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A 10-Year Ecological Monitoring of Soils and *Triticum aestivum* in the Impact Zone of a Power Station

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Abstract: Based on 10 years of environmental monitoring located around the emission zone of an electricity supplier, the main regularities have been studied for the content of heavy metals (HMs), such as Pb, Cd, Zn, Cu, Ni, Mn, and Cr, and 16 priority polycyclic aromatic hydrocarbons (PAHs) in the soils of agricultural landscapes and their accumulation in *Triticum aestivum*. It has been shown that one of the most significant factors for the pollutants accumulation in soils and plants was the prevailing wind direction on the territory and atmospheric transfer of the dust particles of the enterprise with adsorbed pollutants. As the content of pollutants in the soil increased, their accumulation in *Triticum aestivum* increased with each season to a level exceeding maximum permissible concentrations (MPC), especially for Pb, Cd, and benzo[a]pyrene (BaP). The unambiguous influx of pollutants from the soil into the roots and further into the aboveground organs of the plant was typical only for Mn, Cr, and BaP, and the accumulation of other studied pollutants can be explained by their foliar influx. It has been established that *Triticum aestivum* was a more tolerant plant with respect to heavy metals pollution than PAHs.

Keywords: heavy metals; PAHs; *Triticum aestivum*; contamination; thermal power station

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1. Introduction

The National Security and Development Strategies provide an effective policy framework for environmental protection. The directive includes large-scale environmental surveys on the content and forms of various conventional and emerging pollutants along with the assessment criteria for their comprehensive reconnaissance [1]. Efficient management of natural and anthropogenic system contamination with hazardous pollutants is among the most severe challenges of the 21st century [2–6]. Many inorganic and organic compounds are categorized as environmental pollutants that pose a direct threat to human health and disrupt the functioning and degrade the quality of both ecosystem and its individual components [7]. The most hazardous conventional soil pollutants include PAHs, pesticides, organohalides, polychlorinated dibenzo-n-dioxins, dibenzofurans, polychlorinated biphenyls, radionuclides, HMs, and metalloids [8–10].

Largely, the nature of pollution in a particular geographical area is determined by enduring anthropogenic activities. For example, HM input is associated with the extraction of minerals, metallurgical operations, thermal power plants functioning, production of electronic components, textiles, woodworking, and vehicle exhaust emissions [8]. PAH and petroleum compound input into the soil is associated with the extraction, transportation, and processing of fossil fuels, primarily power plants, and the impact of road and rail transport, energy, petrochemistry, and the production of building materials [11–13]. At the same time, mainly chrysene, pyrene, and fluoranthene accumulate in the soils of the

impact zones of thermal power plants during oil spills and oil products, as well as under the influence of vehicles, and heavier compounds, such as, BaP, benzo[k]fluoranthene, benzo[b] fluoranthene, and dibenzo[a]anthracene [12]. Population growth naturally leads to the intensification of industrial production, which leads both to an increase in the anthropogenic load and to the complex synergistic impact of many pollution sources on landscape components. The result of such complex contamination is the appearance of combined contamination with a mixture of various pollutants.

Current efforts are devoted towards the remediation of combined soil contamination caused by the simultaneous exposure of various HM and PAH compounds for several reasons [14–21]. Firstly, the most significant sources of pollutants, such as transport, fuel and energy companies, are widespread. Secondly, the pollution can be traced in the soils of any landscape, even in the remotest regions of the world [22]. Thirdly, the resistance of these substances to degradation in soils makes it possible to assess the duration and intensity of anthropogenic impact. Lastly, HMs and PAHs are characterized not only by toxic effects on living organisms, but also by their serious mutagenic, teratogenic, and carcinogenic effects [23]. One of the most dangerous pollutants is BaP, a carcinogen and mutagen of the first hazard class of compounds [24,25].

Contaminated soils can directly or indirectly pose a threat to living organisms: directly through the negative impact of pollutants on the crops yield and quality and indirectly by accumulating in the human body through the food chain, thereby leading to hazardous health issues. Even a few percent reduction in crop yield due to pollutant exposure can lead to significant long-term losses in crop production and farmer income.

The process of coal burning at thermal power plants results in solid and gaseous products containing various PAH and HM compounds that are released into the atmosphere. The location of agricultural lands near enterprises of the fuel and energy complex leads to progressive processes of technogenic soil pollution, as well as to impacts on the elemental composition of plants as a result of the root and foliar pathways of pollutants. The decrease in the quality and yield of agricultural crops due to the impact of PAHs and HMs is economically unprofitable, and most importantly, environmentally unsafe due to the direct entry of pollutants into the human body through the food chain. Food importers are currently developing standards for the permissible limits of HMs and PAHs in various food products and restricting the import of produce contaminated with these pollutants. Hence, it is vitally important to regularly monitor the soils and plants of agricultural fields subjected to combined contamination with HMs and PAHs. In this study, the long-term monitoring of various pollutants, including HMs and PAHs, in agricultural lands located within the impact zone of the thermal power plant Novocherkassk Power Station (NPS) was carried out. The content of HMs and PAHs in the soils of agricultural landscapes and *Triticum aestivum* plants was studied over a 10-year research period.

