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Identification of Technogenic Magnetic Particles and Forms of Occurrence of Potentially Toxic Elements Present in Fly Ashes and Soil

Małgorzata Wawer

Institute of Environmental Engineering, Polish Academy of Sciences, 34 Skłodowska-Curie St., 41-819 Zabrze, Poland; malgorzata.wawer@ipis.zabrze.pl; Tel.: +48-322716481

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Abstract: Solid fossil fuel power plants are the main source of energy in Poland. In 2018, the most important energy carrier was hard coal with a share of 57.9%, followed by lignite with a share of 18.1%. In addition to CO_2, NO_x and SO_x, the combustion of fossil fuels produces dusts containing, among others, potentially toxic elements (PTEs), e.g., Pb, Zn, Cu, Cr, Cd. Although the currently operating power plants have efficient filter systems, the total dust emission in Poland in 2017 amounted to 341,000 t, of which approximately 36,000 t was from the power plants. PTEs present in the power plant dust are often accompanied by technogenic magnetic particles (TMPs)—mainly iron oxides and hydroxides formed in high-temperature technological processes as a result of the transformations of iron minerals contained in raw materials and additives. The presence of magnetic iron minerals (e.g., magnetite, hematite, maghemite, metallic iron) in the tested ashes from hard coal and lignite power plants was confirmed by scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS) analysis. The sequential extraction analysis showed that most of the analyzed PTEs found in dust after hard coal combustion were mainly related to amorphous and crystalline FeO_x or in the residual fraction and in dust after lignite combustion, mainly in the most mobile fractions.

Keywords: fly ashes; soil pollution; potentially toxic elements; technogenic magnetic particles; sequential extraction

1. Introduction

Current trends and new regulations implemented in the European Union force the gradual reduction in fossil fuels as traditional energy sources, contributing to the diversification of these sources and increasing the share of low-carbon and renewable energy. What is more, the European Commission supports an increase in financing for low-carbon energy, which will also lead to the phasing out of support for fossil fuel projects, including natural gas [1]. Despite these arrangements, new coal-fired power plants and power units are still being designed and opened in Poland, and it is not expected that this source of energy will be abandoned in the near future. Solid fossil fuel power plants are the main source of energy in Poland. In 2018, the most important energy carrier was hard coal with a share of 57.9%, followed by lignite with a share of 18.1%. The share of natural gas in indigenous production amounted to 5.5%, crude oil 1.6%, and the other, mainly renewable energy, sources 16.9% [2]. In addition to carbon dioxide, nitrogen oxides and sulfur dioxide, during the burning of fossil fuels, dusts are formed that contain, among others, potentially toxic elements (PTEs).

Currently operating power plants in Poland must meet a number of requirements related to air protection, consisting of reducing emissions of nitrogen oxides, dust, sulfur oxides and carbon dioxide. Therefore, the units are equipped with flue gas cleaning systems that take into account the interrelationships of denitrification, dust removal and desulphurization systems and meet the

requirements of the best available techniques (BAT). Despite the use of systems with an efficiency of approximately 99.9% for dust removal or 81% for desulphurization, fossil fuel power plants are still a large emitter of pollutants in Poland [3]. The total dust emission in 2017 in Poland amounted to 341,000 t, of which approximately 36,000 t was from power plants [4]. These data show how important the risk is related to the emission of pollutants from the combustion of fossil fuels for energy production. The potentially toxic elements (PTE) emitted along with fine (respirable) dust fractions—PM10 and PM2.5—which can enter the lungs with the air, are especially dangerous for humans. The effect of particulate matter on human health is well known. It is certain that even a relatively short exposure to fine particles containing potentially toxic elements present in the atmosphere may be associated with an increased risk of cardiovascular and respiratory diseases as well as lung cancer [5–9]. Fly ashes emitted by power plants can also be transported over long distances and finally deposited on the surface of buildings, water reservoirs, plants or soils, posing a serious threat to the environment [10–12]. Potentially toxic elements, such as nickel, copper, zinc, cadmium, lead or chromium, accumulated in soil may affect the ecosystem over the next several decades or even centuries, especially when they occur in mobile forms that have a strong negative impact on the environment [13–16]. When insoluble, they are ecotoxicologically inactive as long as the pH remains alkaline or at least neutral [17]. It is also not without significance that before the application of efficient filters and flue gas desulphurization installations, power plants emitted very large amounts of dust. In the early 1990s, the energy sector in Poland emitted over 550,000 t of dust annually [18]. Along with the dust, large amounts of potentially toxic elements, including lead (1400 t/year), cadmium (95 t/year) and mercury (35 t/year), entered the soil [18]. These non-biodegradable elements are still present in the soil and pose a threat to the environment.

A comprehensive analysis of the magnetic properties of the fly ash has shown that all fly ash emitted by power plants contain technogenic magnetic particles (TMPs). TMPs generated in high-temperature technological processes (including the combustion of fossil fuels) from various iron minerals present in raw materials, fuels and additives are transformed into highly magnetic iron oxides [19]. Their presence in the analyzed samples can be quickly detected by simple measurements of magnetic susceptibility. It is also known that TMPs are PTE carriers, which makes them useful for indirect identification of soil contamination with heavy metals [20–23]. Previous studies have shown that from the point of view of human health, the forms of metals and metalloids and their bioavailability are more important than their total content in dust [24–28]. The total content of metals and metalloids does not provide information on the real risk to flora and fauna as it is not known what proportion of PET is in the forms available to living organisms [29]. Therefore, the main objective of the research was to answer the question: is there a difference in the ecological risk associated with the mobility of individual PTEs present in fly ashes from hard coal and lignite power plants? In order to assess the bioavailability of potentially toxic elements present in power fly ash and soils collected in the vicinity of the power plant and to determine which elements are connected with iron oxides (TMPs), speciation analysis based on sequential chemical extraction was carried out according to the Zeien and Brümmer method [30]. Sequential extractions involve the successive digestion of the mineral and organic phases, and thus the release of heavy metals associated with them. Leaching occurs under conditions that simulate both natural and anthropogenic environmental changes [31–33]. Although the Zeien and Brümmer method was developed for soil samples, assuming that fly ash often settles in the soil environment, in this case, it was used for industrial dust samples. Given that fly ashes after solid fossil fuels combustion are common dusts in the atmosphere and they eventually enter the soil, they can be used to assess the environmental risk of dust deposition in soil. A modified risk assessment code (RAC) was used to better assess the risk of fly ash deposition after solid fuel combustion. RAC was introduced by Perin et al. [34] to determine the environmental toxicity of heavy metals. Another question posed was: is it possible to confirm a common source of the technogenic magnetic particles present in fly ash emitted by power plants and accumulated in soil? The combination of mineralogical and chemical analyses together with the geoaccumulation coefficient and risk assessment code allowed for a more

complete understanding of the relationship between the emission hazard and the deposition of fly ash containing potentially toxic elements.

