

Article

# Protected Areas vs. Highway Construction—Problem of Environmental Pollution

Anna Turek \*, Kinga Wieczorek \*, Małgorzata Szczesio and Jakub Kubicki

Institute of General and Ecological Chemistry, Lodz University of Technology, 116 Żeromskiego Str., 90-924 Lodz, Poland; malgorzata.szczesio@p.lodz.pl (M.S.); jakub.kubicki@p.lodz.pl (J.K.)

\* Correspondence: anna.turek@p.lodz.pl (A.T.); kinga.wieczorek@dokt.p.lodz.pl (K.W.); Tel.: +48-42-631-31-23 (A.T. & K.W.)

**Abstract:** Landscape parks are protected areas, attractive to live close to and relax in. In parks, economic and agricultural activities are allowed to a limited extent. The high interest in these areas is the cause of unfavorable changes, including environmental contamination. This paper presents the results of soil quality research in Wzniesienia Łódzkie Landscape Park (Poland). The analyses were performed in 2008, before the construction of the highway in the park began, and after its completion in 2016. The contents of Zn, Cu, Pb, Cd and Ni were determined by flame atomic absorption spectrometry (FAAS). The descriptive statistics, principal component analysis (PCA), cluster analysis (CA), and geographic information system (GIS) were used to assess the impact of different sources on the content of metal in the soil. Over the period of 8 years, there has been an increase in pH and the level of metals, especially nickel. The changes in the metal content result from the different land use, especially abandonment of agricultural activity and emissions related to the construction of the A1 highway.

**Keywords:** soil contamination; highway; landscape park; heavy metals; monitoring; GIS; FAAS



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## 1. Introduction

Soil plays a crucial role in the functioning of terrestrial ecosystems because it serves as a medium for plant growth and the habitat for other organisms. It is commonly believed that protected areas, such as national or landscape parks, are unpolluted areas, safe for living organisms. However, in many cases, these areas are only protected to a limited extent. Therefore, they are often influenced by emissions from the broadly understood human activity. According to the IUCN Guidelines [1], the areas with interaction between humans and nature belong to the V category of protected areas. Landscape parks belong to this category, and are objects of lower protection regime than national parks. The landscape park “covers the area protected because of its specific biotic and abiotic values, as well as preserves the historical and cultural heritage and landscape values in order to maintain and popularize those values in the conditions of sustainable development” [2,3]. The limited scope of the protection of landscape parks means that in Poland, certain forms of economic activity ranging from agriculture and small business to open-cast mining are permitted in these areas [4,5]. The buffer zone (i.e., a protection zone bordering the landscape park, designated to protect against external threats resulting from human activities [6]) around landscape parks is also attractive to investors from the construction industry and potential home buyers. The development of residential buildings is a source of adverse changes in the environment, related to the increase in pollution from municipal sources and excessive exploitation of drinking water intakes. This results in a lower water level, spring water begins to disappear, which in turn affects the flora and fauna of this area. The legally sanctioned growing influence of local authorities on decisions regarding spatial development has negative consequences for protected areas [7,8]. The conflict between the necessity to protect areas valuable for nature and the investment policy is usually

resolved in favor of the latter. The effect of such activities is the reduction in protected areas, including those for the development of the road network. It causes a number of problems, both for the biosphere and the quality of water, soil and air. The reduction in costs related to the maintenance of habitats and wildlife crossings causes losses in the population of valuable flora and fauna species [7,9–11]. The construction of road infrastructure itself is also a major challenge [12]. Works should be planned carefully, not only in terms of technique and economy, but also in the way that protects habitats and reduces stress for wildlife.

Changes in land-use can also have positive effects on the ecosystem. For example, the abandonment of agricultural activity due to the housing and road infrastructure development can increase biodiversity, promote the creation of ecological corridors as well as prevent soil erosion and restore old ecosystems [13]. As the secondary succession progresses, changes in the chemical composition of soils e.g., in the content of organic carbon, potassium, phosphorus and pH are also observed.

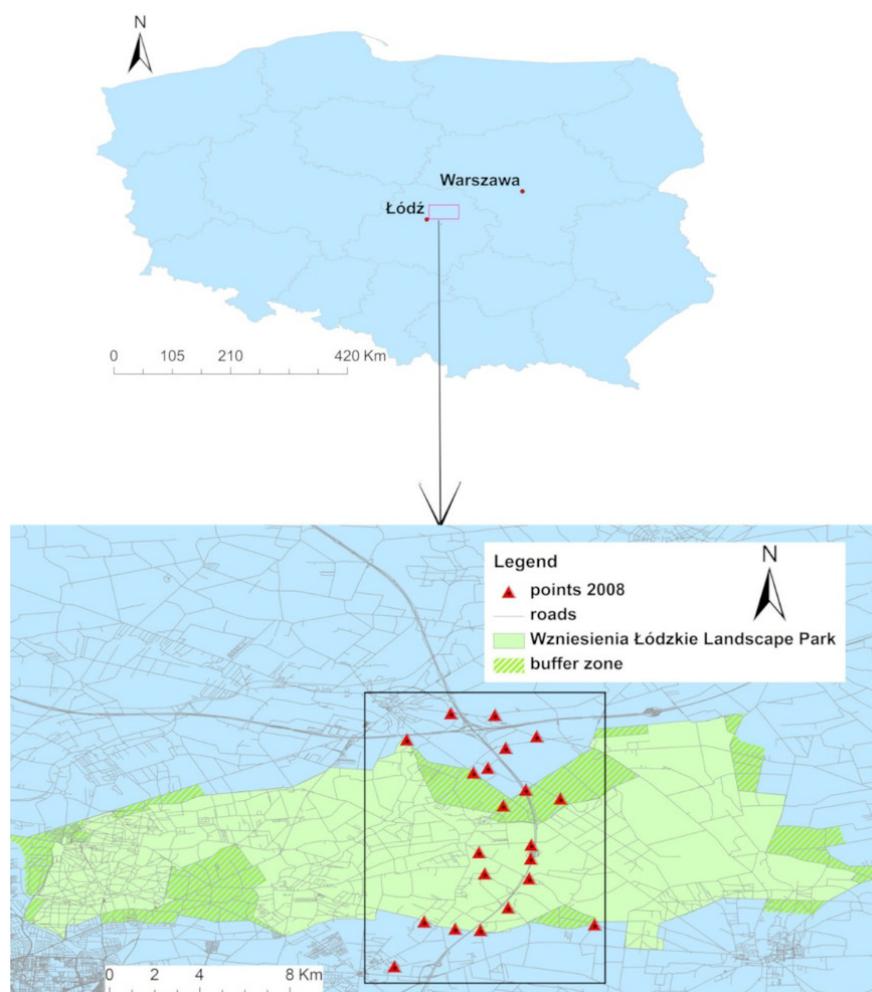
The chemical composition of soils in protected areas is monitored much less frequently than the condition of flora and fauna. Most of the work concerns the impact of road transport on soil pollution with metals, but only few of them present the results of the studies conducted in the protected areas such as landscape parks or national parks [14–17]. The authors emphasize that road transport is a source of metal emissions (mainly Zn, Pb, Cd), with trucks having the largest share. Literature data which deal with chemical effects of construction materials on the environment also point to these materials as a possible source of soil contamination. Different kinds of waste in the form of additives for concrete, cement, asphalt, or alone as road surface substrates, are commonly used as construction elements [18–22]. Waste used as by-products makes it possible to save primary raw materials (economic factor), and at the same time to reduce the amount of stored waste (ecological factor). Such additives may, however, be a source of soil contamination with heavy metals (e.g., Zn, Pb, Cd), as well as K, Na (ashes). The solidification of waste does not completely prevent the leaching of metals into the environment [18]. Factors that affect the susceptibility of metals to leaching are, for example, the type and origin of waste, atmospheric precipitation (especially acid rain), as well as the type of metal binding in the material. It has been found that metals in the amorphous phase are easier to leach than those in the crystalline phase. Secondary fuels used in the production of Portland cement clinker are also a source of heavy metals. Research on the release of heavy metals from cement and concrete has been carried out in Europe since 2005 [22]. Incineration fly ash and incineration bottom ash used in the asphalt mixture are the source of metals (Zn, Pb, Cu, Cr, Cd) migrating to the soil and groundwater [19]. The source of pollution is also the emission of organic and inorganic compounds from the machinery operating on the construction sites.