2. Materials and Methods

Monitoring sites were located up to 2.2 km radius in different directions from the branch of Novocherkassk Power Station (NPS), the largest fuel and energy complex in the Rostov Region (Figure 1) [26]. Despite the close location to NPS, within 2.5 km from the station, there were fields sown with oilseeds and cereal crops. This led to the choice of monitoring sites where common wheat (*Triticum aestivum*) was regularly cultivated. According to the data of long-term meteorological studies, the north-western wind direction prevails in the region under study, causing the greatest distribution of atmospheric emissions from the enterprise. Plants were sampled annually during the 2012–2021 period in the first ten days of July. The crop was in the phase of full ripeness, since it is precisely during this phase that maximum broadcasting of organic pollutants was performed [27,28]. The plants were divided into three parts: roots, stems, and grains for the analysis. The grains were separated from the ear by hand for further analysis. Along with plants, samples of ordinary carbonate chernozem (Haplic Chernozem) were collected, with the following physical and chemical properties: humus content 3.6–4.2%; pH 7.4–7.7; physical clay 50.6–56.3%; silt

40.4–44.6%; $CaCO_3$ 0.5–1.1%; EKO 31–36 cmol kg^{-1}, exchangeable cations (cmol kg^{-1}): Ca^{2+} 31.0–34.2; Mg^{2+} 5.1–6.3; Na^{+} 0.03–0.06.

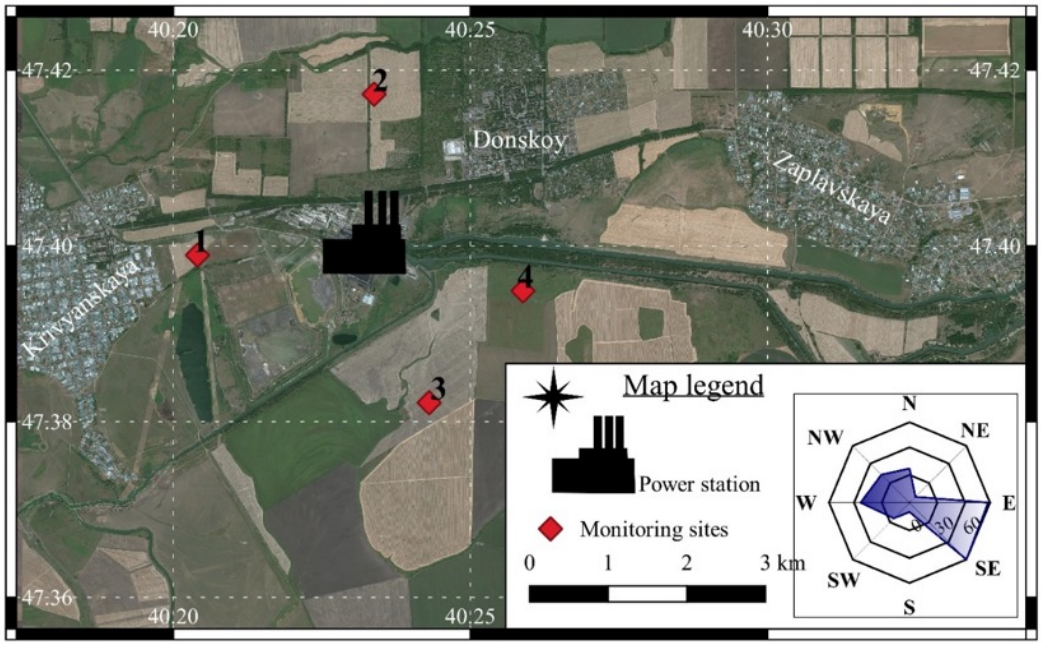

Figure 1. Location map of monitoring sites of agricultural lands located within the impact zone of the Novocherkassk Power Station.

The HMs such as Mn, Zn, Cu, Cr, Pb, Cd, and Ni, presented in the NPS emissions, were determined in plant and soil samples. The total content of HMs in the soil samples was determined by X-ray fluorescence method using X-ray spectrometer (Spectroscan MAX-GV, SPECTRON Ltd., Saint-Petersburg, Russia). The exchangeable form of the metals were extracted into solution with 1 N ammonium acetate buffer (NH_4Ac) at pH 4.8 (soil:solution ratio = 1:5, extraction time 18 h) and measured with an atomic absorption spectrophotometer (KVANT 2-AT, Kortec Ltd., Moscow, Russia) [29,30].

Mineralization of plant samples was carried out by dry ashing method according to [31]. Extraction of HMs from ash was carried out with a 20% HCl solution followed by determination on an atomic absorption spectrometer (KVANT 2-AT, Kortec Ltd., Moscow, Russia).

The extraction of PAHs from soil and plants samples was carried out with *n*-hexane (ultragrade, 99% pure, Sigma-Aldrich, Munich, Germany) [32,33]. The pre-interfering lipid fraction was removed by saponification of 1 g of soil with a 2% KOH alcohol solution. The PAHs in the extract were quantified by high performance liquid chromatography using Agilent 1260 HPLC (Agilent, Santa Clara, CA, USA) with simultaneous fluorescence and ultraviolet detection (Agilent 1260, Waldbronn, Germany, 2015) according to ISO standard requirements [34]. During laboratory experiments, the concentrations of 16 priority PAHs were determined (U.S.E.P. Agency 2009): naphthalene, phenanthrene, anthracene, acenaphthene, acenaphthylene, fluorene, pyrene, chrysene, benzo[a]anthracene, fluoranthene benzo[b]fluoranthene, benzo[k]fluoranthene, BaP, and benzo[g,h,i]perylene. A total content of 16 PAHs were analyzed.

The content of HMs and PAHs in common wheat (*Triticum aestivum*) was analyzed in comparison with the MPC for raw food materials and food products such as "Grain (seeds), flour and cereals, and bakery products" [35]. To assess the level of the soil contamination, a number of standards were used for comparison with the MPC for Mn, Pb, and BaP [36] and for Ni, Cu, Zn, and Cd [37], and standards adopted from Canada [38] were used for Cr, since standard values for this indicator are currently unavailable in Russia. The total content of PAHs in the soil was estimated based on the classification of agricultural land proposed by Maliszewska-Kordybach [39]. In addition, the results of the HM and PAH

total content evaluation were compared with corresponding values in Haplic Chernozem located on the virgin land of the background territory for the dry steppe zone (Table 1).

