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The Determination of Lead and Cadmium Concentration in the Agricultural Soils Alongside Highway 080 of Igdir Province

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ABSTRACT

Gases emitted from both industrial estates and automobile exhausts in agricultural areas cause heavy metal pollution and these metals accumulate in the soil and plants. In this study, 72 soil samples were taken at 5 km intervals from 24 points along the Tuzluca-Iğdır-Nakhchivan route, through which the 080 State Road passes, at 0-10-30 meters perpendicularly inwards from the road and at a depth of 0-20 cm. Total lead (Pb) and cadmium (Cd) accumulations were determined in the samples. The significant decrease in lead and Cd concentrations away from the road indicates that heavy metal deposits have being caused by traffic. The effect of prevailing winds on total Pb and Cd deposition in north and south of the State Highway 080 was statistically insignificant. As the relationships between heavy metal concentrations and soil physical properties were considered, significant negative correlations were found between total Cd concentrations and sand and organic matter contents. Heavy metal pollution index (PI) values were found to be slightly and moderately polluted for Pb and close to highly polluted for Cd according to treshold values. The pollution load index (PLI) values were calculated as a function of the pollution index and according to the PLI results, it was evaluated that Pb and Cd triggered each other in terms of increasing toxic effects. It has been concluded that, with the re-establishment of the Silk Road, the traffic-related pollution will increase in the region.

Keywords: Lead **(**Pb), Cadmium (Cd), Pollution index (PI), Pollution load index (PLI), Igdır Highway 080.

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INTRODUCTION

Environmental pollution especially in soils has serious impacts human and other living organisms' health through the plants, ground water and the atmosphere (Al-Massaedh and Al-Momani, 2020). Human can be exposed heavy metals especially from highway traffic emissions are of very serious damages, and therefore it has been a popular subject for the researchers. Heavy metals can be indigenously or anthropogenically accumulated in soils situating in the vicinity of roadsides (Surucu et al., 2018). Despite soil and water reservoirs are the ultimate accumulation environment; human body, drinking water, plant and foods are the unwanted accumulation media of heavy metals (Wuana and Okieimen, 2011).

Toxic heavy metals mainly lead (Pb), cadmium (Cd) and others such as mercury (Hg), chromium (Cr), tin (Sn), nickel (Ni) and arsenic (As) are perilous pollutants. They are well known to have a negative effect on human health (Al-Massaedh et al., 2018), and are characterized by persistency in the environment and very long biological half-life (Massadeh and Al-Massaedh, 2018). Accumulation of Pb in farmland soils is based on industrial and/or agricultural pollution origin (Keçeci et al., 2020). The principal source of cadmium (Cd) are brake linings and tires (Zechmeister et al., 2005), and redistributed from road asphalt materials (Kluge and Wessolek, 2012) and lubricants (Zechmeister et al., 2005).

As a result of anthropogenic effects, Pb which is emitted to the atmosphere as metal or variety of compounds is one of the most environmentally risky heavy metals (Altınbaş et al., 2008). Despite the bacground concentration is very low for Cd, the weak adsorption nature of it can ease plant uptake at harmfull levels in polluted soils The Cd in the fungicides is transmitted to the soil by spraying. The Cd concentration of crops growing in the vicinity of high ways with heavy traffic could have health risks due to enrichment of Cd associated with vehicle tires and exhaust gas (Kacar, 2009).

State highway baseline data is necessary to define suburbanization and urban spread effects in a developing country. One of them is the amount of heavy metal levels and its migration on the road (Ojuri et al., 2016). Motor vehicle traffic is an anthropogenic action and a primary origin of pollutants emitted to surroundings (Duong and Lee, 2011). The global high vehicular traffic density has led to accelerated emission rates, causing contamination of roadside soils (Modrzewska and Wyszkowski, 2014). Heavy metals emitted from motor vehicles remain suspended in air and deposited along the roadside soil (Yu et al., 2014) with changing distance due to prevailing wind characteristics.

