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Heavy Metal Content in the Soil along the Road No. 7 near Chyżne

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Abstract: The aim of the study was to determine the content of heavy metals (Cr, Cu, Ni, Pb, and Zn) in the soil near Road No. 7, near Chyżne. Soil samples were collected in 12 transects (locations) on the east (downwind) and west (upwind) sides of the road. The samples were taken at a distance of: 5, 50, 100, 300, 500, and 600 m from the edge of the road. Six transects were located in the open area, and another six in the forest. The zinc content in the soil was the highest while that of copper was the lowest. Cr, Cu, Ni, Pb, and Zn concentrations decreased with increasing distance from the road. Differences in the concentration of metals in the soil on the upwind and downwind sides were found. The contents of all tested metals in the soil were higher on the downwind side of the road compared to the concentrations of metals on the upwind side.

Keywords: heavy metals; road pollution; soil; wind direction

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1. Introduction

The role of transport in Poland is systematically growing. Road, rail, and air transport are the most important, while water transport is the least important. Road transport has a negative impact on the natural environment as it contributes to the emission of dangerous and toxic substances [1–7]. Owing to the imperfection of the combustion process and the properties of the fuels used, toxic substances are produced during engine operation, which are then emitted to the environment along with exhaust gases [8]. These substances can be divided into three groups:

- products of imperfect and incomplete combustion: hydrocarbons, carbon mon-oxide, aldehydes;
- nitrogen products from oxidation of the air—NOx;
- products of combusting admixtures and pollutants and other compounds (dust and heavy metals: Cd, Cr, Cu, Pb, Ni, and Zn).

The share of road traffic in total emissions from all sources of atmospheric emissions is approximately thirty percent for carbon monoxide, nitrogen oxides, and aromatic hydrocarbons.

Road traffic also contributes to the emission of metals during: the process of abrasion of tires [8–10]; the wear of catalytic converters and brake linings [4,6,11]; and the use of oils and greases [5,12]. Moreover, the chemical composition of the road surface and the fuel used affect the presence of metals in the roadside environment [7,13].

The content of heavy metals in the soil depends on a number of environmental factors, the most important of which are: distance from the road [14–16]; traffic intensity [2,16]; vehicle speed [6]; altitude and land cover [17–20]; and meteorological conditions, including mainly: prevailing wind direction; air turbulence; and the amount of precipitation [7,17,21]. These factors are very complex and are based on a number of variable parameters. It was found that the distance from the road had the greatest impact on the content of metals in the soil [7]. Metal concentrations in the soil decrease with the increasing distance from the road [1,2,16], and the impact range of road traffic is estimated at several hundred meters [1,22,23]. Vehicle traffic contributes to the high accumulation of metals in near road soils, which is even several times higher than in unpolluted areas [1,2,17,24,25].

A very important factor affecting the spread of metals in the environment is the dominant wind direction. The literature data shows that the location of the road in relation to the prevailing wind direction has an impact on the propagation of traffic pollution, which is particularly important for exposed road sections running through convex landforms, such as mountain ridges and in valleys, where the wind direction coincides with the direction of the valleys [26,27].

Bakirdere and Yaman [7], Viard et al. [17], and Masoudi et al. [21] found higher metal contents in the soil on the upwind side compared to the downwind side. On the other hand, in the opinion of Zechmeister et al. [1], wind may be responsible for the low and significantly diversified concentration of metals in plants within the studied sites. However, in mountain areas with complex landform, the analyses of the directions of the dominant winds are difficult to define owing to the diversity and number of factors affecting the accumulation of heavy metals in the soil [27].

In the scientific literature, there are few studies on the influence of the dominant wind direction on the accumulation of heavy metals in soils. Therefore, this work will contribute to a better understanding of the subject. The aim of the study was to determine the content of Cr, Cu, Ni, Pb, and Zn in the soil along the upwind and downwind sides of Road No. 7, near Chyzne.

