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Heavy Metal Concentrations in Roadside Soils on the Białystok-Budzisko Route in Northeastern Poland

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Abstract: Civilization development has contributed to environmental pollution. In recent years, the number of vehicles has increased significantly; according to the Central Statistical Office, the number of passenger cars in Poland in 2000 was nearly 10 million, while in 2020 it was slightly more than 25 million. The study aimed to determine the content and spatial distribution of trace elements (Fe, Mn, Cd, Pb, Cr, Ni, Zn and Cu) in the roadside topsoil along the trunk road Białystok–Budzisko on different types of land use (urban, rural, agricultural and forestal areas). Forty-five soil samples were collected from a 160 km road section, at intervals of approximately 4 km. Metal contents were analyzed by atomic absorption spectrometry. The concentrations of metals in roadside soils occurred in the following order: Fe > Mn > Zn > Cr > Cu > Pb > Ni > Cd. The average contents of Cd, Zn, Cu, and Pb were higher than the geochemical background values of the Polish soils. Moreover, the values of the I_{geo} showed for Cd moderate to strong, while for Zn, Cu and Pb, moderate soil contamination. The study indicates that significant metal-binding factors in the studied roadside soils are Fe and Mn oxides. The crucial source of metals is road transport, depending on its intensity, which means amount, type, and speed of vehicles. Moreover, based on the analysis of the course of the factor values and their dynamics, it was observed that the areas where typical activities connected with the population take place (urban and agricultural areas) are additional sources of heavy metals. The results of this paper are relevant to the prevention and control of heavy metal pollution in roadside soils. The study can contribute to reducing the concentration of toxic elements in ecosystems due to vehicle emissions with appropriate land-use policies.

Keywords: soil pollution; motor transportation; elemental concentration; urban areas; rural areas; agricultural areas; forestal areas

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1. Introduction

The development of civilization has contributed to severe environmental pollution [1–3]. In addition to industry and agriculture, road transport is a primary source of trace element pollution. In recent years, the number of cars has increased significantly, which is associated with increased contamination of the soil environment and surface and groundwater with heavy metals [4–6]. According to the Central Statistical Office, the number of passenger cars in Poland in 2000 was almost 10 million, while in 2020 it was slightly above 25 million [7]. Pollution from road transport is considered a major environmental risk factor responsible for premature deaths worldwide [4,8]. Most heavy metals come from exhaust gases, car oil leaks, tire and brake disc wear, and corrosion of vehicle metal parts [9–15]. There is a misconception that air pollution related to traffic is only a consequence of the effect of incomplete fuel combustion, when, in fact, it is dominated by emissions of non-combustion particles generated by abrasion of brake and clutch pads and discs, corrosion of vehicle bodies and road infrastructure, and deterioration of road surfaces [16–21].

For a long time, soil was considered a repository of pollutants due to adsorption processes that affect binding to inorganic and organic contaminants [5,22]. The level of heavy metal contamination of soils depends on its type, climate [23], anthropogenic activity [24,25], and atmospheric conditions [13], including wind direction and speed, type of precipitation, type of terrain [14] and type of vegetation [26].

Surface layer of roadside soil near roads with heavy traffic in urban areas is a good indicator of heavy metal pollution from atmospheric dust [27,28]. Metals such as Cd, Cu, Pd and Zn enter the environment through the consumption of brake pads, lubricating and industrial oils [9,22], while Cr and Ni enter through the wear of metal parts and chrome accessories [29]. Moreover, heavy metal content in soils along the road is strongly related to traffic and decreases with distance from the road [13]. Furthermore, the authors [30] showed a correlation between vehicle traffic volume and metal content in roadside soils, but some studies [31] do not confirm this relationship. Soil contamination caused by vehicular transport has received much scientific attention in recent years [32–42] and should be monitored to preserve environmental quality and prevent degradation.

The above considerations encouraged us to conduct the study. The objectives of the study were: (1) to determine the content and spatial distribution of trace elements: iron (Fe), manganese (Mn), cadmium (Cd), lead (Pb), chromium (Cr), nickel (Ni), zinc (Zn) and copper (Cu) in the top layer of roadside soils along the trunk road Białystok-Budzisko in different types of land use (urban, rural, agricultural and forestal areas), (2) application of I_{geo} (Geoaccumulation Index), CF (Contamination Factor) and PLI (Pollution Load Index) indices to determine possible heavy metal contamination, and (3) application of multivariate statistical methods to identify the processes governing metals and their distribution trends in soils.

The results and analysis can be used to prevent heavy metal pollution from road transport as one of the main sources of soil contamination. The paper can contribute to reducing the concentration of toxic elements in the food chain and ecosystems in general that end up there due to vehicle emissions.

2. Materials and Methods

2.1. Study Area and Sampling

The analyzed road is located in northeastern Poland and is a part of Via Carpatia international route, running from Lithuania (Klaipeda) through Poland, Slovakia, Hungary, Romania, and Bulgaria to Greece (Thessaloniki). The analysis of heavy metal contents in soil samples along trunk road No. 8 leading from Białystok to Budzisko was carried out on the length of about 160 km. The route runs from the center of Białystok through Korycin, Skindzierz, Suchowola, Białobrzegi, the Augustów bypass, and Suwałki to the Polish-Lithuanian border crossing in Budzisko. The intensity of vehicle traffic in the studied road section ranges from 6753 to 21670 vehicles per day. The study area is marked by natural values and is narrowly transformed by man (Table 1). The entire surface of the analyzed area is covered by Quaternary formations of the Central Polish glaciation developed in the form of silts, clays and till of slow-glacial sands and gravels. The average annual temperature is about +6.8 °C, while the average wind speed is 2.8 $m \cdot s^{-1}$. Weak and moderate winds are most common. The winds are primarily from the west and southwest directions [43]. The mean annual precipitation varies from a minimum value of 456.4 mm to a maximum of 748.9 mm [44].

The research points were located in 4 types of areas. The first groups consisted of soils from urban (1–5, 15, 24, 35–39) and rural (6, 7, 11–14, 18, 23, 45) residential areas through which the road passes. The next groups include agricultural (9, 16, 19–21, 25–32, 40, 42, 44) and forestal (8, 10, 17, 22, 33, 34, 41, 43) areas near the analyzed route (Figure 1, Table 1). A total of 45 soil samples were collected close to the edges of the road (160 km road section, at intervals of approximately 4 km) at a depth of 0–10 cm (surface samples). Each sample was collected at the roadside 2 m from the edge of the roadway [45]. The samples did not contain road construction materials. According to the studies [26,46,47], the highest element concentrations are found in soils near the road itself and decrease proportionally with increasing distance from the road. Soil samples were collected in October 2019 on both sides of the road, several unit samples each and then mixed thoroughly to obtain a bulk sample for each research point. All samples were collected with a stainless-steel spatula and placed in polyethene bags (approximately 1 kg).

