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Environmental consequences of a galvanising plant fire

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Abstract: The aim of the study is to determine the concentration of selected heavy metals in soil contaminated with galvanising fume resulting from a fire in a galvanising plant. Surface horizon of soil exposed to contamination by toxic fumes due to the fire of a galvanising plant in Dębska Wola near Kielce (SE Poland) was analysed. Soil samples were collected in an agricultural area of 12 ha after the plant's failure in 2019 and three years after the fire in 2022. Grain-size distribution, pH and concentration of zinc, lead and cadmium were determined. The acceptable values of pollutants were significantly exceeded in soil (Zn_{max} – 2007.3 mg·kg^{-1} DM, Pb_{max} – 509.5 mg·kg^{-1} DM, Cd_{max} – 17.1 mg·kg^{-1} DM in 0–5 cm horizon) and reduced in control samples (Zn_{max} – 756.1 mg·kg^{-1} DM, Pb_{max} – 320.1 mg·kg^{-1} DM, Cd_{max} – 15 mg·kg^{-1} DM). In the organic-mineral horizon the concentrations declined by an average of Zn – 41.8%, Pb – 26.1% and Cd – 16.3%, while in the mineral horizon by 27.8% (Zn), 26.7% (Pb) and 15.6% (Cd). Industrial plants, in which thermal treatment of molten metals is conducted, pose a real threat to the environment in the case of a failure. In order to minimise the effects of potential leaks, their location should be thoroughly considered. The course and consequences of accidents should be monitored during the event (such as fire) and in the long term (*e.g.* with the use of bioindicators).

Keywords: agricultural soils, ecological risk, environmental monitoring, geoaccumulation, toxic metals

INTRODUCTION

Soil, as an element of natural environment, is exposed to various anthropogenic pressures and climate change, which modify its physical, chemical and biological properties and severely limit the capacity to neutralise pollutants (Bednarek, Dziadowiec and Pokojowska, 2002; Moscatelli *et al.*, 2017). Toxic substances that are persistent, have complicated transformation and interact with soil materials are particularly dangerous (Latosińska, Kowalik and Gawdzik, 2021). Migration of heavy metals, petroleum products and pesticide misuse alter the soil ecosystem balance (Rashid *et al.*, 2023). Harmful gases and dusts deposited near industrial plants are among significant soil pollutants (Fritsch *et al.*, 2010; Costa da Silva *et al.*, 2021; Kozłowski, Szwed and Żelezik, 2021; Świercz, Gandzel and Tomczyk-Wydrych, 2021). A serious threat to ecological safety is posed by the pollution of soils with heavy metals, due to their features, such as accumulation, persistence and low mobility in soils (Chen *et al.*, 2022). Moreover, there is a close relation between soil chemistry and dynamics of soil water, which has further consequences for the products of soil processes in annual cycles (Gavrilescu, 2021). Catastrophic events can release unlimited amounts of elements, necessary for plant growth in small doses, but dangerous if in excess (Elemike *et al.*, 2019; Kumar *et al.*, 2019; Alengebawy *et al.*, 2021). Zinc is an example of such element; both its deficiency, as well as excess, is harmful to plants and animals (Kabata-Pendias and Mukherjee, 2007).

Zinc is one of the most common trace metals in the Earth's crust. It is deemed essential for the organisms, as it is a protein cofactor and acts as an agent in the regulation of immunomodulatory factors (Haase and Rink, 2014).

The content of zinc at the level of 100 mg·kg^{-1} dry mass is assumed to inhibit nitrification process, while the content of

1,000 mg·kg^{-1} dry mass disturbs microbiological processes (Roohani *et al.*, 2013; Lee, 2018). While comparing the effect of zinc on organisms to the effects caused by other metals with similar chemical properties, one may claim that it belongs to the group of relatively harmless metals. While overexposure of organisms to Zn has a toxic effect, acute zinc poisoning is rare. Large doses of exogenous zinc having the effect of reducing copper absorption are seen as a process posing the main risk (Terrin *et al.*, 2020). Furthermore, excessive zinc content from anthropogenic sources present in the soil has an impact on the shift in biodiversity of microorganisms of Gram-positive and Gram-negative groups, such as *Bacillus* sp., *Streptococcus* sp., *Pseudomonas* sp. or *Enterobacter* sp., which in turn affects the diversity in bioavailability of other metals (Plum, Rink and Haase, 2010). The accumulation in the surface layer of the soil of anthropogenic (above normative) contents of lead, cadmium and zinc, defined as low mobility under appropriate conditions (*e.g.* at low pH for sandy soils), may result in them being absorbable by plants, which poses a potential threat to living organisms, including into the food chain. Quantitative description of changes in soil structure and properties requires research on long term monitoring plots, enabling determining natural spatial variability, modified by a strong anthropogenic pressure.

The aim of the research conducted in the area of galvanising plant failure near Kielce was to:
- determine the total concentration of selected heavy metals in soil after the fire and after the period of 3 years,
- determine the changes in soil environment – changes in selected metal concentrations,
- assess the ecological risks in the studied area.