Roadside agricultural soils are substantial storage for the direct pollution from vehicle sources, which could easily come in contact with pedestrians and people residing within the surrounding of the roads either as suspended dust or direct inhalation. The concentration of heavy metals in soils can be a secondary origin of water pollution in a cycled ecological situation (Cheung et al. 2003). In this study, it was investigated that total lead (Pb) and cadmium (Cd) deposition on soil samples taken diagonally from both of the West (080-05) and East (080-06) sections in Tuzluca-Igdir-Aralik-Dilucu region of State Highway 080 as well as changes in heavy metal accumulation inward from the highway based on the distance, the effect of prevailing winds on heavy metal deposition in the north and south of the highway, and the relationships between heavy metal concentrations and some physical and chemical properties of the soils.

MATERIALS AND METHODS

The study field was located between the West section of the highway 080-05 from (40º04´-43º64´) the district of Tuzluca till Igdır city center (39º92´-44º07´) and the East section of the highway 080-06 ends up at the Dilucu custom (39º65´-44º79´) in Aralik district. Total distance is about 130 km long. The number of motor vehicles traveling in the field for 2019 is 24259, most of which are trucks with diesel engine (Anonymous, 2021a).

Igdir province and its surrounding, which have a microclimate and a vegetation period between 137-191 days according to the Frost Calendar of Turkey (Şimşek et al., 2017), therefore this ecosystem has distinctly different properties than the the Eastern Anatolia Region in terms of climatic conditions and plant variety. Igdir plain with an average height of 850 m above the sea level is surrounded by altitudes of 1200-2000 meters. The two-thirds of Ararat, the highest mountain of Turkey (5137 m) is located within borders of Igdir province. This topographic nature 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 Aralık district (Karaoğlu et al., 2018).

The soil samples were taken diagonally from 24 points, on State Highway 080, at 5-km intervals, at a perpendicular distance of 0-10-30 meters from the highway, and at 0-20 cm soil depth. Figure 1 shows the map of the sampling nodes.

