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COMPREHENSIVE RISK ASSESSMENT NEAR THE ZŁOTNIKI CHEMICAL WORKS S.A.

Rapid industrial development is connected with technical improvement and modern solutions which diminish its adverse environmental impact globally. Although this progress is significant and does not degrade the environment the historical contaminants are still present which can significantly affect human health. Therefore, it is crucial to focus on the areas where industrial activities lasted a long time. Among industries, the chemical sector can have a severe environmental impact, including process production and waste. Hence, this study aimed to assess Złotniki Chemical Works S.A. impact on the environment and residents' health risks as this plant was present in this area for years. Findings show significant environmental impact and possible health risks to inhabitants due to high metal concentrations in the studied soil samples. High concentrations of lead, zinc, and copper were recorded. Despite advanced technologies, continuous industrial activity monitoring is crucial for local community safety and environmental protection.

1. INTRODUCTION

The adverse impact of environmental pollution stemming from the rapid advancement of industry and technology, compounded by natural environmental factors is a pervasive global issue. Its ramifications are intricate and touch nearly every individual.

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Among the most frequently cited health risks associated with environmental hazards are cancer, allergies, immune system disorders, metabolic abnormalities, and reproductive issues [1].

The chemical industry, which encompasses the production of fertilizers for agriculture among its crucial sectors plays a vital role in the economy. Nevertheless, it harbors numerous hazards due to the utilization of harmful substances in production processes and the generation of waste products. Chemical compounds employed in industrial facilities can pose significant threats to both the environment and living organisms, including humans. In recent times, chemical plants within the European Union have increasingly adopted novel technologies aimed at minimizing their environmental footprint [1].

Consequently, research efforts have been directed toward evaluating the current and historical pollution levels associated with these plants, particularly during periods when their environmental impact was pronounced.

This work aimed to assess the impact of the Chemical Works S.A. on the environment along with an assessment of health risks. Due to the proximity of residential buildings and a watercourse, the aim was to comprehensively assess the quality of soil around the plant, therefore the research involved determining the concentration of selected elements in soil and employing the selected indices and formulas to assess the possible health risk. The research hypothesis assumed that the Złotniki Works may harm the environment and living organisms and pose a health risk to the inhabitants of the surrounding areas.

2. EXPERIMENTAL

Study area. Złotniki Works are located within the city of Wrocław, at Żwirowa Street. In their vicinity, there is railway line number 275, which is a part of the former Wrocław–Berlin railway line. The company is located next to the section of the railway between the Wrocław Żerniki and Wrocław Leśnica stations. The roads leading to the plant are Żwirowa Street and the internal road leading from Piołunowa Street. The closest buildings are residential houses located to the north at Żwirowa Street, approximately 200 m from the company. Residential estates located to the east, i.e., the direction of the prevailing winds, are approximately 500 m away from the "Złotniki" Works. There are low single-family buildings and Primary School No. 24. Złotnicki Park, which is a place of rest and recreation for residents of the surrounding housing estates, is located approximately 250 m to the northeast. The Bystrzyca River flowing from the north and west of the Złotniki Works is approximately 200 m from the company premises. The river flows northwards, and on its left bank, at a distance of 230 m from the buildings of the Złotniki Works, there is a NATURA 2000 protected area Łęgi nad Bystrzycą protecting riparian forests, oak-hornbeam forests, and meadows. The company's premises cover a 10-hectare, fenced, and almost completely developed usable area.

Fig. 1. Soil sampling sites created in ArcGIS

Soil samples were taken from locations that were important in terms of pollutant transport: along the access road, close to the plant, and further away, assuming that pollutants were carried away by the wind. Złotniki Works was established on the site of the former Goldschmieden's chemical factory which produced soda and aluminum oxide. In the interwar period, the factory was one of the two largest producers of aluminum sulfate. After World War II, the factory was nationalized and became part of the Wrocław Inorganic Industry Plant. In the late 1940s, the plant began producing aluminum sulfate, which remained the company's main product until 2004. Since the 1940s, the plant produced, among others aluminum-ammonium and aluminum-potassium alum, various grades of aluminum sulfate, magnesium nitrate, nickel sulfate, magnesium sulfate, multi-component fertilizer solutions, calcium nitrate, sodium aluminate, aluminum polychlorides, mixed aluminum-iron coagulants. In the 1990s, aluminum sulfate production technology was changed, installations were modernized, the company was computerized and modernized, and the construction of modern laboratories began. Currently, Złotniki Works is a producer of calcium and magnesium fertilizers.