Table 1. General characteristics of the study area.

Type of Land Use	Research Points	Characteristics
urban	1–5, 15, 24, 35–39	points located in cities with large populations, Białystok (296,628), Suwałki (69,626), Augustów (30,373), and along roads passing through smaller towns, near single- or multi-family housing and services
rural	6, 7, 11–14, 18, 23, 45	points next to the road that runs through smaller villages, close to single-family and farm buildings
forestal	8, 10, 17, 22, 33, 34, 41, 43	points located near road that passes through large forest complexes, including naturally valuable areas protected by the Natura2000 programme (Knyszyn Forest, Biebrza Valley, Augustów Primeval Forest, Suwałki Landscape Park)
agricultural	9, 16, 19–21, 25–32, 40, 42, 44	points near land used for cultivation or used for grazing animals kept for farming purposes

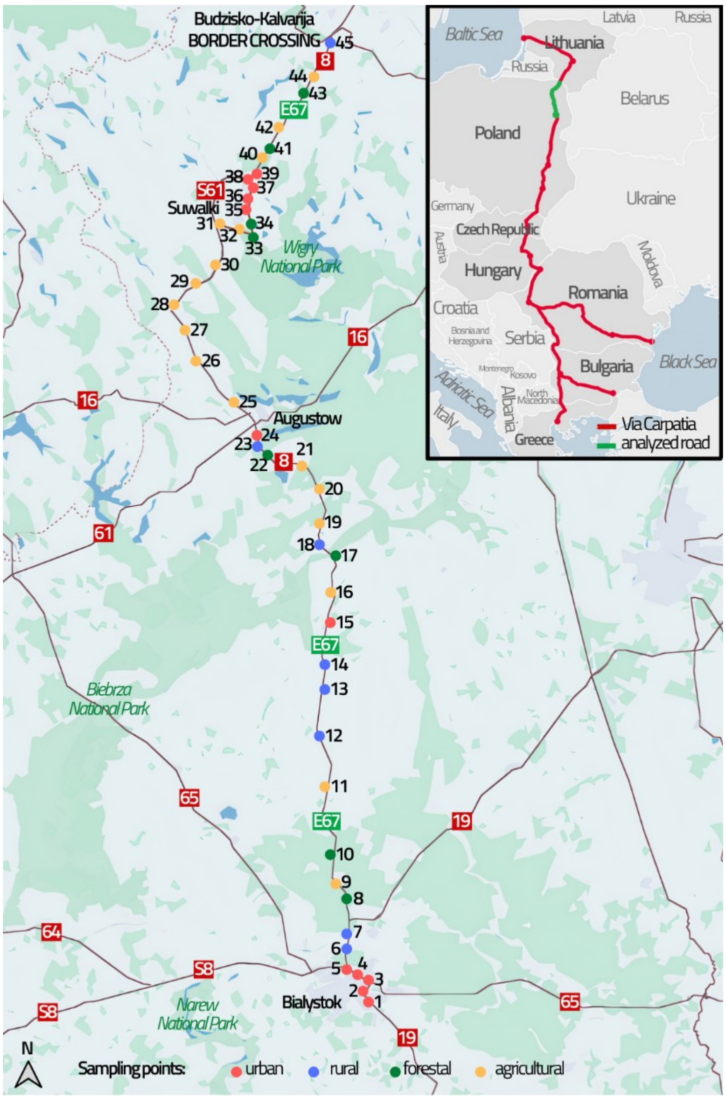

Figure 1. Location of research points on the road from Białystok to Budzisko, northeastern Poland.

2.2. Sample Processing and Analysis

The samples were transported to the laboratory and stored at 20 °C before further testing activities. The samples were sieved through a 2 mm polyethene sieve to remove stones and organic debris, then ground in an agate mortar and sieved through a 0.20 mm mesh polyethene sieve. All steps were carried out without contact with metal elements to avoid contamination of the samples. Samples of soil (1 ± 0.01 g) were weighed for mineralization. The samples were mineralized with aqua regia (HNO_3:HCl = 1:3) in a microwave digestion system (Ethos Easy, Milestone, Italy). The concentration of Cd, Ni, Pb, Zn, Cr, Fe, Cu, and Mn was quantified by atomic absorption spectrometry using an AAS ICE 3500 Thermo Scientific (Thermo Scientific Portable Analytical Instruments Inc., Tewksbury, MA, USA). The precision of the measurements was verified using the standard reference material certificate No. 0217-CM- 700I-04, 7003. The measurement results of the standard reference material showed good agreement with the certified values (Fe = 97%, and Mn = 94%, Zn = 96%, Cu = 101%, Cr = 80%, Pb = 95%, Ni = 89%, Cd = 109%). The pH value was measured in 1:2.5 (w:v) deionized water [48]. Soil organic matter (OM) content was quantified by mass loss during soil burning at 400 °C [49]. The influence of ignition temperature on the results obtained appears in many publications [50–52]. According to [49], a better fit is observed at 375 ± 5 °C, which is related to the presence of clay minerals in the soils. On the other hand, the temperature between 400–430 °C does not cause errors in the results of organic content in soils containing carbonates [49].

2.3. Assessment of Roadside Soil Contamination

The geochemical background, which depends primarily on geological conditions, is used to evaluate and compare the level of metal contamination of soils. Metal concentrations were compared with the geochemical background defined by Turekian and Wedephol [53] as the average content of elements in the Earth's crust, which can only provide general information about the extent of anthropogenic impact on the environment. It is also crucial to consider the regional mineralogical composition of the parent geological material, i.e., information on the initial natural concentrations of heavy metals, which may vary to a large extent depending on the geological surface structure present in the study area [54]. Metal concentrations of roadside soil were also compared with the parent geogenic component, i.e., the local soil background in Poland—these are Quaternary surface sediment [55].

Indices were also used to assess the condition of soils. One commonly used rate is the Geoaccumulation Index (I_{geo}). Other indicators proposed in this study include the Contamination Factor (CF) and the Pollution Load Index (PLI) [1,2,42,56,57] (Table 2).

Table 2. Interpretation of the values and classes of indices used.

