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Research Article

Heavy Metal Pollution in the Agricultural Soils alongside Highway 080 of Igdir Province

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Abstract

Natural soils have been polluted by variety of human activity such as urbanization, industrialization and excessive fertilizer and pesticide usage. However, the agricultural soils alongside the highways, especially those of international ones, are relatively at higher risk of heavy metal pollution depending on the intensive track traffic. Therefore, total of 72 soil samples from the 24 sampling sites were taken at 5 km interval to elucidate the vehicle-induced heavy metal pollution on the international highway 080 in Igdir, Turkey. After characterising the soil samples, their total and DTPA extractable or plant available concentrations were determined. The results showed that the concentrations of total and available heavy metals were highly dependent on the distances from the highway. In general, the closer distance to highway resulted in higher element concentrations. Iron and zinc were the most affected elements ($p>0.01$), and followed by nickel ($p<0.05$), manganese and copper (close to $p= 0.05$). The zone from 0 to 10 m away from the highway was the most polluted area. Pollution indices (PI) were in descending order as Ni>Cu>Zn>Fe>Mn for the total concentrations and Cu>Zn>Mn>Fe>Ni for the available fractions. The pollution load indices (PLI) were generally higher than the pollution indices (PI) of total micronutrients except nickel (Ni) values, and were generally lower than the pollution indices (PI) of available ones. It can be concluded that Ni and Cu were likely to reach environmentally risky levels in relatively shorter time.

Keywords: Heavy metals, total and available deposits, pollution index, pollution load index, Highway 080.

Iğdır ili 080 Devlet Karayolu Boyunca Tarım Topraklarında Ağır Metal Kirliliği

Öz

Doğal topraklar, kentleşme, sanayileşme ve aşırı gübre ve pestisit kullanımı gibi çeşitli insan faaliyetleri ile kirlenmiştir. Bununla birlikte, özellikle uluslararası olanlar olmak üzere otoyolların yanındaki tarımsal topraklar, yoğun yol trafiğine bağlı olarak nispeten daha yüksek ağır metal kirliliği riski altındadır. Bu nedenle, Türkiye Iğdır'da 080 uluslararası karayolunda araç kaynaklı ağır metal kirliliğini aydınlatmak için 24 örnekleme noktasından toplam 72 toprak numunesi 5 km aralıklarla alınmıştır. Toprak numunelerinin özellikleri belirlendikten sonra, toplam ve bitki tarafından alınabilir miktarları DTPA ile ekstrakte edilerek ölçülmüştür. Sonuçlar, toplam ve alınabilir ağır metal konsantrasyonlarının büyük ölçüde otoyola olan mesafelere bağlı olduğunu göstermiştir. Genel olarak, otoyola daha yakın mesafe, daha yüksek element konsantrasyonları ölçülmüştür. Uzaklıktan en çok etkilenen elementler demir ve çinko olmuştur ($p> 0.01$) ve bunları nikel ($p <0.05$), manganez ve bakır ($p = 0.05$'e yakın) izlemiştir. Otoyoldan 0 ila 10 m uzaklıktaki bölge en kirli bölge olmuştur. Kirlilik indeksleri (PI), toplam konsantrasyonlar için Ni> Cu> Zn> Fe> Mn ve alınabilir değerler için Cu> Zn> Mn> Fe> Ni şeklinde sıralanmıştır. Kirlilik yük endeksleri (PLI) genel olarak nikel (Ni) değerleri dışında toplam mikro besinlerin kirlilik endekslerinden (PI) daha yüksek ve genellikle alınabilir değerlerin kirlilik endekslerinden (PI) daha düşük hesaplanmıştır. Ni ve Cu'nun nispeten daha kısa sürede çevre açısından riskli seviyelere ulaşma ihtimalinin yüksek olduğu sonucuna varılabilir.

Anahtar Kelimeler: Ağır metaller, toplam ve alınabilir birikimler, kirlilik endeksi, kirlilik yük endeksi, 080 Devlet Karayolu.

1. Introduction

Soil is an active and necessary natural part of lithosphere comprimizig various forms of organisms from microscopic to huge trees. Soil encloses both macro and micro nutrients which are significant sustenance for the biosphere and aids in maintaining the stability of biodiversity and habitat.

A great deal of the metal(loid)s is classified as micronutrients, namely their small quantities are necessary for growing of plants and/or animals. Exemplarily, copper (Cu), manganese (Mn), molybdenum (Mo), nickel (Ni) and zinc (Zn) are the heavy metals which are vital for higher plants. Chromium (Cr), Cu, cobalt (Co), Mn, Mo, selenium (Se), vanadium (V) and Zn are the micronutrient heavy metal(loid)s for animals and humans. Iron (Fe), not usually taken into account as a risky heavy metal due to very low solubility in soils, is essential for both plants and animals. Either deficiency or toxicity of micronutrients have adeverse influences over plant and animal health, such as limitation in growth, physiological stress and, in utmost cases, the decease of yield. In many parts of the world, the deleterious effects of deficicency of esential heavy metal(loid)s are economically more considerable than their toxicities in the soils [1].