2. Materials and Methods

2.1. Study Area

The study area was situated along the state Road No. E77 (national road DK7) be-tween the villages Jablonka and Chyzne, county Nowy Targ in Sothern Poland, and in the vicinity of the border crossing to Slovakia. Geographical coordinates: the latitude and longitude and elevation are 49°43′ N, 19°67′ E and 649 m above sea level. According to Koppen classification, the area is by temperate continental climate (Dfb). The data for the average annual precipitation, temperature, and wind speed are about 115 mm, 7.5 °C and 10 km/h, respectively [28]. The dominant wind directions are S (1319 h per year), SSW (956 h per year) and W (759 h per year) for the analyzed area [29,30]. The simulated meteorological data are available for the Jabłonka, Chyzne, and Czarny Dunajec locations [31].

Road No. E77 plays an important role in the transit traffic towards southern Europe. The traffic density on the road section between Jablonka and the state border was about 5000 vehicles per day in 2015 and the speed limit was 90 km per hour [32,33].

2.2. Sampling

The samples were collected in 12 transects near the Slovak state border. The transects were located perpendicularly to the road, on the eastern and western side of the road, in the open area: meadows and pastures, as well as in the woodland.

With respect to the prevailing wind direction, the transects were located upwind "non-road emission source" (E transects) and downwind "from road emission source" (W transects) relative to the road (Figure 1). Each transect included six sampling sites at the following distances from the edge of the road: 5, 50, 100, 300, 500, 600 m (Figure 2). In order to avoid the influence of local pollution sources sampling sites were situated at least 500 m from housing estates. The reference area was situated south of Chyzne village in the Jelesnia stream valley, at the minimal distance of about 5 km from roads and individual houses.

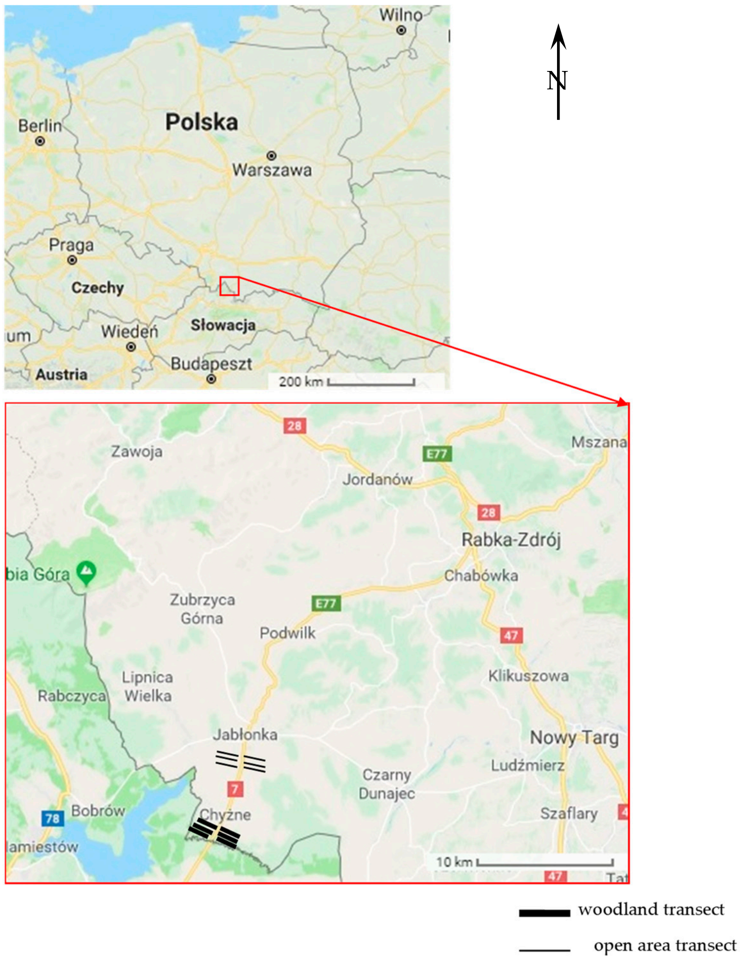

Figure 1. Location of sampling sites.