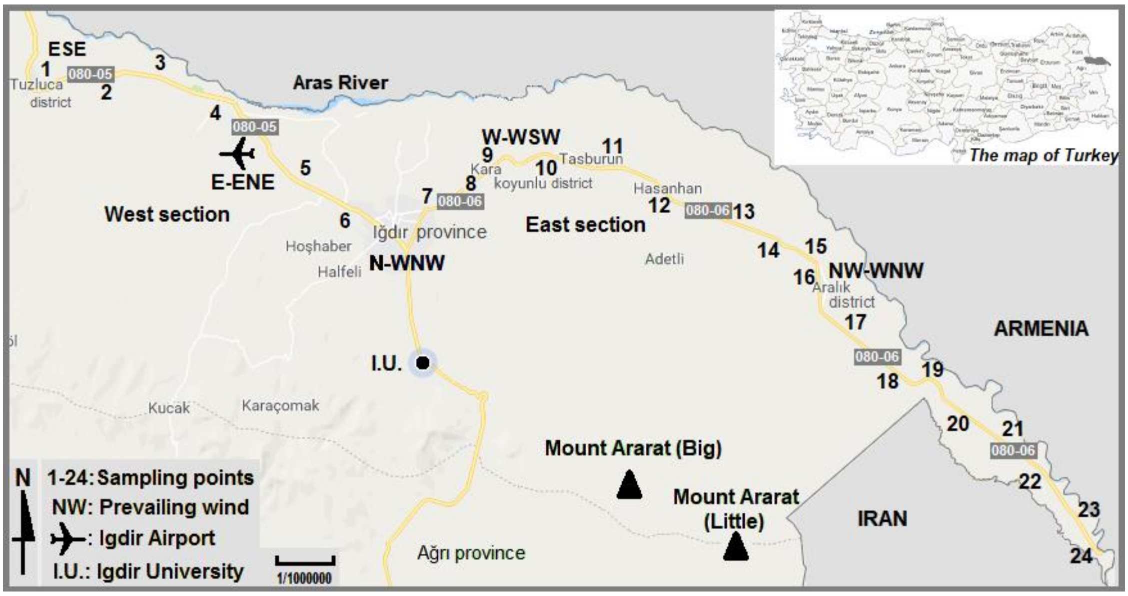

Figure 1. The map of study field

The soil samples were air-dried and passed through 2-mm plastic sieve. Then the following parameters were determined: texture (%) by Bouyoucos hydrometer method (1951); soil reactions (pH) in 1:2.5 soil water suspension with a glass electrode (Richards, 1954);

carbonate equivalent by a manometric method using Scheibler Calcimeter (Allison and Moodie, 1965); organic matter by Walkley-Black method (Walkley, 1947); the electrical conductivity ($EC.10^3$) in 1:2.5 soil/water extract using the EC-meter (Dellavalle, 1992).

In order to determine the total amounts of Pb and Cd in the samples, they were digested with 3 M HCl + 1 M HNO_3 acids (Orbey et al., 2012). The concentrations of Pb and Cd in the extract were determined by means of an ICP-OES (Thermo Scientific iCAP6000).

Table 1 shows the concentrations of Pb and Cd for the earth's crust, soil, average and upper limit values according to different references and researchers which were used in the evaluation of the pollution indices.

Table 1. Values for Pb and Cd in different environments (mg kg^{-1})

Heavy metal	Crust	Soil	Mean	Upper limit
Lead	14.8[1]	1-200[2] 150[3] 250[4]	15[2]-16[1]	300[6] 50[7]
Cadmium	0.1[1]	0.06[3] 0.2[1] 0.1-1.0[5]	0.2[1] <0.5[5]	3[4,6] 0.4[7]

[1]Sposito, 2008; [2]Kacar, 2009; [3]He et al., 2005; [4]Rowell, 1994; [5]Lodenius, 1989; [6]Anonymous, 2005 (pH>6), (The Ministry of Environment and Urbanization); [7]Anonymous, 2021b (European Commission Directorate General for Environment).

The pollution index (PI) was determined with Pb and Cd concnetrations of 72 sampling nodes by using the following equation (Wei et al., 2009) in order to assess the level of heavy metal pollution (Siti Norbaya et al., 2014).

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

Where, C_n is the measured concentration of each heavy metal and B_n is the average concentrations accepted for each heavy metal. There are different values for B_n. In this study, average values in soil (Sposito, 2008) in Table 1 were taken as basis in the pollution indices (PI) for Pb and Cd. The pollution index (PI) for each heavy metal is classified as low ($PI \leq 1$), medium ($1 < PI \leq 3$) and high pollution ($PI > 3$) (Wei et al., 2009).

The method proposed by Tomlinson et al. (1980) was used to calculated pollution load index (PLI) for a specific region. In this method, the heavy metals studied can be considered as force multipliers for each other. This index can be explained as a practical way to relate contamination level of varied regions. The equation of pollution load index (PLI) is:

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

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

$$PLI = \sqrt[2]{(PI1 \text{ x } PI2)}$$

Where n is the number of heavy metals (two in this study) and PI is the pollution index. This equation has been used as easy and relative method to analyse extent of heavy metal contamination.

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

In order to determine the statistical significance of total Pb and Cd concentrations changing with perpendicular distance in the sampled soils, as well as the effect and importance of the prevailing winds on the heavy metal concentrations, the analysis of variance was applied. Pearson parametric regression analysis was performed to delineate the coherence between the physical and chemical properties of the soils and heavy metal concentrations.