Sample preparation. Three sites of sampling were selected (1–3), and the wind rose for the city of Wrocław was taken into account along with choosing sites potentially most exposed to pollutants. Soil samples were collected according to the standard (PN-R04031:1997 *Soil Chemical-Agricultural Analysis – Sampling*) in summer 2023. Samples of ca. 1 kg of soil were taken from depths of 0–30 cm at each site, and then each sample was placed in separate airtight containers and mixed. Figure 1 shows sampling sites (ArcGIS program). Table 1 describes sampling sites along with their geographic coordinates.

Table 1

Location and characteristics of sampling sites near the Złotniki Chemical Plant

Sample	Type of terrain	Geographic coordinates
1	moderately wooded area	51°8′4.89″N, 16°52′27.65″E
2	wasteland – meadows	51°8′1.29″N, 16°52′27.42″E
3	farmlands	51°8′0.62″N, 16°52′36.43″E

Chemical analysis. The content of the following elements was assessed: Hg, Fe, Pb, Cr, Ni, Cd, Zn, and Cu. The soil samples were first dried and then sieved through a 1 mm sieve. Aliquots were then created from the samples, each weighing approximately 0.2 g. The prepared samples were poured with 8 cm^3 of 65% nitric acid, thus subjecting them to the mineralization process. The content of heavy metals in the obtained filtrates was determined using atomic spectrometry according to the PN-ISO 11047, 2001 norm.

Health risk assessment. Average daily dose (*ADD*) is expressed as the mass of a pollutant per unit of body weight over time. The potential exposure dose is the product of the contaminant concentration, inhalation rate, exposure time, exposure frequency, and exposure duration divided by the product of the averaging time and body weight. The calculated exposure to studied metals from the environment was estimated based on the amount of the harmful element per 1 kg of body weight during one day [3]. All data used for calculations are summarized in Table 2. The following equations were used to calculate *ADD*:

$$ADD_{\mathrm{ing}} = C\frac{\mathrm{Ing}R\; EF\; ED}{BW\; AT} \tag{1}$$

$$ADD_{\mathrm{inh}} = C\frac{\mathrm{Inh}R\; EF\; ED}{PEF\; BW\; AT}\times 10^{6} \tag{2}$$

$$ADD_{\mathrm{term}} = C\frac{SL\; SA\; ABS\; EF\; ED}{BW\; AT} \tag{3}$$

where: ADD_{ing} – average daily dose absorbed orally, ng/(kg·day), ADD_{inh} – average daily dose absorbed by inhalation, ng/(kg·day), ADD_{derm} – average daily dose absorbed through the skin, ng/(kg·day), C – average metal concentration in soil, mg/kg, Ing$R$ – daily accidental soil intake, mg/day, Inh$R$ – daily lung ventilation, m^3/day, EF – contact frequency, day/year, ED – duration of contact, year, BW – average body weight, kg, AT – averaging period, day, PEF – particle emission factor, m^3/kg, SL – coefficient of dust adherence to the skin, mg/(cm^2·day), SA – skin surface exposed to soil, cm^2, ABS – percutaneous absorption coefficient.

Table 2

Acceptable values of the parameters in question according to US EPA [3]

Parameter	Adults	Children
Ing$R$, mg/day	100	200
EF, day/year	7.6	20
ED, year	6	70
AT, day	2190	25550
BW, kg	15	70
Inh$R$, m^3/day	180	180
PEF, m^3/kg	$1.36 \cdot 10^9$	$1.36 \cdot 10^9$
ABS	0.001	0.001
SL, mg/(cm^2·day)	0.2	0.7
SA, cm^2	2800	5700

To assess non-carcinogenic health risks, the hazard quotient (HQ_i) index was used. As the HQ coefficient increases, the intensity of the impact of a studied element on health also increases. $HQ_i \geq 1$ means the possibility of negative health effects. The non-carcinogenic risk is the quotient of the average daily exposure dose and the reference dose (RfD) [4]. The RfD values used for calculations are listed in Table 3.