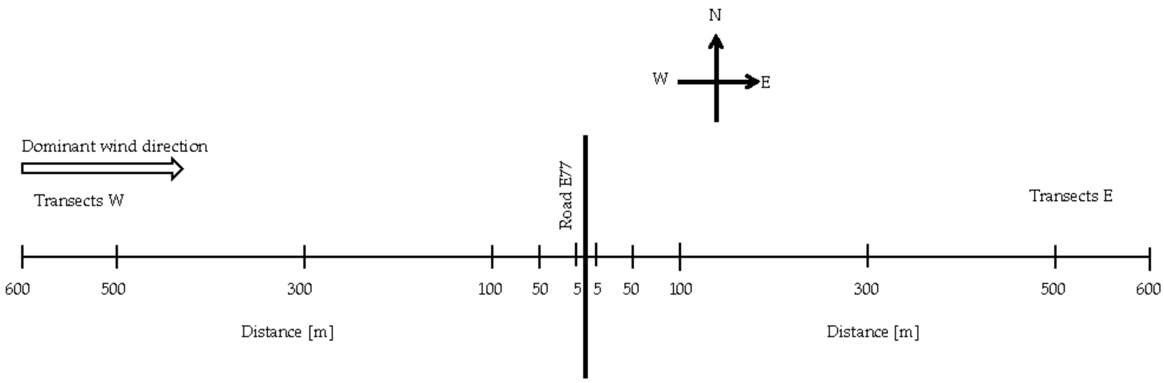

Figure 2. Scheme of sampling transect.

2.3. Material

In all, 72 soil samples from a depth of 0–10 cm were taken for the study. The sampling sites were located on both sides of Road No. 7 near Chyzne. One side of the road was the downwind side and the other side upwind. Samples of the soil were taken within six transects located in the open area and also six transects in the woodlands (Figure 1). The samples were taken in September 2021. The material was placed in polyethylene bags.

2.4. Methods

2.4.1. Chemical Analysis

In order to determine the content of heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn) in the sampled soil material (top soil, up to 10 cm), the following laboratory work was carried out, in accordance with the methodology used for collecting and preparing samples for chemical analyses [34,35]:

- Manually cleaning the collected samples by removing foreign material (dry leaves, twigs, grass, etc.);
- Drying the samples at 70 °C;
- Grinding soil samples in a ceramic mortar and sieving through a sieve with a mesh diameter of 2 mm;
- Mineralization, which is performed to completely break down soil samples into simple, solid compounds—1 g of the dried sample material was digested with a modified Aqua Regia solution of equal parts concentrated HCl, HNO_3, and DIH_2O for one hour in a heating block or hot water bath. The resulting solution was filtered and stored in sealed polyethylene containers until sent for spectrometric analysis;
- The determination of the total content of heavy metals using the inductively coupled plasma mass spectrometry (ICP-MS) method in the Bureau Veritas laboratory. The use of the Bureau Veritas methodology made it possible to accurately determine the metal content in the soil material, with the following detection limits (mg kg^{-1}) for Cd: 0.01, Cr: 0.5, Cu: 0.01, Ni: 0.1, Pb: 0.01 and Zn: 0.1. The STD DS11 and STD OREAS262 standards were used as reference materials.

2.4.2. Statistical Analysis of the Data

To describe precisely the investigated data, we used the following descriptive measures: mean, median, standard deviation (SD), and the difference between first and third quartile (Interquartile Range—IQR) and min-max. To describe precisely the investigated data I used the following descriptive measures: mean, median, standard deviation (SD), lower (Q1) and upper (Q3) quartile and min-max. The normality of the distribution of consecutive variables was checked using the Shapiro-Wilk test. If normality can be assumed, then I have compared mean values using the Student's t-test for two independent variables, or ANOVA for more than two such variables. In the opposite case, I used non-parametric tests, i.e., U Mann-Whitney's test for two independent variables. Here, I assume the significance level $p = 0.05$; however, I also highlight statistically significant results for $p = 0.01$ and $p = 0.001$, respectively. p-values corresponding to significant results were marked in bold. In the case of $p < 0.001$ we always denote $p = 0.001$. All calculations and graphs were carried out using the R (version 4.0.2, Vienna, Austria).