Table 1. The content of HMs and BaP and 16 priority PAHs total amount (∑16 PAHs) in the soils of the background dry steppe zone of southern Russia.

Mn	Cr	Ni	Cu	Zn	Pb	Cd	BaP	∑16 PAHs
			mg kg^{-1}				μg kg^{-1}	
814.5	96.5	61.4	51.9	71.7	27.7	0.6	16	218

To assess the resistance of reed plants under conditions of technogenic pollution with HM and PAH, the accumulation coefficient (AC) and the translocation factor (TF) of plants were calculated. The AC represents the ratio of the concentration of the pollutant in the dry mass of a plant to the content of its exchangeable forms in the soil [40]. The TF1 value allows assessment of the barrier functions of a plant under pollution and is defined as the ratio of the pollutant concentration in the stems to the concentration in the roots [41]. Additionally, for assessment of the pollutant's translocation intensity from stem to grains, TF2 was calculated as the ratio of the pollutant's concentration in the grain to their concentration in the stems.

Statistical analysis of the obtained results, as well as the compilation of graphic material, was carried out using STATISTICA 10 and Sigmaplot 12.5.

3. Results

It was observed that the maximum technogenic load was in the soil samples from monitoring sites No. 1 (2.0 km W) and No. 2 (1.5 km N). The highest concentration of HMs and PAHs were observed in the soils of the aforementioned plots, which is especially significant for the soil of plot No. 1 (H) (Figures 2–4) over the entire monitoring period.

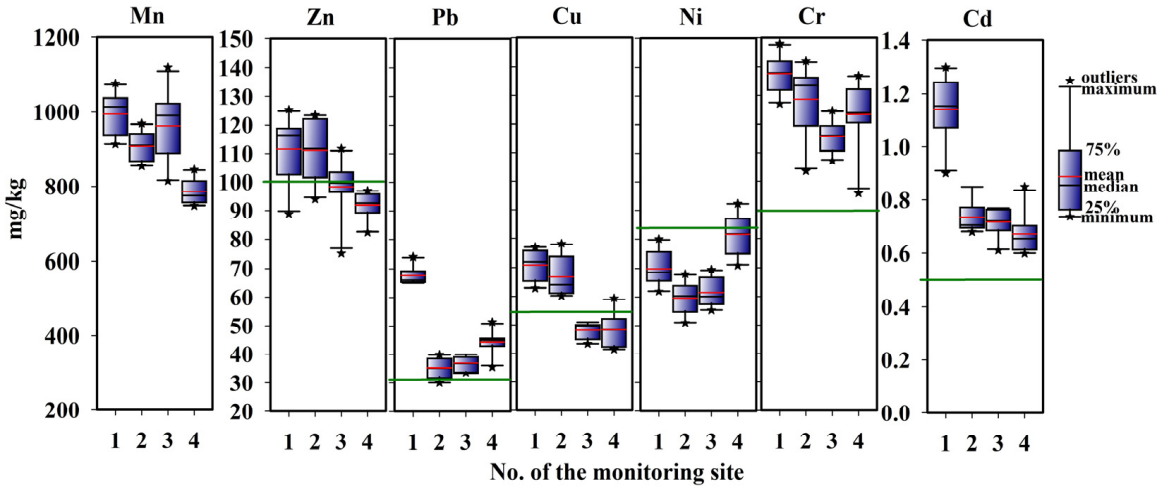

Figure 2. The total concentration of HMs in agricultural fields soil located near the power station over a 10-year monitoring period. Green line is the maximum permissible concentrations (MPC). *—outlier.

Over this 10-year period of monitoring studies, we observed that, on average, the total content of all HMs exceeded the background concentrations of elements in the soil except for Ni. Despite the excess, the concentration of HMs in the soil of agricultural fields decreased, with a similar tendency in the series of the background territory, i.e., Mn > Cr > Zn > Ni > Cu > Pb > Cd. The concentration of Pb, Cr, and Cd exceeded the MPC in the soils of all monitoring sites, while for Zn and Cu, MPCs were exceeded only in

sites located in the priority western and northern directions from the power plant (No. 1 and No. 2). Concentrations of Mn and Ni above that of the MPCs was not detected in any monitoring sites throughout the entire period of study (Figure 2).

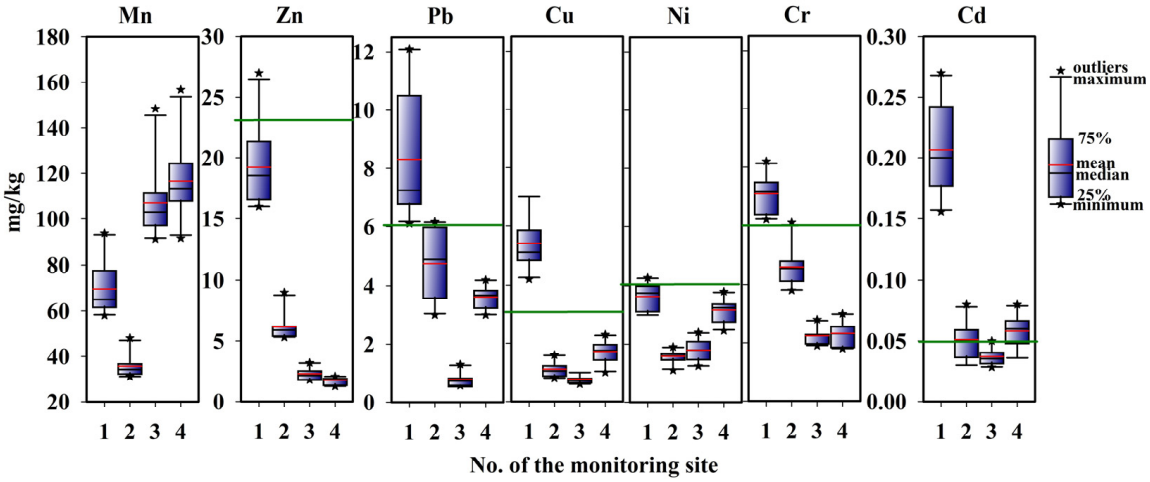

Figure 3. The concentration of HMs exchangeable forms in the soils of agricultural fields located near the power station over a 10-year monitoring period. Green line is the maximum permissible concentrations (MPC). *—outlier.