Regardless of their essentiality for plant growth, excessive occurence of heavy metals in tissues and organs adversely affects the development of plants at vegetative and generative stages [2]. Many metals are necessary for human life at low concentrations and these metals can be toxic at high concentrations. These essential metals are iron (Fe), magnesium (Mg), zinc (Zn), copper (Cu), and manganese (Mn), etc. These are the key elements for maintaning biochemical processes taking place in a living body [3].

In many developing and developed countries, vehicular pollution is a critical environmental issue especially in the over-crowded places. Transports in big cities are predicted to be liable for 70% of carbon monoxide (CO), 50% of hydrocarbon (CxHy), 30-40% of nitrogen dioxide (NO_2), 30% of suspended particulate matter, and 10% of sulphur dioxide (SO_2) of the total pollution, of which two-thirds is provided by exhost emission alone [4]. The different kind of motor vehicles release a number of toxic metals into the vicinity of highways. The heavy metals participate in biological cycle and their surplus or deficit ensues in nuisance of the metabolism and obstructed vegetation [5].

It is very difficult to remove heavy metals incorpaorated in the soil environment. Retention of heavy metals by soil colloids affects the plant uptake and their downward movement in soil profile [6], which reduces the quantity and quality of crop production [7]. Heavy metals have been difficult to deal with not only in air and soils but also in treatment waters [8].

This study considers the agricultural lands along the State Highway 080 which provides the connection of Tuzluca-Igdir-Nakhichevan for total and DTPA-extractable Ni, Fe, Mn, Zn, and Cu. The influence of highway deposits were evaluated perpendicular distance from the highway by taking into consideration the prevailing wind, side effects being in the right and left handside of the highway, soil physical and chemical properties, and the West (080-05) and East (080-06) sections of the State Highway.

2. Material and Method

2.1. Materials

2.1.1. Site Description

The study field was located between the West section of the highway 080-05 from the west entrance (40º04´-43º64´) of the district of Tuzluca in the west of the province Igdir towards the province Igdir (39º92´-44º07´) and the East section of the highway 080-06 to the Dilucu customs (39º65´-44º79´) of the district of Aralik in the east of the province Igdir and was approximately 130 km long. The number of motor vehicles traveling in the field for 2019 is 24259, most of which are diesel motor vehicles [9].

2.1.2. Soil Samples

Total of 72 surface (0-20 cm) soil samples were taken diagonally from 24 points (Figure 1) situating 40°04′-43°68′ and 39°66′-44°80′ alongside the State Highway 080, at 5 km intervals, at a perpendicular distance of 0-10-30 meters from the highway.

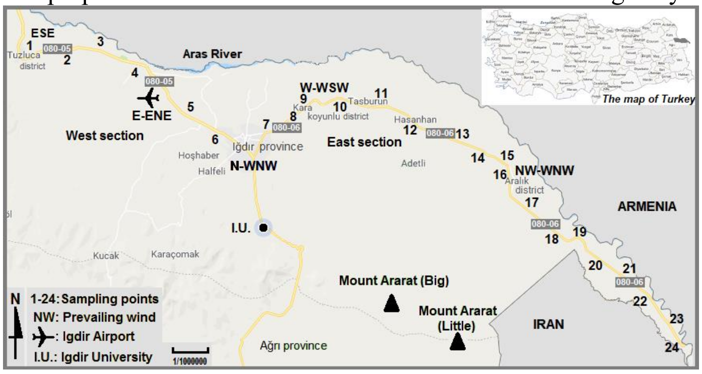

Figure 1. The map of study field

2.1.3. Igdir Province

Igdir province and its surrounding, which have a microclimate feature and a vegetation period between 137-191 days according to the Frost Calendar of Turkey [10], have different properties in the Eastern Anatolia Region in terms of climatic conditions and biological diversity.

Igdir plain situates 850 m above the sea level and is surrounded by mountains with altitudes of 1200-2000 meters. Therefore the plain has a plate-like appearance. This geological structure of Igdir province can sometimes be advantageous (agricultural diversity) and sometimes causes difficulties (drainage problem, salinity, cold air mass subsidence).

As a result of the assessments on the monthly prevailing wind directions of automatic meteorological stations (2014-2017), the annual prevailing wind direction was determined as ESE for Tuzluca district; E-ENE for Igdir airport; N-WNW for Igdir province; W-WSW for Karakoyunlu district; and NW-WNW for Aralik district [11].