2. Materials and Methods

As part of the study, eight samples of fly ashes were analyzed, four samples from a hard coal power plant (electrical generating capacity of 1492 MW/1532 MW; equipped with electrostatic precipitators, non-catalytic nitrogen oxide reduction system and wet flue gas desulphurization installation) located in Southern Poland and four samples from a lignite power plant (electrical generating capacity of 368 MW; equipped with electrostatic precipitators and wet flue gas desulphurization installation) located in central Poland (names of power plants protected by a confidentiality agreement). Fly ashes were collected from different areas of electrostatic precipitators by power plant employees. Samples taken from subsequent horizons of the soil profile in the forest located in Jaworzno near the coal-fired power plant were also analyzed. A site with undisturbed soil horizons was selected for sampling in a pine forest that had been growing for over 50 years. About 500 g of samples were taken with a plastic spatula from individual levels in a shallow soil pit. Jaworzno is located in Southern Poland in the Upper Silesia industrial region. In Jaworzno, apart from sand, limestone, dolomite and hard coal deposits, there were also zinc-lead ores, which were exploited from the 12th century. Moreover, until the 1970s, a zinc smelter operated in the city [35].

The low field magnetic susceptibility (κ) of soil samples was measured with the use of Bartington MS2 apparatus with MS2B sensor (Bartington Instruments Ltd., Witney, UK) to calculate the mass-specific (χ) magnetic susceptibility with the following equation:

$$\chi = \kappa/q \ (\times 10^{-8} \ m^3 \cdot kg^{-1}) \tag{1}$$

where q is the density of the sample placed in a standard 10cc Bartington plastic container. This parameter confirms the presence of magnetic particles in the sample. Sequential chemical extraction described by Zeien and Brümmer [30] has been used to determine the potential mobility and bioavailability of metals in the samples. It is a seven-step chemical extraction procedure from the soluble/exchangeable fraction to the residual fraction, in which the next steps use solutions of increasing aggressiveness. Metal mobilization decreases in the order: soluble > exchangeable > carbonate > Fe–Mn oxide > organic > residuum [36,37].

The extracting agents, as well as their operationally defined fractions, are presented in Table 1.

Table 1. Sequential extraction procedure.

Step	Fraction	Extractants	Equilibration
F1	Soluble + Exchangeable fraction	1 M NH_4NO_3, pH 7.0	S:L* 1:25, shaking for 24 h at room temperature
F2	Easily mobilizable fraction (bound to carbonate)	1 M NH_4OAc, pH 6.0	S:L* 1:25, shaking for 24 h at room temperature
F3	Manganese oxide fraction (bound to Mn (hydr)oxides)	0.1 M NH_2OH-HCl + 1 M NH_4OAc, pH 6.0	S:L* 1:25, shaking for 30 min at room temperature
F4	Organic fraction (bound to soil organic matter-SOM)	0.025 M NH_4EDTA, pH 4.6	S:L* 1:25, shaking for 90 min at room temperature
F5	Amorphous iron oxide fraction (bound by low crystalline Fe (hydr)oxides)	0.2 MNH_4-Oxalate buffer, pH 3.25	S:L* 1:25, shaking for 4 h at room temperature
F6	Crystalline iron oxide fraction (bound by crystalline Fe (hydr)oxides)	0.1 M ascorbic acid in 0.2 M NH_4-Oxalate, pH 3.25	S:L* 1:25, shaking for 30 min at water bath on 96 °C
F7	Residual fraction (mineral form)	Aqua regia (HCl + HNO_3)	S:L* 1:25

*S:L—sample to liquid ratio.

After each extraction step, the tube containing the solid samples and the extractant was centrifuged for 15 min at 1700 g. Then, the solution was filtered through 0.45 µm cellulose acetate filter paper. The residual samples were used for the subsequent extraction steps.

The content of selected elements (Zn, Cu, Pb, Cr, and Cd in fly ashes and Fe, Mn, Zn, Pb, Cd, Cu, Cr, Co and Ni in soils) in individual fractions was determined with the flame atomic absorption spectrometer (Avanta model, GBC Scientific Equipment Pty Ltd, Melbourne, Australia). The quality assurance and quality control procedures were performed using soil certified reference materials (GBW 08303 and BCR-176R), the percentage recovery for the six observed elements ranged from 93% to 107%.

Selected fly ash samples were subjected to scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS) analysis. The SEM/EDS analysis was performed in high vacuum with the use of an environmental scanning electron microscope Philips XL 30 ESEM/TMP equipped with an energy dispersive detector (EDAX detector, Sapphire type, Ametek, Inc., Berwyn, PA, USA). For SEM/EDS analysis, the technogenic magnetic particle (TMP) fraction was enriched by magnetic separation. For this purpose, the beaker with the sample and isopropanol was placed in an ultrasonic cleaner. The sample was sonicated for 30 min to break up agglomerates. Then, the magnetic fraction was separated with a hand magnet. After separation, the magnetic fraction was dried in an oven at 40 degrees to evaporate the isopropanol.