MATERIALS AND METHODS

STUDY AREAS

The analysed area is located in south-eastern Poland (Świętokrzyskie Province) on a 12 ha fragment of arable field. Its western part is adjacent to the Termetal galvanising plant in Dębska Wola, Morawica Commune (Fig. 1). The plant specialises in hot-dip galvanising of steel structures. Its failure in 2019 caused the emission of great amounts of zinc vapours. The soils in the study area are brown earth soils made of Pleistocene light clays, sandy and occasionally loamy sands. Its adsorbing capacity and base saturation are low (Filonowicz, 1968; Juszczyk *et al.*, 2006).

DATA COLLECTION

Soil samples from 0–5 cm horizon (TOP) and 5–20 cm horizon (BOTTOM) were collected twice. For the first time sampling took place on 2–5 October 2019, soon after the plant's failure, and control samples were collected on 3–4 October 2022. Samples were taken from the same plots (Fig. 1), chosen due to prevailing western and south-western winds on the day of the fire (Świercz *et al.*, 2023). Each sample was taken from a plot of 2×2 m and weighted about 1,000 g, which corresponded to min. 5–8 punctures of an Egner's stick. Unhumidified organic matter was removed before sampling. The structure of the soil profile is typical for brown soils – for agricultural areas: Ap-Bbr-Cca (points 1–6, 9–15), for forests: O-A-Bbr-Cca (points 7–8) (FAO, 2015; PTG and UWP, 2019).

CHEMICAL AND DATA ANALYSIS

The soil samples were transported to the laboratory of Przedsiębiorstwo Geologiczne Sp. z o.o. in Kielce to perform an assay of selected heavy metals and physical and chemical properties. The specimens had been initially dried at room temperature (not exceeding 40°C), then mechanically pulverised in an agate mill, and sieved through a sieve assembly, resulting in grains no larger than 2 mm. The granulometric composition assay was carried out using aerometric and sieve analysis (Polski Komitet Normalizacyjny, 1998), while the soil pH (Polski Komitet Normalizacyjny, 2013) was measured with a pH meter (Elmetron Zabrze, Poland with pH-EPS-1 electrode). Prior to carrying out chemical analysis to examine the composition of selected metals (Zn, Pb, Cb), the samples were subjected to wet mineralisation using hydrochloric acid (15 cm^3) and nitric acid (5 cm^3) per 1 g of soil. The mineralisation process took 2 h at a temperature of 120°C using a CEM Mars 6 mineralizer (Matthews, NC, USA). The cooled-down solution was filtered and diluted with 30 ml of deionised water. Agilent Tech. 51100 SVDV (Santa Clara, CA, USA) emission spectrometer was used for chemical analyses. Method validation was carried out based on certified reference material – Loamy Sand 4, CROM036-050 (Manchester, NH, USA).

The values of elemental concentrations which were measured and the certified values were compared (Tab. 1). All the results obtained for this reference material were statistically close to the certified values (p < 0.05). All relative standard deviations of measured replicates were within ±5%.

Fig. 1. Location of the study area with research plots; source: own elaboration

Table 1. Comparison the results with certified materials Loamy Sand 4, CRM036-050

Metals	Measured value ±*SD*	Certified value ±*SD*	Relative difference (%)
	mg·kg^{-1}		
Cd	0.90 ±0.20	1.0 ±0.15	99.0
Pb	10.60 ±0.90	9.90 ±0.40	115.0
Zn	42.23 ±0.70	40.41 ±0.30	98.0

Explanation: *SD* = standard deviation.
Source: own elaboration.

The results were analysed in Statistica ver. 13 software (Tibco Software Inc.). The direction of air mass flow, visualised with the NOAA Hysplit model (Air Resources Laboratory, NOAA's Office of Atmospheric Research, National Oceanic and Atmospheric Administration), was presented in the paper Świercz *et al.* (2023). Concentration maps of studied parameters were plotted in Surfer ver. 18.3.3 (Golden Software, LLC, Golden, CO, USA). The interpolation was carried out using the kriging method, which allows for a significant refinement of the mesh (research area) despite irregularly placed measurement points, which allows for an accurate reflection of the analysed surface. The following indicators were calculated in order to assess the degree of soil contamination with metals: the index of geoaccumulation (I_{geo}) and the ecological risk factor (E_r^i) (Müller, 1969; Salminen *et al.*, 2005; Zhiyuan *et al.*, 2011; Barbieri, 2016).

Geoaccumulatin index (I_{geo}) was calculated using the Equation (1):

$$I_{\text{geo}} = \log_2 \frac{C_i}{1.5B_i} \quad (1)$$

where: C_i = content of a given heavy metal in soil; B_i = geochemical background for a given heavy metal; 1.5 = natural variations in the content of a particular heavy metal in the environment resulting from differences in geological structure.