2.2. Methods

2.2.1. Physical and Chemical Analyses

The soil samples were air-dried and passed through 2-mm plastic sieve. Then the following parameters were determined: texture (%) by Bouyoucos hydrometer method [12]; soil reactions (pH) in 1:2.5 soil water suspension with a glass electrode [13]; carbonate equivalent by a manometric method using Scheibler

Calcimeter [14]; organic matter by Walkley-Black method [15]; the electrical conductivity ($EC.10^3$) in 1:2.5 soil/water extract using the EC-meter [16].

2.2.2. Total-Available Micronutrient Analyses

After the total amounts of nickel, iron, manganese, zinc and copper micronutrient elements investigated in the sampled soils were extracted with 3 M HCl + 1 M HNO_3 acid, they were read at ICP-OES, determined at ppb level, and converted to mg kg^{-1} [17].

The available concentrations of Fe, Mn, Zn and Cu in the soils were extracted by 0.005 M DTPA + 0.01 M $CaCl_2$ + 0.1 M TEA mixture at pH to 7.3, then the element concentrations were determined by means of atomic absorption spectrophotometer (Agilent FS 240) [18, 19]. In order to evaluate the degree of pollution for the microelements in soils, their composition, lower and upper limits, and threshold values for optimal plant requirements were given in Table 1.

Table 1. Total and DTPA-extractable micronutrient concentrations (mg kg^{-1})

ME	Soil	Average[1]	Upper limit[2]	Critical values in plant[3]
Ni	40[4]	13	75	10.0[6,7]
Fe	-	18000	-	4.50
Mn	3000[5]	330	-	14.0
Zn	300[4]	48	300; 50[6]	0.54
Cu	20[4]	17	140; 15[6]	0.20

ME: Micronutrient elements;
[1][20]; [2][21]; [3][22]; [4][23]; [5][24]; [6][25]; [7][26].

2.2.3. Heavy Metal Pollution Index (PI)

The pollution index (PI) of nickel, iron, manganese, zinc and copper at 72 sampled points for the total and available concentrations was calculated of by using the following equation [27] in order to assess the level of heavy metal pollution [28].

$$PI = Cn/ Bn \quad \text{(I)}$$

Where, C_n is the measured quantity of each heavy metal and B_n is the upper limit values accepted for each heavy metal. Despite there are different values for B_n in the literature the average values in soil [20] given in Table 1 were taken as basis in the pollution indices (PI) for nickel, iron, manganese, zinc and copper. The pollution index (PI) for each heavy metal is classified as low ($PI \leq 1$), medium ($1 < PI \leq 3$) and high pollution ($PI > 3$) [27].

2.2.4. Pollution Load Index (PLI)

Tomlinson et al. [29] suggested an equation so as to calculate pollution load index (PLI) for a specific region. According to this process, the heavy metals analysed can be considered as force multipliers for each other. This index can be explained as a practical way to state contamination level of varied regions. The equation of pollution load index (PLI) is:

$$PLI = \sqrt[n]{(PI1 \text{ x } PI2 \text{ x } PI3 \text{ x} \ldots \text{x } PIn)} \quad \text{(II)}$$

However, it was used for this study as given below:

$$PLI = \sqrt[5]{(PI1 \text{ x } PI2 \text{ x } PI3 \text{ x } PI4 \text{ x } PI5)}$$

Where n is the number of heavy metals (five in this study) and PI is the pollution index. This equation has been used as easy and holistc way of evaluating relative level of heavy metal contamination.

2.2.5. Pollution and Pollution Load Indices Graphics

It was thought to be more useful to draw graphics belonged to pollution and pollution load indices instead of graphics related to deposits of heavy metals. The graphics of pollution and pollution load indices for 0, 10 and 30 meter inward from the highway were drawn and interpreted.

2.2.6. Statistical Analyses

The analysis of variance was performed in order to determine the statistical significance of changes of the total and available nickel, iron, manganese, zinc and copper pollution in the sampled soils based on the perpendicular distance inward from the highway as well as the effect of the prevailing winds on heavy metal deposit and its significance degree. On the other hand, correlation analysis was performed to determine the coherence between the physical and chemical properties of the soils and traffic-induced heavy metal deposition.

3. Results and Discussion

3.1. Physical and Chemical Analysis Results

The texture of the experiental soils were classified as sandy loam (SL), clayey loam (CL), silty clay loam (SCL) and clay (C). The samples 1, 2, 3, 4, 13, 16, 17, 19, 20, 21, 22, 23, and 24 had a sand percentages between 73-78% and therefore light textured; the samples 5, 6, 7, 8, 9, 10, 11, 14, 15, and 18 had a silt percentage between 42-48% and a clay percentage range of 31-39% and thus medium textured; and the rest of 12 soil samples had very clay content between 48-51% and thus heavy textured [30]. The pH values were ranged between 7.4-10.5 and were defined to be neutral and alkaline (slightly alkaline, moderately alkaline, strong alkaline). Carbonate contents ($CaCO_3$) varied between 1.4-15.2% and they classified as low calcareous, calcareous, medium calcareous, and high calcareous. Organic matter contents were between 0.1-1.7% and therefore they were poor in organic matter in very low to low class [31]. Electrical conductivity ($EC.10^3$) values were recorded between 2.3-18.4 mmhos cm^{-1} and varied between very mild saline and extreemly saline [32].