RESULTS AND DISCUSSION

The soil samples 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 high sand percentages (73-78%) and light textures; the samples 5, 6, 7, 8, 9, 10, 11, 14, 15, and 18 had high silt (42-48%) and clay (31-39%) percentages and medium textured and the sample 12 had very high clay (48-51%) percentages and heavy textured (Demiralay, 1993). The pH were ranged between 7.4-10.5 and the pH classes were neutral to alkaline (slightly alkaline, moderately alkaline, strong alkaline). Lime ($CaCO_3$ equivalent) contents varied between 1.4-15.2% and they showed a distribution among low calcareous, calcareous, medium calcareous and highly calcareous classes. Organic matter (OM%) contents were in OM poor class with 0.1-1.7% range (Aydın and Sezen, 1995). Electrical conductivity (EC) values (2.3-18.4 dS cm^{-1}) ranged between mildly saline and extreemly saline (Aydemir, 1992).

Heavy Metal Concentrations

Total Pb and Cd concentrations in 72 soil samples generaly had an average concentration around the reference level of 16 mg kg^{-1} for Pb and 0.2 mg kg^{-1} for Cd (Sposito, 2008). The calculated pollution indices and pollution load indices (PLI) (Tomlinson et al., 1980) were given in Table 2.

The highest heavy metal concentrations were measured in the soil samples just on the vicinity of the highway. Lead and cadmium concentrations decreased inwards from the highway and this result strengthened the idea that pollution was caused by traffic. In general, the pollution indices (PI) of both heavy metals calculated by the reference mean concentrations in the soil (Sposito, 2008) were classified as low (PI<1) to medium pollution ($1<PI\leq3$). Majority of soil samples showed a PI below 1 indication little environmental risks but the sampling sites 3 and 12 had a PI 1.30 and 1.24 with moderate environmental risks. However, Cd posed higher environmental treat with larger number of sampling nodes having a PI over 1 in moderate pollution class. The sampling node 3 was the hot point for Cd with a PI 2.7.

The pollution load indices (PLI) were also in a very similar manner to PI that the higher PLI were recorded wit the closer distance to the road. The samples 1, 2, 3, 12, 14, 17, 23 and 24 showed relatively higher PLI at just road side. At some hot points the deposition were higher due possibly to plate like topograpy. In some of these sampling points, Pb concentrations were high and some of their Cd concentrations were high, and consequently pollution indices and pollution load indices were higher. According to these results, it can be said that weaker coherence of Pb and Cd occurrence at any sampling node can induce smaller PI or PLI values which can be indication of the different pollution source.