The ecological risk factor (E_r^i) was calculated according to the methodology for assessing the toxicity of heavy metals in water, soil and air (Eq. 2) (Hakanson, 1980; Biasioli, Barberis and Ajmone-Marsan, 2006; Biasioli and Ajmone-Marsan, 2007; Ajmone-Marsan and Biasioli, 2010; Rahman, Saha and Molla, 2014; Fodoué *et al.*, 2022).

$$E_r^i = T_i C_{Fi} \quad (2)$$

where: T_i = metal toxic response factor for an individual substance (T_{Cd} = 10, T_{Pb} = 5, T_{Zn} = 1), C_{Fi} = contamination factor of an individual heavy metal.

The degree of soil contamination was assessed according to the scale presented in Table 2.

Table 2. Ecological risk index (E_r^i) and geoaccumulatin index (I_{geo}) classes in relation to soil quality

E_r^i	Soil quality	I_{geo}	Soil quality
<40	low potential ecological risk	≤0	unpolluted
40–80	moderate potential ecological risk	0–2	unpolluted to moderately polluted
80–160	considerable potential ecological risk	2–3	moderately to highly polluted
160–320	high potential ecological risk	3–4	highly polluted

Source: own elaboration.

RESULTS

The average pH value in soil samples from the organic-mineral horizon 0–5 cm (TOP) in 2019 was pH_{H2O} = 4.68 and pH_{KCl} = 4.45. In the samples from the mineral horizon 5–20 cm (BOTTOM) the values were lower: pH_{H2O} = 4.45 and pH_{KCl} = 4.31. In 2022 the average pH value from the 0–5 cm horizon was pH_{H2O} = 4.77 and pH_{KCl} = 4.54, while in the 5–20 cm horizon pH_{H2O} = 4.5 and pH_{KCl} = 4.33 (Tab. 3). The grain-size distribution was dominated by sand fractions, constituting from 58 to 82% (approx. 71.4% on average). Silt accounted for 38.2% and clay 8–19%.

Zinc concentration in soil (TOP) in 2019 amounted to 638.3 mg·kg^{-1} (mean), while in the direct vicinity of the plant it exceeded 2,000 mg·kg^{-1}, and in the most distant sample it was approximately 100 mg·kg^{-1}. Zn concentrations were lower in the deeper layer – BOTTOM (max. 909.5 mg·kg^{-1}, min. 42.3 mg·kg^{-1}).

In 2022 the content of zinc ranged from 110.9 to 756.05 mg·kg^{-1}, and the average value was 371.52 mg·kg^{-1} (0–5 cm horizon). In the samples from the 5–20 cm horizon the content of zinc ranged from 43.8 to 578.67 mg·kg^{-1}, with the average value of 150.35 mg·kg^{-1} (Tab. 4).

In both diagnostic horizons the concentrations of lead were the highest in samples collected in 2019 from the plot no. 1 (TOP – 509.7 mg·kg^{-1}, BOTTOM – 290.7 mg·kg^{-1}), with the average values of 184.3 mg·kg^{-1} (TOP) and 114.3 mg·kg^{-1} (BOTTOM). The lowest values were noted in samples no. 12 (TOP – 109 mg·kg^{-1}) and 15 (BOTTOM – 41 mg·kg^{-1}). In the samples collected in 2022 the content of lead ranged from 90.11 to 320.11 mg·kg^{-1} in the 0–5 cm horizon (average of 136.19 mg·kg^{-1}) and from 41.22 to 200.67 mg·kg^{-1} in the 5–20 cm horizon, with the average value of 83.05 mg·kg^{-1}. The mean content of cadmium in the samples from 2019 was 9.8 mg·kg^{-1} in the 0–5 cm horizon and 6 mg·kg^{-1} in the 5–20 cm horizon. The highest Cd concentrations, as in the case of other analysed metals, were detected in samples collected in the closest vicinity of the plant (plot no. 1 – 17.1 mg·kg^{-1} TOP, plot no. 2 – 11.6 mg·kg^{-1} BOTTOM), with the average values of 9.8 mg·kg^{-1} (TOP) and 6 mg·kg^{-1} (BOTTOM). The content of cadmium in the samples collected in 2022 ranged from 3.90 to 15.04 mg·kg^{-1} (TOP) and from 1.05 to 10.50 mg·kg^{-1} (BOTTOM), with the average values of 8.16 and 5.08 mg·kg^{-1}, respectively. The lowest Cd concentrations in the first and the second analysis were noted in plots no. 12 and 15 (Tab. 4, Fig. 2).