3.2. Micronutrients Analysis Results

Total and available concentrations of heavy metals in 72 soil samples evaluated, by pollution indices (PI) calculated from the averages and background level of 13 for Ni; 18000 for Fe; 330 for Mn; 48 for Zn and 17 Cu [20], and according to critical values in plant 10 for Ni; 4.5 for Fe; 14 for Mn; 0.54 for Zn and 0.2 for Cu [22] were given in Table 2 as maximum, minimum and average values.

Table 2. Total and DTPA-extractable micronutrient concentrations and pollution indices (PI)

ME	D	Total (mg kg^{-1})			PI			DTPA-ext (mg kg^{-1})			PI		
		Max.	Min.	Ave.	Max.	Min.	Ave.	Max.	Min.	Ave.	Max.	Min.	Ave.
Ni	0	224.9	21.9	123.5	17.3	1.7	9.5	1.4	0.1	0.3	0.1	0.0	0.0
	10	181.4	20.6	100.9	13.9	1.6	7.8	1.9	1.4	0.8	0.2	0.1	0.1
	30	152.1	19.9	85.9	11.7	1.5	6.6	2.9	0.1	1.5	0.3	0.0	0.2
Fe	0	33843.8	7347.8	20595.8	1.9	0.4	1.1	5.8	0.4	3.1	1.3	0.1	0.7
	10	28611.4	6653.6	17632.5	1.6	0.4	0.9	5.9	1.0	3.4	1.3	0.2	0.7
	30	26984.2	6065.1	16524.6	1.5	0.3	0.9	4.7	0.8	2.8	1.0	0.2	0.6
Mn	0	892.1	135.3	482.2	2.7	0.4	1.6	37.2	0.8	19.0	2.7	0.1	1.4
	10	807.0	142.8	474.9	2.4	0.4	1.4	27.7	1.9	14.8	2.0	0.1	1.1
	30	741.7	126.0	433.8	2.2	0.4	1.3	28.2	1.4	14.8	2.0	0.1	1.1
Zn	0	125.8	50.6	88.2	2.6	1.1	1.8	1.2	0.0	0.6	2.2	0.0	1.1
	10	115.5	47.0	81.3	2.4	0.9	1.7	1.4	0.0	0.7	2.6	0.0	1.3
	30	99.0	45.1	72.1	2.1	0.9	1.5	1.2	0.0	0.6	2.3	0.0	1.2
Cu	0	55.4	16.2	35.8	3.3	0.9	2.1	4.9	0.2	2.5	24.6	0.9	12.7
	10	70.3	3.9	37.1	4.1	0.2	2.2	4.1	0.4	2.2	20.3	1.7	11.0
	30	51.9	3.4	27.6	3.0	0.2	1.6	6.7	0.6	3.7	33.6	3.2	18.4

ME: Micronutrient elements; D: Distance from highway (m); PI: Pollution indices; 0-10-30: Distances from highway (m).

Total nickel concentrations were higher than the reported soil mean concentration of 13 mg kg^{-1} [20] at all sampling points. Consequently, pollution index values ranged between 1.5-17.3, and were classified as “medium pollution” (1<PI≤3) and” high pollution” (PI>3). Available Ni concentrations were lower than the critical level for plant 10 mg kg^{-1} at all sampling points. In this approach, pollution index values were between 0.0-0.3, and were “low pollution” (PI<1). The reason for such behaviour is the alkaline pH and low organic corbon content of the experimental soils. This nature of the soils limits the solubility and availability of Ni in soils [18].

The reported soil average total Fe concentration (18000 mg kg^{-1}) was lower than those obtained in the experimental soils. Therefore, pollution index values were in the range of 0.3-1.9, and the pollution classes were low (PI≤1) to medium (1<PI≤3) pollution. Despite quite high-water table in the region, DTPA-extractable Fe concentrations were well under the sufficiency level (4.5 mg kg^{-1}) for plant [22] at majority of sampling points. So, PI values were in the safe range between 0.1-1.3. Very high pH, low orgaic matter content and carbonate content are the factors limiting its plant availability along with heavy soil texture [33].

Majority of sampling sites had a total Mn concentration above the reported average concentration of 330 mg kg^{-1} [20]. Thus, PIs were reckoned between 0.4-2.7 in low pollution (PI≤1) and medium pollution (1<PI≤3) classes. DTPA-extractable Mn however were classified as deficient at many sampling sites showing a concentration of <14 mg kg^{-1}. This infact resulted in low pollution class (PI≤1) in majority, to lower extent in medium polluition level (<PI≤3. Despite the total Mn level comparatively higher than the literature average Mn concentration its plant availability highly limited by soil and other environmental conditions which enable to buffer excessive mobility of this element in the soil and reduce plant availability.