Table 2. Pb and Cd concentrations, pollution and pollution load indices

SN	Pb (mg kg^{-1})			Pb			Cd (mg kg^{-1})			Cd			PLI_0	PLI_{10}	PLI_{30}
	0	10	30	PI_0	PI_{10}	PI_{30}	0	10	30	PI_0	PI_{10}	PI_{30}			
1	13.27	7.86	3.62	0.83	0.49	0.23	0.26	0.23	0.19	1.3	1.15	0.95	1.04	0.75	0.46
2	11.06	8.55	5.60	0.69	0.53	0.35	0.42	0.13	0.15	2.1	0.65	0.75	1.20	0.59	0.51
3	20.82	14.12	9.88	1.30	0.88	0.62	0.54	0.25	0.19	2.7	1.25	0.95	1.87	1.05	0.77
4	10.58	10.03	13.63	0.66	0.63	0.85	0.24	0.24	0.19	1.2	1.2	0.95	0.89	0.87	0.90
5	8.91	6.40	8.89	0.56	0.40	0.56	0.20	0.08	0.15	1	0.4	0.75	0.75	0.40	0.65
6	10.99	7.95	7.93	0.69	0.50	0.50	0.22	0.19	0.18	1.1	0.95	0.9	0.87	0.69	0.67
7	5.51	7.22	6.56	0.34	0.45	0.41	0.20	0.16	0.12	1	0.8	0.6	0.59	0.60	0.50
8	5.97	4.71	2.00	0.37	0.29	0.13	0.11	0.10	0.03	0.55	0.5	0.15	0.45	0.38	0.14
9	8.55	8.05	8.25	0.53	0.50	0.52	0.21	0.20	0.20	1.05	1	1	0.75	0.71	0.72
10	8.44	5.70	7.57	0.53	0.36	0.47	0.21	0.13	0.18	1.05	0.65	0.9	0.74	0.48	0.65
11	8.74	6.96	5.92	0.55	0.44	0.37	0.18	0.13	0.10	0.9	0.65	0.5	0.70	0.53	0.43
12	19.76	11.79	13.5	1.24	0.74	0.84	0.16	0.14	0.11	0.8	0.7	0.55	0.99	0.72	0.68
13	8.73	4.30	4.63	0.55	0.27	0.29	0.16	0.14	0.09	0.8	0.7	0.45	0.66	0.43	0.36
14	12.48	7.62	5.58	0.78	0.48	0.35	0.26	0.17	0.18	1.3	0.85	0.9	1.01	0.64	0.56
15	8.53	7.60	4.95	0.53	0.48	0.31	0.24	0.17	0.18	1.2	0.85	0.9	0.80	0.64	0.53
16	5.80	4.94	4.59	0.36	0.31	0.29	0.05	0.05	0.04	0.25	0.25	0.2	0.30	0.28	0.24
17	12.44	7.06	4.20	0.78	0.44	0.26	0.32	0.22	0.09	1.6	1.1	0.45	1.12	0.70	0.34
18	8.40	6.18	6.86	0.53	0.39	0.43	0.26	0.23	0.13	1.3	1.15	0.65	0.83	0.67	0.53
19	7.87	7.96	6.18	0.49	0.50	0.39	0.17	0.18	0.13	0.85	0.9	0.65	0.65	0.67	0.50
20	10.85	6.82	6.05	0.68	0.43	0.38	0.25	0.17	0.12	1.25	0.85	0.6	0.92	0.60	0.48
21	7.46	7.36	8.74	0.47	0.46	0.55	0.26	0.23	0.20	1.3	1.15	1	0.78	0.73	0.74
22	6.65	6.57	6.74	0.42	0.41	0.42	0.25	0.14	0.14	1.25	0.7	0.7	0.72	0.54	0.54
23	15.11	9.27	9.30	0.94	0.58	0.58	0.26	0.19	0.13	1.3	0.95	0.65	1.11	0.74	0.61
24	12.16	10.57	9.04	0.76	0.66	0.57	0.26	0.18	0.15	1.3	0.9	0.75	0.99	0.77	0.65

SN: Sample number; 0-10-30: Distances from highway (m); PI: Pollution indices; PLI: Pollution load indices.

The graphics of indices of pollution (PI) and pollution load (PLI) are shown in Figure 2, 3 and 4 for 0, 10 and 30 meter distance from the highway, respectively. Generally, the pollution index (PI) value of Cd were higher than the Pb ones therefore Cd showed larger environmental risk than Pb. The relative mobilitiy of Cd is higher than the one for Pb, therefore soils around the highway is to receive some Cd from other pollution sources most probably wheathered Cd can be transferred towards road side due to topography, as well as traffic induced pollution. PLI values were mostly found lower than PI of Cd and higher than PI of Pb except several sampling points. In other words, PLI values exemplified both PI values of Pb and Cd. It was commented that as a result of multiplier effect of PLI, PLI values can be used for each sampling point in lieu of PI value of Pb and Cd.