This study attempts to assess the impact of land management changes on the content of cadmium, copper, lead, nickel and zinc in the soils of Wzniesienia Łódzkie Landscape Park (PKWŁ—Park Krajobrazowy Wzniesień Łódzkich) (Poland). Selected elements are widespread in the environment, they can be introduced into soils with waste and municipal sewage; they are also most often mentioned as the main pollutants emitted from agricultural sources, industry and means of transport. These metals are also listed as the priority pollutants on the US EPA's list. The aims of the study were: (1) monitoring the content of metals in soils in 2008 and 2016; (2) examining the impact of a large road investment on the level and distribution of potentially mobile trace metal fractions in the PKWŁ area. The following research hypotheses were assumed: (a) the construction of the highway increased soil contamination; (b) the road investment does not change the soil quality or is only one of the factors of such a change.

## 2. Materials and Methods

### 2.1. Study Area

Wzniesienia Łódzkie Landscape Park (Figure 1) was established in 1996. It is located on the north-eastern outskirts of the Łódź agglomeration. The western part of PKWŁ lies within the boundaries of the city and forms a large urban forest complex—Łagiewnicki Forest. PKWŁ covers an area of 11,580 ha, and additionally 3083 ha is a buffer zone. The purpose of PKWŁ is to preserve the most valuable part of the upland landscape, unique in central Poland, with a border zone of the Łódź Heights, shaped under the Pleistocene glaciation. Another goal is to protect natural resources, including the partially preserved natural flora. The PKWŁ area is covered with Pleistocene glacial and fluvioglacial sediments (gravel, sand and clay), and locally Holocene ones. The Quaternary layer reaches 150 m in some places. Under the Quaternary layer there are Mesozoic (Cretaceous, Jurassic) sediments, and locally also Paleogene and Neogene ones [23–26]. In the area of PKWŁ there are Cambisols (Eutric and Dystric), Albic Luvisols, Brunic Arenosols, Gleyic Phaezems and locally—Dystric Gleysols and Stagnosols, Histosols and Technosols. Two Natura 2000 sites (Buczyna Janinowska code PLH100017 and Wola Cyrusowa code PLH100034) have been established in the park. The sources of the Bzura River—one of the main rivers in the region (166 km in length) and its tributary—Moszczenica (55 km)—are located in PKWŁ. At the time PKWŁ was created, arable land, orchards and grasslands amounted to 6384 ha. About 3845 ha were covered by forests with the largest forest complex, Las Łagiewnicki, located within the city of Łódź.

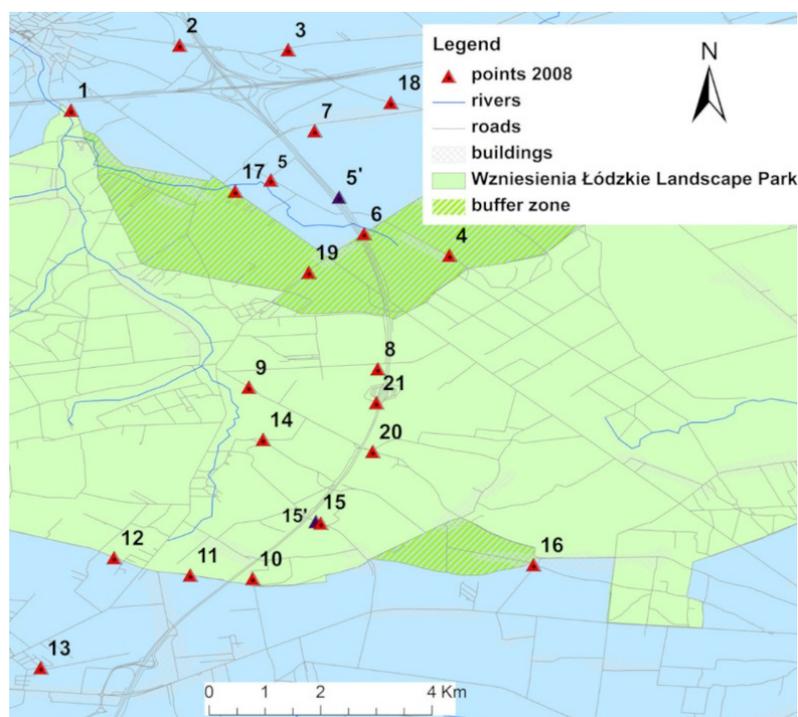


**Figure 1.** Location of PKWŁ.

PKWŁ is located in the municipalities of Łódź, Nowosolna, Brzeziny, Dmosin, Stryków and Zgierz (it borders with these localities), and its location in central Poland and the vicinity of the Łódź agglomeration pose a number of threats [7,9]. The first factor is the rapid urbanization of the area attractive in terms of landscape values and the vicinity of Łódź. This problem results from the lack of spatial development plans for part of the PKWŁ area. The expansion of residential and recreational buildings worsened the landscape values (fencing the area, installation of transmitters, power lines). The problem was also the increase in emissions of municipal pollutants (sewage, waste) and over-exploitation of water resources. Lowering of the groundwater table resulted in the disappearance of numerous springs on the slopes of the hills. Changes in water conditions and an increase in population had a negative impact on the flora and fauna. The last element of the transformation of this area was the construction of A1 highway section (north to south direction) running through the center of PKWŁ. In the vicinity of the northern border of the park, there is also a junction of A1 and A2 highways and a logistics hub. Currently, the area of PKWŁ is not particularly exposed to industrial pollution. Since the collapse of industry in the 1990s, small and medium sized enterprises have dominated in Łódź.

## 2.2. Soil Sampling

Soil samples were collected twice in 2008 (before commencing the construction of A1 highway section) and in 2016 (after 1–2 months of its functioning). The distance between the studied area and the center of Łódź is 10–20 km. In 2008, sampling sites were randomly selected within 2 km of the mapped construction route (Table 1, Figure 2). At each of the locations, one composite sample, consisting of 15–20 sub-samples, was taken. The total mass of soil collected at a given site was about 0.5 kg. Samples were taken using the Egner's stick from 20 cm of the top layer of soil. The location of sampling points was determined by handheld Global Positioning System (GPS) (MobileMapper 50). Soils were dried at room temperature, passed through a 2 mm stainless steel mesh and stored in Ziplock bags.



**Figure 2.** Location of sampling sites (5' and 15'—points 2016).

Table 1. Description of sampling sites.