Geoaccumulation Index (I_{geo})		Contamination Factor (CF)		Pollution Load Index (PLI)	
Value	Soil Quality	Value	Soil Contamination	Value	Pollution Status
Igeo ≤ 0	uncontaminated	CF < 1	low	PLI = 0	denote perfection
0 < Igeo < 1	uncontaminated to moderately contaminated	1 ≤ CF < 3	moderate	0 < PLI ≤ 1	only baseline levels of pollution
1 < Igeo < 2	moderately contaminated	3 ≤ CF< 6	considerable	PLI > 1	deterioration of soil quality
2 < Igeo < 3	moderately to strongly contaminated	CF ≥ 6	very high		
3 < Igeo < 4	strongly contaminated				
4 < Igeo < 5	strongly to extremely contaminated				
Igeo ≥ 5	extremely contaminated				

A geochemical index, proposed by Müller [58], is used to determine the degree of soil contamination:

$$I_{geo} = \log_2[C_n / (1.5 \times B_n)] \quad (1)$$

where C_n is measured concentration of the analyzed metal ($mg \cdot kg^{-1}$), B_n means geochemical background (local background of Polish soils) of a given element [55]. The constant 1.5 is the correlation coefficient of the background matrix due to lithological variability.

Another rate that allows evaluating the degree of soil condition is the Contamination Factor (CF), defined as the ratio of the concentration of the analyzed metal to the background content [59] (in this paper—the local value for Polish soils) [55]:

$$CF = C_{metal} / C_{background} \quad (2)$$

where C_{metal} means the concentration of a metal at a research point and $C_{background}$ is the geochemical background value of the metal.

Soil quality can also be assessed by calculating the Pollution Load Index (PLI), which is a comprehensive measure of contamination by more than one element [60] and refers to the contaminant load at the sampling site rather than the number of pollutants assessed [61]:

$$PLI = (CF_1 \times CF_2 \times \ldots \times CF_n)^{1/n} \quad (3)$$

where n is the number of elements determined in the samples.

2.4. Statistical Analysis

Statistical analyses began with the calculation of basic statistics of available data such as arithmetic mean, median, minimum, maximum, standard deviation, and coefficient of variation. The Shapiro-Wilk test was applied to assess the normality of the distributions of the variables analyzed. The results were considered statistically significant with an error probability of $p < 0.05$. Due to the lack of normal distributions, the nonparametric Spearman correlation test between variables was applied. A broad set of data made it possible to use a multivariate statistical method (factor analysis, FA) to reduce their number and identify the processes governing the metals. The number of factors was determined on the basis of the "scree plot" and the "Kaiser criterion". In many cases, this method was applied to identify sources of environmental contamination [62,63]. Multivariate statistical techniques such as factor analysis (FA) are used in various studies, including soil environments [64,65] or road dust [66–68] to distinguish between natural and anthropogenic impacts [68]. Therefore, in interpreting the results of factor analysis, it was assumed that the associations of a primary variable with a factor are strong when the absolute values of its loadings exceed 0.70. Puckett and Bricker [63] and Evans et al. [69] applied a similar value. The purpose of factor analysis is to interpret the effects of factors on the variables, but sometimes to perform further analysis on a reduced data set, we need to estimate the values of unobservable variables (factors 1, 2, 3). These estimates are called factor values. This article presents the distribution of factor values along the study road. The STATISTICA 13.1 software (TIBCO Software Inc., Palo Alto, CA, USA) was used for statistical calculations of the resulting data.

3. Results and Discussion

3.1. Metal Content of Roadside Soils

The basic descriptive statistics of heavy metal and organic matter (MO) content and pH_{H_2O} values in surface roadside soils from 45 research points are listed in Table 3. The factors affecting the mobility of metals in roadside soils are organic matter and pH, as shown by many authors [26,70,71]. The pH value of the investigated soils ranged from 4.45 pH (point 34—near a forest near Suwałki) to 8.14 pH (point 27—Szkocja). A part of the soils, approximately 18% of all samples, had a very acid or acid reaction, ranging from 4.45 to 6.09. All these soils came from forestal areas. Acid soils may increase the environmental risk associated with metal mobilization and increase their contribution to the biogeochemical cycle [72]. Studies have not shown a strong correlation between pH and metal contents in soils (Table 4). Some authors [73] showed that the mobility of trace elements in soil depends on changes in soil pH, while others [74] did not show clear correlations between the pH of roadside soils and the metal content in their study. About

80% of samples were with neutral or alkaline pH values found within urban, rural and agricultural areas.

Table 3. Descriptive statistics of metal concentrations [mg·kg^{-1}], pH and MO [%] in roadside soils (SD—standard deviation, CV—coefficient of variation, - (dash)—not applicable).

Parameter (n = 45)	Geochemical Background	Average	Median	Min	Max	SD	CV [%]	S-W Test
Fe	47,200 [a] 12,900 [b]	4604.89	4380.00	1350.00	9210.00	1801.99	39	0.043
Mn	850 [a] 289.0 [b]	155.86	150.98	61.80	323.92	55.39	36	0.116
Zn	95 [a] 30.0 [b]	74.80	63.18	26.46	215.02	42.97	57	0.000
Cr	90 [a] 27.0 [b]	14.24	13.80	8.13	29.47	2.94	21	0.000
Cu	45 [a] 7.1 [b]	9.65	7.52	0.51	41.39	7.83	81	0.000
Pb	20 [a] 9.8 [b]	9.43	8.08	4.10	23.49	4.18	44	0.000
Ni	68 [a] 10.2 [b]	6.56	6.58	4.60	11.68	1.21	18	0.000
Cd	0.3 [a] 0.18 [b]	1.12	1.14	0.83	1.36	0.11	10	0.741
pH	-	-	-	4.45	8.14	0.88	12	-
MO	-	4.69	4.50	2.24	9.13	1.70	36	0.013
traffic p/d	-	10,583.64	9530.00	6753.00	21,670.00	3493.30	33	0.000

Geochemical background according to: [a] [74], [b] [54].

Table 4. Spearman correlations between heavy metal concentrations and soil properties.

	traffic	pH	MO	Cu	Cd	Ni	Pb	Cr	Zn	Mn	Fe
traffic	1.00										
pH	−0.11	1.00									
MO	−0.05	−0.44	1.00								
Cu	−0.02	0.03	−0.03	1.00							
Cd	−0.17	−0.09	0.21	0.28	1.00						
Ni	−0.02	0.14	0.00	0.37	0.00	1.00					
Pb	0.41	−0.31	0.26	0.30	0.19	0.16	1.00				
Cr	−0.04	0.03	−0.18	0.43	0.03	0.50	0.33	1.00			
Zn	−0.07	0.00	0.07	0.69	0.16	0.42	0.38	0.34	1.00		
Mn	−0.48	0.17	−0.25	−0.05	0.01	0.35	−0.14	0.33	0.04	1.00	
Fe	−0.24	0.21	−0.13	0.32	0.12	0.61	0.00	0.55	0.39	0.66	1.00

The average content of organic matter (OM) in soils was 4.69% ± 1.70. The MO content in 75% of samples was in the range of 2.24–6.00%. The most abundant in MO soils (9.13%) was point 13 in Skindzierz (rural area). In rural areas, in addition to agriculture, there are activities related to the livelihood of the people living there, which may be associated with the high content of organic matter in the soils studied. The study showed a low dependence (Spearman correlation) between organic matter (OM) and contents of the following metals: Cd (0.21), Pb (0.26), and Mn (−0.25). Similar results were obtained in other studies [75,76]. The high values of correlation coefficients between the studied metals and the lack of highly significant relationships with pH and organic matter may indicate the anthropogenic enrichment of the studied soils in these elements.