Besdies two sampling sites the total Zn concentration of the soil samples were above the reported total average Zn level of 48 mg kg^{-1} [20]. This resulted relatively higher PIs ranging between 0.9-2.6 in low to medium pollution classes. However, their available concentrations were proportionally lower with a PI range of 0.0-2.6 in the same abovementioned pollution classes. There are also a number of factors limiting its plant avalability.

The experimental soils are richer than the reported soil Cu level (17 mg kg^{-1}). Therefore, some soil samples exerted a PI (0.2-4.1) above 3 which may cause some environmental risks. Available copper values were lower than sufficiency threshold of 0.20 mg kg^{-1} at all sampling points except one point. This extreme point showed a PI 33.6 which has environmentally serious risk.

The total PIs for the maximum ones were ordered as Ni>Cu>Mn>Zn>Fe; on the other hand, the available pollution indices for the maximum ones were ordered as Cu>Zn>Mn>Fe>Ni. Due to alkaline soil pH, high carbonate, low organic matter content, total concentration is to show natural occurrence order of the elements, however, added heavy metals other than the structural components of mineral phases can exert larger mobility. Therefore, Cu and Zn may be regarded as the risky elements in terms of antropogenic inclusion such as traffic, agricultural practices and industrial activities.

The pollution load indices (PLI) were generally higher than the pollution indices (PI) of total micronutrients except nickel (Ni) values, and were generally lower than the pollution indices (PI) of available ones. According to these results, PLI had a multiplier effect on total values of micronutrients, however it had not an multiplier effect on available ones because of factor limiting the mobility of these microelements.

3.3. Interpreting of Graphics

The graphics of indices of pollution (PI) and pollution load (PLI) belong to total and available micronutrients concentrations are shown in Figure 2, 3, 4, 5, 6 and 7 for 0, 10 and 30 meter distance from the highway. In graphics of total indices, nickel (Ni) values were omitted by virtue of being higher than the others (Table 2) and causing heterogeneity and/or irregularity in graphics of total ones. Similarly, in graphics of available indices, copper (Cu) values were removed for the same reason (Table 2). Those should be included becasuse there are environmentally problemetaic locations for those elements.

The indices of sampled points for total and available micronutrients were well monitored than their concentrations in graphics. Because values of indices were lower and more homogeneous due to mathematical equations.