Table 3

Reference doses [ng/(kg·day)] [5]

Metal	RfD_{inh}	RfD_{derm}	RfD_{ing}
Cu	$4 \cdot 10^4$	$4 \cdot 10^4$	$4 \cdot 10^4$
Zn	$3 \cdot 10^5$	$6 \cdot 10^4$	$3 \cdot 10^5$
Pb	$3.52 \cdot 10^3$	$5.25 \cdot 10^2$	$3.5 \cdot 10^3$
Fe	0.7	0.7	0.7

Simultaneous human exposure to several non-carcinogenic elements or via several routes of exposure requires the calculation of the HQ_i index separately for each element and for each route of exposure. The quotients calculated in this way are summarized and the sum is the hazard index (HI). $HI \geq 1$ means that negative health effects are possible.

$$HQ_i = \frac{ADD}{RfD_i} \tag{4}$$

$$HI = \sum_{i=1}^{n} HQ_i \tag{5}$$

The excess cancer risk *ECR* index was used to assess the carcinogenic risk. It involves estimating the risk based on studies of the likely development of cancer in the human body throughout life. The *ECR* index is the result of metal concentration, contact frequency, exposure time, and individual risk divided by the average body weight along with the average time (number of days of a person's life exposure). The inhalation unit risk (*IUR*) for Ni, Pb, Cr, Cd are $2.6\cdot10^{-4}$, $1.2\cdot10^{-5}$, 0.012, and $1.8\cdot10^{-3}$ $(\mu g/m^3)^{-1}$, respectively (Integrated Risk Information System, IRIS) [3]. The exposure time (*ET*) was assumed to be 14 years for adults and 8 years for children, respectively. If the *ECR* ranges between 10^{-6} and 10^{-4}, there is a low risk of cancer [4].

$$ECR = \frac{C\,ET\,EF\,ED\,IUR}{BW\,AT} \tag{6}$$

where: C – average metal concentration in soil, mg/kg, ET – exposure time, year, EF – contact frequency, day/year, ED – duration of contact, year, IUR – inhalation unit risk, $\mu g^{-1}/m^{-3}$, BW – average body weight, kg, AT – average period, day.

Table 4

Values of geochemical background [mg/kg] [7]

Metal	Geochemical background	Metal	Geochemical background
Hg	0.056	Ni	18.6
Fe	30890	Pb	17
Cd	0.102	Zn	52
Cr	35	Cu	14.3

Calculation of soil pollution indices. A single pollution index (*PI*) allows us to determine the enrichment of the studied soil with the analyzed elements taking into account the geochemical background [6] (Table 4). It determines which of the analyzed element poses the greatest threat to soil and is calculated according to:

$$PI = \frac{C_n}{B_n} \tag{7}$$

where: C_N – element concentration in the sample, mg/kg, B_N – geochemical background of the corresponding element, mg/kg.

Table 5 defines 5 classes of soil pollution according to the *PI* index.

Table 5

Classes of soil pollution [8]

Range of *PI*	Level of soil pollution
$PI \leq 1$	none
$1 < PI \leq 2$	small
$2 < PI \leq 3$	moderate
$PI > 3$	high

The pollution load index (*PLI*) was used to calculate the total soil pollution in the study area. It shows the pollutant load of the analyzed soil to notice the trend of deterioration of soil conditions in the studied area due to the accumulation of toxic elements in the soil. The PLI index is calculated as follows:

$$PLI = \left(PI_1\, PI_2 \cdots PI_n\right)^{1/n} \tag{8}$$

where: n – number of elements, PI_i – pollution index of a given element.

Table 6 shows soil pollution level according to the PLI index.