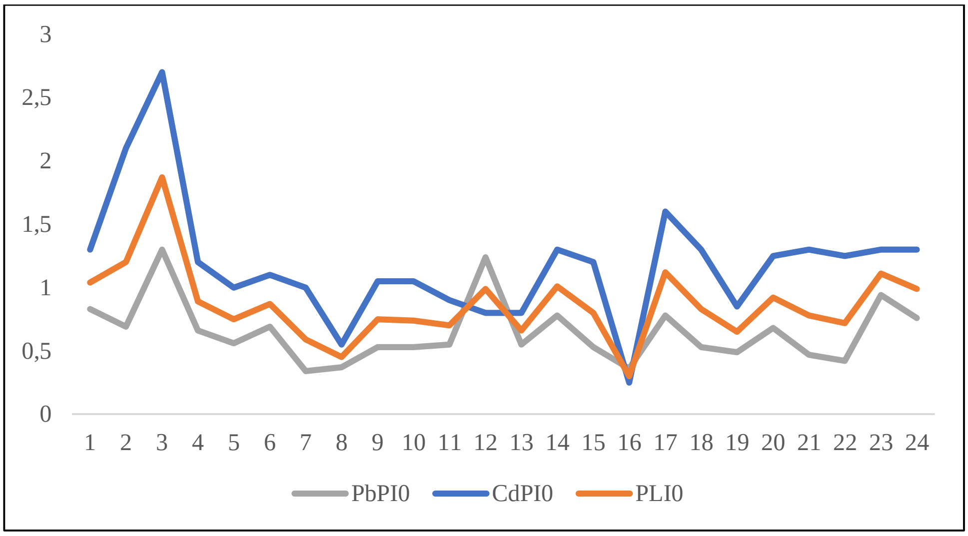

Figure 2. Pollution indices alongside the road at 0 meter distance

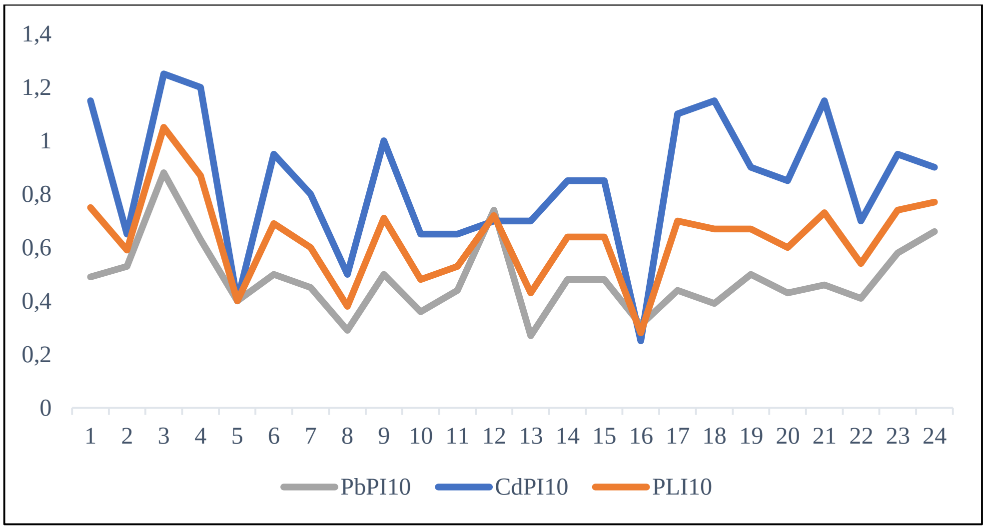

Figure 3. Pollution indices graphic for 10 meter distance from highway

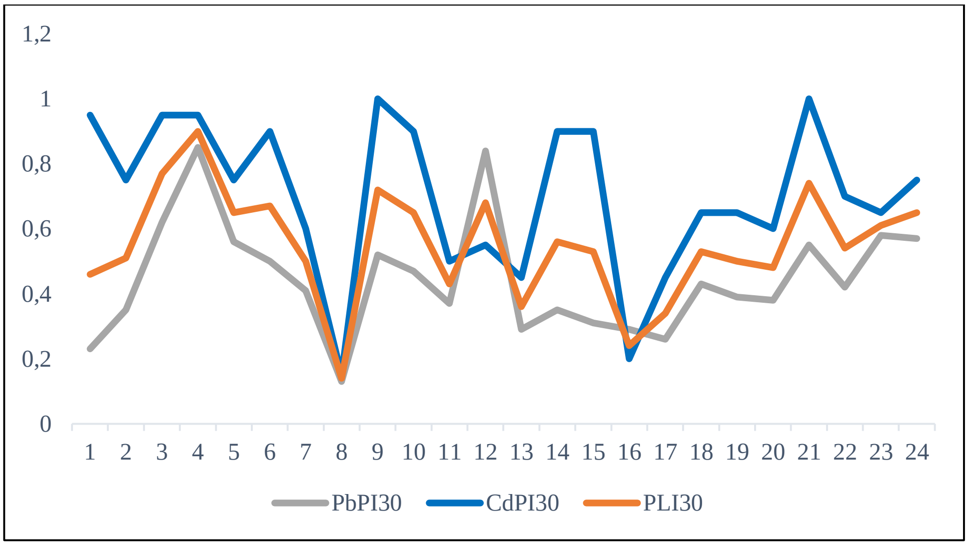

Figure 4. Pollution indices graphic for 30 meter distance from highway

The indices of sampled points for Pb and Cd were well monitored than their concentrations in graphics. Because the pollution indices show relative degree of pollution at any point by considering either single element or both elements.

When the graphics are considered, it is easily become aware of that both 8th and 16th sampling points are of very low index values. The reason for this fact could be intensive vegetation cover at 8th sampling point and high frequency of strong wind and light soil texture at 16th sampling point. Ligt soil texture such as S, SL and LS with 54-97% sand content (Karaoğlu et al., 2017) reduces the heavy metal adsorption and/or strong wind blow away the exhost gases and limit deposition of the metals on the soils nearby the road.

Conversely, 3, 12, 14 and 17th sampling points are of high index values than the others. Although 3 and 17th sampling points had sandy texture, they had high heavy metal deposits owing to very heavy traffic according to General Directorate of Highways' Traffic Volume Maps (Anonymous, 2021a). 12 and 14th sampling points had clayey and silty texture, respectively. That's way retention of material especially heavy metal was high level in them due to their textural features.

