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Assessment of Heavy Metals Contamination and Ecological Risk of Roadside Agricultural Soil, Used for Sunflower (*Helianthus annuus L.*) Cultivation

Dafinka Pangarova, Ekaterina Serafimova*

University of Chemical Technology and Metallurgy, Sofia, Bulgaria

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ABSTRACT

The present study is an attempt for comprehensive assessment of the pollution intensity and corresponding ecological risk of heavy metals including Cd, Co, Cr, Cu, Fe, Ni, Pb, Zn and Sb for agricultural soil, located alongside the national road II-81 in Bulgaria, used for the sunflower (Helianthus annuus L.) cultivation, by various factors and indices calculation.

In total, 18 surface soil samples (0 - 20 cm depth) were collected at distances 11 m, 36 m and 61 m from the road edge at two sunflower plants' growth stages: vegetative (V-3) and maturity (R9).

The total concentrations of heavy metals of soil samples, collected at two different sunflower growth stages were used for assessment of the potential ecological risk. Based on the results for the potential ecological risk index, pollution load index, enrichment factor, contamination factor and the degree of contamination, calculated from the average total concentrations, considerable pollution of the tested agricultural soil was observed, mainly with Sb.

The values of enrichment factor show that with the exception of Fe, Cr and Ni the rest of the tested heavy metals are mostly from anthropogenic sources. There are strong, not statistically significant correlations between the enrichment factors, ecological risk index, pollution load index and contamination degree and the distance from the road edge and strong correlations between enrichment factors of heavy metals related to the road traffic emissions and the distance from the road edge. The values of the factors and indices above mentioned are lower at the growth stage R9 than at the growth stage V-3 that shows the sunflower capacity of accumulation of the tested heavy metals.

Keywords: heavy metals, agricultural soil contamination, sunflower, ecological risk, roadside, road traffic, pollution load index, contamination degree.

INTRODUCTION

It is well known fact that worldwide the continuous industrialization and human social, economic and agricultural activities have been accompanied by the increased pollution of the soil since a wide range of contaminants from these areas affected soil quality [1 - 3].

Nowadays, heavy metals pollution is the biggest threat for soil quality, negatively affecting the human health. Road traffic is one of the primary sources of trace metal pollution in roadside agricultural soils, that has negative

**Correspondence to: Ekaterina Serafimova, University of Chemical Technology and Metallurgy, 8 Kliment Ohridski blvd., 1797 Sofia, Bulgaria, E-mail: ekaterina_sr@uctm.edu.*

impact on human health [2, 4 - 6].

Heavy metal emissions from road traffic have been investigated in detail in a wide range of studies [7 - 14] and a well-known example is the lead additives in fossil fuels for internal combustion engines. Since the banning of petrol containing tetraethyl lead, one of the problems related to vehicle emissions has been solved to some extent, but with the accumulation of scientific research in the field of road traffic emissions, more heavy metals are covered, namely from the platinum group [15 - 17] and antimony [18 - 21].

The aim of this study is to assess comprehensively the pollution intensity and corresponding ecological risk of heavy metals including Cd, Co, Cr, Cu, Fe, Ni, Pb, Zn and Sb for agricultural soil, located alongside the national road II-81in Bulgaria, used for the sunflower (*Helianthus annuus L.*) cultivation, by various factors and indices calculation.

The selection of the road II-81 for present investigation is based on the fact that it is representative of second-class roads in Bulgaria in terms of road traffic load and the soils near the carriageway of second-class roads are used very often for cereals and technical crops, including sunflower, cultivation.

The soil used for sunflower cultivation has been selected because in the scientific literature there are published data from laboratory and field studies on the bioaccumulation of heavy metals by sunflower plant. According to these data it could be concluded that sunflower has a marked potential for accumulation of a number of heavy metals such as Ni, Cu, As, Pb, and Cd [22, 23]. Due to its ability to accumulate large amounts of heavy metals from the soil, the plant is considered a “hyper-accumulator” [24, 25].