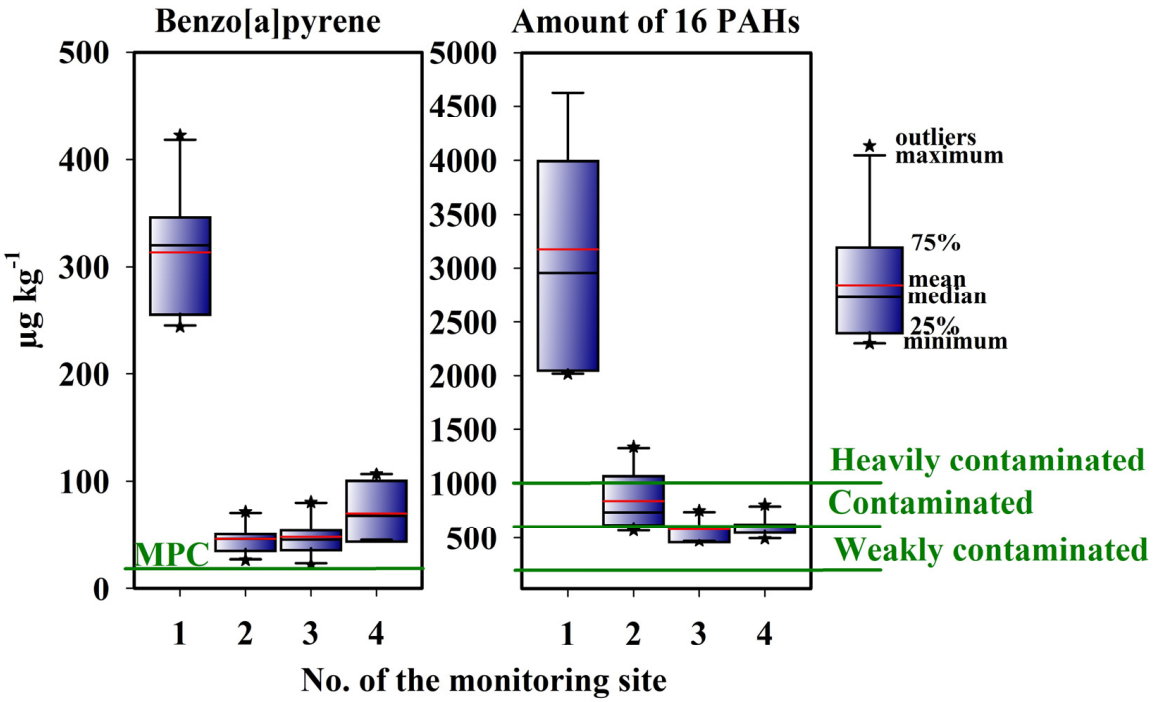

Figure 4. The content of benzo[a]pyrene and the total amount of 16 priority PAHs in the soils of agricultural fields located near the power station over a 10-year monitoring period. *—outlier.

Overall, the distribution patterns of HM exchangeable forms had similar tendencies in the total concentration of elements in the soil of agricultural fields (Figure 3). However, MPC was exceeded by HM exchangeable forms only in the monitoring site No. 1 for Pb, Cu, Cr, and Cd throughout the entire study period, which indicated the technogenic origin of the established concentrations for these elements. The decreasing order of the HMs mobile forms content somewhat differed from their total content: Mn > Zn > Cr > Pb > Cu > Ni > Cd.

In contrast, an increase in the amount of Pb and Cu was observed in the existing series of exchangeable forms.

The concentration of BaP and the total amount of 16 priority PAHs exceeded the background values throughout the study. At the same time, the highest concentration of polyarenes was observed for the soil of monitoring site No. 1 (2.0 km W), which was subjected to the greatest technogenic load due to its location in the prevailing wind direction and minimal distance from the enterprise. For the entire period of monitoring studies, the content of BaP on average exceeded the MPC by more than 16 times. The total concentration of 16 priority PAHs in soil from monitoring site No. 1 (2.0 km W) corresponded to heavily polluted soils. Soils from site no. 2 (1.5 km N) corresponded to polluted ones, according to the classification proposed by Maliszewska-Kordybach [40]. Finally, soils from site no. 3 (2.2 km S) and no. 4 (2.1 km E) related to the category of polluted and slightly polluted soils, respectively (Figure 4). Grouping by soil pollution with the total amount of 16 priority PAHs was determined based on data from [39].

During the observation period, the concentration of almost all the studied pollutants increased in soils (Table 2). Significant increase was also found in the concentration of exchangeable forms of Pb, Cu, Ni, Cd, as well as BaP in the soils from monitoring site No. 1, located on the windward side of the NPS. The soils from monitoring sites No. 2 and No. 3 were characterized by an increase in the content of only exchangeable Pb, Zn, Cu, and BaP (Table 2).

Table 2. Correlation between the content of pollutants in soil and time.