Table 3 shows the results of the analysis of variance made to explain statistically the change of the total Pb and Cd deposits from highway to inward and their significance in the soils taken from the sampling points, and the F test applied since the variances were homogeneous. Total Pb and Cd concentrations continued to decrease inwardly and showed that heavy metal deposition from the traffic would be a significant issue. The decrease in heavy metal concentrations from the highway to inward are very significant for the Pb and very much significant for Cd. Although both of them are related to traffic, the significance level are different between Pb and Cd owing to having high concentration and tolerance values of Pb than those of Cd. According to DUNCAN test results, the concentrations of Pb and Cd at 0 meters to the highway are significantly higher than at 10 and 30 meters.

Table 3. Results of analysis of variance on heavy metal deposits-distance

DV	D	ANOVA					DUNCAN	
							0.05	
		Mean	SD	SN	F	SL	1	2
Pb (T)	0	10.3783	3.93164	24				10.3783b
	10	7.7329	2.23158	24	7.731	0.001	7.7329a	
	30	7.0921	2.79745	24			7.0921a	
	SL						0.472	1.000
Cd (T)	0	0.23500	0.095781	24				0.2371b
	10	0.17125	0.056975	24	9.039	0.000	0.1688a	
	30	0.14792	0.061360	24			0.1404	
	SL						0.157	1.000

DV: Dependent variables; D: Depth; SD: Standard deviation; SN: Sample number; SL: Significant level; T: Total.

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. The effect of prevailing wind did not significantly change the heavy metal concnetrations in the soils (Table 4).

Table 4. The effect of prevailing wind on the heavy metal concentration in soil

Dependent variables	Sum of square	Degree of freedom	Average of square	Standard deviation	F	Significance level
Pb (T)	0.083	1	0.083	3.34775	0.009	0.926
Cd (T)	0.005	1	0.005	0.08134	0.926	0.339

T: Total.