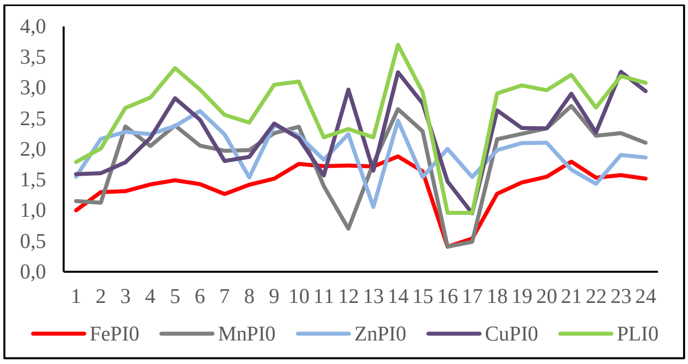

Figure 2. Pollution indices for total micronutrients at 0 m

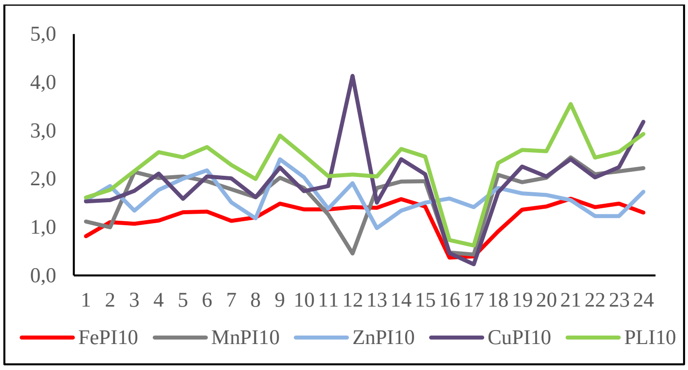

Figure 3. Pollution indices for total micronutrients at 10 m

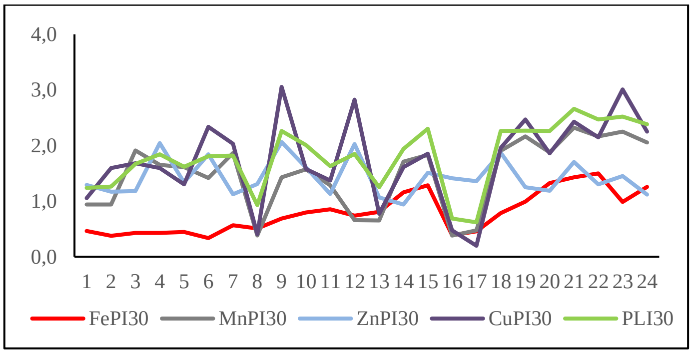

Figure 4. Pollution indices for total micronutrients at 30 m

When the graphics are considered, it is obvious that both 8th, 16th and 17th sampling points are of very low index values. As the reason for this situation, sampling point of 8 took place in intensive vegetation cover and of 16 was in wind erosion region where the soil texture was S as abovementioned, and were S, SL and LS, and the percentages of sand materials were between 54-97 [34]. Vegetation cover was conservator for soil in terms of total micronutrients' particulate deposits and remove some extent of micronutrients from the soils. Sandy soils are really very poor about fine materials, organic matter and other bonding agents, therefore a lot of materials positive and/or negative in terms of soil cannot be held in sandy soils.

On the other hand, values of 12th sampling point were lower for manganese (Mn) than the others. This made us think that there could be a negative relationship between manganese and clay fraction, because this sampling point had high clay content as aforementioned above.

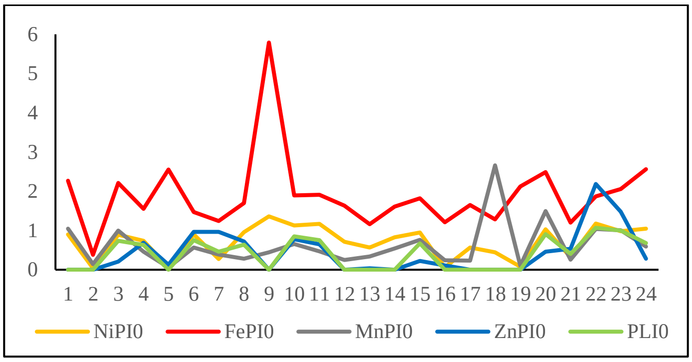

Figure 5. Pollution indices for available micronutrients at 0 m

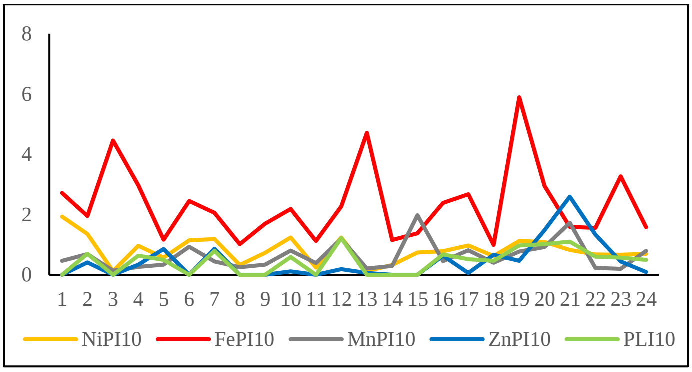

Figure 6. Pollution indices for available micronutrients at 10 m

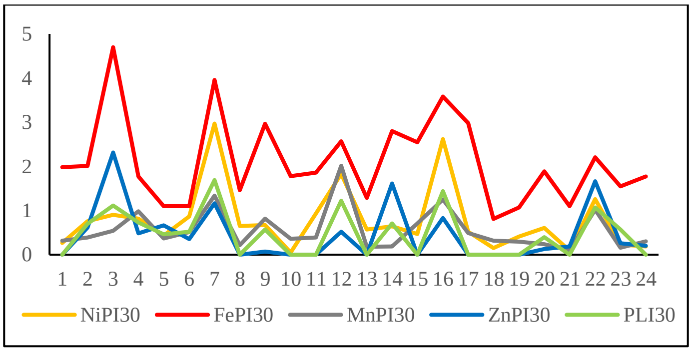

Figure 7. Pollution indices for available micronutrients at 30 m

Available micronutrients indices were generally found higher than the total ones due to having very low tolerable limits (Table 1). Iron (Fe) pollution index values were higher than the others except copper (Cu).

3.4. Statistical Analysis Results

3.4.1. Micronutrients Deposits-Distance Relationships

Analysis of variance were applied to explain the change of the total and available Ni, Fe, Mn, Zn, and Cu concnetrations in the sampled soils inward from the highway. The element concentrations had a tendency to increase towards highway (Table 3) and this suggested that there was traffic induced enrichment of element concentrations.