Table 6

Classes for *PLI* [8]

Class	*PLI*	Level of soil pollution
1	<0	none
2	0–1	small
3	1–2	moderate
4	2–4	high
5	4–8	very high
6	8–16	extremely high

Table 7

Classes of geoaccumulation index I_{geo} according to Müller [9]

I_{geo}	Class	Characteristic
<0	0	not polluted
0–1	1	from not polluted to moderately polluted
1–2	2	moderately polluted
2–3	3	from moderately to strongly polluted
3–4	4	strongly polluted
4–5	5	from strongly to extremely polluted
>5	6	extremely polluted

To assess the level of accumulation of metals in the soil, the I_{geo} geoaccumulation index was used.

$$I_{\text{geo}} = \log_2 \frac{C_n}{1.5B_n} \tag{9}$$

The assessment of soil contamination according to I_{geo} is given in Table 7.

3. RESULTS

3.1. METAL CONCENTRATIONS IN THE SOIL

Metal concentrations in studied soil samples are presented in Table 8. The quality standard of soils around the Złotniki Works was classified into group B according to permissible standards [10]. All exceedances were recorded for soil taken from site 1. This site was located east of the plant, close to the truck parking lot, the access road to the company, and a railway line nearby. The exceedances of the permissible concentrations were approximately 2.5 times higher for Zn, and up to 5 times higher for Cu. High Fe concentrations were also recorded at site 1. The concentrations of other elements such as Ni, Cr, Cd, and Hg did not exceed the norm at any site.

Table 8

Metal content in the soil samples [mg/kg]

Element	Sample 1	Sample 2	Sample 3	Permissible content [10]
Hg	0.1680 ±0.0075	0.2913±0.0032	0.0134±0.0003	2
Fe	21.743±0.029	10.186±0.013	5.888±0.023	–
Cd	1.05±0.36	0.39±0.08	0.33±0.07	4
Cr	39.03±0.56	14.82±0.90	6.08±0.50	150
Ni	40.90±1.06	7.02±0.84	below the limit	100
Pb	401.62±5.37	27.27±1.08	10.34±1.88	100
Zn	765.03±5.88	74.30±0.10	38.48±0.21	300
Cu	779.48±1.61	16.84±0.17	8.86±0.25	150

3.2. HEALTH RISK ASSESSMENT

Tables 9–14 present the results of the *ADD*, *HQ*, and *HI* index for all elements for each site separately.

Table 9

ADD values for all elements for site 1 [ng/(kg·day)]

ADD	Hg	Fe	Cd	Cr	Ni	Pb	Zn	Cu
	Adults							
ADD_{ing}	$2.37\cdot10^{-1}$	$3.06\cdot10^{1}$	1.48	$5.5\cdot10^{1}$	$5.76\cdot10^{1}$	$5.66\cdot10^{2}$	$1.08\cdot10^{3}$	$1.10\cdot10^{3}$
ADD_{inh}	$1.70\cdot10^{-5}$	$2.20\cdot10^{-3}$	$1.06\cdot10^{-4}$	$3.96\cdot10^{-3}$	$4.15\cdot10^{-3}$	$4.07\cdot10^{-2}$	$7.75\cdot10^{-2}$	$7.90\cdot10^{-2}$
ADD_{derm}	$4.72\cdot10^{-3}$	$6.11\cdot10^{-1}$	$2.95\cdot10^{-2}$	1.10	1.15	$1.13\cdot10^{1}$	$2.15\cdot10^{1}$	$2.19\cdot10^{1}$
	Children							
ADD_{ing}	$5.52\cdot10^{-1}$	$7.15\cdot10^{1}$	3.45	$1.28\cdot10^{2}$	$1.34\cdot10^{2}$	$1.32\cdot10^{3}$	$2.52\cdot10^{3}$	$2.56\cdot10^{3}$
ADD_{inh}	$3.02\cdot10^{-5}$	$3.91\cdot10^{-3}$	$1.89\cdot10^{-4}$	$7.02\cdot10^{-3}$	$7.35\cdot10^{-3}$	$7.22\cdot10^{-2}$	$1.38\cdot10^{-1}$	$1.40\cdot10^{-1}$
ADD_{derm}	$3.09\cdot10^{-3}$	$4.00\cdot10^{-1}$	$1.93\cdot10^{-2}$	$7.19\cdot10^{-1}$	$7.53\cdot10^{-1}$	7.39	$1.41\cdot10^{1}$	$1.44\cdot10^{1}$