No.	Latitude	Longitude	Site Feature		pH-H <sub>2</sub> O		pH-KCl		Organic Matter [%]		Textural Classification [27,28]
			2008	2016	2008	2016	2008	2016	2008	2016	2008/2016
1	51°53'17" N	19°36'31" E	grassland	grassland	6.3	6.2	4.9	5.7	5.1	5.3	sandy loam
2	51°53'55" N	19°37'34" E	cropland	fallow <sup>(1)</sup>	7.0	7.1	6.4	6.9	2.9	3.2	sandy loam
3	51°53'52" N	19°38'37" E	cropland	cropland	5.7	6.3	4.1	5.3	3.8	3.7	sandy loam
4	51°51'51" N	19°40'11" E	cropland	cropland	5.7	7.5	4.2	7.4	4.4	4.3	sandy loam
5	51°52'35" N <sup>(a)</sup>	19°38'27" E <sup>(a)</sup>	pasture	cropland	5.9	5.4	4.8	4.3	3.3	3.0	sandy loam
	51°52'25" N <sup>(b)</sup>	19°39'07" E <sup>(b)</sup>									
6	51°52'04" N	19°39'21" E	cropland	cropland	6.5	7.2	5.2	7.0	3.6	3.7	sandy loam
7	51°53'04" N	19°38'52" E	fallow <sup>(1)</sup>	fallow <sup>(2)</sup>	5.4	6.6	3.8	6.0	4.5	4.3	sandy loam
8	51°50'44" N	19°39'29" E	fallow <sup>(1)</sup>	fallow <sup>(1)</sup>	7.3	6.5	6.4	6.1	3.9	4.5	sandy loam
9	51°50'34" N	19°38'14" E	grassland	grassland	5.8	6.1	4.2	5.4	3.3	3.1	sand
10	51°48'41" N	19°38'16" E	fallow <sup>(1)</sup>	fallow <sup>(3)</sup>	6.5	6.0	5.0	5.1	3.8	4.5	loamy sand
11	51°48'43" N	19°37'40" E	cropland	fallow <sup>(1)</sup>	5.8	7.0	4.4	7.0	3.5	3.8	loamy sand
12	51°48'53" N	19°36'56" E	cropland	cropland	5.4	6.6	4.1	6.1	4.2	4.1	loamy sand
13	51°47'49" N	19°36'13" E	fallow <sup>(1)</sup>	fallow <sup>(2)</sup>	8.0	7.3	7.6	7.3	3.3	3.0	loamy sand
14	51°50'03" N	19°38'22" E	cropland	cropland	6.6	7.1	5.3	6.9	3.2	3.0	loamy sand
15	51°49'14" N <sup>(a)</sup>	19°38'56" E <sup>(a)</sup>	cropland	fallow <sup>(1)</sup>	6.1	5.4	4.7	4.3	3.8	4.0	sandy loam
	51°49'15" N <sup>(b)</sup>	19°38'53" E <sup>(b)</sup>									
16	51°48'49" N	19°40'59" E	cropland	cropland	6.4	5.6	5.1	4.4	3.8	3.7	loamy sand
17	51°52'29" N	19°38'06" E	cropland	cropland	6.0	6.9	4.7	6.6	3.3	3.4	loamy sand
18	51°53'21" N	19°39'37" E	cropland	cropland	5.1	5.7	3.8	4.5	3.6	3.7	sandy loam
19	51°51'41" N	19°38'49" E	cropland	cropland	5.3	7.1	5.2	6.5	4.0	4.0	sandy loam
20	51°49'56" N	19°39'26" E	fallow <sup>(1)</sup>	fallow <sup>(1)</sup>	5.5	5.5	4.0	4.3	3.6	5.6	sandy loam
21	51°50'24" N	19°39'28" E	fallow <sup>(1)</sup>	fallow <sup>(1)</sup>	5.9	6.8	4.8	6.3	2.6	2.9	sandy loam

<sup>(a)</sup> 2008; <sup>(b)</sup> 2016; <sup>(1)</sup> fallow grassland; <sup>(2)</sup> fallow goldenrod; <sup>(3)</sup> fallow bush [12].

2.3. Soil Characterization—Analytical and Statistical Methods

Soil characterization is presented in Table 1. Texture classes of soils were assigned based on the sieve and hydrometer analyses [27,28]. The content of the organic matter (OM) was measured by the gravimetric method (ignition of soil at 500 °C) [29]. Potentiometric determination of soil pH was carried out in the water and 1 mol/L KCl suspensions (soil:extractant ratio 1:2.5 m/V) [30] using the Mettler Toledo Delta 350 pH-meter equipped with the combination pH electrode. In accordance with Polish Standards [31,32], mobile, potentially assimilated fractions of Cd, Cu, Pb, Ni and Zn were determined after the extraction of a 5 g sample with 50 mL 1 mol/L HCl. The total contents of metals were determined after microwave wet digestion (Anton Paar Multiwave 3000, Graz, Austria) with aqua regia and concentrated HF according to the user manual. All reagents were Suprapur or ACS grade. The metal concentration was measured with a flame atomic absorption spectrometry (FAAS, GBC 932 plus spectrometer, Melbourne, Australia). Each sample was measured three times. The mean content of metals is given in Tables 2 and S1. For soil, the certified reference material for extraction metals with 1 mol/L HCl was not commercially available. To guarantee quality, the CRM 7002 Light Sandy Soil (Analytika Co. Ltd., Prague, Czech Republic) was used (Table S2).

The soil contamination levels were estimated by the standard geochemical parameters: contamination factor CF, geoaccumulation index  $I_{geo}$  and enrichment factor EF (Fe was used as a reference value)—Table 3. Furthermore, soil contamination by a potentially assimilated fraction of metals was assessed based on the total index of heavy metal loading  $S_j$  [33,34]—Table 2:

$$S_j = (y_1 + y_2 + \dots + y_j) \tag{1}$$

$$y_j = \sum [(C_j - C_{av})/C_{av}] \tag{2}$$

where:  $C_j$  is the content of metal at each sampling site;  $C_{av}$  is the average content of metal at all sampling sites.

Basic geographic data were acquired from the Head Office of Land Surveying and Cartography [35]. The inverse distance weighted (IDW) [36] of ArcMap 9.2 (Esri Redlands, New York, CA, USA) software was used to interpolate all study parameters and generate geochemical maps [37].

Statistical methods were performed with the Statistica 10 (StatSoft Inc., Tulsa, OK, USA). The distribution normality was assessed by the Shapiro-Wilk’s (S-W) test—Table 2. Spearman’s and Pearson’s correlation coefficients were calculated for non-normal and normal distributed data, respectively (Tables 4 and S3). To visualize the data set, principal component analysis (PCA) and cluster analysis (CA, applying Ward’s method with squared Euclidean distances) were used.

Table 2. Metal contents in soils (extractant 1 mol/L HCl).

No.	Zn [mg/kg]		Cu [mg/kg]		Pb [mg/kg]		Cd [mg/kg]		Ni [mg/kg]		$S_j$	
	2008	2016	2008	2016	2008	2016	2008	2016	2008	2016	2008	2016
1	3.40	7.54	1.48	2.39	7.10	8.43	0.12	0.17	0.32	2.50	−1.52	1.40
2	7.80	6.20	3.98	2.11	10.1	9.66	0.22	0.14	0.80	1.23	2.29	−0.08
3	4.18	2.64	1.51	1.44	8.31	8.28	0.12	0.11	0.47	0.76	−1.00	−1.70
4	4.50	19.0	1.70	3.32	9.50	13.5	0.10	0.32	0.70	1.90	−0.51	4.65
5	11.9	3.42	4.10	1.20	7.90	8.02	0.10	0.08	0.40	0.63	1.31	−2.02
6	6.51	6.21	2.42	2.10	9.13	9.23	0.18	0.18	0.75	1.40	0.81	0.27
7	5.60	9.50	1.40	2.17	8.10	8.75	0.10	0.20	0.70	1.46	−0.62	0.96
8	8.40	5.02	1.70	2.32	9.00	12.1	0.20	0.20	1.10	1.78	1.46	0.94
9	3.40	3.23	1.00	1.09	6.10	5.69	0.10	0.09	0.40	1.11	−1.89	−1.87
10	6.30	6.67	2.00	2.12	10.4	11.9	0.20	0.19	0.60	0.87	0.63	0.25
11	4.20	14.5	1.90	5.51	8.70	12.8	0.10	0.20	0.40	1.02	−1.02	3.38
12	5.10	4.66	1.90	1.74	11.1	11.2	0.10	0.15	0.70	0.96	−0.13	−0.51
13	11.4	4.99	3.10	1.95	12.0	6.42	0.30	0.11	1.50	0.83	4.35	−1.21

Table 2. Cont.