The metal contents varied considerably. The average metal content in the soils at all sampling sites is classified as follows: Fe > Mn > Zn > Cr > Cu > Pb > Ni > Cd. The geochemical background established in [53] was used to assess soil contamination, and the analyses showed that all metals were at natural levels except Cd (100%), Zn (22%) and Pb (4%) (Table 3). In contrast, referring to the local background [54], the analysis showed exceedances for Cd (100%), Zn (96%), Cu (56%), Pb (29%), Mn, Cr and Ni (2%) (Table 3). Fe and Mn, as components of the crust of the earth, occur naturally in virtually all soils [77]. The average Fe content was 4604.89 mg·kg^{-1} ± 1801.99, while Mn content was 155.86 mg·kg^{-1} ± 55.39, the maximum Fe (9210 mg·kg^{-1}) and Mn (323.92 mg·kg^{-1}) contents were registered at point 25 (Szkocja village, agricultural area). Fe is present in road dust and enters the soil due to the abrasion of vehicle brake pads, which are used to accelerate and decelerate the vehicle in heavy traffic. In contrast, soil Mn concentrations are strongly associated with methylcyclopentadienyl manganese tricarbonyl (MMT), which has displaced tetraethyl lead (TEL) used as an anti-knock additive in gasoline and oils [78,79]. Mn in the soil is strongly related to MMT as they correlate with distance from roadways [80]. Furthermore, fugitive and non-combustion emissions, consisting of tire wear or dust resuspension, among others, can also be mentioned as a source of Mn in urban areas [81]. The Zn content ranged from 26.46 mg·kg^{-1} (point 19, Kamień village, agricultural area) to 215.02 mg·kg^{-1} (point 10, Karczmisko nature reserve, forestal area), an average 74.80 mg·kg^{-1} ± 42.97. The main source of Zn in the environment is motor transport. Engine oils may contain this element due to Zn addition to protect the engine against wear and tear. Zinc compounds also act as antioxidants for oil in the combustion chamber [82]. This element is added to car tires as a filler that is released during use. According to various estimates, tires contain about 1.3–1.7% [83] to 4.3% [84] Zn, and during use, a tire loses 1.5 kg of 8 kg of rubber weight due to abrasion [85]. Another source of Zn, especially in urban areas, is zinc sheets for roofing. This material corrodes easily and, due to precipitation, the metal can migrate freely into the soil [82]. The study showed an average Cr content of 14.24 mg·kg^{-1} ± 2.94. It is a prevalent heavy metal in the environment. About 60–70% of Cr emissions are connected with anthropogenic sources. Its presence in the environment depends on the proximity of emission sources and also on meteorological factors. The element is transported long distances mainly by air and then settles on soil [86]. Cr found in road dust can originate from tire friction processes, marking paint, and anticorrosion coatings on vehicles and guardrails [87]. The average Cu content was 9.65 mg·kg^{-1} ± 7.83. This element is low mobile in the soil, strongly dependent on mineral composition, pH, and humus content. It usually accumulates in the upper layers without migrating downward in the soil profile. The source of Cu in soils may be road dust fallout enriched in this element [88]. Brass and copper are components of radiators due to their high corrosion resistance and high thermal conductivity [76,89]. This metal also consequently penetrates the environment, due to automotive oil pump wear or corrosion of metal parts that come in contact with oil [68]. Wear of automotive brake pads and linings is also a cause of Cu release into the environment [90]. The study showed the following Pb and Ni contents in the soil, which fall within the ranges of 4.10–23.49 and 4.60–11.68 mg·kg^{-1}. The presence of Pb in roadside soils may be the result of its addition to gasoline, because it still reflects a significant degree of historical contamination and its long half-life in the soils surrounding the roads, especially those of urban origin [91]. In agricultural areas, the use of compound and phosphate fertilizers and pesticides may be responsible for higher Pb and Ni concentrations [92,93]. The study showed the Cd content in soils ranging from 0.83–1.36 mg·kg^{-1}, with an average of 1.12 mg·kg^{-1} ± 0.11. The Cd content in the soils was also the lowest compared to the other elements analyzed, which is related to the geochemical properties of this metal. All analyzed samples exceeded the geochemical background value, indicating that the soils were enriched in Cd and their origin is anthropogenic. Presumably, the speed of motor vehicles plays a role in the contamination of soils with Cd. In an urban area, vehicles travel much slower than in a non-urban area. The volume of automobile traffic had a massive effect on heavy metal contamination in the soil [13]. The higher speeds reached by cars mean that tires and road surfaces wear out faster, which increases the metal content in roadside soils [10,13]. The Cd found in the soil has high mobility, which poses a risk to human health, especially since this element is extremely toxic. Authors [13,15] found that traffic emissions have a significant impact on soil contamination by Ni, Pb, and Cd along streets. Weather (drought periods or rainfall intensity) may also be a crucial factor that affects metal accumulation in soils near roads.

3.2. Evaluation Methods (I_{geo}, CF, PLI)

To determine the degree of anthropogenic impact on the soils studied, selected indicators of pollution—I_{geo}, CF and PLI—were used, calculating their values regarding the local geochemical background.

The average I_{geo} values, without distinction to several areas, were in the following order: Fe < Mn < Cr < Ni < Pb < Cu < Zn < Cd. All values of this index for elements such as Ni, Cr, Mn and Fe allowed the classification of soils analyzed as class 0, that is, as not contaminated with the above-mentioned metals (Figure 2). The I_{geo} index values for Cd were much higher than any of the other heavy metals and allowed assignment to classes 2 and 3, indicating moderate to severe contamination. Some of the measurement points were also moderately contaminated with Zn, Cu, and Pb.