EXPERIMENTAL

Test zone description

The soil samples have been taken from a farmland located along the right side of the national road II-81, from km 12 + 400 to km 12 + 420, direction Lom. The test zone is far from any industrial heavy metals sources, without trees alongside the road that could serve as screens for road traffic emissions, as it is shown in Fig.1(a).

The main characteristics of the road II - 81 sections are as follow: in the studied sections are listed in the Table 1.

From the information listed in the Table 1 it follows that this is a high traffic intensity road with high percentage of heavy tracks. It can be supposed that the main anthropogenic sources for

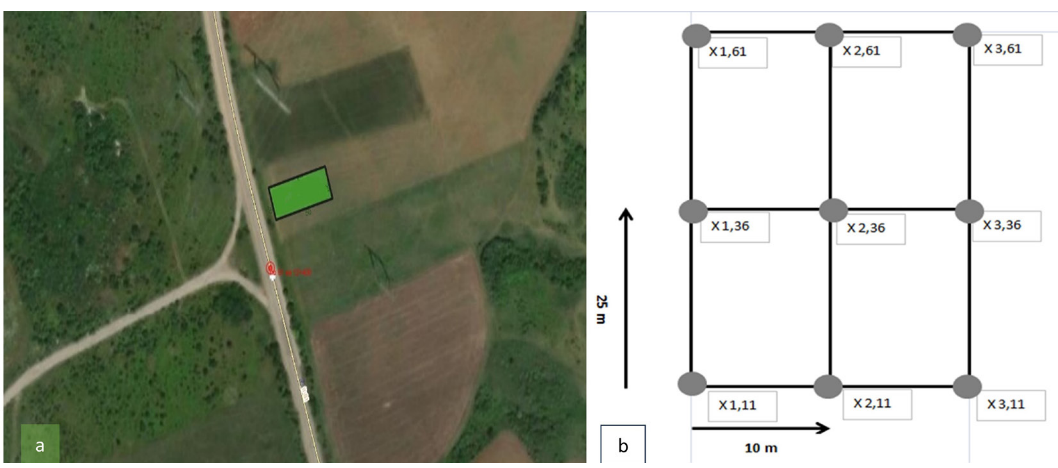

Table 1. Main characteristics of the test zone.

Characteristic	Description/Value
Road profile	Embankment
Embankment height, m	2
Cross section	GD 10,50, two lanes
Traffic lane width, m	3.75
Grade, %	>4
Average daily traffic, veh./24 h	5385
Heavy vehicles, %	10
Test zone area, m^2	1000

heavy metals in the test zone soil are road traffic and agricultural activities.

In Fig. 1(b) is given the diagram of the wind rose at the test zone [26]. From the diagram is visible that the highest wind frequencies are from the West and from the North-West. This means that primary and secondary accumulation of heavy metals on the test zone could be expected.

Sampling

The soil samples were taken during June and August 2020 at depth 0 - 20 cm, according to Ordinance No 3 from 2008 [27].

Sample preparation and heavy metals determination

The soil samples were dried at room temperature for 48 h and at 105 ± 5^{o}C in an oven for additional 24 h. The dried samples were grinded by agate mortar and sowed through a sieve 3 mm. Subsequently the samples were homogenized, subdivided by quartering and sowed through a sieve 2 mm. The prepared representative soil samples have been stored at 4^{o}C in refrigerator, until the digestion for heavy metal extraction and determination.

Soil samples digestion and heavy metals' extraction has been carried out with 10 % solution of HCl and concentrated HNO_3 under heating for 15 min in sand bath, followed by filtering and dilution to 100 mL in volumetric flasks.

Heavy metal determination has been carried out by atomic absorption spectrometer "Perkin-Elmer" 5000 with modulus for work with acetylene/air flame. Obtained concentration in mg/l has been transformed in mg/kg.

Evaluation methods for assessment of heavy metals contamination and ecological risk

Heavy metal concentrations of soil samples taken at the two sunflower (SF) growth stages are compared with the background, protective and maximum permissible concentrations of heavy metals in agricultural soils according to Ordinance No 3 from 2008 [27] with the exception of that of Sb, which is according to Hakanson [28].