No.	Zn [mg/kg]		Cu [mg/kg]		Pb [mg/kg]		Cd [mg/kg]		Ni [mg/kg]		S <sub>j</sub>	
	2008	2016	2008	2016	2008	2016	2008	2016	2008	2016	2008	2016
14	3.60	5.27	1.50	2.37	6.90	7.31	0.10	0.13	0.50	1.32	−1.36	−0.34
15	3.20	2.88	1.10	1.99	7.40	17.2	0.10	0.09	0.70	1.04	−1.26	−0.37
16	6.10	4.03	2.30	1.80	12.4	8.61	0.10	0.12	0.20	1.07	−0.39	−0.95
17	9.17	7.41	2.72	2.28	12.1	10.2	0.21	0.19	0.78	0.89	2.02	0.28
18	2.87	3.71	1.34	1.56	7.53	8.74	0.06	0.11	0.29	1.15	−2.11	−1.09
19	5.33	6.24	2.62	2.32	8.81	9.71	0.17	0.20	0.99	1.17	0.97	0.37
20	5.70	6.23	1.40	1.57	7.80	8.56	0.10	0.14	0.70	0.96	−0.64	−0.67
21	3.20	2.51	1.45	1.26	7.20	7.40	0.10	0.11	0.52	1.01	−1.39	−1.68
Range [mg/kg]	2.87–11.9	2.51–19.0	1.00–4.10	1.09–5.51	6.10–12.4	5.69–17.2	0.06–0.30	0.08–0.32	0.20–1.50	0.62–2.50		
Mean [mg/kg]	5.80	6.28	2.03	2.12	8.94	9.70	0.14	0.15	0.64	1.19		
Median [mg/kg]	5.33	5.27	1.70	2.10	8.70	8.75	0.10	0.14	0.70	1.07		
S–W Test (p)	0.02	0.00	0.01	0.00	0.20	0.09	0.00	0.02	0.08	0.01		
CV [%]	45.2	63.5	42.6	43.7	20.4	27.5	43.5	36.5	46.7	36.2		

Table 3. Geoaccumulation index (I<sub>geo</sub>), contamination factor (CF), enrichment factor (EF) of total metal contents in soils.

No.		Zn [mg/kg]		Cu [mg/kg]		Pb [mg/kg]		Cd [mg/kg]		Ni [mg/kg]	
		2008	2016	2008	2016	2008	2016	2008	2016	2008	2016
1	CF	0.75	0.80	0.61	1.24	1.99	2.23	8.15	11.83	1.21	2.81
	EF	1.77	1.13	1.44	1.76	4.70	3.16	19.31	16.78	2.86	3.99
	I <sub>geo</sub>	−1.00	−0.91	−0.39	−0.08	0.41	0.57	0.74	0.90	−0.32	0.91
2	CF	1.19	1.43	1.14	2.52	2.12	2.24	8.00	17.30	2.12	2.07
	EF	1.90	3.28	1.81	5.78	3.38	5.14	12.76	39.77	3.37	4.77
	I <sub>geo</sub>	−0.33	−0.07	−0.12	0.22	0.50	0.58	0.73	1.06	0.50	0.47
3	CF	0.62	0.41	1.20	0.93	1.48	1.63	7.89	10.18	1.68	1.90
	EF	1.38	0.92	2.66	2.09	3.29	3.66	17.48	22.78	3.73	4.25
	I <sub>geo</sub>	−1.27	−1.87	−0.10	−0.21	−0.02	0.12	0.72	0.83	0.16	0.34
4	CF	1.09	1.39	1.58	1.42	1.74	2.16	11.29	11.31	3.38	3.69
	EF	1.45	2.39	2.10	2.43	2.30	3.72	14.99	19.47	4.49	6.35
	I <sub>geo</sub>	−0.46	−0.11	0.02	−0.03	0.21	0.53	0.88	0.88	1.17	1.30
5	CF	1.26	0.41	0.67	0.88	1.82	1.96	8.28	13.80	1.63	1.79
	EF	2.56	1.09	1.36	2.35	3.72	5.22	16.89	36.72	3.32	4.76
	I <sub>geo</sub>	−0.26	−1.88	−0.35	−0.23	0.28	0.39	0.74	0.96	0.12	0.25
6	CF	1.08	0.86	0.94	1.14	2.20	2.12	10.66	12.46	1.43	2.55
	EF	1.78	1.29	1.54	1.70	3.62	3.17	17.58	18.64	2.35	3.82
	I <sub>geo</sub>	−0.48	−0.79	−0.20	−0.12	0.55	0.50	0.85	0.92	−0.07	0.77
7	CF	0.74	1.08	0.46	1.26	1.84	2.34	8.73	13.10	1.20	2.20
	EF	1.67	1.70	1.05	1.98	4.17	3.68	19.80	20.59	2.72	3.45
	I <sub>geo</sub>	−1.02	−0.47	−0.51	−0.08	0.29	0.64	0.77	0.94	−0.32	0.55
8	CF	1.46	0.88	0.97	1.18	3.04	4.00	8.10	11.31	1.65	2.40
	EF	2.21	1.09	1.47	1.46	4.61	4.98	12.27	14.08	2.51	2.99
	I <sub>geo</sub>	−0.04	−0.77	−0.19	−0.11	1.02	1.42	0.73	0.88	0.14	0.68
9	CF	0.76	0.60	0.99	0.77	2.41	2.28	4.44	10.58	1.62	1.82
	EF	1.79	1.45	2.33	1.87	5.70	5.51	10.53	25.63	3.83	4.42
	I <sub>geo</sub>	−0.99	−1.32	−0.18	−0.29	0.68	0.60	0.47	0.85	0.11	0.28
10	CF	1.11	1.11	0.94	1.35	3.24	3.55	12.02	13.47	1.48	2.18
	EF	1.46	1.59	1.23	1.93	4.26	5.07	15.81	19.24	1.95	3.11
	I <sub>geo</sub>	−0.43	−0.43	−0.20	−0.04	1.11	1.24	0.90	0.95	−0.02	0.54

Table 3. Cont.

No.		Zn [mg/kg]		Cu [mg/kg]		Pb [mg/kg]		Cd [mg/kg]		Ni [mg/kg]	
		2008	2016	2008	2016	2008	2016	2008	2016	2008	2016
11	CF	0.89	1.81	0.53	1.48	2.22	2.16	9.73	12.22	1.13	2.14
	EF	2.03	2.75	1.21	2.26	5.06	3.30	22.16	18.62	2.58	3.25
	I <sub>geo</sub>	−0.75	0.27	−0.45	−0.01	0.57	0.53	0.81	0.91	−0.41	0.51
12	CF	0.82	0.65	0.88	0.95	2.45	2.23	9.51	12.34	1.30	1.92
	EF	1.80	1.23	1.93	1.79	5.34	4.21	20.78	23.26	2.83	3.62
	I <sub>geo</sub>	−0.87	−1.21	−0.23	−0.20	0.71	0.57	0.80	0.92	−0.21	0.36
13	CF	1.83	0.46	1.85	1.27	3.96	3.35	10.10	16.14	2.28	2.80
	EF	2.47	0.94	2.51	2.59	5.36	6.80	13.67	32.76	3.09	5.68
	I <sub>geo</sub>	0.28	−1.69	0.09	−0.07	1.40	1.16	0.83	1.03	0.60	0.90
14	CF	0.87	0.86	0.77	1.51	1.96	1.83	8.68	14.41	1.46	2.76
	EF	1.82	1.25	1.62	2.18	4.12	2.65	18.27	20.85	3.08	3.99
	I <sub>geo</sub>	−0.79	−0.80	−0.29	0.00	0.38	0.29	0.76	0.98	−0.03	0.88
15	CF	0.88	1.03	1.28	1.55	1.68	2.45	4.44	6.94	1.68	2.05
	EF	1.21	1.80	1.76	2.71	2.30	4.28	6.10	12.14	2.31	3.58
	I <sub>geo</sub>	−0.77	−0.54	−0.07	0.01	0.16	0.71	0.47	0.67	0.16	0.45
16	CF	1.08	1.00	0.94	1.17	2.33	2.18	11.79	13.00	1.75	2.73
	EF	1.62	1.75	1.40	2.04	3.48	3.80	17.61	22.71	2.62	4.77
	I <sub>geo</sub>	−0.47	−0.58	−0.20	−0.11	0.63	0.54	0.90	0.94	0.23	0.86
17	CF	0.99	0.99	0.72	1.27	2.16	1.44	11.79	13.61	1.31	1.71
	EF	2.33	2.45	1.69	3.14	5.10	3.57	27.84	33.76	3.10	4.25
	I <sub>geo</sub>	−0.60	−0.60	−0.32	−0.07	0.53	−0.06	0.90	0.96	−0.19	0.19
18	CF	0.50	0.58	0.57	0.94	1.84	2.04	7.89	10.56	1.45	1.96
	EF	1.48	1.47	1.71	2.39	5.49	5.16	23.56	26.70	4.32	4.97
	I <sub>geo</sub>	−1.60	−1.37	−0.42	−0.20	0.29	0.44	0.72	0.85	−0.05	0.39
19	CF	0.82	1.01	0.55	1.18	1.77	1.81	9.68	9.00	1.91	1.83
	EF	2.09	2.20	1.40	2.57	4.53	3.93	24.76	19.55	4.87	3.97
	I <sub>geo</sub>	−0.88	−0.57	−0.44	−0.10	0.24	0.27	0.81	0.78	0.34	0.29
20	CF	0.63	0.81	0.60	0.99	1.66	1.59	2.85	9.94	1.51	2.12
	EF	1.31	1.79	1.26	2.19	3.48	3.53	5.95	22.00	3.16	4.68
	I <sub>geo</sub>	−1.25	−0.89	−0.39	−0.18	0.15	0.09	0.28	0.82	0.01	0.50
21	CF	0.91	0.85	1.83	1.43	1.54	1.40	6.44	6.89	1.63	1.99
	EF	1.58	1.48	3.17	2.50	2.67	2.45	11.16	12.02	2.82	3.47
	I <sub>geo</sub>	−0.72	−0.82	0.09	−0.02	0.04	−0.10	0.63	0.66	0.12	0.41