Pollutant	№ Monitoring Site			
	1 (W)	2 (N)	3 (S)	4 (E)
	Exchangeable forms of heavy metals			
Pb	**0.77**	**0.49**	**0.58**	0.01
Zn	0.35	**0.45**	**0.77**	0.31
Cu	**0.59**	**0.46**	**0.56**	0.11
Ni	**0.79**	−0.07	0.28	−0.21
Mn	0.36	−0.18	0.25	0.31
Cd	**0.45**	0.33	0.33	0.41
Cr	0.32	0.06	0.17	0.18
	The total content of heavy metals			
Pb	−0.10	0.15	−0.07	0.05
Zn	0.35	−0.09	−0.28	−0.05
Cu	0.34	0.40	0.37	−0.07
Ni	0.07	−0.12	0.13	−0.17
Mn	−0.17	0.06	−0.17	−0.12
Cd	−0.04	0.42	0.31	0.35
Cr	−0.31	−0.27	0.31	−0.22
		PAHs		
Sum of PAHs	−0.17	0.06	−0.17	−0.12
BaP	**0.65**	**0.74**	**0.54**	0.27

Note: bold indicates significant correlations obtained as a result of calculating the Spearman correlation coefficient at $p < 0.05$.

The accumulation of HMs and PAHs in various organs of common wheat (*Triticum aestivum*) reflected the pollutants content in the soil. The highest concentrations of HMs and PAHs were observed in plants growing on monitoring site no. 1 (W), where the MPC in wheat grain exceeded for Zn, Cu, Pb, and Cd by 1.6, 2.1, 19.8, and 6.0 times, respectively (Table 3). Site No. 4 was characterized by the lowest content of most HMs in wheat plants, which can be attributed to its remoteness from the emission source (2.1 km) compared to sites no. 1 and no. 2 and the location of this point on the leeward side of the NPS. The consistency of data obtained confirms the anthropogenic origin of the increased concentrations of elements in plants. On average, over the entire observation period, Pb,

Cd, and BaP concentrations exceeded the MPC in wheat grains regardless of the sampling location, as well as Zn and Cu in plants from monitoring site no. 1 (W) (Table 3).

Table 3. Concentration of HMs, BaP, and 16 priority PAHs total amount (∑16 PAHs) in various parts of different parts of wheat sampled from agricultural fields located near the power station (2012–2021).

№	Parameter	Mn	Zn	Cr	Cu	Pb	Ni	Cd	БаП	∑16 PAHs
					mg kg^{-1}					μg kg^{-1}
					Root					
1 (W)	mean	56.2	**81.2**	21.0	**21.5**	**9.4**	9.8	**0.6**	63.6	734.7
	min/max	42.0/67.0	61.9/126.6	16.0/28.0	12.0/26.9	7.0/11.6	7.9/13.9	0.3/0.8	44.5/100.5	404.8/996.0
2 (N)	mean	40.5	55.8	11.7	6.0	**12.5**	7.8	**0.7**	15.6	392.6
	min/max	22.0/61.0	41.3//63.0	7.7/15.0	2.7/8.0	8.4/20.4	5.7/8.8	0.4/1.0	10.4/26.9	237.2/545.9
3 (S)	mean	53.6	48.9	7.2	11.1	**2.7**	3.2	**0.4**	13.4	369.6
	min/max	23.4/71.3	33.6/77.3	5.0/8.1	1.5/14.4	1.8/3.8	1.7/4.1	0.1/0.5	8.4/26.7	223.1/494.1
4 (E)	mean	20.7	42.8	6.6	3.4	**5.5**	2.8	0.1	21.1	407.7
	min/max	11.5/32.2	32.6/59.1	5.2/9.8	1.4/4.8	3.9/6.5	2.4/6.4	0.04/0.2	12.4/35.6	295.8/576.7
					Stem					
1 (W)	mean	60.6	**80.5**	19.5	**24.9**	**16.2**	9.1	**0.6**	16.3	101.8
	min/max	36.6/74.2	52.0/163.3	9.4/47.7	6.0/89.5	2.4/30.1	4.5/15.0	0.2/1.0	9.4/22.8	66.8/146.4
2 (N)	mean	37.7	48.3	11.6	5.7	**11.8**	7.7	**0.7**	10.4	127.4
	min/max	18.4/83.3	32.0/82.1	6.9/16.0	2.4/11.0	5.0/18.2	3.3/12.8	0.3/1.1	6.0/16.9	74.7/205.7
3 (S)	mean	47.3	44.7	11.3	12.8	**4.8**	3.1	**0.4**	10.2	166.6
	min/max	31.3/84.9	29.6/86.2	2.1/17.0	2.0/57.3	0.6/9.1	2.4/5.8	0.1/0.8	6.4/17.1	80.3/230.1
4 (E)	mean	20.3	42.9	7.6	3.0	**5.1**	2.8	0.1	16.2	188.0
	min/max	9.6/47.9	14.1/94.5	3.9/10.6	1.5/4.6	3.4/6.5	2.2/4.0	0.04/0.4	8.4/27.6	118.5/324.4
					Grains					
1 (W)	mean	54.7	**82.8**	20.9	**21.2**	**9.9**	8.7	**0.6**	**4.1**	71.8
	min/max	23.7/112.3	33.3/217.0	10.7/32.3	14.0/39.6	3.5/37.4	4.7/21.6	0.3/1.7	2.5/5.9	46.1/109.7
2 (N)	mean	40.4	48.4	10.6	9.8	**12.5**	10.1	**0.6**	**2.8**	99.1
	min/max	14.5/62.4	27.2/108.4	5.9/25.8	1.7/16.0	2.8/33.8	1.4/31.2	0.3/1.6	2.1/4.1	49.7/146.5
3 (S)	mean	46.0	43.3	5.7	10.0	**2.5**	3.2	**0.4**	**3.3**	126.3
	min/max	26.0/116.5	21.2/69.9	4.0/10.7	2.0/25.7	1.2/4.0	2.1/5.7	0.1/1.5	2.3/5.8	55.4/214
4 (E)	mean	23.2	43.3	6.3	4.0	**9.7**	3.2	**0.2**	**4.5**	139.0
	min/max	8.6/32.7	23.8/84.7	4.0/13.9	1.5/6.4	0.8/35.8	2.1/4.0	0.04/0.3	2.2/7.1	65.8/231.1
MPC		-	50	-	10	0.5	-	0.1	1.0	-

Note: bold values indicates exceeding MPC.