The number of the samples taken for the calculations is presented in Table 1.

To investigate the existence of monotonic relationships between two variables, Spearman's correlation coefficient was used. This coefficient takes values from -1 to 1. The statistically significant result concerning Spearman's correlation coefficient proves the existence of monotonic dependencies between the variables. If the coefficient becomes positive, it means that as one variable grows, the value of the other variable grows as well. However, if the correlation is negative, it means that as the value of one parameter increases, the value of the other parameter decreases as well. The correlation can be low, moderate, high, or very high. It may also not be present. The following classification of the correlation strength was used:

- $|r| = 0$—no correlation,
- $0 < |r| \leq 0.3$—very weak correlation,
- $0.3 < |r| \leq 0.5$—weak correlation,
- $0.5 < |r| \leq 0.7$—moderate correlation,
- $0.7 < |r| \leq 0.9$—high correlation,
- $0.9 < |r| < 1.0$—very high correlation,
- $|r| = 1$—full correlation.

In the study, soil samples from places near the road were collected, and then concentrations of Cr, Cu, Ni, Pb, and Zn in them, respectively, were analyzed. There were 12 transects; half came from the forest (N = 36) and the other half from the open area. Similarly, the division of wind directions was half-and-half (upwind and downwind). Samples were taken at distances of 5, 50, 100, 300, 500, and 600 m, respectively. At each distance of 5, 50, 100, 300, 500, and 600 m, 12 samples (16.7%) were taken.

Table 1. Characteristics of calculation parameters.

Variable	Parameter	Total (N = 72)
Transect	12 (6 in the forest and in the open area, and 6 on the upwind and downwind sides)	N = 6 for each transect
Land cover	Forest	50% (N = 36)
	Open area	50% (N = 36)
Wind direction	Upwind	50% (N = 36)
	Downwind	50% (N = 36)
Distance (m)	5	16.7% (N = 12)
	50	16.7% (N = 12)
	100	16.7% (N = 12)
	300	16.7% (N = 12)
	500	16.7% (N = 12)
	600	16.7% (N = 12)
Distance (m) divided	Equal or smaller than 100	50% (N = 36)
	More than 100	50% (N = 36)

3. Results

The average concentration of Cr was 47.41 (±13.53; standard deviation), in the case of Cu 19.53 (±6.4), in the case of Ni 27.39 (±8.72), in the case of Pb 34.93 (±13.09), and, finally, in the case of Zn 62.35 (±20.49) (mg kg^{-1}). These results are presented in Table 2.

Table 2. Mean concentrations, standard deviations, median (Q1–Q3) and min-max of heavy metals in the soils in mg kg^{-1}; n = 72.

Metal	Parameters	Concentration (mg kg^{-1})
Cr	Mean (SD)	47.4 (13.5)
	Median (Q1–Q3)	43.7 (35.5–59.8)
	Min-Max	28.0–72.1
Cu	Mean (SD)	19.5 (6.4)
	Median (Q1–Q3)	18.6 (14.1–27.0)
	Min-Max	9.6–28.9
Ni	Mean (SD)	27.4 (8.7)
	Median (Q1–Q3)	25.8 (19.8–37.5)
	Min-Max	14.0–40.8

Table 2. *Cont.*

Metal	Parameters	Concentration (mg kg^{-1})
Pb	Mean (SD)	34.9 (13.1)
	Median (Q1–Q3)	30.6 (23.7–49.7)
	Min-Max	18.4–56.1
Zn	Mean (SD)	62.4 (20.5)
	Median (Q1–Q3)	60.6 (43.2–83.5)
	Min-Max	30.0–90.2

3.1. Relationship with Land Cover

Statistically significant differences between types of the land cover for Cu concentration ($p < 0.05$, U Mann-Whitney test) and Ni concentration (mg kg^{-1}) ($p < 0.05$, U Mann-Whitney test), respectively, were obtained. We can observe that greater concentration of these metals occurred in the open area. These results are presented in the Figure 3.