In the spatial distribution of pollutants a concentric pattern around the plant is visible in the case of the samples collected in 2019 and a longitudinal pattern in the case of the samples from 2022 (Fig. 3, 4). In 2019, the concentrations of zinc exceeding 300 mg·kg^{-1} were noted in the plots located 500 m (T) and

Table 3. Tested soil's physical properties in the years 2019 and 2022

Sample No.	Organic-mineral horizon 0–5 cm				Mineral horizon 5–20 cm							Grain-size group
	pH_{H2O}		pH_{KCl}		pH_{H2O}		pH_{KCl}		% fraction content (ø in mm)			
	2019	2022	2019	2022	2019	2022	2019	2022	2–0.05	0.05–0.02	<0.002	
1	4.21	4.25	4.02	4.10	4.00	4.33	3.89	3.90	75	15	10	Pg
2	4.19	4.22	4.00	4.13	4.04	4.10	3.88	3.97	68	16	16	Gp
3	4.53	4,57	4.20	4.43	4.12	4.14	3.98	3.98	72	42	14	Gp
4	4.06	4.23	3.89	3.99	4.00	4.20	3.87	4.00	82	32	14	Pg
5	4.24	4.66	4.01	4.23	4.06	4.12	4.00	3.98	78	34	12	Pg
6	4.32	4.36	4.12	4.08	4.10	4.13	4.01	4.05	71	46	17	Gp
7	4.57	4.55	4.43	4.45	4.23	4.41	4.01	4.12	60	58	18	Gl
8	4.21	4.23	4.01	4.11	4.09	4.10	3.78	3.99	58	59	17	Gl
9	4.90	5.00	4.26	4.40	4.30	4.30	4.12	4.05	61	20	19	Gl
10	5.20	5.40	5.00	5.10	5.00	4.90	4.98	4.75	77	34	11	Pg
11	5.10	5.20	4.98	5.00	5.00	4.90	4.89	4.82	80	29	9	Pg
12	4.90	5.00	4.72	4.81	4.76	4.65	4.53	4.50	82	26	8	Pg
13	5.20	5.20	5.03	5.10	4.87	4.90	4.74	4.77	72	62	17	Gp
14	5.33	5.40	5.06	5.10	5.12	5.20	4.99	5.00	76	41	17	Gp
15	5.19	5.30	5.00	5.10	5.04	5.13	5.00	5.07	59	59	18	Gl
Min.	4.06	4.22	3.89	3.99	4.00	4.10	3.78	3.90	58	15	8	–
Max.	5.33	5.40	5.06	5.10	5.12	5.20	5.00	5.07	82	62	19	–
Mean	4.68	4.77	4.45	4.54	4.45	4.50	4.31	4.33	71.40	38.20	14.47	–
SD	0.46	0.46	0.46	0.44	0.45	0.40	0.48	0.43	8.42	15.98	3.62	–

Explanations: ø = diameter, *SD* = standard deviation.
Source: own study.

Table 4. Content of Zn, Pb and Cd (in $mg \cdot kg^{-1}$ DM) in soil in the years 2019 and 2022

Sample No.	Organic-mineral horizon 0–5 cm						Mineral horizon 5–20 cm					
	Zn		Pb		Cd		Zn		Pb		Cd	
	2019	2022	2019	2022	2019	2022	2019	2022	2019	2022	2019	2022
1	1761.08	687.33	509.70	301.34	17.11	15.04	909.45	578.67	290.67	98.56	10.90	8.99
2	2007.34	756.05	420.89	320.11	13.55	11.71	701.09	470.67	210.56	126.89	11.60	10.50
3	1093.66	696.67	307.56	146.66	14.88	13.11	400.64	249.66	230.87	200.67	7.90	5.66
4	1117.23	700.67	196.78	104.55	15.77	13.67	260.66	190.76	130.67	109.66	6.90	5.80
5	766.90	509.77	147.80	131.40	12.66	11.07	198.76	162.60	100.33	90.66	7.09	6.43
6	630.11	420.87	140.89	120.33	12.09	7.68	120.78	100.66	98.78	58.90	8.11	5.55
7	456.89	290.87	110.87	98.77	9.87	6.78	82.89	70.98	70.09	55.67	5.11	5.00
8	400.09	320.23	120.77	100.07	7.99	6.00	70.79	56.90	67.98	57.90	4.68	3.56
9	222.19	200.87	110.98	98.78	7.09	6.00	67.55	66.78	79.89	70.98	6.78	5.44
10	190.80	180.87	130.89	100.56	8.01	7.55	56.90	52.60	120.33	90.99	7.12	6.12
11	201.56	160.87	113.90	98.77	7.33	6.56	69.78	60.77	90.67	80.45	3.45	3.40
12	305.05	287.08	109.07	95.43	4.56	4.09	45.89	46.67	50.80	50.11	3.78	3.40
13	170.89	120.89	111.77	90.11	5.71	4.90	56.04	57.80	55.89	52.33	3.04	3.00
14	129.89	128.89	122.55	123.56	4.71	4.30	47.90	45.99	60.45	60.80	2.89	2.31
15	120.99	110.90	110.73	112.45	4.90	3.90	42.33	43.80	40.97	41.22	1.02	1.05
Min.	120.99	110.90	109.07	90.11	4.56	3.90	42.33	43.80	40.97	41.22	1.02	1.05
Max.	2007.34	756.05	509.70	320.11	17.11	15.04	909.45	578.67	290.67	200.67	11.60	10.50
Mean	638.31	371.52	184.34	136.19	9.75	8.16	208.76	150.35	113.26	83.05	6.02	5.08
SD	603.42	238.89	126.26	72.59	4.28	3.76	264.75	165.04	73.80	40.72	2.98	2.46

Explanations: *SD* = standard deviation.
Source: own study.