For all elements at site 1, the exposure route with the highest exposure to contaminants is the oral route. The highest doses, for all exposure routes, were determined for Pb for both adults and children; for children, this dose was higher and amounted to as much as $1.32\cdot10^3$ ng/(kg·day). The highest dose was recorded for Cu for children through oral route and it was $2.56\cdot10^3$ ng/(kg·day). For all elements, for both groups, the highest dose was in the case of the oral route of exposure, the next was the dermal route and the lowest doses were recorded for the respiratory route.

Table 10

HQ and *HI* values for all elements for site 1

Parameter	Hg	Fe	Cd	Cr	Ni	Pb	Zn	Cu
	Adults							
HQ_{ing}	$5.92\cdot10^{-6}$	$7.66\cdot10^{-4}$	$3.70\cdot10^{-5}$	$1.37\cdot10^{-3}$	$1.44\cdot10^{-3}$	$1.41\cdot10^{-2}$	$2.69\cdot10^{-2}$	$2.75\cdot10^{-2}$
HQ_{inh}	$4.26\cdot10^{-10}$	$5.51\cdot10^{-8}$	$2.66\cdot10^{-9}$	$9.89\cdot10^{-8}$	$1.04\cdot10^{-7}$	$1.02\cdot10^{-6}$	$1.94\cdot10^{-6}$	$1.98\cdot10^{-6}$
HQ_{derm}	$3.94\cdot10^{-7}$	$5.09\cdot10^{-5}$	$2.46\cdot10^{-6}$	$9.14\cdot10^{-5}$	$9.58\cdot10^{-5}$	$9.41\cdot10^{-4}$	$1.79\cdot10^{-3}$	$1.83\cdot10^{-3}$
HI	$6.31\cdot10^{-6}$	$8.17\cdot10^{-4}$	$3.94\cdot10^{-5}$	$1.47\cdot10^{-3}$	$1.54\cdot10^{-3}$	$1.51\cdot10^{-2}$	$2.87\cdot10^{-2}$	$2.93\cdot10^{-2}$
	Children							
HQ_{ing}	$1.38\cdot10^{-5}$	$1.79\cdot10^{-3}$	$8.63\cdot10^{-5}$	$3.21\cdot10^{-3}$	$3.36\cdot10^{-3}$	$3.30\cdot10^{-2}$	$6.29\cdot10^{-2}$	$6.41\cdot10^{-2}$
HQ_{inh}	$7.55\cdot10^{-10}$	$9.77\cdot10^{-8}$	$4.72\cdot10^{-9}$	$1.75\cdot10^{-7}$	$1.84\cdot10^{-7}$	$1.80\cdot10^{-6}$	$3.44\cdot10^{-6}$	$3.50\cdot10^{-6}$
HQ_{derm}	$2.58\cdot10^{-7}$	$3.34\cdot10^{-5}$	$1.61\cdot10^{-6}$	$5.99\cdot10^{-5}$	$6.28\cdot10^{-5}$	$6.16\cdot10^{-4}$	$1.17\cdot10^{-3}$	$1.20\cdot10^{-3}$
HI	$1.41\cdot10^{-5}$	$1.82\cdot10^{-3}$	$8.79\cdot10^{-5}$	$3.27\cdot10^{-3}$	$3.42\cdot10^{-3}$	$3.36\cdot10^{-2}$	$6.41\cdot10^{-2}$	$6.53\cdot10^{-2}$

HQ and *HI* values were not above 1 for any analyzed elements for all studied sites, therefore the possibility of negative effects related to human exposure to a studied element is not real.

The values of *ADD* calculated for soil samples from site 2 indicate the highest oral exposure for both adults and children. The highest values for oral exposure were found for Zn for children: $2.44\cdot10^2$ ng/(kg·day), for adults $1.05\cdot10^2$ ng/(kg·day), respectively.