Where [38]: CF < 1 low contamination; 1 ≤ CF < 3 moderate contamination; 3 ≤ CF < 6 considerable contamination; CF ≥ 6 very high contamination; EF < 2 minimal enrichment; 2 ≤ EF < 5 moderate enrichment; 5 ≤ EF < 20 significant enrichment; 20 ≤ EF < 40 very high enrichment; EF ≥ 40 extremely high enrichment; I<sub>geo</sub> < 0 unpolluted (class 0); 0 ≤ I<sub>geo</sub> < 1 unpolluted to moderately polluted (class 1); 1 ≤ I<sub>geo</sub> < 2 moderately polluted (class 2); 2 ≤ I<sub>geo</sub> < 3 moderately to strongly polluted (class 3); 3 ≤ I<sub>geo</sub> < 4 strongly polluted (class 4); 4 ≤ I<sub>geo</sub> < 5 strongly to extremely polluted (class 5); I<sub>geo</sub> ≥ 5 extremely polluted (class 6). Geochemical background [20]: Fe 12,900 mg/kg; Zn 30 mg/kg; Cu 7.1 mg/kg; Pb 9.8 mg/kg; 0.18 mg/kg; Ni 10.2 mg/kg.

Table 4. Pearson’s and Spearman’s correlation coefficients of metal mobile fractions (in 2008 and 2016).

2008 Year	Zn	Cu	Pb	Cd	Ni	pH
Zn	1.00					
Cu	<b>0.80</b>	1.00				
Pb	<b>0.69</b>	<b>0.72</b>	1.00			
Cd	<b>0.64</b>	<b>0.62</b>	0.53	1.00		
Ni	0.53	0.38	0.39 <sup>(1)</sup>	<b>0.67</b>	1.00	
pH	0.46	<b>0.59</b>	0.28	<b>0.67</b>	0.41	1.00
2016 Year	Zn	Cu	Pb	Cd	Ni	pH
Zn	1.00					
Cu	<b>0.82</b>	1.00				
Pb	0.45	0.54	1.00			
Cd	<b>0.86</b>	<b>0.81</b>	<b>0.62</b>	1.00		
Ni	0.42	<b>0.57</b>	0.21	0.49	1.00	
pH	0.46	<b>0.56</b>	−0.03 <sup>(1)</sup>	0.51	0.32	1.00

<sup>(1)</sup> Pearson’s correlation; p < 0.01 bold; p < 0.05 italics.

### 3. Results and Discussion

#### 3.1. Soil Characterization and Metal Distribution Maps

The samples collected in 2016 contain 2.9 to 5.3% of organic matter (OM) i.e., slightly more than the average content of OM in arable soils in central Poland [39], and comparable to the content of OM determined in 2008 (Table 1). In the case of different types of fallow (grassland, goldenrod, bush), the direction of changes in the OM level is usually similar to the one described by Kozak et al. [13]. The change in land use from cropland to fallow grassland (sites 2, 11, 15), and longer abandonment of agricultural activity (sites 1, 8, 20, 21) are associated with a certain increase in the content of organic substances. On the contrary, the conversion of grassland fallow to goldenrod resulted in a reduction in the organic matter content. In terms of grain size, clay sands and sandy loams with a low clay fraction dominate. They are typical of soils formed on post-glacial sediments. The reaction of the examined soils in 2008 and 2016 is varied and ranges between 5.1 to 8.0 (pH-H<sub>2</sub>O), 3.8 to 7.6 (pH-KCl), 5.4 to 7.5 (H<sub>2</sub>O) and 4.3 to 7.4 (KCl), respectively. The pH measurement in the KCl suspension is more reliable in terms of determining the current state of soil acidification, due to the fact that it includes two fractions of hydrogen ions: (1) H<sup>+</sup> ions which are the result of the current balance in the solid-liquid phases of the soil, and (2) hydrogen ions which are held the least by the soil solid phase and can relatively easily pass into the liquid phase in dynamically changing soil conditions. In terms of pH-KCl, the soils collected in 2008 are usually either very acidic (38% of the samples) or acidic (48% of the samples). In 2016, the acidification decreased noticeably, the pH increased in 15 sites (i.e., in over 70% of the samples), and in the remaining locations the pH was lower by a maximum of 0.7 pH units. Thus, in 2016, slightly acidic to alkaline soils dominated (Figure 3). Several factors could have influenced this direction of pH changes, including a change in the type of land management as the main one [13]. The long-term use of fertilizers, especially those containing nitrogen, is a major factor in soil acidification [40,41]. In some of the sites in PKWL, agricultural activity was abandoned due to the planned road investments, and before the construction started, the soil turned into fallow. Depending on the degree of plant succession, the pH may then increase or decrease compared to the arable soil [13]. Presumably, the increase in pH may be related to the abandonment of soil fertilization. Moreover, deacidification of the soil can be also expected in connection with the road investments carried out in the park, e.g., dusting of calcium-based building materials, and the use of building material with the addition of solidified waste (the pH of the waste leachate depends on waste origin and method of stabilization [21,42]). The increase in both pH-H<sub>2</sub>O and pH-KCl in the period between 2008 and 2016 in most of the studied sites (Table 1, Figure 3) applies to both locations near and further away from the construction area. Therefore, it should be assumed that the increase in pH is the result of not only the construction of the highway itself, but also the limitation of land cultivation in this part of the park.

Metal extraction was performed with 1 mol/L HCl according to Polish Standards [31,32]. As proved in previous works [43–46], it is an extractant that leaches potentially mobile metal fractions from soil. At the same time, it does not affect the silicate minerals, and therefore does not release sparingly soluble metal fractions strongly bound to the solid phase of the soil. Hence, extraction with diluted hydrochloric acid can be used to determine mobile fractions of metals. It was found that HCl extracts fractions of metals that are water soluble, exchangeable and bounded with carbonates. Moreover, a strong correlation between the content of heavy metals in soil and in plants growing on it was recognized. The results of the determination of metals on all sites are given in Table 2. In 2008, the concentration of mobile forms of metals changed in the following range: Pb > Zn > Cu > Ni > Cd (except for site 5, where the zinc content was higher than that of lead). In 2016, this trend was generally maintained, although at sites 4, 7 and 11, the concentration of zinc was higher than that of lead, and at sites 1 and 9, the content of nickel was slightly higher than that of copper. In 2016, the average content of all metals analyzed in the study area increased by about 4.5% (Cu), 7 to 8.5% (Cd, Zn, Pb) and by over 85% (Ni) compared to 2008.