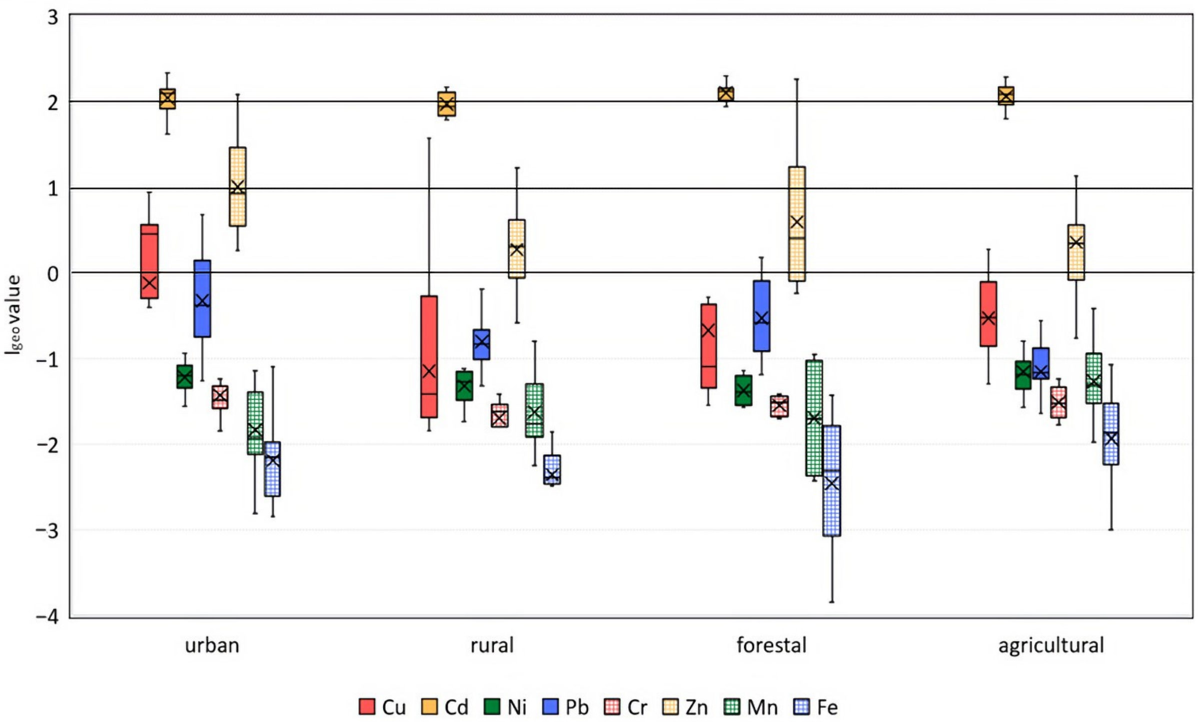

Figure 2. Box plot for I_{geo} of heavy metals in roadside soil.

The average CF index values took a series similar to I_{geo}: Fe < Cr < Mn < Ni < Pb < Cu < Zn < Cd. The results suggest that the soil is not contaminated (Fe, Mn, Cr, Pb, Ni) or moderately (Zn and Cu) contaminated near the road (Figure 3). The results indicated a very high contamination of the studied area with Cd.

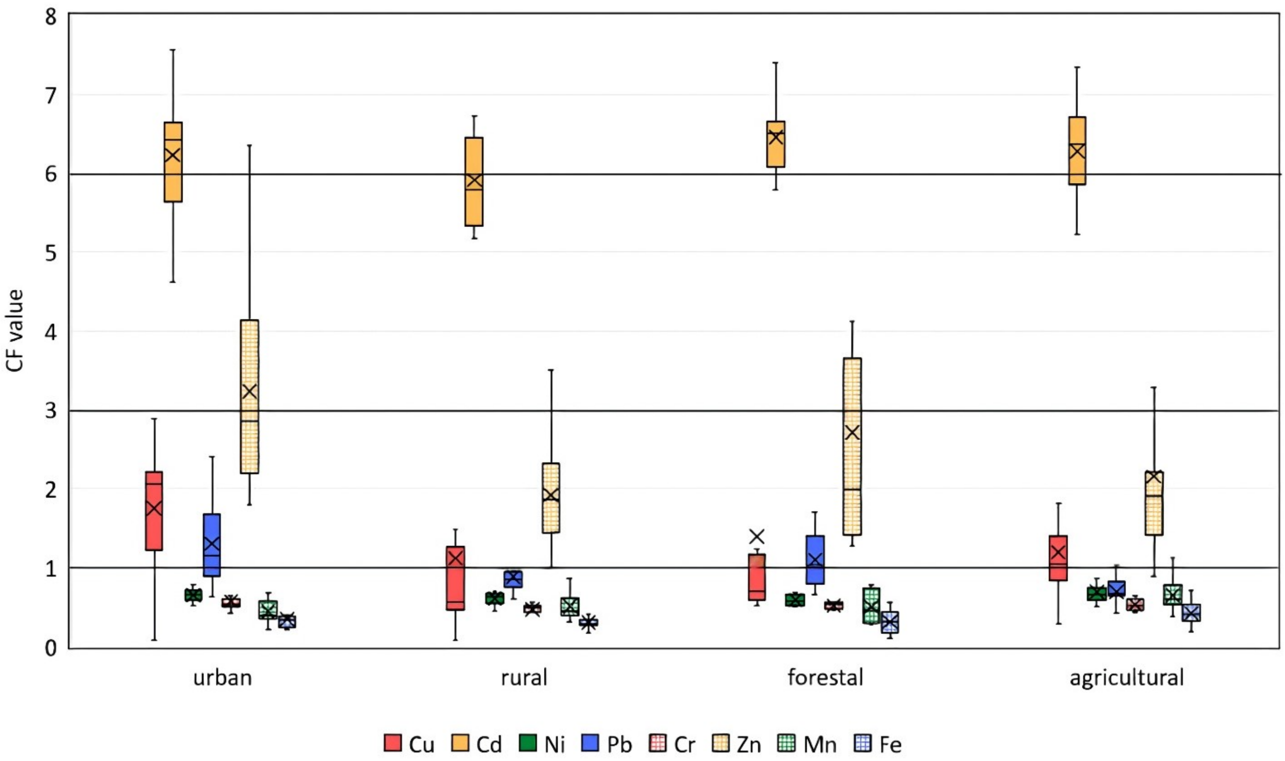

Figure 3. Box plot for CF of heavy metals in roadside soil.

The PLI detects the deterioration of soil quality due to heavy metal contamination. The PLI values in the research indicate no and minimal metal pollution, although there are also areas along the route where contamination is present. Among the sites where PLI > 1, the points in urban areas dominate (Figure 4).