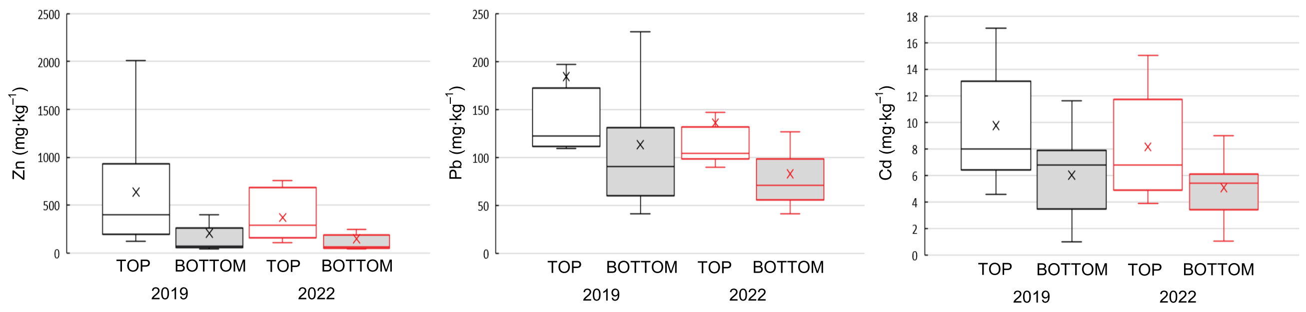

Fig. 2. Distribution of selected statistics of Zn, Pb and Cd concentrations in soil samples collected in 2019 and 2022; × = mean concentration, vertical lines = range between the lowest and the highest content, source: own study

150 m (B) from the plant. In the case of lead, values above 100 mg·kg^{-1} occurred in all the samples from the 0–5 cm horizon and in the distance of 365 m from the emission source in samples from the 5–20 cm horizon. Elevated content of cadmium was recorded in all the samples, with values exceeding 6 mg·kg^{-1} (average value from the 5–20 cm horizon sample) in the samples located up to 600 m from the plant. Maps with the results of chemical analyses of the samples collected in 2022 present significantly limited area with elevated concentrations of studied pollutants. Contour lines joining plots with Zn concentrations above 200 mg·kg^{-1} in the 5–20 cm horizon of soil delimit an area equal to 1/5 of the studied area. The area is even smaller in the case of Pb content of 100 mg·kg^{-1}. A longitudinal pattern of metal distribution in soil is visible for cadmium; however, the reduction in the case of Cd is significantly lower than for Zn and Pb. The reduction in the content of cadmium in the samples collected after three years from the plant's failure amounted to 16.3% in the 0–5 cm horizon and 15.6% in the 5–20 cm horizon.