As no geochemical background values are available for the fraction of extracted metals using 1 mol/L HCl, or other acids of similar concentration, it is difficult to assess the degree of soil contamination with mobile forms of the examined elements. Therefore, complex index of soil contamination with heavy metals  $S_j$  was calculated [33,34]—Table 2. Index  $S_j$  is based on raw data and gives information about the sites which are the most loaded with metals. In 2008, the highest loads of pollutants occurred at sites 2, 5, 8, 13 and 17 ( $S_j$  1.3–4.4), while in 2016—at points 1, 4 and 11 ( $S_j$  1.4–4.7). On the other hand, locations 1, 9, 14, 15, 18 and 21 ( $S_j$  from  $-2.1$  to  $-1.3$ ) and 3, 5, 9, 13, 18 and 21 ( $S_j$  from  $-2.0$  to  $-1.1$ ) were the least polluted in 2008 and 2016, respectively. The variability in pollutant loads may have various sources, but the following seem to be the most probable: (i) change in soil use, (ii) road investments carried out in the studied area. The first factor is related to the abandonment of agricultural activities and the decrease in the amount of fertilizers added into the soil. Consequently, such areas should be characterized by an unchanged or lower metal content. On the other hand, fallow land is sometimes treated by residents as a sort of garbage dump, which leads to uncontrolled pollution. Increased metal content may also come from materials used for mid-field road hardening (e.g., slags) [47], and in the case of lead, an increase in leaching of metal from cement with solutions rich in NaCl used as a de-icing agent is also observed [17]. Another form of land use after the abandonment of cultivation is residential and recreational use, and the associated loads of household pollutants (waste, sewage, dust emissions from heating devices) and components of building materials. The distribution of the analyzed metals (mobile fractions) is shown in Figure 4.

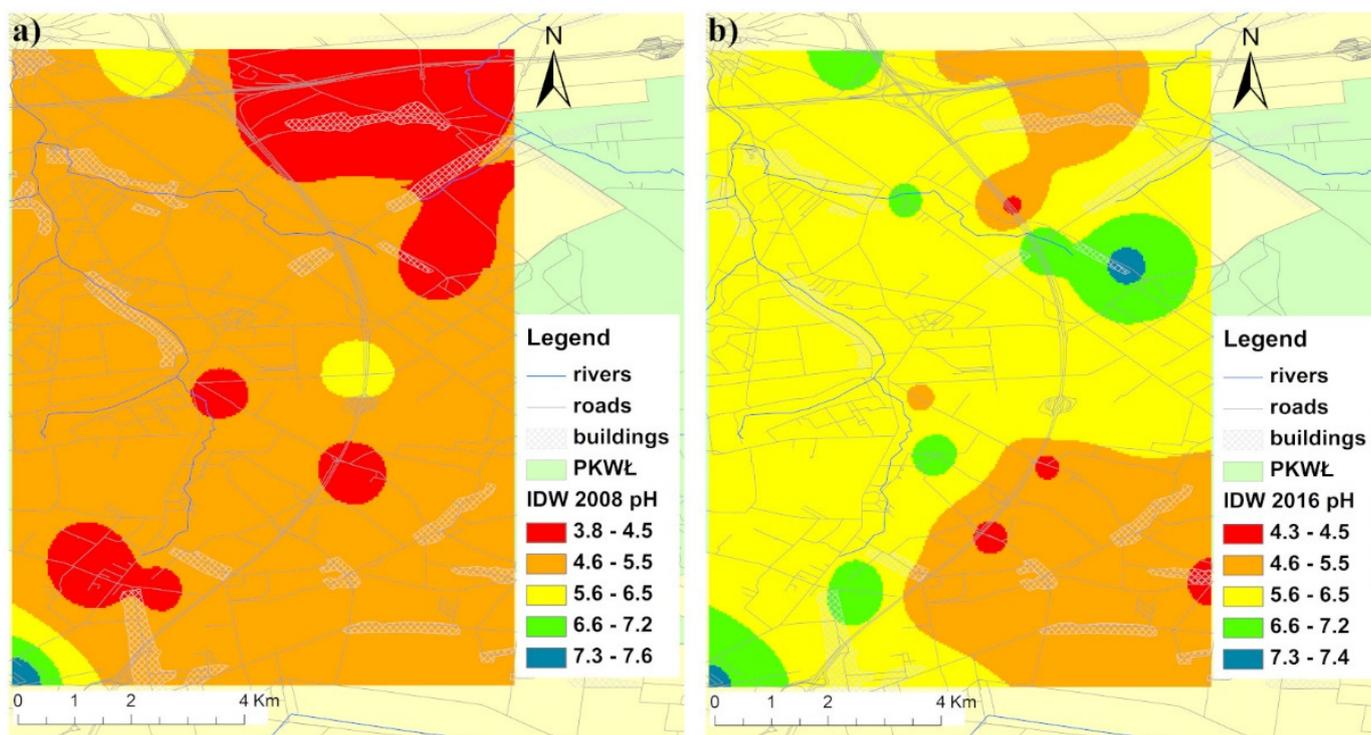


Figure 3. Spatial distribution of (a) pH (2008); (b) pH (2016).

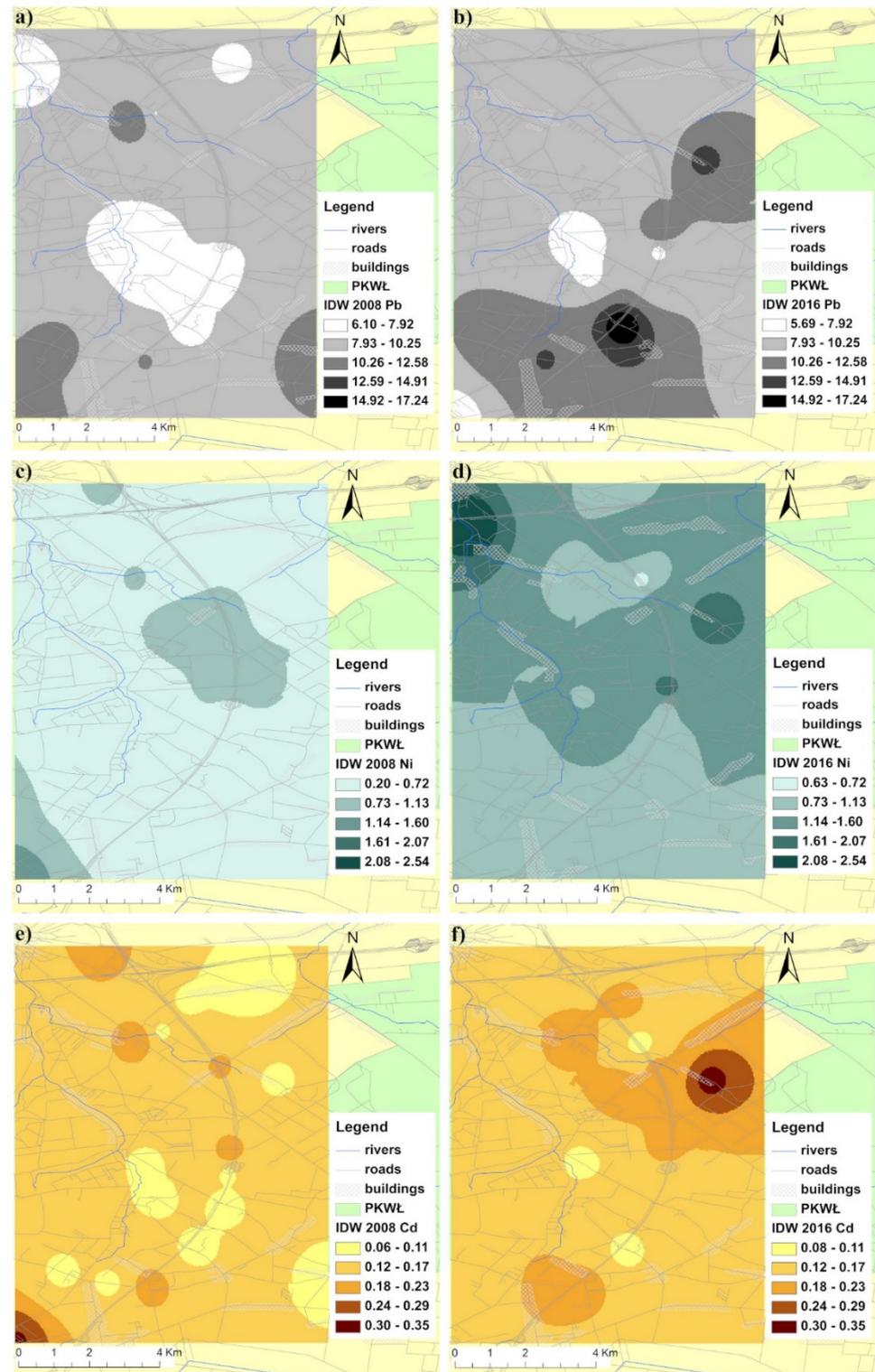
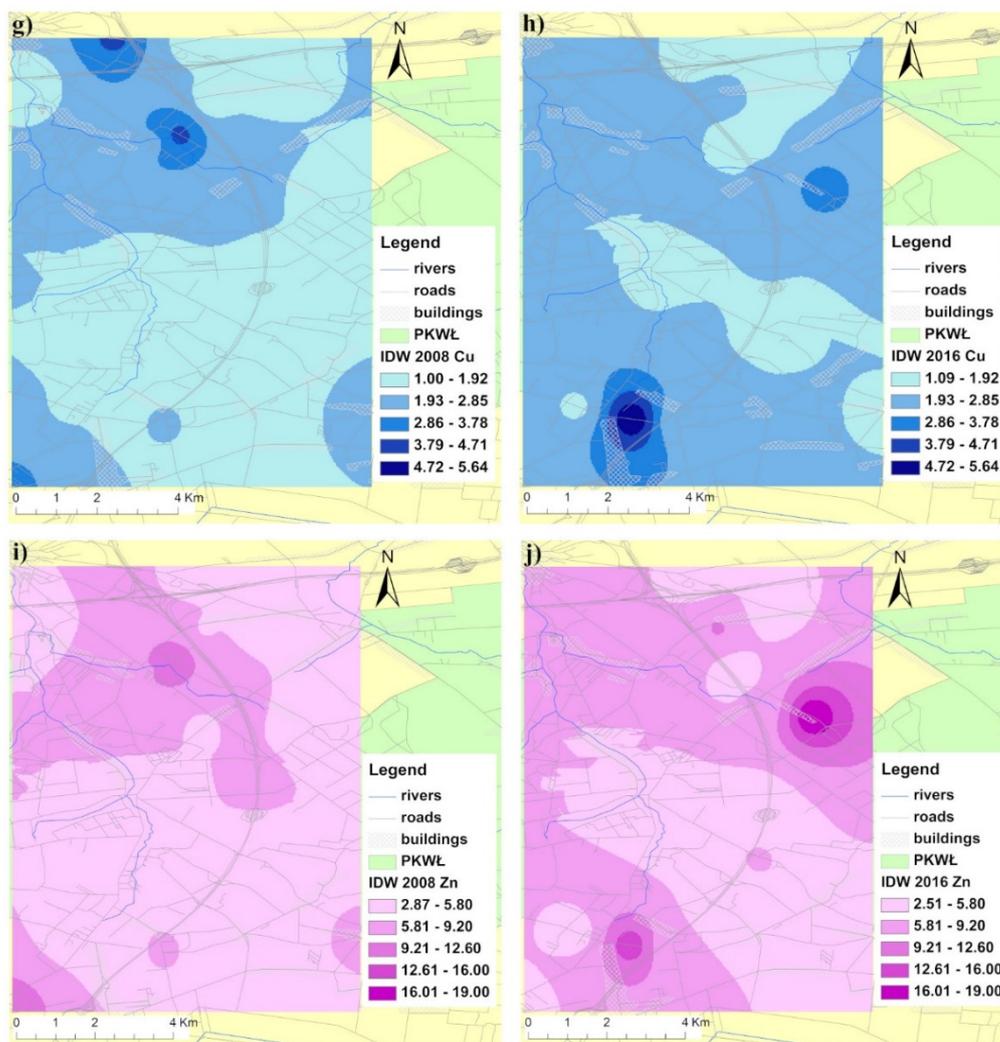