The geoaccumulation index (I_{geo}), introduced by Müller [38], helps to determine the degree of PTE accumulation in soil in relation to the geochemical background content. I_{geo} was calculated for the upper horizons of analyzed soil from the following formula:

$$I_{geo} = \log 2 \, (CEL/1.5 \, C_{background}) \tag{2}$$

where CEL is the element content determined in soil samples, and $C_{background}$ is the geochemical background concentration of the metal. Factor 1.5 is the correction factor that compensates the natural (lithological) fluctuations in the geochemical data. Background values were taken from Kabata-Pendias and Pendias [39] for limestone and dolomites, which are the bedrock in this region. According to Müller [38], soil is: $I_{geo} \leq 0$ uncontaminated; $0 < I_{geo} < 1$ uncontaminated to moderately contaminated; $1 < I_{geo} < 2$ moderately contaminated; $2 < I_{geo} < 3$ moderately to heavily contaminated; $3 < I_{geo} < 4$ heavily contaminated; $4 < I_{geo} < 5$ heavily to extremely contaminated; $I_{geo} \geq 5$ extremely contaminated.

A risk assessment code (RAC) was used to evaluate the environmental risk associated with the percentage of bioavailable fraction of metals in soil and sediments. This index is expressed as the percentage of exchangeable fraction (determined by the European Community Bureau of Reference (BCR) method) in the sample. As we used the Zeien and Brümmer method in these studies, which allows the identification of two fractions considered to be easily available—easy soluble and exchangeable fraction—the RAC was determined on the basis of their percentage. Therefore, the RAC was defined as the sum of the percentage of fractions F1 and F2 in the samples. For this purpose, the share of individual fractions in the sample was converted into percentages. When the percentage ratio of the sum of F1 and F2 to the total metal concentration was <1%, the heavy metal was considered to have no adverse impact on the environment. If the ratio was in the range of 1–10%, the risk was low, medium—in the range of 11–30%, and 31–50%—high. A ratio higher than 50% indicates that the risk to the environment is very high as the heavy metal is readily released from the sample matrix [40,41].

3. Results and Discussion

3.1. Fly Ashes Analysis

SEM/EDS analysis carried out on fly ashes after hard coal combustion (Figure 1) showed that a large part of the observed particles were spherical and the composition corresponded to iron oxides (magnetite and maghemite) or aluminosilicates. Quartz grains were also observed, some of which contained admixtures of aluminum and calcium. Spheres with a composition similar to magnetite or in the form of a coating on an aluminosilicate core are typical of magnetic minerals that are formed during

the combustion of coal containing weakly magnetic sulfides (e.g., pyrite and marcasite) [19,42,43]. Similar forms were observed in the magnetic fractions of fly ash after lignite combustion (Figure 2). There were numerous spherical particles of aluminosilicates with admixtures of iron, barium, potassium, and magnesium. These forms of TMPs are typical of coal combustion processes [19].
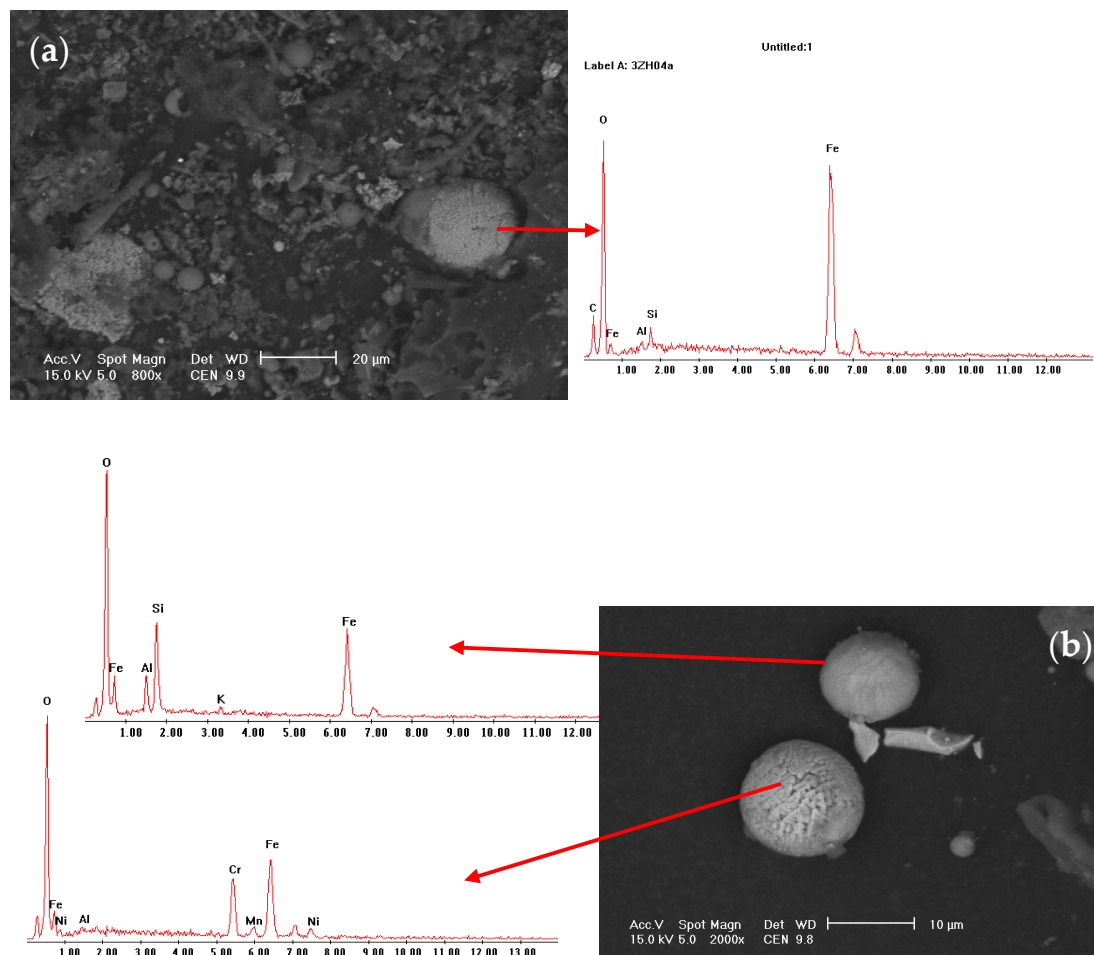
Figure 1. Magnetic phase of fly ashes after hard coal combustion: (**a**) aluminosilicate sphere with a thin coating of magnetite; (**b**) the upper spherule consists of aluminosilicates with a thin coating of iron oxide, the lower spherule consists of iron oxide, chromium, nickel and trace amounts of manganese.