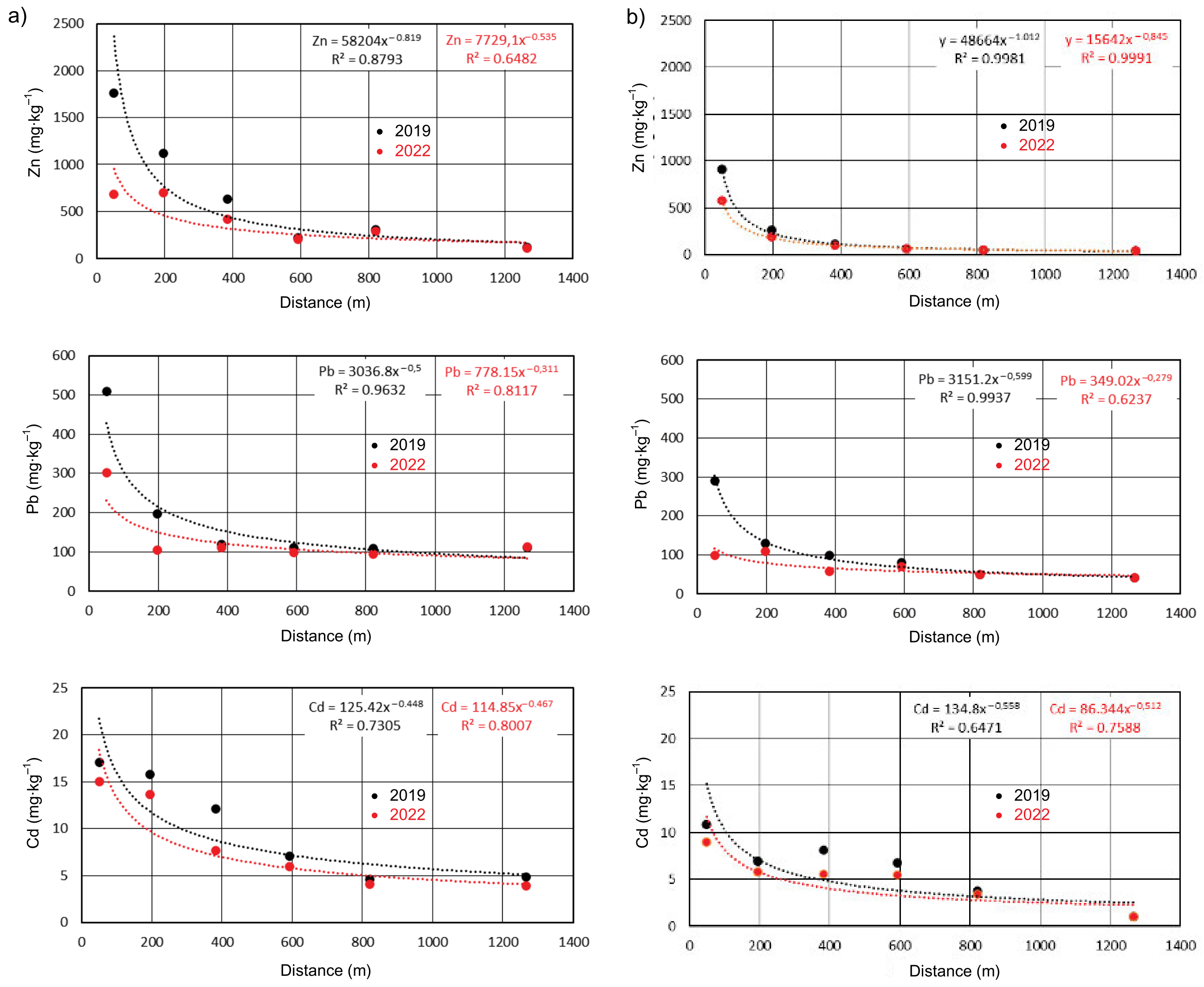

Fig. 3. Zn, Pb, Cd concentrations depending on the distance from the emission source: a) TOP, b) BOTTOM; source: own study

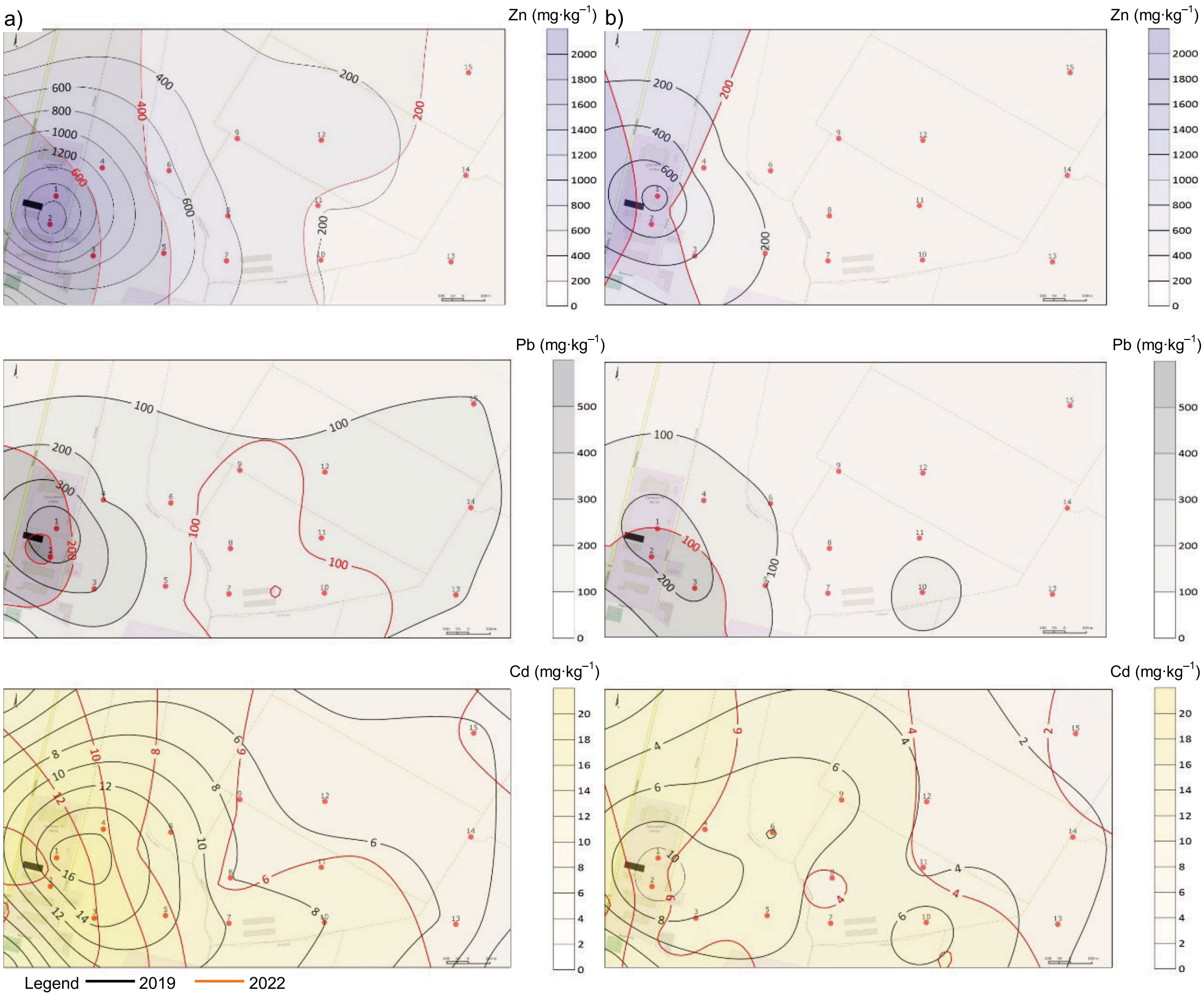

Fig. 4. Concentration maps of Zn, Pb and Cd: a) TOP, b) BOTTOM; source: own study