Figure 4. Cont.



**Figure 4.** Spatial distribution of metal concentrations [mg/kg]: (a) Pb (2008); (b) Pb (2016); (c) Ni (2008); (d) Ni (2016); (e) Cd (2008); (f) Cd (2016); (g) Cu (2008); (h) Cu (2016); (i) Zn (2008); (j) Zn (2016).

There was an increase in the content of all metals at sites 1, 4, 7, 11 and 18, as well as 14 (except Pb), 19 (except Cu) and 20 (except Cu and Zn). The increase in the level of metals is observed both on fallow land and arable land, near the highway and at points away from the construction site. It should also be taken into account that most of the local roads were used as access roads to the construction site, hence the risk of contamination of the surrounding areas with emissions from vehicles delivering construction materials. An additional factor may be wind-blown dust.

The average shares of potentially mobile fractions in relation to the total content of metals in 2008 and 2016 were, respectively: Zn—20% and 23%, Cu—35% and 24%, Pb—44% and 47%, Cd—9% and 7%, Ni—4% and 5%. In the case of nickel, cadmium and copper, the total content of metals in 2016 increased for 19, 18 and 16 examined sites, respectively (Table S1). For the remaining metals, changes in concentrations concerned about 50% of the samples. An increase in the content of metals was favored by a significant soil deacidification in 2016. In order to assess soil contamination, three indices CF, EF and  $I_{geo}$  were calculated (Table 3). In most cases,  $I_{geo}$  values correspond to 0 and 1 class, with class 0 dominating for zinc and copper. Soils moderately contaminated with lead, nickel and cadmium (class 2) are present at a few sites only. Similarly, most of the CF and EF values for zinc and copper correspond to the lowest ranges, i.e.,  $CF < 3$  (low or moderate contamination) and  $EF < 5$  (minimal or moderate enrichment). The spatial distribution of

the mobile fractions of Cu and Zn also had a similar trend (Figure 4), and it was bound up with agricultural activity. With the exception of a few points, soils are moderately contaminated (CF) with nickel and lead. EF values correspond to moderate (Ni, Pb) or significant (Pb) enrichment. Although lead is not an easily migrating metal, the high share of mobile fractions (almost 50%) in the analyzed soils may indicate a significant influence of anthropogenic sources [43]. On the contrary, almost all sites are very highly contaminated with cadmium ( $CF \geq 6$ ) and are characterized by significant or very high enrichment with Cd ( $EF > 5$ ). No heavy contamination was found based on Polish legislation for agricultural soil [48]. Only in the case of cadmium, the limit values for arable soils (i.e., 2 mg/kg for  $pH\text{-KCl} \leq 6.5$  and 3 mg/kg for  $pH\text{-KCl} > 6.5$ ) were exceeded at sites 4, 10, 16 and 17 (2008), and 2, 4, 6, 11, 13, 14 and 17 (2016). Based on the Shapiro-Wilk test, it was found that the normal distribution occurs for lead (2008 and 2016 samples) and nickel (2008 samples). In addition, the normal distribution was found in the case of pH determined in 2016. The non-normal distribution was found in the agricultural soil [49]. Higher values of the coefficient of variation ( $51\% < CV \leq 100\%$  [50]) for Zn (2016) indicate the presence of point sources of this element in the studied area. In other cases, there is moderate variability in terms of metal content ( $21\% < CV \leq 50\%$ ), and for Pb (2008) low variability can even be considered ( $CV \leq 20\%$ ).

Table 4 presents metal and pH correlation coefficients. In 2008, strong or moderate correlations [51] occurred among all the variables, except for Ni/Cu, Ni/Pb and Pb/pH. Therefore, it should be assumed that the pollutants came from several common sources [38,49], but the emissions had a similar qualitative composition. Most likely, these are emissions related to road transport [52–54] and agricultural activities [55,56]. In 2016, the correlation coefficients changed significantly in some cases, but they are still strong or moderate except for the Ni/Pb, Ni/pH and Pb/pH pairs. It should therefore be assumed that other sources of contamination have appeared or the quantitative relationships of contamination from the previously existing sources have changed. This hypothesis is confirmed by the lack (apart from a few examples) of interrelationships among the analytes in the samples from 2008 and 2016 (Table S3).

### 3.2. Principal Component Analysis (PCA) and Cluster Analysis (CA)

The principal component analysis (PCA) was performed on the basis of a dataset covering all parameters (metal mobile fractions and pH) determined in 2008 and 2016. Four principal components (PCs) can be extracted, which explain 81.89 % of the variability (Table 5). Relevant factor loadings are shown in Table S4.

