	•
15							•	•	•	•					■	■	•		•	•
16							•		•	•					■	■	•	•	•	•
17				+			•	•		•				•	■	■	•		•	•
18							•		•				•			■	•	•	•	•
19							•	•	•	•				•		■	•	•	•	•
20							•	•	•	•			•	•		■	•	•	•	•

Legend

	$I_{geo} \leq 0$	Uncontaminated
•	$0 < I_{geo} < 1$	Uncontaminated/moderately contaminated
+	$1 < I_{geo} < 2$	Moderately contaminated
■	$2 < I_{geo} < 3$	Moderately/strongly contaminated
	$3 < I_{geo} < 4$	Strongly contaminated
	$4 < I_{geo} < 5$	Strongly/extremely contaminated

SP: Sampling Point; D: Dry Season; W: Wet Season

Figure 8. Statistics of I_{geo} of soil in (**a**) dry and (**b**) wet season.



3.3. Contamination Factor, Degree of Contamination, Modified Degree of Contamination and Pollution Load Index

The assessment of the overall contamination of the studied agricultural soil was based on C_f^i. In the dry season, the soil was classified as slightly contaminated with Fe, Mn and Cd, moderately contaminated with Zn, Cr, Pb and Ni, considerably contaminated with Cu and highly contaminated with As and Hg. In the wet season except for Cu and Cd, the contamination factor of all other metals decreased. However, there was a very limited change in the overall scenario. Cr was additionally added to the first category, Cd shifted from a slightly contamination to moderately contamination factor and Cu fell into the highly contaminated group. Overall the C_d values of the soil of the study area during the dry and wet seasons were 5,751.26 and 2,444.42, respectively. The maximum values of the contamination degree denoted very high contamination. The mC_d as proposed in the present study is based on integrating and averaging all the available analytical data for a set of soil samples. This modified method can therefore provide an integrated assessment of the overall enrichment and contamination impact of groups of pollutants in the soil. During the dry and wet seasons the mC_d varied as 575.13 and 244.44, respectively thus revealing an ultra high degree of contamination. Because of heavy rainfall, dilution and other run-off during thewet season, metals from the upper layer of the soil were flushed out to some extent through the canal into the adjoining vast flood zone and hence all the indices values were lower in this season compared to the dry season. The PLI values indicated immediate intervention to ameliorate pollution in both seasons. Average C_f^i, C_d and mC_d of the soil is given in Table 7.

Table 7. Average C_f^i, C_d , mC_d and pollution load index (PLI) of soil over two seasons.

	Dry Season	**Wet Season**
Fe	0.65	0.36
As	2715.36	1708.96
Mn	0.40	0.36
Cu	4.68	7.72
Zn	2.95	2.72
Cr	1.42	0.97
Pb	1.38	1.24
Hg	3021.98	717
Ni	2.40	1.77
Cd	0.02	3.49
C_d	5751.26	2444.42
mC_d	575.13	244.44
PLI	1801.3	50,047.5

3.4. Correlations Matrix

Pearson correlation analysis [42] was performed between all the variables. The level of significance ($p \leq 0.05$ and $p \leq 0.01$) of multi-element correlation for soil samples was determined and the results are given in Table 8. The listed r values indicated the high degree of positive correlations and significant linear relation between various pairs of metals, reflecting their simultaneous release and

identical source from the DEPZ zone, transport and accumulation in soil. The inter-metallic correlation coefficients in the soil samples with $p < 0.05$ during the dry season were: Fe-Ni, As-Pb, Cu-Zn, Cu-Cr, Cu-Cd, Zn-Pb, Zn-Cd and Cr-Cd. In the wet season the correlation trends were: Fe-As, Fe-Cr, Fe-Ni, As-Cr, Cu-Zn, Cu-Cr, Cu-Ni, Cr-Pb, Cr-Ni and Pb-Ni. The significant correlations indicate that they may have originated from common sources, presumably from other industrial (chemicals, paints) activities. The correlation of As with Cr and Fe indicate their common source from tannery industries. The strong association of Cd, Zn, and Cu indicates common sources, and these metals may have been derived from anthropogenic sources, especially the paint industry and municipal sewage system.

Table 8. Correlation coefficient matrix for the metals in soil around DEPZ during the dry and wet seasons.

	Fe	As	Mn	Cu	Zn	Cr	Pb	Hg	Ni	Cd
Dry Season										
Fe	1						.		.	
As	0.467 *	1								
Mn	0.553 *	−0.048	1							
Cu	−0.004	−0.078	0.174	1						
Zn	0.112	−0.020	0.226	0.964 **	1					
Cr	0.016	−0.096	0.164	0.972 **	0.957 **	1				
Pb	0.263	0.512 *	−0.224	0.558 *	0.570 **	0.469 *	1			
Hg	0.185	0.079	0.281	−0.047	−0.129	−0.088	−0.165	1		
Ni	0.579 **	0.193	0.142	0.161	0.248	0.213	0.393	−0.010	1	
Cd	−0.041	−0.122	0.217	0.978 **	0.941 **	0.960 **	0.410	−0.064	0.060	1
Wet Season										
Fe	1									
As	0.753 **	1								
Mn	0.557 *	0.223	1							
Cu	0.315	0.417	0.535 *	1						
Zn	0.110	0.173	0.511 *	0.889 **	1					
Cr	0.750 **	0.571 **	0.555 *	0.703 **	0.525 *	1				
Pb	0.548 *	0.454 *	0.125	0.489 *	0.323	0.668 **	1			
Hg	0.082	0.037	0.371	−0.158	−0.101	0.150	0.081	1		
Ni	0.623 **	0.547 *	0.539 *	0.599 **	0.473 *	0.672 **	0.622 **	−0.092	1	
Cd	0.296	0.351	−0.069	0.003	−0.326	0.132	0.029	−0.091	0.099	1

* Correlation is significant at the 0.05 level (2-tailed); ** Correlation is significant at the 0.01 level (2-tailed).

4. Conclusion

Soil is a great geochemical reservoir for contaminant as well as a natural buffer for transportation of chemical materials and elements in the atmosphere, hydrosphere, and biomass. For this, it is the most important component of the human biosphere. As soil is an important constituent of the human biosphere, any harmful change to this segment of the environment seriously affects the overall quality of human life. The most adverse effect of heavy metals is that they can be introduced into the food chain and threaten human health. Agricultural products growing on soils with high metal concentrations are represented by metal accumulations at levels harmful to human and animal health as well as to the bio-environment. The impact of anthropogenic heavy metal contamination on agriculture soil around DEPZ was evaluated in this study using seasonal variation and indices. All the indices more or less revealed that the study area was seriously affected by different metals. Dry seasons

resulted in some multi-fold higher values of the overall indices. These metals with high concentrations in the studied soils may have been mixed with groundwater by leaching. High concentrations of heavy metals in soils around industrial facilities originate from an anthropogenic source which is associated with unrestrained solid release and untreated or poorly treated fluid wastes from these industrial facilities. To control soil contamination, legislative measures must be taken, legally binding the individual industries, forbidding discharge of untreated or poorly treated industrial effluents. Lowering the quality of soil health due to these industries can only be restricted if a zero discharge system ETP is implemented throughout the DEPZ. Immediate steps including regular monitoring of toxic metals in the agricultural soil is needed to check the environmental quality. Wastewater discharged from DEPZ could be recycled for the remediation of pollution in a sustainable and eco-specific way. Moreover different remediation measures should be taking promptly to remove excising metal contamination.

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