The content of individual analyzed elements in dust from hard coal and lignite power plants differed and was higher in samples of ash after hard coal combustion (except for cadmium) (Table 2). The content of zinc in ashes after burning lignite ranged from 159 to 164 mg·kg^{-1}, and the content in ashes after burning hard coal was higher and ranged from 187 to 244 mg·kg^{-1}. Total lead content ranged from 73 to 114 mg·kg^{-1} in ashes from the lignite power plant and from 97 to 117 mg·kg^{-1} in ashes from the hard coal power plant. The cadmium content in both types of analyzed dust ranged from 4 to 18 mg·kg^{-1}, and chromium from 80 to 105 mg·kg^{-1}. Copper content in ashes from the lignite power plant ranged from 50–60 mg·kg^{-1}. In ashes after hard coal combustion, the copper content was slightly higher and ranged from 78 to 91 mg·kg^{-1}. Although the above values are high, it should be taken into account that the ash samples were collected from various electrostatic precipitators where these dusts were trapped and not emitted to the atmosphere. However, until the 1990s, power plants were not equipped with such efficient filters and most of the pollutants emitted ended up in the air and eventually deposited in the soil.

Table 2. Total content of analyzed potentially toxic elements (PTEs) (mg·kg^{-1}) in dusts.

PTEs	Dust after Hard Coal Combustion				Dust after Lignite Combustion			
	S1	S2	S3	S4	S1	S2	S3	S4
Zn	213	188	199	245	165	159	161	163
Pb	117	97	102	112	75	73	100	115
Cd	6,3	16	11	4.4	7	16	5.8	19
Cu	79	78	83	92	52	56	53	59
Cr	82	92	105	106	90	88	88	88

Sequential analysis showed that in dust after burning hard coal (Figure 3), in the first four tested fractions, zinc was released in small amounts (up to 6%), and most Zn was associated with iron oxides (between 50% and 76% of the Zn released during chemical analysis), with much more being released in the sixth stage of extraction, i.e., the one associated with crystalline iron oxides, and therefore also with TMPs. The remaining part of Zn was associated with an aluminosilicate and silicate phase (F7). In the case of zinc present in ashes after burning lignite (Figure 4), only small amounts were present in forms that were easily soluble, exchangeable, and bound to MnO_x. The vast majority of Zn was found in the F4 fraction—bound to organic matter (42–50%). According to da Silva et al. [44] and Karakaśeva et al. [45], this fraction is temporarily unavailable and could be released if conditions become oxidative. Zinc in the dusts after lignite combustion was also associated with fractions F5 (bound to amorphous FeO_x) and F6 (bound to crystalline FeO_x) (14–22%).
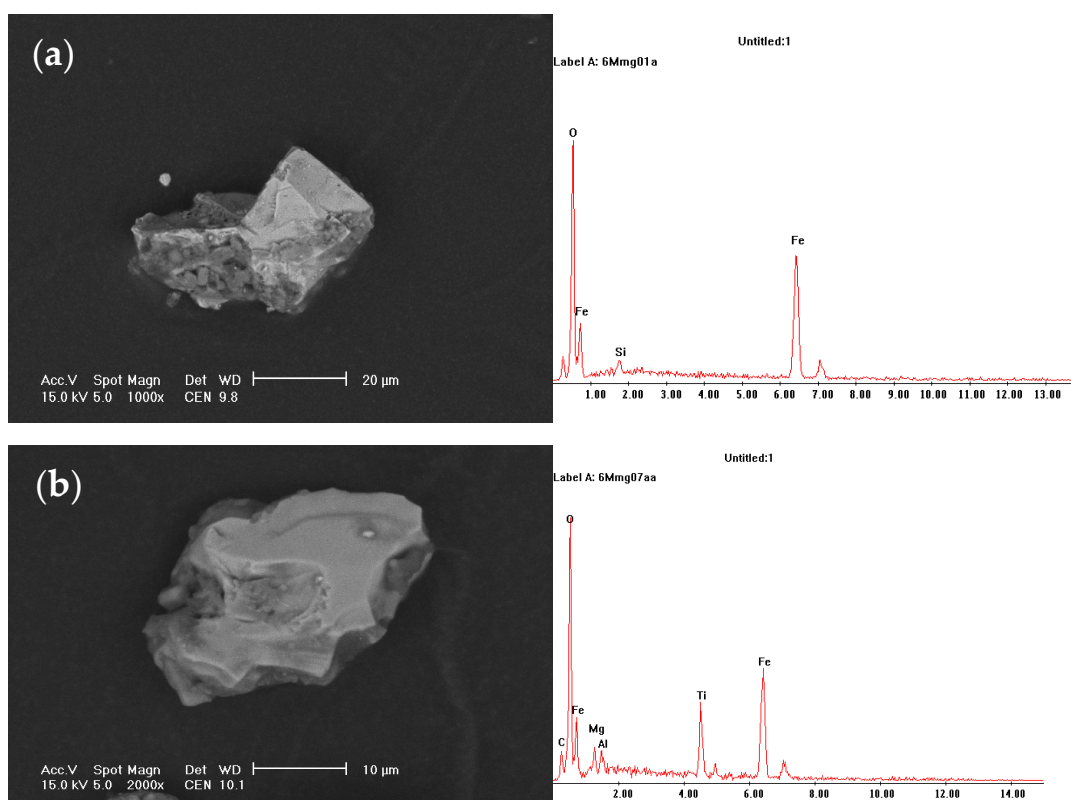
Figure 2. Iron oxide with a structure similar to maghemite (**a**) and (**b**) iron oxide with an admixture of titanium, magnesium and aluminum, present in fly ash after lignite combustion.