Pearson correaltion analysis was performed to delineate the relationships between heavy metal concentrations and soil physico-chemical properties (Table 5). It was determined that there were significant correlations between Cd and sand content and negative very significant correlations between Cd and organic matter. This means that as the amount of sand in the soil increases, the Cd concentration will increase, on the contrary, as the amount of organic matter increases, the Cd concentration will decrease. The reason for this is that Cd is the element with the highest water solubility among heavy metals that is way, it spreads rapidly in nature (Seven et al., 2018). Since the sand material does not have an electrically specific surface, Cd is thought to be more active in sandy soils. The correlations between Pb and soil properties were insignificant. Because, highly soluble lead compounds turn into insoluble lead compounds in the soil and the soluble lead concentration in the soil is around 0.05-5 ppm (Özkan, 2009).

Table 5. Correlation coefficient between soil properties and heavy metal concentrations

Heavy metals	Soil properties				
	Sand (%)	pH (1:2,5)	Lime (%)	OM (%)	EC (dS m^{-1})
Pb (T)	0.110	-0.061	-0.060	-0.143	-0.026
Cd (T)	0.216*	-0.112	0.116	-0.301**	0.106

T: Total; *p<0.05; **p<0.01.

CONCLUSION

Environmental pollution and environmental protection awareness were discussed frequently in the global and scientific sense in the 1960s and emphasized the need to resolve environmental problems as soon as possible in order to sustain ecosystem and economic life (Hacıoğlu Deniz, 2009). The environment that is most affected by environmental pollution and cannot be cleaned is the soil. The negative effects of the industrialization period on soils have been in the form of excessive heavy metal accumulations.

Since Pb and Cd, which are selected as research subjects, are very common in the daily life of people, they have negative effects on all living things and especially on humans as heavy metals. As a result of anthropogenic effects, the lead being the first heavy metal to damage the ecosphere and being released into the atmosphere as a metal or compound is the most important heavy metal that causes environmental pollution as it has the toxic effect (Çepel, 1997; Kahvecioğlu et al., 2003) and Pb compounds have the ability to deposit in soils and to stay in soil for a long time (Alloway, 2013). Since Cd in contaminated soils can be absorbed in large quantities by food plants depending on its concentration in the soil, it is the greatest concern in terms of its entry into the food chain (Jarup, 2003).

The soils of the study field were classified as sandy loam (SL), clayey loam (CL), silty clay loam (SCL) and clay (C) texture; the pH values were ranged between neutral and alkaline; lime ($CaCO_3$ equivalent) contents showed a distribution among low calcareous, calcareous, medium calcareous and highly calcareous classes; organic matter (OM%) contents were in poor class; electrical conductivity (EC) values ranged between mildly saline and extreemly saline.

In a great majority of the sampled soils, clay% and organic matter% were very low and poor in soil colloids and therefore by elements. This is desirable for heavy metals and undesirable for nutrients. High lime% and consequently high pH values of the study soils will be able to cause uselessness of nutrients (zinc, iron, manganese etc.) and chlorosis disease, and high electrical conductivity values will be able to lead to physiological drought.

It was determined that total Pb deposits were lower than limit values and pollution indices (PI) were low and moderate contaminated, which is a positive situation for soils of study field. The most important reason for this is that most of the vehicles in traffic are diesel engine vehicles. Total Cd deposits were mostly above the limit values and the pollution indices were moderate and close to high contaminated, indicating that Cd pollution is higher. However, each measurement value for Pb and Cd is a potential toxic effect. Statistically, the fact that the decrease of Pb and Cd values inward from the highway was very significant and the higher Pb and Cd values were measured in the samples taken from the side of the highway shows that current heavy metal deposits are caused by traffic. The high pollution load index (PLI) values at some sampling points suggested that Pb and Cd accumulations triggered each other.

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.

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