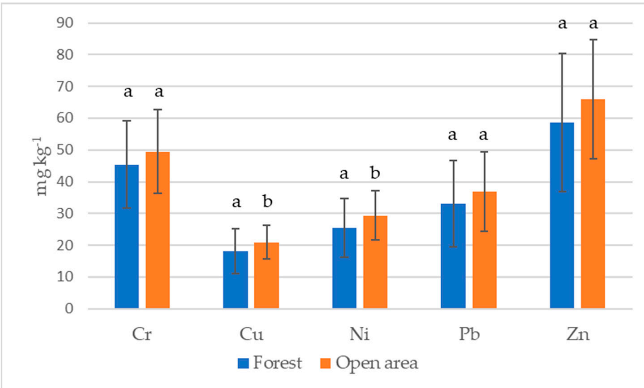

Figure 3. Comparison of mean element concentration against land cover. Bars marked with the same letters within one element indicate no difference according to U Mann−Whitney test (n = 36).

3.2. Relationship with Wind Direction

Statistically significant differences between the wind direction category for every element have been found using the U Mann-Whitney test ($p < 0.05$). We can observe that greater concentration of these elements occurred in downwind sides (Figure 4).

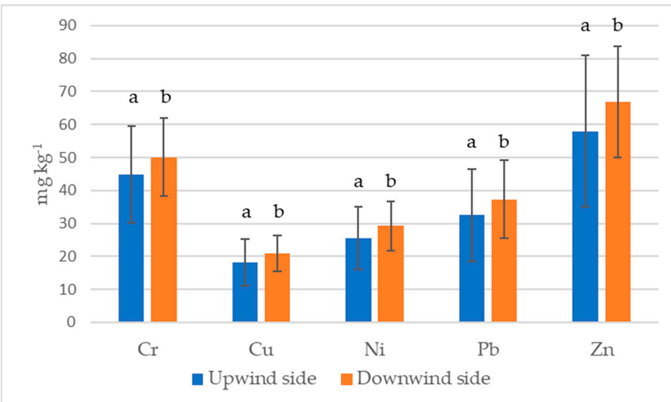

Figure 4. Comparison of mean element concentration against wind direction. Bars marked with the same letters within one element indicate no difference according to U Mann−Whitney test (n = 36).

3.3. Relationship with Distance

Statistically significant differences between shorter (smaller or equal than 100) and longer distance for every element were obtained ($p < 0.01$). We can observe that greater concentration of elements occurred closer to the road. These results for selected metals are presented in Figure 5.

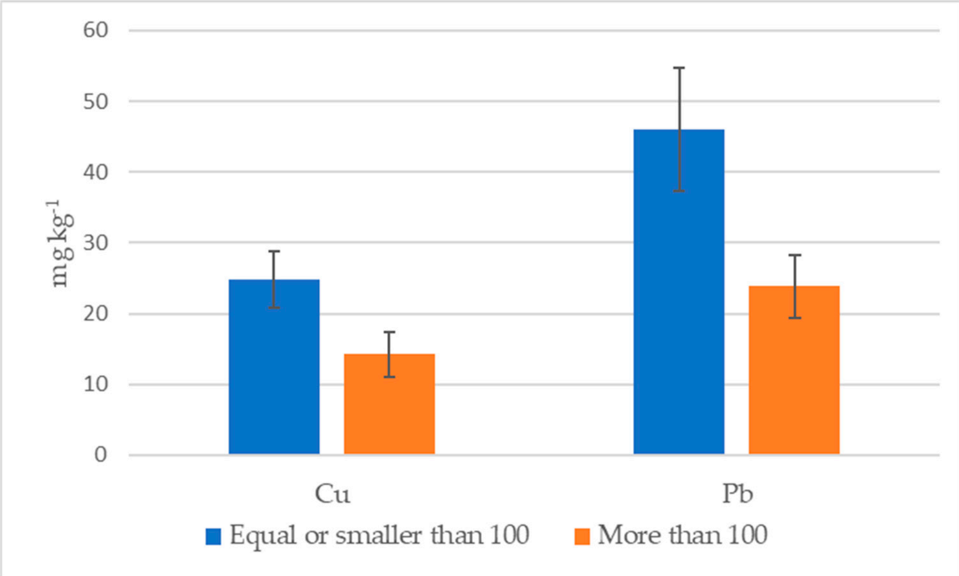

Figure 5. Comparison of Cu and Pb concentration against distance. Relationship distance—land cover (forest).