A large proportion of the lead present in dust was also present in the mobile fractions. It shows that Pb was weakly bound onto dust particles and could be easily released to soil and plants through ion exchange [27,46]. Lead contained in ashes after lignite combustion was gradually released at almost all stages, and the greatest amount was recorded in fraction F4. In the samples originating

from hard coal combustion, lead was mainly present in the last three fractions, the most of which (43–59%) was present in fraction F6, probably connected with magnetic minerals. Depending on the level of exposure, lead may adversely affect the nervous system, kidney function, immune system, reproductive and developmental systems, and the cardiovascular system. What is more, once taken into the body, lead is distributed throughout the body in the blood and accumulates in the bones [47]. Lead is also bioavailable for plants, but is mainly retained in the roots [48,49].

In ashes from the hard coal power plant, cadmium was mainly released in the first three stages of extraction or was present in the residual fraction. In the case of ashes after lignite combustion, cadmium was released at various stages, but also significant amounts were present in fractions F1, F2, F5 or F7. The fact that in the fly ash from coal-fired power plants cadmium was mainly present in the first three most mobile fractions may be a major threat. This suggests that it was bound to the dust particles mainly by surface adsorption forces and could easily be released into the environment after the deposition of industrial dust on the soil surface. Previous studies by Kuokkanen et al. [50] have shown that cadmium is very volatile and can pass through flue gas channels. In this way, it precipitates on the surface of particulate matter or is emitted into the atmosphere [51]. Cadmium and its inorganic compounds are classified as probably carcinogenic to humans [52].
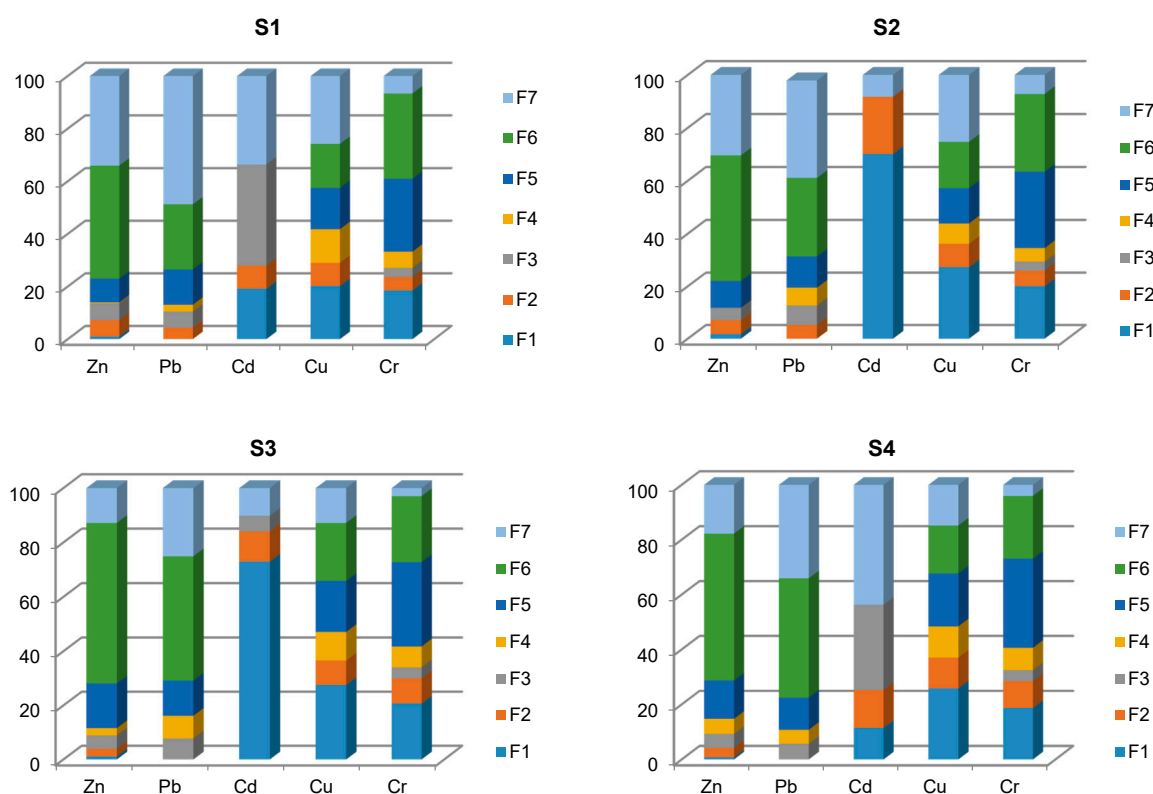

Figure 3. Sequential extraction of fly ashes after hard coal combustion (%).

Copper in ash from the lignite power plant was mainly released at the fifth stage of extraction (39–53%). This indicates that it was mainly associated with amorphous iron oxides; however, up to 20% copper was also present in the mobile fractions (F1 and F2). At the sixth stage of extraction, copper in these dusts was not released at all, which may mean that it is not associated with the crystalline phase of magnetic particles, which was also shown by mineralogical studies. In the ashes after hard coal combustion, Cu was present in almost all fractions except fraction F3, associated with manganese oxides.

Additionally, in both types of dust, chromium was mainly associated with fractions F5 and F6 and to a lesser extent with F1. This means that it was mainly connected with amorphous and crystalline