Table 3. Results of analysis of variance on micronutrients deposits-distances

DV (T)	D	Mean	Standard deviation	SN	F	p	DV (A)	D	Mean	Standard deviation	SN	F	p
	0	149.36	55.5807	24				0	0.7163	0.40163	24		
Ni	10	126.77	44.0927	24	5.285	0.007	Ni	10	0.8192	0.43126	24	0.226	0.798
	30	106.51	35.0405	24				30	0.7879	0.73489	24		
	0	26110.6	6572.39	24				0	1.9008	0.97499	24		
Fe	10	22464.9	6024.94	24	21.446	0.000	Fe	10	2.3400	1.24848	24	0.997	0.374
	30	14249.7	6665.24	24				30	2.1192	0.98677	24		
	0	625.09	217.230	24				0	8.7567	7.89201	24		
Mn	10	560.96	193.734	24	3.014	0.054	Mn	10	8.7600	6.63197	24	0.129	0.880
	30	487.22	204.950	24				30	7.8663	6.50021	24		
	0	94.742	18.5978	24				0	0.2342	0.29852	24		
Zn	10	77.800	16.3223	24	14.590	0.000	Zn	10	0.2379	0.33985	24	0.014	0.986
	30	68.600	15.9836	24				30	0.2492	0.34310	24		
	0	38.272	10.5068	24				0	2.3879	1.34859	24		
Cu	10	33.136	12.8375	24	3.281	0.051	Cu	10	2.4167	1.01607	24	1.008	0.370
	30	29.658	13.2746	24				30	2.8596	1.46360	24		

DV: Dependent variables; D: Distance from highway; SN: Sample number; p: Significant level;
T: Total; A: Available.

The distance from the highway is very significant factor for total traffic-induced pollution load of Fe, Zn, Ni; and about the significance threshold for Mn and Cu with a p 0.054 and 0.051, respectively. These suggested that Fe, Zn, and Ni had higher traffic dependency than the the other elements. The availability of the elements however had larger dependency to traffic due to the added elements on to the indigenous occurrence has a tendency to be more mobile [35].

3.4.2. Relationships Between Micronutrients Concentrations and Prevailing Winds

In this study, the samplings were conducted diagonally, and 12 of the 24 sampling points took place on the north of the highway and the other 12 took place on its south. Figure 1 shows the prevailing wind directions recorded in the study field. Analysis of variance were applied to determine the effect of prevailing winds on micronutrient concentrations. The effect of the prevailing winds was insignificant for all microelements in total and DTPA-extractable ones, except for the available iron concentrations were significant (p=0.037) and the total zinc concentrations were close to significance level (p=0.069) (Table 4).

Table 4. Micronutrients deposits-prevailing winds relationships

DV	Sum of square	DF	Mean of square	SD	F	p
Ni (T)	558.003	1	558.003	48.36317	0.265	0.609
Ni (A)	0.245	1	0.245	0.53790	0.826	0.327
Fe (T)	6875416.882	1	6875416.882	8068.29315	0.164	0.686
Fe (A)	4.993	1	4.993	1.07745	4.520	0.037
Mn (T)	31542.347	1	31542.347	210.40453	0.744	0.391
Mn (A)	50.753	1	50.753	6.94920	1.026	0.315
Zn (T)	953.971	1	953.971	19.99973	3.413	0.069
Zn (A)	0.053	1	0.053	0.32320	0.488	0.487
Cu (T)	104.137	1	104.137	12.60675	0.689	0.409
Cu (A)	4.147	1	4.147	1.29027	2.548	0.114

DV: Dependent variables; DF: Degrees of freedom; SD: Standard deviation;
p: Significant level; T: Total; A: Available.

3.4.3. Relationships Between Micronutrients concentrations and soil properties

The Spearman correlation analysis was performed to delineate the relations between the physical and chemical properties of the soils and micronutrients' concentrations (Table 5).

The correlations were positive and very significant between total nickel and carbonate content and $EC.10^3$; negative significant between total nickel and sand%; positive and very much significant between total iron and carbonate content, positive significant between total iron and $EC.10^3$; positive and very significant between total manganese and carbonate content and $EC.10^3$; negative significant between total zinc and sand percentage and pH; positive and very much significant between total copper and carbonate content; positive and very significant between total copper and $EC.10^3$. The occurrence of carbonate minerals in soils is an indication of the soil wheathering degrees. The ongoing dry climate with 260 mm annual precipitation results in accumulation of carbonates in soils. The presence of carbonates is to further immobilize heavy metals originating from either wheathering processes or pollution [18].

There was positive correlation between the available fractions of heavy metals and organic matter exept for Zn and Cu. Ni and Fe were inversely related to $EC.10^3$, whereas Mn and Cu positively correlated to $EC.10^3$. The $EC.10^3$ in the experimental soils is to increase with the salinity and alkalinity. The alkaline condition immobilize Fe and Ni. High pH on the other hand is to solubilize organic matter which chelate Zn and Cu stronger [18]. This nature can mobilize to some extent these two heavy metals.