DISCUSSION

The Old-Polish mining and metallurgy played a crucial role in the economic development of the country in the 19th century. The leading industrial centres, located in Upper Silesia and Świętokrzyskie Mountains, significantly affected soils, mainly due to zinc–lead ore mining (Cabała *et al*., 2020, Kalicki *et al*., 2020). Definitely, the permissible levels of Zn concentration, *i.e.* 15–240 mg·kg^{-1} DM, are not exceeded in most Polish soils. However, the standards are often exceeded in cities, allotment gardens, as well as industrial areas, including galvanising plants (Diatta, Chudzińska and Wirth, 2008; Bosiacki, Bednorz and Spiżewski, 2022; Binner *et al*., 2023). An event of a catastrophic nature in the industrial infrastructure in Dębska Wola near Kielce in 2019 caused a number of consequences for the natural environment. One of the consequences was a release of toxic galvanised metal fumes into the atmosphere with unknown characteristics of impact on the air quality in the area affected by the fire. The chemical composition of soil transformed significantly due to the deposition of pollutants around the plant and within neighbouring crop fields. Significant growth in the concentration of Zn, Pb, and Cd was reported in its near-surface, most biologically active layer. Possible reference values for the analysed samples are soil tests from Morawica municipality, carried out in the scope of monitoring performed by of District Chemical and Agricultural Station in Kielce (Pol. Okręgowa Stacja Chemiczno-Rolnicza) in 2010 and 2014 (Pasieczna (ed.), 2012; Pasieczna and Markowski, 2015). Assay results of zinc in the range of 40.2 to 81.2 mg·kg^{-1}, of lead (40.4–85.2 mg·kg^{-1}), and of cadmium (0.33 to 5.2 mg·kg^{-1}) obtained in this period within the entire soil profile qualified it as free of pollutants. The chemical composition analysis of organic and mineral layer samples carried out in 2019 showed a significant growth of mean concentrations of certain metals in comparison to soil monitoring test results from previous years; a 10-fold increase for zinc, a 3.5-fold for cadmium, and a 3-fold increase in the concentration of lead. A comparison of test results from 2019 and 2022 with World Reference Values (WRV) (Kabata-Pendias, 2010) and state regulations (Rozporządzenie, 2016) is presented in Table 5.

The limits of the WRV (Kabata-Pendias, 2010) are even more restrictive (Zn – 62 mg·kg^{-1}, Pb – 25 mg·kg^{-1}, Cd – 1.1 mg·kg^{-1}); therefore, the results obtained in this study were complying with the acceptable standards only in 4 samples from 2019 and 8 samples from 2022 in the case of zinc. The concentrations of lead in all the samples significantly exceeded the reference values (WRV). Only one sample (no. 15) remained below 1.1 mg·kg^{-1} for cadmium in both sample series. According to the guidelines of the Institute of Soil Science Cultivation in Puławy (Pol. Instytut Uprawy Nawożenia i Gleboznawstwa –

Table 5. Trace element concentrations ($mg \cdot kg^{-1}$) in soils by world reference values (WRV) and Polish soil value references with indicators

Metals	WRV (Rozporządzenie, 2016)	Polish soil value references 0–25 cm (Kabata-Pendias, 2010)	I_{geo} mean (TOP/BOTTOM)		I_{geo} max. (TOP/BOTTOM)		E_r^i (TOP/BOTTOM)	
			2019	2022	2019	2022	2019	2022
Cd	1.1	2	5.24/4.54	4.84/4.11	6.05/5.49	5.87/5.35	97.5/60.2	81.57/50.81
Pb	25	100	2.71/2.01	2.15/1.44	4.18/3.37	3.51/2.84	921.7/566.3	680.96/415.26
Zn	62	300	5.24/4.54	3.10/1.51	5.84/4.70	4.43/4.04	638.3/208.8	371.51/150.35

Explanations: I_{geo} = geoaccumulatin index, E_r^i = ecological risk index.
Source: own study and literature.