Correlations between the content of pollutants in the soil and in the wheat were found (at $p < 0.05$) (Table 4). A significant correlation was observed between the content of Mn, Cr, and BaP in the soil and various plant parts. The results demonstrated a significant correlation of Zn and Pb between soil and root, as well as between soil and the stem. For other studied pollutants, including Cu, Ni, and Cd, as well as 16 priority PAHs, significant relationships can be traced only between the concentrations in soil and roots. In this case, the lack of significant correlations indicates either the presence of a selective element-static barrier on the path of pollutant migration in the soil–roots–stems–grain system or foliar input of HMs and PAHs into the aboveground organs of wheat.

Table 4. Correlation between the content of pollutants in soil and various parts of wheat plants (*Triticum aestivum*).

Plant Part	Soil								
	Mn	Zn	Cr	Cu	Pb	Ni	Cd	BaP	∑16 PAHs
Roots	**0.52**	**0.81**	**0.87**	**0.58**	**0.79**	**0.51**	**0.52**	**0.90**	**0.81**
Stems	**0.51**	0.48	**0.51**	0.44	**0.51**	0.07	0.09	**0.67**	0.28
Grain	**0.54**	0.40	**0.80**	0.34	0.40	0.33	0.22	**0.66**	0.20

Note: bold values indicate significant correlations obtained as a result of calculating the Spearman correlation coefficient at $p < 0.001$.

Relationships between the absorption of pollutants during the period of plant growth and the duration of exposure to the pollutant were determined (Table 5). It was shown that as one approaches the source of emission, the relationship between the content of pollutants in plants increases, which is more typical for roots.

Table 5. Relationship between pollutant uptake during plant growth and the duration of pollutant exposure.

Pollutant	№ Monitoring Site											
	1 (W)	2 (N)	3 (S)	4 (E)	1 (W)	2 (N)	3 (S)	4 (E)	1 (W)	2 (N)	3 (S)	4 (E)
	Root				Stem				Grains			
Mn	**0.80**	**0.77**	0.50	0.65	**0.73**	**0.66**	0.50	0.64	**0.54**	**0.72**	0.31	0.65
Zn	**0.70**	0.53	0.11	**0.75**	**0.70**	0.64	0.17	**0.71**	**0.72**	0.61	0.07	**0.70**
Cr	−0.05	**0.78**	−0.04	**0.70**	−0.10	0.31	0.07	**0.75**	0.12	**0.74**	−0.27	0.26
Cu	**0.75**	−0.30	**0.78**	**0.79**	−0.22	−0.06	0.37	0.33	**0.70**	0.13	0.62	**0.72**
Pb	**0.79**	**0.72**	−0.19	0.16	−0.08	0.65	0.14	−0.19	**0.71**	0.11	0.06	0.06
Ni	**0.70**	0.57	**0.75**	0.01	−0.14	0.13	−0.20	−0.01	0.03	0.06	−0.09	0.29
Cd	0.58	**0.73**	−0.35	0.74	0.60	0.64	−0.30	0.69	0.60	0.60	−0.30	0.55
BaP	**0.79**	0.25	0.36	−0.16	0.38	0.15	0.20	−0.12	0.30	0.15	0.26	−0.10
16 PAHs	**0.72**	**0.74**	0.66	0.32	0.61	0.63	0.51	0.30	0.64	0.66	0.60	0.03

Note: bold values indicate significant correlations obtained as a result of calculating the Spearman correlation coefficient at $p < 0.001$.

Determination of the significance in the *Triticum aestivum* barrier mechanisms preventing the pollutants migration in the soil–root–stem–grain system, as well as the analysis of the HM and PAH redistribution coefficients (AC) between the soil and various plant organs, was carried out. The accumulation of pollutants in plants and the intensity of their migration from the soil to the grains were different for various types of contaminants: inorganic and organic, and HMs and PAHs, respectively. The AC of Mn, Ni, and Cr was characterized by relatively lower values and did not depend on the proximity to the emission source. The redistribution coefficients of elements in the root–stem (TF1) and stem–grain (TF2) systems were lower than those in the soil–root system (Figure 5) Overall, the values of TF1 and TF2 for various HMs in wheat (*Triticum aestivum*) were at par with each other. However, there was an increased variability in the intensity of Pb and Cu accumulation, which may be correlated with their content increasing in the soil over the monitoring period (Table 3, Figure 5). In this case, the PAHs migration intensity into common wheat organs was lower than that of HMs. The redistribution coefficients of PAH AC, TF1, and TF2 were below 1. The redistribution coefficients of the 16 PAHs total content decreased in the following order: soil–root (AC) > root–stem (TF1) > stem–grain (TF2). A similar trend was also observed for BaP accumulation in wheat (*Triticum aestivum*) from monitoring site No. 1, while for plants from other monitoring sites, TF1 values slightly exceeded AC, which might be due to the lower technogenic load and subsequently a reduced barrier function (Figure 5).

Using clustering of the data obtained over a 10-year monitoring period, pollutant groups were identified that have similar patterns of migration in the soil–roots–stems–grains system under a technogenic load emerging from a point emission source (Figure 6). According to the pollutant's accumulation nature in the roots, two clusters were identified. The first cluster represented by HMs did not perform vital physiological functions (viz. Cd and Pb), while the second cluster represented all other studied pollutants, including PAHs. More importantly, the content of the HMs exceeded the MPC in grains (Table 3).