iron oxides but also some part was probably bounded in the form of surface adsorption. Chromium is considered to be one of the top 20 contaminants on the Priority List of Hazardous Substances in the past 15 years [53]. However, the results of the analyses indicate that in the tested samples it appeared in an immobile form, so it should not pose a threat.
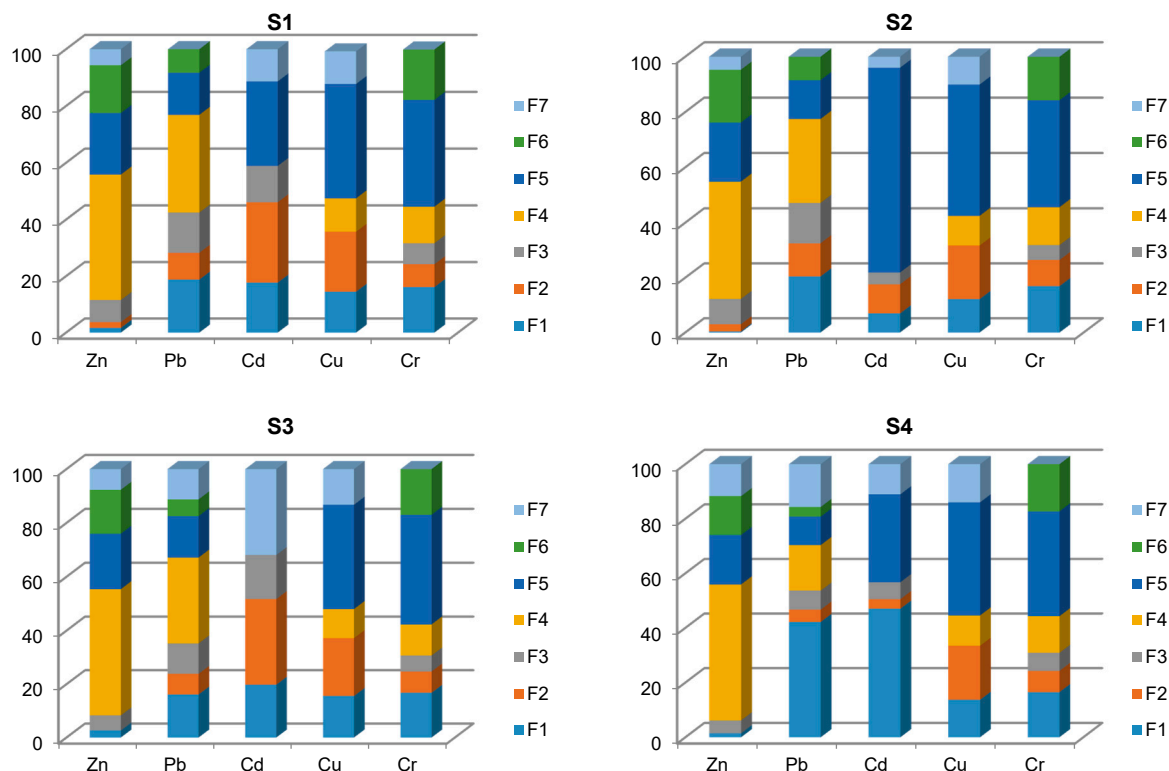

Figure 4. Sequential extraction of fly ashes after hard coal combustion (%).

TMPs, which are mostly stoichiometrically imperfect iron oxides of the magnetite–maghemite series with different chemical compositions, may contain significant amounts of PTEs. Their potential toxicity in the soil environment depends on their mobility, and this in turn is associated with forms of their binding to magnetic iron oxides. Chromium and zinc present in fly ashes after hard coal combustion, as well as copper, cadmium, and chromium in fly ashes after lignite combustion, were undoubtedly associated with iron oxides forming technogenic magnetic particles. These results are supported by previous findings by Magiera et al. [17].
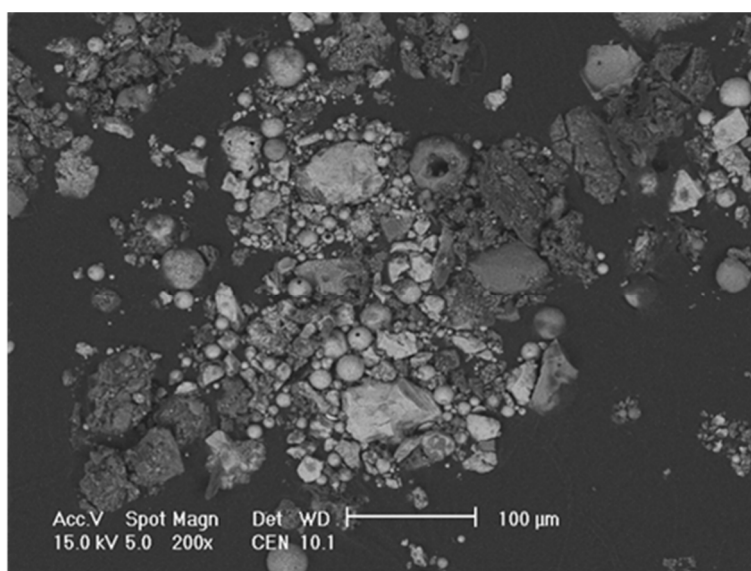
3.2. Soil Samples Analysis

SEM/EDS observation performed on soil samples revealed that the magnetic phase of iron was observed in the form of spheres as well as in the form of sharp-edged particles (Figure 5). Spheres, similar to the case of fly ash, came from high temperature combustions of fossil fuels and the sharp-edged, angular particles could be of detrital origin or related to non-exhaust traffic emissions [54,55].

Following the same methodology as for fly ashes, soil samples from the region affected by coal-fired power plant emissions, which contain significant amounts of dust deposited in the soil as a result of over a century of plant activity, were analyzed. The content of the analyzed elements differed in individual soil layers (Table 3). The higher content of the analyzed elements was found in the organic soil horizons; Oi, Oe, Oa/Ah (0–1 cm, 1–6 cm and 6–15 cm deep, respectively). The highest content of Pb and Fe was found in the Oa/Ah horizon (712 and 16,600 mg·kg^{-1}, respectively). Manganese and zinc contents were higher in the Oe horizon (250 and 450 mg·kg^{-1}, respectively), and the highest content of lead—712 mg·kg^{-1}—was noticed in the Oa/Ah horizon. In the deeper layers of the soil, the content of the above-mentioned metals was much lower. In the E, E/B and B horizons (20–25 cm;

25–40 cm and >40 cm deep, respectively) only trace amounts of Mn, Cd, Pb, Cu, Cr and Ni were found. This shows that most of the pollutants were retained only in the organic horizon, which confirms previous reports that organic matter accumulates and retains pollutants [16,56]. Despite the relatively high content of Fe, Mn, Zn, Pb and Cu in soil samples, the limit value specified in Polish regulations was exceeded only in the case of lead in the Oa/Ah horizon (500 mg·kg^{-1} of lead for forest soil) [57]. The values of magnetic susceptibility were also higher in organic horizons (up to 154 ×10^{-8} m^3 ·kg^{-1}), which indicates the presence of technogenic magnetic particles.

Figure 5. Particles with the composition of iron oxides (light colors of the particles in the photo), darker gray particles are aluminosilicates observed in soil samples.

Table 3. Total content of analyzed PTEs (mg·kg^{-1}) in soil horizons.