Additionally the pollution level and ecological risk of the studied heavy metals have been comprehensively evaluated by calculation of the potential ecological risk index (RI), pollution load index (PLI), enrichment factor (EF), contamination factor (Cf) and contamination degree (Cd) from the average heavy metal concentrations.

In Table 2 are listed formulas of calculations, terms and classifications for different factors and indices.

Data processing

All data for the heavy metal concentrations, factors and indices have been processed by Descriptive Statistic and Correlation from Analysis Tools Pack of MS Excel Professional Plus 2021.

RESULTS AND DISCUSSION

Average total heavy metal concentrations

The average total concentration of studied heavy metals in the soil samples taken at the two SF growth stages V - 3 (three leaves at least 4 cm long) and R9 (maturity) are presented in Table 3 [32].

As can be seen from the presented results, the

Table 2. Description and classification of used factors and indices.

Factor/Index	Terms	Clasification
Enrichment factor [29] $E_f^i = \frac{\frac{C_{i,soil}}{C_{Fe,soil}}}{\frac{C_{i,background}}{C_{Fe,backround}}}$	$C_{i,\ soil}$=*Concentration of i-th heavy metal in soil* $C_{i,\ background}$=*Concentration of i-th heavy metal in sedimentary rocks* $C_{i,\ Fe}$=*Concentration of Fe heavy metal in soil* $C_{Fe,\ background}$ =*Concentration of Fe in in sedimentary rocks*	E_f≤1 – no enrichment, natural; *1<*E_f< 3– minor enrichment, anthropogenic *3<*E_f< 5– moderate enrichment; *5<*E_f< 10– moderately severe enrichment; *10<*E_f< 25–severe enrichment; *25<*E_f< 50– very severe enrichment; E_f>50– extremely severe enrichment.
Contamination factor [30]		
$C_f^i = \frac{C_{i,soil}}{C_{i,background}}$	$C_{i,\ soil}$=*Concentration of i-th heavy metal in soil* $C_{i,\ background}$=*Concentration of i-th heavy metal in sedimentary rocks*	$C_{f\leq}$1 – low; *1<*C_f< 3– moderate *3<*E_f< 6– considerable; C_f>6– very high.
Contamination degree [30]		
$CD = \sum_{i=1}^{n} C_f^i$	C_f^i=*Contamination factor of i-th heavy metal in soil*	*CD*≤ 8 – low degree of contamination; *8<CD*< 16– moderate degree of contamination; *16<CD*< 32– considerable degree of contamination; *CD* >32– very high degree of contamination.
Polution load index [31]		
$PLI = \sqrt[n]{\prod_{i=1}^{n} C_f^i}$	C_f^i=*Contamination factor of i-th heavy metal in soil*	*PLI*≤ 1 – non-polluted; *PLI*>1– polluted.
Potential ecological risk index [29]		
$RI = \sum_{i=1}^{n} C_f^i \times T_r^i$	C_f^i=*Contamination factor of i-th heavy metal in soil;* T_r^i= *toxic-response factor of i-th heavy metal:* *Cu=5;Zn=1; Pb=5; Cd=30; Ni=5; Co=5, Cr=2; Sb=18*	*RI* ≤150 – low risk; *150<RI*< 300–moderate risk; *300<RI*< 600– severe risk; *RI*>600– serious risk.

Table 3. Average total heavy metal concentration in soil samples taken at the two SF growth stages.

Distance, m	Average total heavy metal concentration, mg/kg								
	SF stage V-3								
	Cu	Zn	Pb	Cd	Cr	Fe	Ni	Co	Sb
11	51.35	233.63	44.19	1.51	47.21	22745.50	54.67	22.24	8583.21
36	49.85	109.48	30.01	1.66	47.84	23800.90	76.70	31.73	5237.27
61	46.15	156.49	73.16	0.92	24.52	24036.89	55.12	41.30	4616.32
Distance, m	SF stage R9								
	Cu	Zn	Pb	Cd	Cr	Fe	Ni	Co	Sb
11	67.63	259.59	65.17	0.57	18.71	25893.53	8.71	20.44	9713.49
36	117.28	98.97	43.71	0.25	18.66	26038.22	4.20	23.59	4830.90
61	103.74	228.80	28.89	0.24	9.96	26340.50	5.99	35.11	6878.19

total average concentrations decrease in the range Fe > Sb > Zn > Cu > Pb > Ni > Cr > Co > Cd at stage V-3 and in the range Fe > Sb > Zn > Cu > Pb > Co > Cr >> Ni > Cd at stage R9.