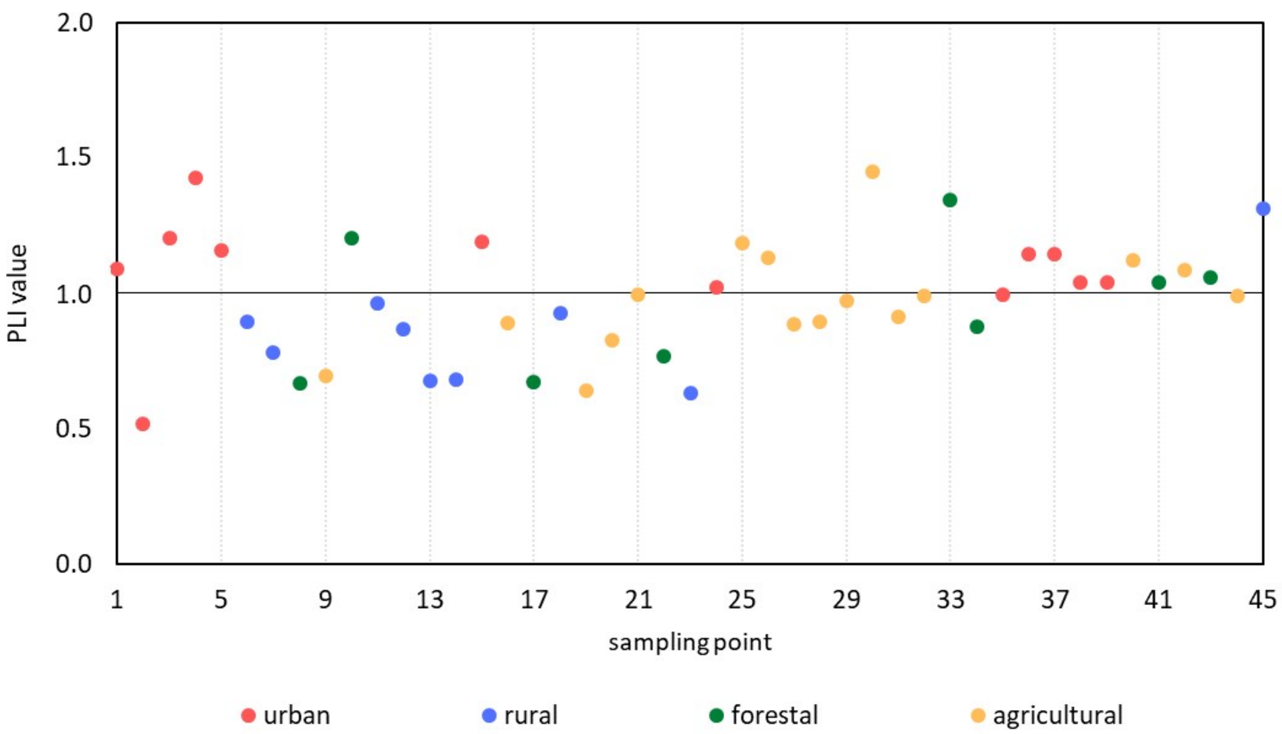

Figure 4. Cross plot of heavy metal PLI in roadside soil.

3.3. Spatial Distribution of Metals in Roadside Soils

The analysis of the content of heavy metals in soils according to different sources from the literature (Table 5) shows the differentiation of the results within and between particular groups. The average amount of Cd in the analyzed roadside soils was usually higher compared to the studies of other authors, which reflect the I_{geo}, CF and PLI values. The contents of Cu, Ni, Pb, Cr, Zn, and Mn were generally lower or at levels similar to those of the references cited in the table; nevertheless, it should be noted that none of the mentioned works performed an analysis of the amount of Fe in the soils.

Table 5. Literature values of metal concentrations in soils near the roadway ($mg \cdot kg^{-1}$).

Fe	Mn	Zn	Cu	Cr	Pb	Ni	Cd	Location	Reference
Residential Areas (urban and rural)									
NA	512.2	274.6	41.6	56.1	44.2	34.7	0.34	Shanghai, China	[32]
NA	92–599	10–88	4–20	18–29	16–144	7–20	0.06–0.59	Melbourne, Australia	[33]
NA	741	NA	21.0	36	17	NA	0.54	Toronto, Canada	[34]
NA	NA	142	52.3	70.9	104	40.3	0.31	Siena, Italy	[35]
Forestal Areas									
NA	NA	NA	1.32–11.25	NA	7.88–54.27	NA	0.096–1.19	Vilnius-Klaipėda highway, Lithuania	[36]
NA	470	133	39.9	39.0	76.3	24	0.477	Hangzhou, China	[45]
NA	NA	71.4	16.8	NA	39.1	28.6	0.123	Liaoning Province, China	[38]
NA	NA	52.56	18.82	86.80	25.68	25.96	0.44	Yunnan Province, China	[39]
Agricultural Areas									
NA	83–1122	10.5–1547	NA	3.7–75.3	7.1–50.1	2–27	NA	Poland	[40]
NA	NA	13.1–152.9	1.5–226.2	NA	6.6–101.3	NA	0.1–1.54	Poland	[41]
NA	NA	78.2	20.2	NA	40	29.8	0.136	Liaoning Province, China	[38]
NA	NA	11.4–489	7.4–146	2.4–50.5	6.1–66.1	2.83–113	0.06–2.08	Thailand	[42]

ND—not detected, NA—not available.

Figure 5 shows significant diversity in the contents of individual elements in the roadside soils. In the case of most metals, relatively high concentrations were observed in the vicinity of Białystok, Augustów, and Suwałki, that is, urban areas with naturally high car traffic intensity. Additionally, these locations have a more compact pattern of detached houses heated by fossil fuels. Significant amounts of Mn, Cr, Ni, and Cd were observed in agricultural areas. There is considerable Cd contamination of the regions along the road, and high levels of Cd can be registered at all consecutive points from 32 to the end of the analyzed route, which may explain the intensive traffic in the border areas.