Państwowy Instytut Badawczy – IUNG-PIB) (Kabata-Pendias *et al.*, 1993; Kabata-Pendias and Piotrowska, 1995), the soils in Dębska Wola, contaminated with heavy metals due to the failure of an industrial plant, were classified as class VI on a six-point scale (very heavily polluted soils). The I_{geo} values calculated for Cd and Zn in 2019 classified the soils as heavily or extremely contaminated. The lowest value of geoaccumulation was calculated for the mean concentrations of Pb (moderately to heavily contaminated). The values of I_{geo} calculated for the samples collected in 2022 were much lower. In the case of Zn and Pb they classified soil as moderately to heavily polluted, while in the case of Cd – heavily polluted. The ecological risk factor E_r^i was also high – significantly high for Cd and very high for Pb and Zn in 2019 (TOP). In 2022 E_r^i was very high in the case of Zn and Pb in the 0–5 cm horizon and for Pb – in the 5–20 cm horizon. In the case of Cd the risk was moderate and considerable in TOP and BOTTOM horizons (Tab. 5).

Significantly lower average contents of lead (20.23 $mg \cdot kg^{-1}$; max 23.3 $mg \cdot kg^{-1}$) and cadmium (0.58 $mg \cdot kg^{-1}$; max 0.8 $mg \cdot kg^{-1}$) were detected in the top horizon of soil (0–30 cm) from Stalowa Wola, Poland, exposed to long-term pressure from metallurgical plant (Świdawska-Urbańska and Zalewski, 2019). Similarly, in other regions of the world, where soils for agricultural use subjected to multidirectional pressures were analysed, metal concentrations generally did not exceed WRV (Baran and Wieczorek, 2012; Alsafran *et al.*, 2021; Al-Taani *et al.*, 2021; Huang *et al.*, 2021; Santos, Soares and Alleoni, 2022). Higher contents of metals were noted in soils from the areas of long-term impacts from plants with significant metallic emissions (mines and smelters). In the samples of soils around the Apiai smelter in Brazil (Jin *et al.*, 2015) the concentrations of Zn, Pb and Cd were extremely high, amounting to 14,062, 37,781 and 144 $mg \cdot kg^{-1}$, respectively. The average soil content of metals in the area under the impact of zinc and lead mine in Sidi village, China, were 1,190 mg $Zn \cdot kg^{-1}$ and 1,852 mg $Pb \cdot kg^{-1}$ (Hooda, 2010). Studies carried out in the areas of environmental contamination confirm the elevated risk of adverse health effects due to consumption of plants, in particular wheat and rice, grown on soils polluted with Zn, Cd and Pb (Amirmoradi *et al.*, 2012). Zinc supplied to the human body with food is a significant microelement, involved in numerous metabolic processes, ensuring normal skin and mucosa function. Exposure to zinc in galvanisation and alloy- and smoke-pot-producing plants may be a cause of metal fume fever with symptoms similar to flu, while overexposure is also claimed to be one of the causes leading to neoplastic diseases (Jabłońska-Trypuć, 2007). Within 3 years of the galvanising plant failure and the release of significant amounts of Zn into the environment, a significant reduction in the content of this element in the soil was observed. This state can be explained by the migration of the element to deeper soil levels, at relatively low pH values and intense rainfall (with daily rainfall totals from May to June 2019 in the range of 40–70 mm – data from Institute of Meteorology and Water Management in Kielce-Suków (Pol. Instytut Meteorologii i Gospodarki Wodnej – Państwowy Instytut Badawczy). Many years of research indicate that zinc in the first year of fertiliser application at a dose of 2–30 $kg \cdot ha^{-1}$, depending on the granulometric composition of the soil (Alloway, 2009), is taken up by the plant's root system to a maximum of 6% of the total content in the soil (Prasad and Freitas, 2003). The so-called "residual" zinc is taken up more effectively in the following years, especially in more compact soils. In sandy soils with low humus content, the migration of Zn within the profile takes place faster, although this element is not very mobile (Alloway, 2009). Ultimately, it is in absorbed by plants to a lesser extent (Lakshmi *et al.*, 2012). Lead and cadmium, as extremely toxic metals, are not involved in any physiological function in the human body, they accumulate mainly in kidneys and lead to nephropathy and neoplasms (Marchewka, 2009).

CONCLUSION

Industrial plants, in which thermal treatment of molten metals is conducted, pose a real threat to the environment in the case of a failure. In order to minimise the effects of potential leaks, their location should be thoroughly considered. The course and consequences of accidents should be monitored during the event (such as fire) and in the long term (*e.g.* with the use of bioindicators). The contamination of brown earth soils in the area of galvanising plant with heavy metals (lead, zinc and cadmium) was significantly reduced. Samples collected in 2022 exhibit much lower concentrations of toxic elements than those from 2019. The average reduction in the case of the organic-mineral horizon (0–5 cm) noted for zinc amounted to 41.8%, lead – 26.1% and cadmium – 16.3%. Similar values were recorded in the samples from mineral horizon (5–20 cm), where the average content of zinc was reduced by 27.8%, lead – 26.7% and cadmium – 15.6%. A significant decrease in the content of the tested elements in samples taken from a field exposed to toxic vapour deposition was caused by an increase in their solubility and bioavailability in acidic soil conditions.

CONFLICT OF INTERESTS

All authors declare that they have no conflict of interests.

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