It should be pointed out that Sb concentration is very high. According to the literature review such a high concentration is common for soils located near antimony mines or shooting ranges. Having in mind that the test zone is far from any industrial sources of contamination it could be presumed that the sources in this case are road traffic and shooting. As the land is used for grains and sunflower cultivation and is located in semi-mountainous region it is possible to be used for birds hunting.

Comparison between the test results and the norms for heavy metal concentrations in Ordinance No 3 from 2008 shows that at the stage V-3 with the exception for chromium the concentrations for the rest of the studied heavy metals are above the norms for background concentrations. The concentrations of Cd, Cu, Pb and Co are higher than the norms for protective concentrations either at all or at some of the distances from the road edge. The same is true for the heavy metal concentrations of the soils samples, taken at the stage R9, with the exception for that of Ni and Cd.

Enrichment factors

In Table 4 and Table 5 are presented results for heavy metal enrichment factors of the soil samples, taken at the SF growth stages V-3 and R9.

As can be seen from the presented results, at the stage V-3 with the exception of chromium the enrichment factors for the rest of tested heavy metals are higher than one. This means that they come from anthropogenic sources. According to the classification in Table 2, the enrichment factors for heavy metals at this initial stage classify between minor enrichment to extremely severe enrichment (in case of Sb). With the exception of Cu and Sb, the enrichment factors for the rest of the studied heavy metals of soil samples taken at the stage R9 are lower than those at the stage V-3. Therefore, it could be presumed that the sunflower plant has the ability to accumulate most of the studied heavy metals.

Degree of contamination, pollution load index and ecological risk

The results for the calculated degree of contamination, pollution load index and ecological risk at the two SF growth stages are presented in Table 6. Comparison between the results and the classification in Table 2 shows that the soil

Table 4. Heavy metal enrichment factors of soil samples taken at the SF stage V-3.

Distance, m	Enrichment factor							
	Cu	Zn	Pb	Cd	Cr	Ni	Co	Sb
11	1.3841	5.1352	3.8014	6.1069	0.8748	1.8589	2.6898	7090.7
36	1.2666	4.0630	2.4829	4.5463	0.4313	2.0348	3.7343	5368.8
61	1.2630	3.3621	2.4851	4.1374	0.4308	2.3544	4.6922	4608.1

Table 5. Heavy metal enrichment factors of soil samples taken at SF stage R9.

Distance, m	Enrichment factor							
	Cu	Zn	Pb	Cd	Cr	Ni	Co	Sb
11	1.5967	5.2520	5.1145	2.0480	0.3155	0.2613	2.1522	6862.3
36	1.6407	4.6219	4.0073	0.8608	0.1606	0.2595	1.8346	5460.9
61	1.4971	2.6348	3.9959	0.8611	0.3037	0.2320	2.4669	4033.5

Table 6. Heavy metals contamination and ecological risk of soil samples taken at the two SF growth stages.

CD-V-3	CD-R9	PLI-V-3	PLI-R9	RI-V-3	RI-R9	Distance
5738	6488.971	5.687252	5.231866	103182.8	116656.07	11
3505.22	3229.357	4.122609	2.826548	63051.36	58027.115	36
3091.677	4595.128	3.932274	2.460272	55530.77	82589.914	61

Table 7. Correlation matrix of heavy metals enrichment factors and the distance from the road edge at the SF stage V-3.