Based on the results of the pollutants accumulation in the stems, two clusters were identified. Similar results were obtained by clustering the content of pollutants in the grains. For the above-ground parts of the plant, two clusters were identified, the first of which was represented by organic pollutants, while the second was represented by inorganic pollutants (Figure 6).

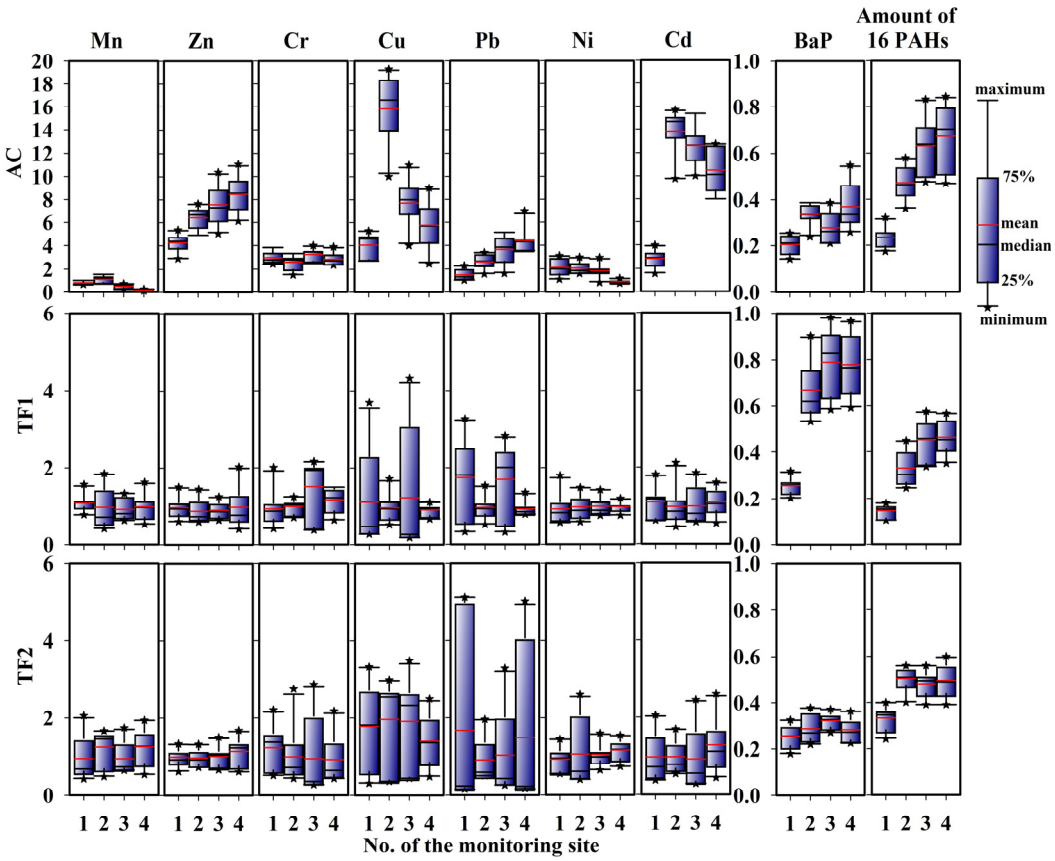

Figure 5. Accumulation coefficient (AC), translocation coefficients of pollutants between at the root-stem (TF1), and stem–grain (TF2) boundary of various pollutants in wheat (*Triticum aestivum*) over a 10-year monitoring period. *—outlier.

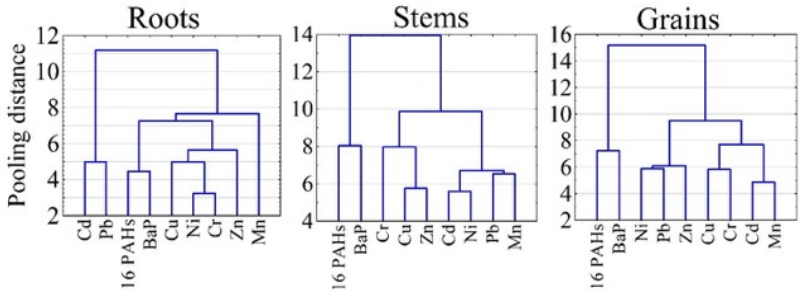

Figure 6. Clustering of pollutants in different parts of the plant over a 10-year monitoring period.

4. Discussion

For the study area, the greatest accumulation of pollutants in the W and N directions was due to the prevailing wind direction, which was previously discussed in studies performed for soils located around emission sources [42–45]. Categorically, higher PAH content was observed in soils located in the vicinity of power stations [20,46]. Due to the continuous mutually exclusive processes of accumulation and destruction of PAHs in the environment, their concentration in the soil characterizes the intensity of the emission source over time [32,47–50]. Interestingly, the increase in the mobility of HMs in soils are most likely a consequence of continuous exposure to atmospheric emissions from the power station. Similarly, an increase in the concentration of Pb, Zn, Cu, and Cd was observed during a fifteen-year monitoring of agricultural soils located near areas with heavy industrialization [51]. Soil contamination with Cd, Pb, and Zn has been extensively reported near smelters, power plants, and highways [20,52,53]. These elements can be

considered as the indicators for diagnosing the ecological state of soils [52]. The increase in the content of BaP in soils over a 10-year monitoring period was primarily a consequence of an increase in the intensity of the technogenic load from a point source, such as thermal power plant NPS. The above-mentioned hypothesis was validated by the change in the strategy of soil self-purification through microbiological degradation to the process of "soil aging", i.e., stable sorption of PAHs by the organic–mineral matrix [48,54–56]. Nadal et al. also observed an increase in the content of PAHs in the soils of the impact zones over time near chemical and petrochemical plants [57].