**Table 5.** The eigenvalues and the proportion of variances explained by the principal components (PC1-PC4).

	Eigenvalue	% of Variance	Cumulative % of Variance
PC1	4.22	35.19	35.19
PC2	3.44	28.69	63.88
PC3	1.26	10.52	74.41
PC4	0.90	7.48	81.89

PC1 includes the metals investigated in 2008, and pH (2008 and 2016). The variables assigned to PC1 have negative factor loadings. The loadings of all variables from 2008 are high ( $-0.91 \div -0.70$ ), whereas for pH (2016) the relationship is moderate ( $-0.58$ ). All parameters analyzed in 2016 are with negative loadings on PC2. Their factor loadings are more varied ( $-0.90 \div -0.52$ ), and two groups of analytes can be distinguished: (1) Zn, Cd and Cu, which have a significant influence on the PC2, and (2) Pb, Ni and pH—having a moderate effect on this PC. PC3 shows moderately positive loadings for Ni (2016), and negative—for Pb (2008 and 2016), whereas PC4 shows moderately positive loadings for both Ni (2008) and Pb (2016). On the loading plots PC2-PC3 and PC1-PC3 opposite correlations are observed between Pb(2008)/Ni(2008), and Pb(2016)/Ni(2016), respectively.

The pedogenic origin of lead and nickel is represented by PC3, as evidenced by the positive factor loading of siderophile Ni and the negative charges for Pb (chalcophile) [57]. PC4 represent additional anthropogenic sources of lead and nickel, such as coal burning dust air-transported over long distances, phosphate fertilizers, and also historical contamination (e.g., vehicle transport or pesticides) [55,58–61]. Figure S1 presents factor scores obtained from PCA for sampling sites. The results of the principal component analysis are consistent with the maps of the spatial distribution of metals (Figure 4). The GIS maps clearly show these changes that took place in the soil environment in the studied period.

As shown in Figure 5, three clusters of sampling sites with similar properties were created using the cluster analysis (CA). Cluster 1 includes points 4, and 11, where in 2008 to 2016, the highest increase in pH and the content of metals, especially for zinc and copper, was observed. In the case of these sites, the highest values of the contamination index  $S_j$  4.7 (site 4), and 3.4 (site 11) were also found in 2016. Both sites are at local roads and the use of soil 4 did not change during the studied period. An increase in the metal contents at point 4 may be caused by contamination from the means of transport (cars, buses), as the site is located on the route to the nature reserve. Potential sources of metals are e.g., lubricating oil (Cd, Pb, Ni), diesel fuel (Cd, Ni), tires (Zn, Cd, Pb), bearing wear (Pb, Cu), and brakes (Ni, Zn, Cu) [61]. Another source of metals could be the dust carried by wind from the construction site located to the west of this site (in Poland, wind from the west is dominant). Point 11 was located near the construction site and the adjacent road was probably used to transport building materials. A significant increase in soil pH in points 4 and 11 could be caused by the emission of alkaline dust from the highway construction site. These points should be regarded as the main hot-spots. Cluster 2 contains soils from 2008 for which the  $S_j$  index was positive, and two sites with the value of this index close to 0 i.e., points 12 ( $S_j = -0.1$ ) and 16 ( $S_j = -0.4$ ). In most cases, the content of metals in these sites decreased between 2008 and 2016. Cluster 3 gathers soils for which  $S_j$  in 2008 was negative (within the range from  $-0.6$  to  $-2.1$ ), which means that these were the samples with the lowest total pollutant load. In some of these sites, the metal content increased in 2016.

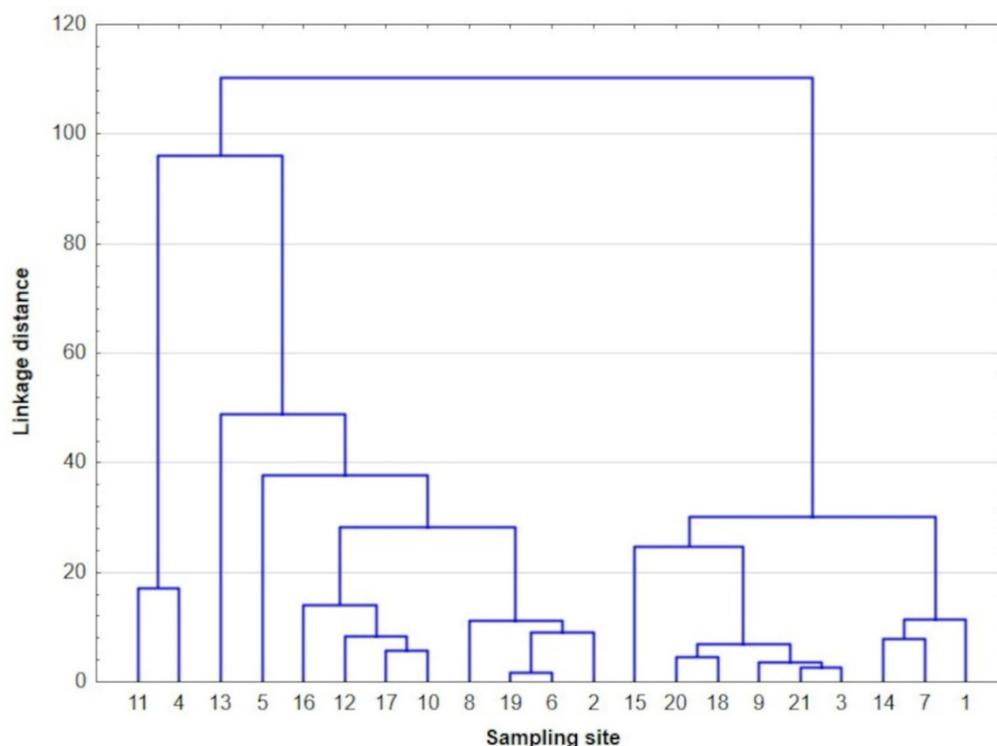


Figure 5. Dendrogram depicting clustering of sampling sites.

#### 4. Conclusions

In 2008 to 2016, soil pH increased significantly in the study area, and in 2016, slightly acidic to alkaline soils prevailed. Presumably, the increase in pH was related to dust emissions from the transport of building materials and from the highway construction site.

The contents of metal mobile fractions in 2008 and 2016 decreased in the following order: Pb > Zn > Cu > Ni > Cd at most of the investigated sites. In 2016, about half of the sites showed an increase in the content of mobile forms of Cd, Cu, Pb and Zn. The nickel content increased in all examined points (except number 13). The retention of metals is supported by soil pH. Strong correlations between Cu and Zn in 2008 and Cd, Cu, and Zn in 2016 suggest that these elements originated from the same sources. PCA and CA coupled with the GIS helped to follow the changes in the distribution of metals in the studied area, and to extract some hot-spots.

To sum up, road investments in protected areas, apart from ecological aspects, influence changes in soil chemistry. The construction of the highway cannot be indicated as the only source of soil contamination with metals in the area and in the buffer zone of PKWŁ. Nevertheless, the increase in pH and metal contents in the large part of the study area can be attributed to the construction works and the increase in road traffic. However, the possible impact of changes in the management of PKWŁ and the increase in the number of inhabitants on the level of chemical soil contamination should be taken into account. The increase in urbanization is a problem for protected areas. Therefore, areas with natural and recreational values should be systematically analyzed in terms of changes in the chemical composition of abiotic elements of the environment.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min12070838/s1>, Table S1: Total content of metals in soils (mg/kg); Table S2: Results of metal determination in CRM 7002 Light sandy soil (extract by cold 2 mol/L HNO<sub>3</sub>); Table S3: The Pearson's and Spearman's correlation matrix for raw dataset (2008 and 2016); Table S4: Factor loadings of variables (2008 and 2016); Figure S1: Factor scores obtained from PCA for sampling sites.

**Author Contributions:** Conceptualization and methodology, A.T. and J.K.; software, M.S. and K.W.; validation, A.T. and J.K.; formal analysis, A.T., K.W., J.K. and M.S.; writing—original draft preparation, A.T.; statistical methods K.W.; visualization, M.S. and K.W.; supervision, A.T. and K.W. All authors have read and agreed to the published version of the manuscript.

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**Data Availability Statement:** All data presented in the article.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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