Table 5. Regression analysis for micronutrients concentrations-soil properties

HM (T)	Soil properties					HM (A)	Soil properties				
	Sand (%)	pH (1:2.5)	$CaCO_3$ (%)	OM (%)	$EC.10^3$ (dS m^{-1})		Sand (%)	pH (1:2.5)	$CaCO_3$ (%)	OM (%)	$EC.10^3$ (dS m^{-1})
Ni	-0.198*	0.080	0.676***	0.062	0.534***	Ni	-0.054	-0.192	-0.149	0.081	-0.041
Fe	-0.085	0.160	0.490***	0.100	0.244*	Fe	0.183	0.056	-0.150	0.016	-0.026
Mn	-0.028	0.101	0.599***	-0.107	0.637***	Mn	-0.089	-0.184	0.100	0.044	0.021
Zn	-0.259*	-0.200*	-0.040	0.107	0.016	Zn	0.167	0.049	0.078	-0.289**	0.336**
Cu	-0.188	0.046	0.519***	0.116	0.297**	Cu	-0.028	-0.160	-0.144	0.111	0.001

HM: Heavy metal; T: Total; A: Available; OM: Organic matter; *$p<0.05$; **$p<0.01$; ***$p<0.001$

Heavy metal pollution, which is released as an aerosol into the atmosphere as a result of human activities and deposits in the soil, is a serious problem worldwide. The aerosols are dispersed in the atmosphere and transported a few kilometers from their outlet and enter the soil as dry or wet-depositions [36, 37]. Heavy metals in the soil are considered as substances that leave a strong trace on the monitoring of human activities such as industrial waste, exhaust gas emissions and aerosols. Heavy metals are the most dangerous one among anthropogenic pollutants due to their toxic effects and resistance [38, 39].

Soil, which has an important place in terrestrial ecosystem, cannot clean itself once it has been polluted. Micro elements in the soil structure create pollution only when they exceed a certain limit value [40]. There is a risk of toxic effects when total and particularly available microelement concentrations are above the critical values for plants and the concept of heavy metal makes sense at this point. Natural pollution originated from the parent material [41] faces as an artificial pollution increasing as a result of anthropogenic effects.

For Ni, one of micronutrient elements, the total value in the soils is reported to be 10-100 mg kg^{-1} [42], 100 mg kg^{-1} is the upper limit [43, 44] and 45 mg kg^{-1} as average of earth's crust [45], they were measured to be higher than 100 mg kg^{-1} at 55 sampling points of the study field and showed high contamination. All of the available nickel values measured in the study were lower than 10 mg kg^{-1} critical value [22] and showed a lesser extent of environmental risk.

There is no upper limit value determined for total iron, which is the 3rd most common element in the lithosphere with 43200 mg kg^{-1}, and it was measured to be higher than the average value of 16000 [20] at 51 sampling points of the studied field and showed a moderate contamination. Available iron values measured in this study were higher than the critical value of 4.5 mg kg^{-1} [22] at 4 sampling points and showed moderate contamination.

Total manganese was reported as 716 mg kg^{-1} in lithosphere and 330 mg kg^{-1} in soil [20] and up to 3000 mg kg^{-1} in soil [24] and measured to be higher than the average value of 330 mg kg^{-1} [20] at 58 sampling points of the study field, showed moderate contamination. The available manganese values measured in this study were higher than the critical value of 14.0 mg kg^{-1} [22] at 13 sampling points and showed moderate contamination.

Total zinc was reported to be 65 mg kg^{-1} in the earth's crust and averagely 48 mg kg^{-1} in the soil [20] and maximum of 300 mg kg^{-1} [23], and was measured to be higher than 50 mg kg^{-1} [25] except for 1 sampling point of the road sites, and therefore the soils showed moderate contamination. The available zinc concentrations measured in the study were higher than the critical value of 0.54 mg kg^{-1} [22] at 9 sampling points and showed the moderate contamination.

Total copper was reported to be 25 mg kg^{-1} in the earth's crust and averagely 17 mg kg^{-1} in the soil [22] and was measured to be higher than 15 mg kg^{-1} [25] except for 6 sampling points of the study field, and showed the moderate and high contamination. The available copper values measured in the study were higher than the critical value of 0.20 mg kg^{-1} [22] except for 1 sampling point and showed moderate and high contamination.

4. Conclusions and Recommendations

Highway 080 will be able to a part of Silk Road (historical) near future. This concern about heavy metal pollution will be then dramatic hazard if some precautions are taken by our government such as increasing electrical vehicles, railway transportation, tax increase for diesel engines etc.

Total and available micro nutrients in the soil should be monitored regularly. Total deposits can be transformed into available forms and may have a toxic effect if they exceed the limit values.

It is thought that the positive and very important correlations between the number of carbonates and salt in the soil and the total/DTPA-extractable micronutrients. These relations also indicate possible reclamation of the polluted soils.

It should be state that Ni and Cu had potential to reach environmentally risky levels in relatively shorter time.

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