Concentrations of all samples taken only from the forest were significantly lower among greater distances ($p < 0.001$). These results (mean values and SD) are presented in the Table 3.

Table 3. Comparison of elements from the forest against distance.

Metal	Parameter	Concentration (mg kg^{-1})		*p*-Value
		Equal or Smaller than 100 m (N = 18)	More than 100 m (N = 18)	
Cr	Mean (SD)	57.2 (8.7)	33.4 (3.8)	<0.001
Cu	Mean (SD)	24.2 (4.4)	12.1 (2.3)	<0.001
Ni	Mean (SD)	33.1 (6.5)	17.7 (2.9)	<0.001
Pb	Mean (SD)	44.4 (9.9)	21.8 (3.0)	<0.001
Zn	Mean (SD)	78.4 (9.6)	39.0 (7.8)	<0.001

3.4. Relationship with Distance—Land Cover (Open Area) Only for Chemical Elements from the Open Area

Statistically significant differences between shorter and longer distance (m) for concentration of samples taken only from the open area were proved to be significant ($p < 0.001$) in each case. We can observe that for distances which were closer to the road, concentrations of elements were greater as well. These results (mean values and SD) are presented in the Table 4.

Table 4. Comparison of elements from the open area against distance.

Metal	Parameter	Concentration [mg kg^{-1}]		*p*-Value
		Equal or Smaller than 100 m (N = 18)	More than 100 m (N = 18)	
Cr	Mean (SD)	61.1 (6.3)	37.9 (5.7)	**<0.001**
Cu	Mean (SD)	25.5 (3.4)	16.4 (2.2)	**<0.001**
Ni	Mean (SD)	36.2 (3.8)	22.6 (3.3)	**<0.001**
Pb	Mean (SD)	47.7 (7.1)	25.9 (4.6)	**<0.001**
Zn	Mean (SD)	83.1 (5.1)	48.9 (8.8)	**<0.001**

3.5. Relationshipdistance—Wind Direction (Upwind)

It was proved that there is a statistically significant difference between shorter and longer distance (m) for concentration of every chemical element from places with the upwind direction ($p < 0.001$). Greater concentration of these elements occurs closer to the road. The average concentrations of metals in the soil (calculated for N = 18) were almost twice as high at distances up to 100 m (for 5, 50, and 100 m from the road) than at distances greater than 100 m, i.e., for 300, 500, and 600 m from the road (Figure 6).

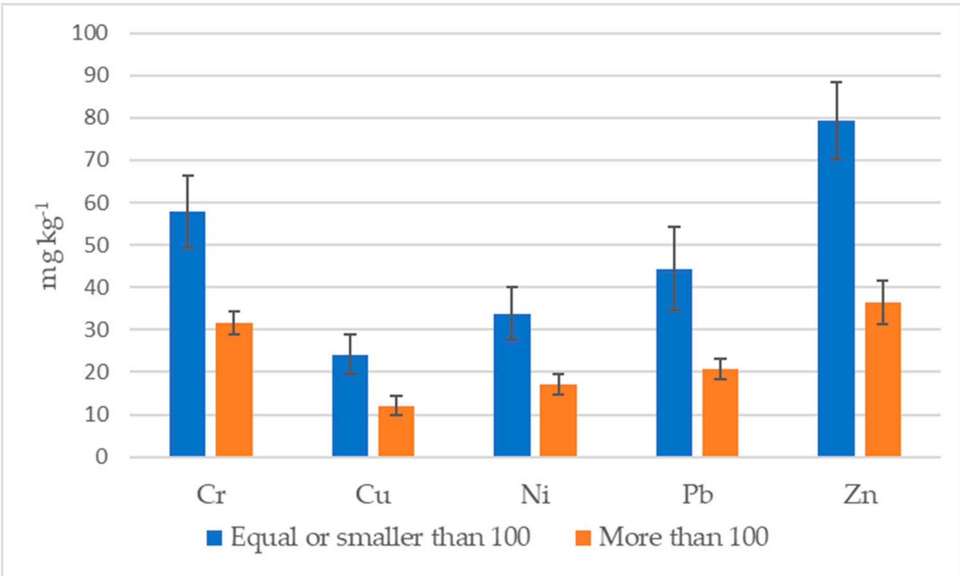

Figure 6. Comparison of mean element concentration against distance—for metals from the sides with the upwind direction.