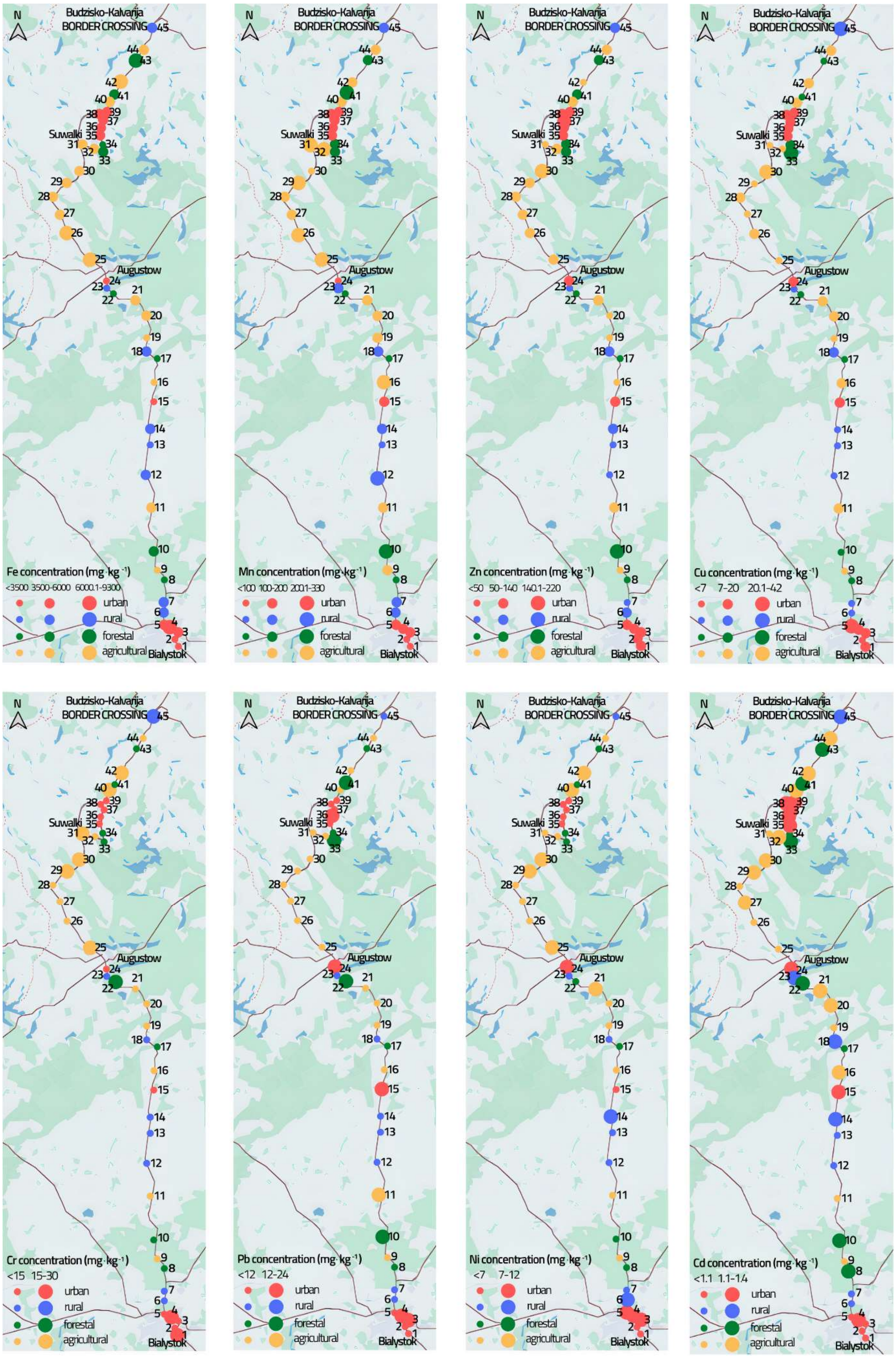

Figure 5. Spatial diversity of the metals along the route analyzed, taking into account the type of land use at the research points.

3.4. Identification of Pollution Sources Using Statistical Analyses

Analyses began with basic statistics of the metals studied in roadside soils. As shown in Table 2, the CV values of all metals followed the order Cu (81%) > Zn (57%) > Pb (44%) > Fe (39%) > Mn (36%) > Cr (21%) > Ni (18%) > Cd (10%). The high CV value for Cu, Zn and Pb indicates high variability and suggests that the sources of metals may have external origins. Moreover, it suggests a common source of Cu, Ni, Pb, Cr, Zn, and Fe, which may be vehicle traffic. However, the analysis of Spearman correlation coefficients between vehicle traffic volume and the content of the metals studied does not support the above thesis. Studies [94–96] also did not show a direct relationship between vehicle traffic volume and the content of some metals in soils. Presumably, this is associated with stationary sources of some metals that are not directly related to automobile traffic, for example, the presence of Zn, Cu, and other metals in the metal roadside covers. The statistical relationship between Cu and Zn (r = 0.69) in the soils studied can confirm the above hypothesis (Table 4). According to [97,98], the correlations between the contents of some components enable indicating their potential sources. A strong positive correlation between almost all metals indicates similar sources. Generally, an increase in elemental contents compared to background levels indicates anthropogenic influences [98]. Metals such as Cd, Cu, Pb, and Zn are good indicators of soil contamination because they are present in gasoline, automotive components, lubricating oils, and industrial exhaust [22]. The surface of roadside soil near heavy traffic in urban areas is an indicator of heavy metal pollution from precipitation [27,28,99]. Based on Spearman correlation, only the correlation between traffic volume and Pb contents (r = 0.41) was found, which is related to the past when traffic volume had a close relationship with the amounts of Pb emitted to soils near roads. The study [100] also indicates a relationship between the Pb and Zn content in the road soils and automobile traffic. In the past, leaded gasoline was applied to power motor vehicles. Typically, higher metal content is expected in the soil in areas with higher traffic intensity, although the literature is inconclusive [101]. The low values of the correlation coefficient between metal content indicate that they may come from different sources [102]. Research shows [103] that the most contaminated soils are located near roads with a high traffic volume; on the other hand, among Cd, Cu, Pb, and Zn, only Pb was significantly correlated with the intensity of road traffic. The authors [94,104] showed no significant relationship between traffic volume and Zn or Cu content in the soils studied. Correlations between Fe, Mn and Ni, Cr and Zn (r = 0.33–0.66) were noted. The results obtained confirmed the observations [105,106] that claim that metals form very stable complexes with Fe and Mn oxides.

The multivariate analysis confirmed the above thesis. In addition, it allowed one to determine which metals are most important in soil contamination and what their crucial sources are. Based on the multivariate analysis, three factors that constitute about 60% of the global variability of the phenomena and processes occurring in the analyzed system were determined on the basis of the "scree plot" and the "Kaiser criterion". Table 6 shows the sets of factor loadings that shape the interpretable factors (e.g., processes). Factor 1 accounts for 24% of the total variance and is positively correlated with Ni, Mn, and Fe. Factor 2 explains 19% of the variance and is positively correlated with Cu, Pb, and Zn, while factor 3 explains 16% incident to traffic volume. Factor 1 is not related to the effects of incomplete combustion of fuel, but the processes of abrasion of brake pads, brake and clutch discs, corrosion of car bodies and road infrastructure, as well as deterioration of the road surface [19–21,107]. The presence of Fe and Mn is significant, which may indicate processes of binding and immobilization of Ni by oxides of the mentioned metals. As mentioned above, currently Mn is added to fuels instead of the previously used Pb, which may indicate the direct impact of motor traffic on the soils studied. However, previous analyses of Spearman correlation coefficients do not support this thesis.

Table 6. Grouping of elements tested based on multivariate analysis (FA).