Horizon	Depth	χ	Fe	Mn	Zn	Pb	Cd	Cu	Cr	Ni	Co
	cm	10^{-8} m^3·kg^{-1}					mg·kg^{-1}				
Oi	0–1	57	3884	193	354	231	3.5	47	5	8	4.5
Oe	1–6	154	9890	250	450	385	5	75	10	14.5	2.5
Oa/Ah	6–15	81	16,605	203	418	713	7.2	77	9.5	15	5.8
Ah	15–20	90	3620	23	249	239	7.5	33	4.5	24	2.8
E	20–25	6.2	94	2.8	40	5.5	1	4.5	1	2	0
E/B	25–40	3.7	114	4	51	5	1.4	6	3.5	5.5	0
B	<40	1.7	121	1.8	32	0	1.6	1.5	4.3	0	0

Compared to the content of elements determined in fly ash samples, the content of zinc and lead was several times higher in the soil. This may be due to the long-term deposition of fly ash in this region, as evidenced by the fact that higher levels of the analyzed elements were found in the upper soil levels. At present, emissions are very limited (approximately 148 t/year), but in the end of the 1990s, the Jaworzno power plant was emitting over 2500 tons of dust per year. It is also not without significance that from the 12th century various deposits were exploited and processed in this area, starting with calamine (zinc ore containing silver), then zinc and lead ores, iron and ending with coal. Human activities on such a large scale have caused numerous changes and disturbances to the environment in this area. The fact that the topsoil was characterized by a higher content of the analyzed metals than the subsoil makes it possible to exclude the natural (lithogenic) origin of these elements and undoubtedly indicates human activity as their source [58]. Previous research conducted in this area by Rachwał [59] as well as by Cabała et al. [60] in the neighboring region (Łosień (Dąbrowa Górnicza)) has revealed similar and even higher content of these elements in the soil.

In all the analyzed soil samples, iron was mainly present in the crystalline and amorphous iron oxides (up to 48 and 26%, respectively) (Figure 6). In the uppermost layer of forest litter (Oi sub-horizon), in the first three phases of the analysis, 80% Mn, almost 60% Zn and 54% Cd were extracted, in the Oe sub-horizon it was: 68%, 46% and 58%, respectively, and in the Oa/Ah: 46%, 37% and 58%. These three elements were released most easily in the upper soil layers, probably associated with organic matter or with the solid phase with weak surface adsorption forces [61]. In the latter case, the carrier of these particles could be industrial dust falling onto the soil surface. In the organic layers of analyzed soil, more than 40% of lead and 30% of copper was found in the F4 fraction, which confirms that soil organic matter (SOM) has the ability to retain heavy metals. The remaining part of the lead present in the samples was related to the F2, F3, and F5 fractions. Copper in soil samples was also associated with amorphous FeO_x (more than 20% in analyzed horizons), and chromium—with crystalline FeO_x in organic layers (42–60%). Nickel and cobalt were found mainly in the F6 and F7 fractions, i.e., they were associated mainly with crystalline iron oxides as well as aluminosilicates and silicates.

Sequential extractions, simulating both natural and anthropogenic environmental changes, have shown that the danger of releasing PTEs associated with power plant dust into the soil is significant, especially in acid forest soils. A major threat may be the fact that a large part of the metals and metalloids that are components of the fly ash are associated with the first fractions in which metals are easily released and can be considered potentially bioavailable [61]. These elements can be transported over long distances together with fly ash particles.
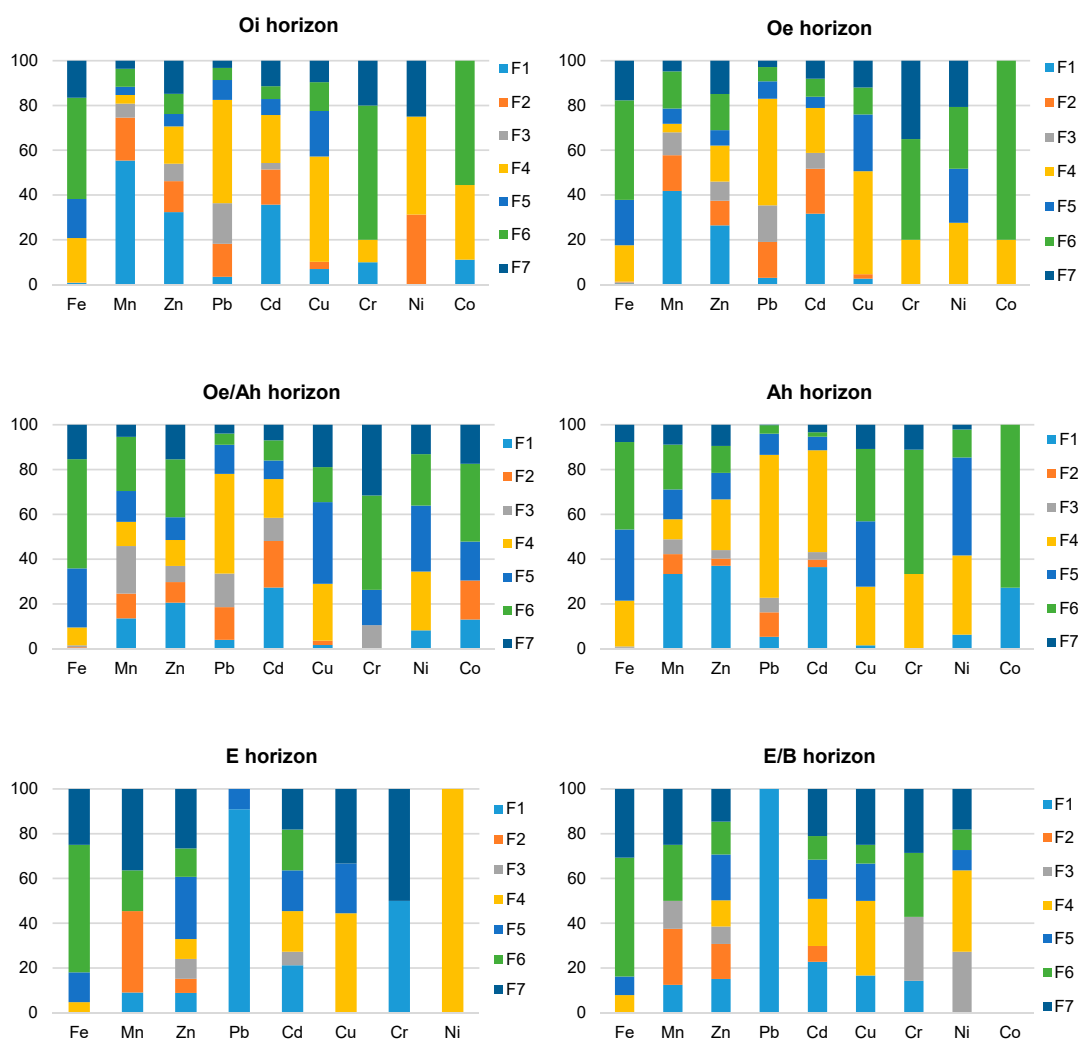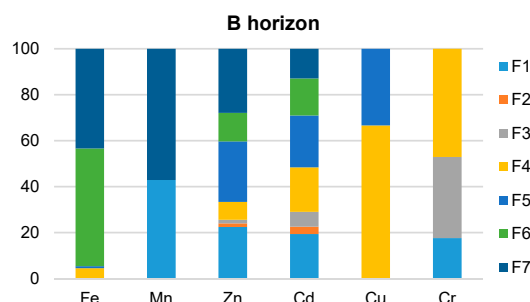