3.6. Relationship Distance—Wind Direction (Downwind)

We can observe that greater concentration of all elements from sides with a downwind direction occurs closer to the road ($p < 0.001$). The average concentrations of metals in the soil (calculated for $N = 18$) were higher at a distance up to 100 m (for 5, 50, and 100 m from the road) than at distances greater than 100 m, i.e., for 300, 500, and 600 m from the road (Figure 7).

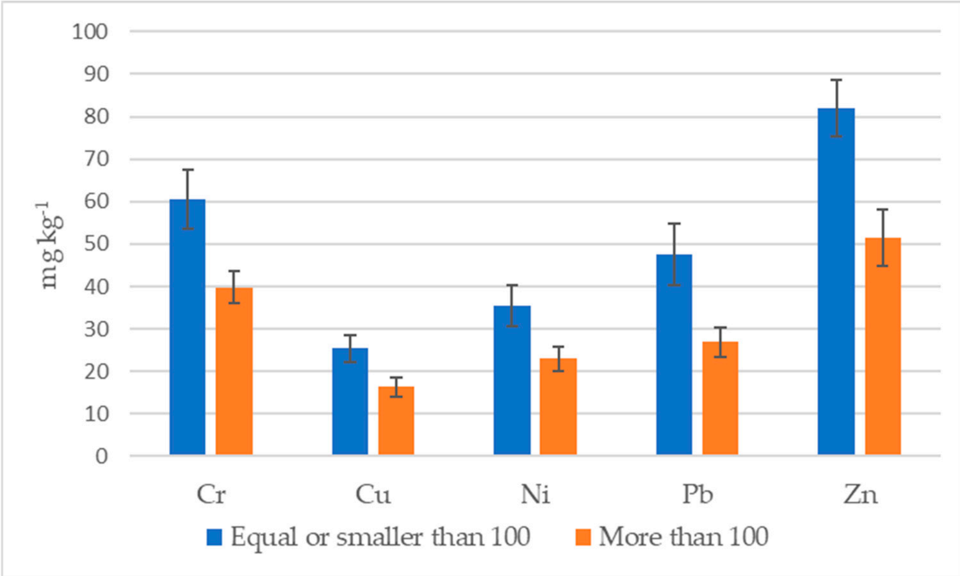

Figure 7. Comparison of mean element concentration against distance—for metals from sides with a downwind direction.

The values of the average concentrations of all tested metals in the soil were higher on the downwind side of the road compared to the values of the contents of metals in the soil collected on the upwind side of the road.

3.7. Spearman's Correlation Coefficients

Spearman's correlation coefficients between the concentration of the tested metal in the soil and the distance from the road have been calculated. The data are presented in Table 5.

Table 5. Spearman correlation coefficient (*p*-Value) $N = 36$.

Metal (mg kg^{-1})	**Distance (m)**				
	Overall	**Forest**	**Open Area**	**Upwind**	**Downwind**
Cr	−0.891 **(<0.001)**	−0.898 **(<0.001)**	−0.913 **(<0.001)**	−0.930 **(<0.001)**	−0.908 **(<0.001)**
Cu	−0.861 **(<0.001)**	−0.905 **(<0.001)**	−0.882 **(<0.001)**	−0.903 **(<0.001)**	−0.888 **(<0.001)**
Ni	−0.858 **(<0.001)**	−0.892 **(<0.001)**	−0.913 **(<0.001)**	−0.901 **(<0.001)**	−0.879 **(<0.001)**
Pb	−0.879 **(<0.001)**	−0.891 **(<0.001)**	−0.911 **(<0.001)**	−0.910 **(<0.001)**	−0.911 **(<0.001)**
Zn	−0.895 **(<0.001)**	−0.918 **(<0.001)**	−0.912 **(<0.001)**	−0.915 **(<0.001)**	−0.919 **(<0.001)**

All of the above Spearman correlations between metal concentrations in soil samples and distance from the road were, independently of land cover or wind direction, negative and high or very high. It means that as distance from a road increased metal concentration in the soil samples decreased.