Elements	Factor 1	Factor 2	Factor 3
Fe	0.83	0.26	0.06
Mn	0.87	−0.21	−0.02
Zn	0.21	0.71	−0.26
Cu	0.11	0.70	−0.27
Cr	0.24	0.57	0.36
Pb	−0.20	0.76	−0.01
Ni	0.73	0.35	0.21
Cd	0.09	0.19	−0.64
pH	0.26	−0.11	0.53
MO	−0.28	0.09	−0.51
traffic	−0.42	0.36	0.71
Variance [%]	24	19	16

Similar to the first factor, the second factor with non-fossil sources is related to the functioning of motor transport. It indicates the presence of Cu and Zn in the soils, but the scale of the phenomenon is already smaller than the first factor (which explains 19% of the variability). Additionally, the presence of Zn may be an effect of tire grinding against the road surface during the braking of motor vehicles. The second factor also shapes the Pb content in the investigated soils and is correlated with it. The elevated concentration of Pb is related to the past when this element was added to gasoline in the form of complex compounds as an antiknock agent and to increase its octane number [85,108]. Previous analyses of Spearman correlation coefficients have shown a relationship between automobile traffic volume and Pb content. The former factor can be described in part as geogenic and the latter as anthropogenic.

Figure 6 shows the dynamics of the changes in factors values at each research point. The highest factor values representing factor 1 were on the road between research points 25 and 33. The average traffic volume is not the highest on this section of the road compared to the others, which is the result of the collected data. As shown earlier, factor 1 correlated with Ni, Fe, and Mn. Therefore, an additional source of detected metals was sought. Spatial analyses of the areas through which the road passes showed that the section of the road between points 25 and 33 passes through agriculturally used land. This road section from Augustów to Suwałki is part of the E67 expressway and the Via Carpatia route. Except for previously identified sources of Fe and Mn, soil minerals contained in the bedrock and various organic and mineral compounds supplied to the soil, for example, as a result of mineral-organic fertilization on agricultural lands, are other sources [109].

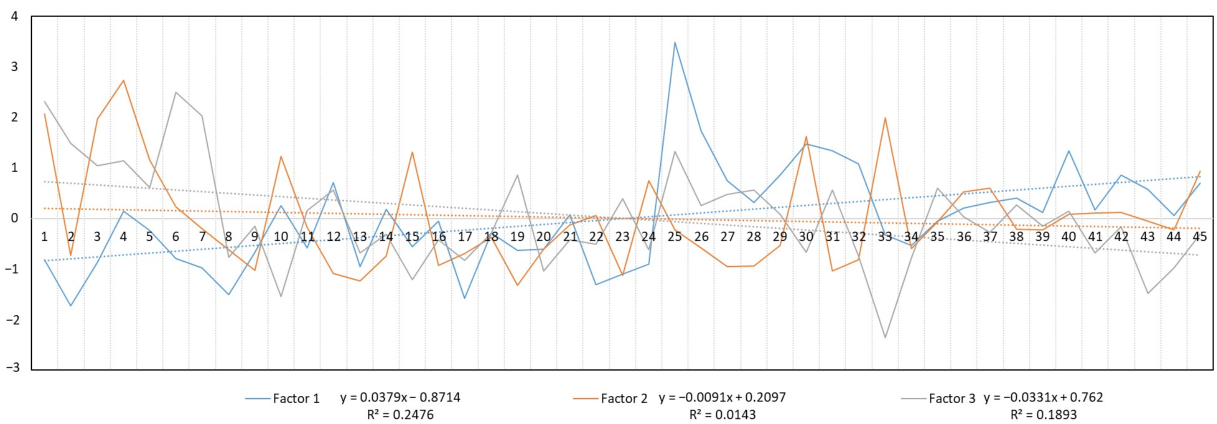

Figure 6. Factor scores in research points.

The high values representing factor 2 are evident on the road section between points 3 and 6. These points were located in the urbanized area of Białystok. As shown earlier, factor 2 has an anthropogenic character associated, in particular, with the traffic and urban infrastructure of Białystok. The most important sources of heavy metals in cities include: (i) dust and aerosol particles (from fossil fuel combustion, motor vehicles, etc.); (ii) corrosion of metal structures, including galvanized roofs and fences; (iii) use of man-made building materials; (iv) agricultural and garden activities (use of fertilizers and composts); (v) deposition of solid or liquid waste on the surface of soils; and (vi) use of paints and other decorative materials [110]. High concentrations of some metals were found in road soils of the cities of Białystok, Suwałki, and Augustów. The course of factor values (Figure 6) related to factor 2, correlated with Cu, Pb, and Zn, is conditioned by intensive car traffic, also in the past (gasoline with Pb) in the cities. The lowest factor values (F3) associated with car traffic intensity were recorded at points 10, 33 and 43, which are placed in forestal areas. In general, an upward trend of factor 3 is evident along the road studied, which is related to a gradual increase in car traffic towards the state border (Budzisko).

Research indicates that most heavy metals can accumulate and pose a risk to human and animal health, especially when they reach levels higher than those naturally occurring in surface soils [111]. Various studies have shown that heavy metals such as Pb, Cd, and Ni are responsible for some diseases that have fatal effects on humans and animals. Due to their accumulation and long-term retention by plants and animals, metals become very dangerous [112]. Therefore, an appropriate land-use policy must be applied that would prohibit the use of roadside land, especially those within a distance of about 30 m on both sides of the road, for agricultural purposes and livestock grazing to reduce the concentration of toxic elements in the food chain and ecosystems due to vehicle emissions [113].

4. Conclusions

The study determined the content and spatial distribution of heavy metals (Fe, Mn, Cd, Pb, Cr, Ni, Zn and Cu) in the top layer of roadside soils along the trunk road Białystok–Budzisko.

Metal concentrations in roadside soils occurred in the following order: Fe > Mn > Zn > Cr > Cu > Pb > Ni > Cd. The mean content of Cd, Zn, Cu, and Pb was higher than the geochemical background values of the Polish soils. Moreover, the values of I_{geo} indicated moderate to strong contamination with Cd, while the soils were moderately contaminated with Zn, Cu, and Pb. The dynamics of changes of the factor values at each research point presented in this paper showed the highest factor values for points located in agricultural and urban areas.

The level of urbanization, road age, atmospheric conditions, and agricultural production on soils can significantly affect the distribution of trace metals in roadside soils, but the crucial source of metal pollution is road transport, depending on its intensity, number, type and speed of vehicles.

The results of this paper are relevant to the prevention and control of heavy metal pollution in roadside soils. The work can contribute to reducing the concentration of toxic elements appearing in the food chain and ecosystems due to vehicle emissions. We suggest that the first step in this direction should be an appropriate land-use policy that would prohibit the use of roadside land, on either side of the road, for agriculture and livestock grazing.

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