	Ef Cu	Ef Zn	Ef Pb	Ef Cd	Ef Cr	Ef Ni	Ef Co	Ef Sb	Distance
Ef Cu	1								
Ef Zn	0.9297	1							
Ef Pb	0.9996	0.9192	1						
Ef Cd	0.9852	0.979	0.9802	1					
Ef Cr	0.9997	0.9202	1	0.9806	1				
Ef Ni	-0.788	-0.959	-0.771	-0.882	-0.772	1			
Ef Co	-0.816	-0.545	-0.831	-0.705	-0.83	0.2862	1		
Ef Sb	0.9617**	0.9951**	0.9538**	0.9944**	0.9545**	-0.926	-0.626	1	
Distance	-0.879*	-0.993**	-0.865*	-0.947**	-0.866*	0.9863**	0.4406	-0.976**	1

** Strong correlation [33]*

***Very strong correlation [33]*

samples, taken at both SF stages are polluted, they are with very high degree of contamination and pose serious ecological risk for the ecosystems and humans, mainly due to antimony.

Correlations

In Tables 7, 8 and 9 are presented correlation matrices for Pearson correlations between heavy metals enrichment factors, degree

Table 8. Correlation matrix of heavy metals enrichment factors and distance from the road edge at the SF stage R9.

	Ef Cu	Ef Zn	Ef Pb	Ef Cd	Ef Cr	Ef Ni	Ef Co	Ef Sb	Distance
Ef Cu	1								
Ef Zn	0.8595	1							
Ef Pb	0.2268	0.6927	1						
Ef Cd	0.2179	0.6861	1	1					
Ef Cr	-0.688	-0.221	0.5505	0.5581	1				
Ef Ni	0.937	0.9839	0.5527	0.545	-0.392	1			
Ef Co	-0.975	-0.726	-0.006	0.0028	0.8314	-0.837	1		
Ef Sb	0.6808	0.9595**	0.8678*	0.8633*	0.0629	0.8937*	-0.502	1	
Distance	-0.677	-0.958**	-0.87*	-0.866*	-0.068	-0.891*	0.4977	-1***	1

** Strong correlation [33]*
***Very strong correlation [33]*
*>*** Functional relationship, statistically significant at confidence level α= 0, 05, n=3 [33]*

Table 9. Correlation matrix of CD, PLI and RI of soils samples taken at the two SF growth stages and the distance from the road edge.

	CD-V-3	CD-R9	PLI-V-3	PLI-R9	RI-V-3	RI-R9	Distance
CD-V-3	1						
CD-R9	0.839	1					
PLI-V3	0.999	0.863	1				
PLI-R9	1	0.851	1	1			
RI-V-3	1	0.838	0.999	1	1		
RI-R9	0.839	1	0.863	0.851	0.838	1	
Distance	-0.929**	-0.578	-0.911**	-0.920**	-0.930**	-0.57	1

***Very strong correlation [33]*

of contamination, pollution load index and ecological risk of the soil samples taken at the two SF stages and the distance from the road edge.

As could be seen from the results in Table 7 and Table 8 for all the heavy metals, generated from road traffic emissions, the enrichment factors are strongly, negatively correlated with the distance from the road edge. With the exception of antimony all of the rest correlations are not statistically significant. This shows that heavy metals enrichment of the soil is due to more than one anthropogenic source. It should be pointed out an existence of a very positive strong correlation between some of the studied heavy metals, emitted from the road traffic, which shows similar emission source.

From the results for the correlation coefficients in Table 9 it follows that there are strong to very strong, not statistically significant negative correlations between different indices and the distance from the road edge and therefore road traffic has a significant role in the soil contamination by heavy metals.

CONCLUSIONS

Basing on the obtained results could be driven the next main conclusions:

- Most of the heavy metals in the tested soil samples are from anthropogenic sources;
- There are strong, not statistically significant correlations between EF, RI, PI and Cd and the distance from the road edge. The exception is EF for Sb where the correlation with the distance from the road edge is statistically significant at confidence level α = 0.05. Therefore, the road traffic is a significant source for the soil contamination by heavy metals in the test zone;
- The values of factors and indices for soil pollution and ecological risk are lower at the growth stage R9 than at the growth stage V-3 which shows the sunflower capacity of accumulation of the studied heavy metals.

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