Figure 6. *Cont.*

Figure 6. Sequential extraction of soil samples (%).

3.3. Geoaccumulation Index and Risk Assessment Code

Calculation of the geoaccumulation index (Table 4) showed that, according to Müller [38], in comparison with the background values, the soil was heavily to extremely contaminated with Pb (I_{geo} 4.57 to 6.19) and heavily contaminated with Zn, Cd. Additionally, the Oe and Oa/Ah horizons were heavily contaminated with Cu, while the Oi and Ah horizons were moderately contaminated with this metal. I_{geo} value for cobalt suggested that organic horizons of soil were uncontaminated to moderately contaminated. The analyzed soil was not contaminated by Fe, Mn, Ni and Cr, as evidenced by low I_{geo} values.

Table 4. Background values of elements (mg·kg^{-1}) commonly found in limestone and dolomites according to Kabata-Pendias and Pendias [39] and geoaccumulation index (Igeo) calculated for the upper horizons of soil.

Soil Horizon	Fe	Mn	Zn	Pb	Cd	Cu	Cr	Ni	Co
Background	7000	600	17.5	6.5	0.35	6	10.5	13.5	1.6
I_{geo} Oi	−1.44	−2.22	3.75	4.57	2.74	2.38	−1.66	−1.34	0.91
I_{geo} Oe	−0.09	−1.85	4.1	5.3	3.24	3.06	−0.66	−0.48	0.06
I_{geo} Oa/Ah	0.66	−2.15	3.99	6.19	3.78	3.09	−0.73	−0.41	1.26
I_{geo} Ah	−1.54	−5.32	3.25	4.61	3.83	1.85	−1.81	0.25	0.2

The results of the risk assessment code analysis, which allows the identification of the potential threat caused by the leaching of potentially toxic elements [41,42], are presented in Table 5. These analyses show that Zn and Pb pose a low risk in the dust after coal combustion, Cr—medium risk, Cu—high risk and Cd—very high risk. Additionally, in dusts after lignite combustion, low risk was associated with Zn and medium risk with Cr. Cadmium, copper and lead may pose a high risk. In the case of soil, risk related to Pb, Ni and Co was medium, to Zn—high and very high to Mn and Cd.

Table 5. Risk assessment category and classification of risk assessment code (RAC) values for elements [40,41] and environmental risk of PTEs leaching from investigated dusts and upper horizons of soil samples.

Category	RAC %	Risk	Hard Coal	Lignite	Soil
I	<1	No risk	-	-	Fe
II	1–10	Low risk	Zn, Pb	Zn	Cu, Cr
III	11–30	Medium risk	Cr	Cr	Pb, Ni, Co
IV	31–50	High risk	Cu	Cd, Cu, Pb	Zn
V	>50	Very high risk	Cd	-	Mn, Cd

4. Conclusions

This research covered fly ash of the power plant after burning hard coal and lignite, as well as soil samples collected in the forest near the power plant. This study showed that the power plant dusts contained technogenic magnetic particles produced during high-temperature processes. TMPs in the

form of sharp-edged particles of iron oxides and aluminosilicates were found in the top layers of forest soil (mostly in the organic horizon). The non-spherical magnetic particles may be associated with other pollution sources (e.g., traffic, metallurgy, etc.) or may be of natural (detrital) origin. The total content of the analyzed PTEs was higher in the fly ash from the coal-fired power plant (except for Cd) than in ash from the lignite burning power plant. The content of zinc and lead in the soil was several times higher than in fly ash, while the content of cadmium and chromium was lower, and the content of copper was at a similar level. The higher content of all analyzed elements together with higher values of magnetic susceptibility in the organic horizons of soils allows the exclusion of their natural (lithogenic) origin and indicates that these elements infiltrated the soil as a result of industrial emissions and could be transported via TMPs. The sequential extraction analysis revealed that a large part of the analyzed toxic elements (Zn, Pb, Cu, and Cr in ash after hard coal combustion, Zn, Cd, Cu, and Cr in ash after lignite combustion, as well as Fe, Ni, Cu, Cr, and Co in soil) were related to F5 and F6 fractions, i.e., structurally incorporated into amorphous and crystalline forms of iron oxides. The geoaccumulation index shows that the upper soil horizons (0–20cm) were heavily to extremely contaminated with Pb, Zn, Cd and Cu. According to the risk assessment code that was used to assess the environmental risk associated with the leaching of potentially toxic elements, Cu in dust from a coal-fired power plant, Cd, Cu, Pb in dust from a lignite-fired power plant and Zn in soil all pose a high environmental risk. Cadmium in dust from a coal-fired power plant and Mn and Cd in soil samples pose a very high risk.

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