It should be noted that, for wheat plants, predominant accumulation of only PAHs was observed in the roots, while HMs were accumulated to a greater extent in the stems and grains. Consequently, there was a long-term multi-element contamination of wheat plants with HMs. However, the total concentration of elements accumulated in the plant was relatively low and did not characterize wheat (*Triticum aestivum*) as an accumulator or hyperaccumulator of HMs. Hyperaccumulators include plants that actively absorb excessively large amounts of one or more HMs from the soil. Under conditions of soil pollution, hyperaccumulators accumulate 100–1000 times more HMs in shoot and leaf tissues than plants that do not belong to this class [58]. Within the same family, different plant species may exhibit similar tolerance to HM pollution [59,60]. As part of the *Poaceae* family, southern reed can be classified as a hyperaccumulator [33] Despite wheat (*Triticum aestivum*) belonging to the *Poaceae* family, it does not have typical features for increased accumulation of HMs in comparison with other species. This was also confirmed in previous studies on this area regarding the accumulation of HMs by plants *Artemisia austriaca* Pall., *Achillea nobilis* L., and *Ambrosia artemisiifolia* L. [26,41]. Consequently, the accumulation of HMs exceeding the MPC, especially for elements that are not essential for catalyzing physiological functions in wheat (viz. Cd and Pb), is primarily due to the intensity of the technogenic load from the emission source [58]. The same may be endorsed for the accumulation of PAHs in plants. This is especially pronounced for the carcinogen of the first hazard class BaP. Artificial soil contamination of Haplic Chernozem by BaP in the amount of 20 ng g^{-1} led to disorientation in the root architecture in spring barley (*Poaceae* family), which subsequently led to losses in yield and quality of the cultivated crop [61].

A significant correlation between the content of Mn, Cr, Zn, Pb, and BaP in the soil and roots, as well as between the soil and aboveground parts of wheat, indicates the migration of these pollutants directly from the soil into the plant. At the same time, the absence of such correlation for Cd, Cu, Ni indicates either the presence of a selective element-static barrier on the path of pollutant migration in the soil–roots–stems–grain system or foliar input of HMs and PAHs into the aboveground organs of wheat. There is also a correlation between the absorption of pollutants during the phenological phases of plant ontogenesis and the duration of exposure to pollutants, since it is only during the growing season that it is transferred from the soil to the aboveground part of the plant [62,63].

The obtained AC values indicated a significant influx of Cd, Cu, Zn, and Pb into the roots of wheat from mobile forms in the soil (Figure 3). Simultaneously, the AC values for these elements increased depending on the proximity of plants cultivated near the emission source; in descending order, No. 1 > No. 2 > No. 3 > No. 4. This trend of pollutant accumulation in the roots indicated that their entry into the root part of wheat was more intense at a lower level of technogenic load due to the absence of the barrier function. The AC of Mn, Ni, and Cr was characterized by relatively lower values and did not depend on the proximity to the emission source. The lower values of TF1 and TF2 are indicating the presence of a definite barrier for limiting HM migration in the root–stem–grain system. The increased variability of the Pb and Cu redistribution coefficients with comparable median values of TF1 and TF2 for different HMs, which was most likely due to an increase in the level of technogenic load over the time. In addition, their accumulation in the aboveground organs may also be attributed to regular foliar exposure to these HMs. At the same time, the increased AC depending on the proximity of plants to the emission source indicated

that their entry into the root part of wheat was more intense at a lower level of technogenic load due to the absence of the barrier function.

The less intense migration of PAHs into plant organs compared to the HMs was due to their lower water solubility [24,64] and indicated the presence of element-static barriers to the migration of soil–root–stem–grain pollutants. Higher values of AC from the sum of the 16 priority PAHs than that of individual BaP exposure may also be attributed to the presence of an individual compound with a higher solubility among the 16 priority PAHs composition (naphthalene, fluorene, phenanthrene, anthracene, acenaphthene, acenaphthylene, pyrene, chrysene, fluoranthene, and benzo[a]anthracene) than BaP [24].

According to cluster analysis, HMs (Cd, Pb) that do not perform physiologically important functions in the plant were combined into a separate group. The presence of Cd in the plant system often interferes with vital biochemical processes including membrane transport, protein binding, and interactions with other elements viz. Ca [65]. Moreover, Pb is an antagonist of Cd, as its uptake provokes an increased accumulation of Ca and Mg in plant tissues [66,67]. Most likely, two mutually exclusive processes occur inseparably from each other, regulating the supply of both metals to the roots, while other elements and PAHs migrated in the roots of wheat without significantly affecting the accumulation of each other through diffusion [65,68].

The intensity of HM and PAH migration from the root to the stem and further to the grain is primarily due to their solubility, which was also evidenced by the results of cluster analysis, namely, the association of PAHs into a group isolated from HMs.

5. Conclusions

An increase in the level of technogenic load on the soils and plants located near a large power station over time (10 years) was observed for Haplic Chernozem soil and common wheat (*Triticum aestivum*). An accumulative effect of emissions from the thermal power plant was reflected in the concentrations of Pb, Zn, Cu, and BaP in soils and plants sampled from the exposed territory. At the same time, the highest technogenic load was recorded in the soil and plant samples from monitoring site No. 1 (2.0 km W), located on the windward side of the emission source. The proximity of agricultural land to the power station significantly contributed to the accumulation of Pb, Cd, and BaP in wheat grains in concentrations exceeding the MPC levels. An increased concentration of pollutants was also observed in the wheat stem over the period. The active presence of plant barrier mechanisms on the soil–root–stem–grain migration pathways was also observed. Barrier functions of common wheat were more significant for PAHs than for HMs, especially on the root–stem and grain–stem migration pathways. Finally, it was demonstrated that soil was not the only primary source of PAHs and HMs entry into plant tissues, but the regular foliar exposure through emissions of the power station, especially in the windward direction, also led to significant accumulation in the plant tissues.

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