4. Discussion

The road has a negative effect on nearby soils. It contributes to their significant contamination, including with heavy metals. Road traffic results in higher pollutant concentrations in the environmental components in the direct proximity to the road. Metal concentrations in soils and plants decrease with distance from the road to reach a background level at a distance ranging widely according to the various authors up to several hundred meters [1,2,36].

In the presented study, metal concentrations in soil samples were significantly correlated with the distance to the road. Data showed considerably higher Cr, Pb, and Zn concentrations in the direct proximity to the road, when compared to the figures reported by Kováčik et al. [37] for the vicinity of traffic roads in Košice, and by Giacomino et al. [38] for the Italian province of Cuneo. The data referring to the distance of 300–600 m matched the data reported by Kabata-Pendias and Dudka [39] for Poland, Marr et al. [40] for Montreal, Diatta et al. [41] for Poznań, Czarnowska and Milewska [42] for Warsaw, and Ligocki et al. [43] for Szczecin.

The existing literature finds differences between upwind and downwind concentrations of particle matter PM [44–47], metal contents in the roadside soils [7,17,21] and in roadside plants [1,17]. However, the results are mixed. Hagler et al. [46] find significant differences in ultrafine particle UFP concentrations between the upwind and downwind sides of the road with the higher amounts of UFP being observed downwind from the road. However, the results in Garcia et al. [44] concerning particle matter PM concentrations near highways show no evidence of a significant upwind source influence. Roorda-Knape et al. [44] and McGee et al. [47] report no correlation between PM concentrations and down/upwind road locations.

Bakirdere and Yaman [7], Viard et al. [17], and Masoudi et al. [21], find Cu, Pb, and Zn in different concentrations in the soils at the upwind and downwind locations from the road at the same distance. The higher pollutant concentrations are usually observed at the downwind side of the road, towards the prevailing wind direction.

Among very few studies on the influence of wind direction on metal concentrations in roadside plants, those performed by Zechmeister et al. [1] and Viard et al. [17] show the differences of some heavy metal contents in plants collected from two sides of the road. The authors conclude that higher values are found downwind from the road.

The prevailing wind direction, across our study area, is a southern one (1319 h per year). Eastern winds are four times less frequent (190 h per year) than Western winds (759 h per year). The differences in prevalence of Western and Eastern winds may explain higher metal pollution on the downwind, eastern side of the southbound road.

Our study revealed statistically significant differences between metal concentrations in the soil at the two sides of the road. The concentrations were higher on the west side (downwind from traffic emission sources). Plant cover influences, to some extent, pollutant dispersion in the vicinity to the road. The samples of the soil were collected in the open area and in the forest. The forest trees may have played the role of natural screen, trapping dust particles, causing disturbances of wind stream, and thus hindering road pollutant propagation. This conclusion is in line with the work of Sucharowa and Suchara [48] who reported the dependence of the metal content in mosses on land cover: open area and woodland. Concentrations decreased with increasing tree density and canopy density. Higher concentrations of all tested metals in the soil were observed in the samples collected in open areas compared to the concentration of metals in the forest.

5. Conclusions

A statistically significant negative correlation was found between the concentrations of heavy metals in the soil and the distance from the road.

The dominant wind direction in the study area was the south-west, which affected the amount of metal accumulation in the described roadside soils. The influence of the dominant wind direction on the concentration of Cr, Cu, Ni, Pb, and Zn was found for a distance greater than 100 m from the road.

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Data Availability Statement: Not applicable.

Conflicts of Interest: The author declares no conflict of interest.

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