Table 11

ADD values for all elements for site 2 [ng/(kg·day)]

ADD	Hg	Fe	Cd	Cr	Ni	Pb	Zn	Cu
	Adults							
ADD_{ing}	$4.1\cdot10^{-1}$	$1.44\cdot10^{1}$	$5.5\cdot10^{-1}$	$2.09\cdot10^{1}$	9.89	$3.84\cdot10^{1}$	$1.05\cdot10^{2}$	$2.37\cdot10^{1}$
ADD_{inh}	$2.95\cdot10^{-5}$	$1.03\cdot10^{-3}$	$3.95\cdot10^{-5}$	$1.50\cdot10^{-3}$	$7.12\cdot10^{-4}$	$2.76\cdot10^{-3}$	$7.53\cdot10^{-3}$	$1.71\cdot10^{-3}$
ADD_{derm}	$8.19\cdot10^{-3}$	$2.86\cdot10^{-1}$	$1.10\cdot10^{-2}$	$4.17\cdot10^{-1}$	$1.97\cdot10^{-1}$	$7.67\cdot10^{-1}$	2.09	$4.73\cdot10^{-1}$
	Children							
ADD_{ing}	$9.58\cdot10^{1}$	$3.35\cdot10^{1}$	1.28	$4.87\cdot10^{1}$	$2.31\cdot10^{1}$	$8.97\cdot10^{1}$	$2.44\cdot10^{2}$	$5.54\cdot10^{1}$
ADD_{inh}	$5.24\cdot10^{-5}$	$1.83\cdot10^{-3}$	$7.01\cdot10^{-5}$	$2.66\cdot10^{-3}$	$1.26\cdot10^{-3}$	$4.90\cdot10^{-3}$	$1.34\cdot10^{-2}$	$3.03\cdot10^{-3}$
ADD_{derm}	$5.36\cdot10^{-3}$	$1.88\cdot10^{-1}$	$7.18\cdot10^{-3}$	$2.73\cdot10^{-1}$	$1.29\cdot10^{-1}$	$5.02\cdot10^{-1}$	1.37	$3.10\cdot10^{-1}$

Table 12

HQ and *HI* values for all elements for site 2

Parameter	Hg	Fe	Cd	Cr	Ni	Pb	Zn	Cu
	Adults							
HQ_{ing}	$1.03\cdot10^{-5}$	$3.59\cdot10^{-4}$	$1.37\cdot10^{-5}$	$5.22\cdot10^{-4}$	$2.47\cdot10^{-4}$	$9.61\cdot10^{-4}$	$2.62\cdot10^{-3}$	$5.93\cdot10^{-4}$
HQ_{inh}	$7.38\cdot10^{-10}$	$2.58\cdot10^{-8}$	$9.88\cdot10^{-10}$	$3.76\cdot10^{-8}$	$1.78\cdot10^{-8}$	$6.91\cdot10^{-8}$	$1.88\cdot10^{-7}$	$4.27\cdot10^{-8}$
HQ_{derm}	$6.82\cdot10^{-7}$	$2.39\cdot10^{-5}$	$9.14\cdot10^{-7}$	$3.47\cdot10^{-5}$	$1.64\cdot10^{-5}$	$6.39\cdot10^{-5}$	$1.74\cdot10^{-4}$	$3.94\cdot10^{-5}$
HI	$1.09\cdot10^{-5}$	$3.83\cdot10^{-4}$	$1.47\cdot10^{-5}$	$5.57\cdot10^{-4}$	$2.64\cdot10^{-4}$	$1.02\cdot10^{-3}$	$2.79\cdot10^{-3}$	$6.33\cdot10^{-4}$
	Children							
HQ_{ing}	$2.39\cdot10^{-5}$	$8.37\cdot10^{-4}$	$3.21\cdot10^{-5}$	$1.22\cdot10^{-3}$	$5.77\cdot10^{-4}$	$2.24\cdot10^{-3}$	$6.11\cdot10^{-3}$	$1.38\cdot10^{-3}$
HQ_{inh}	$1.31\cdot10^{-9}$	$4.58\cdot10^{-8}$	$1.75\cdot10^{-9}$	$6.66\cdot10^{-8}$	$3.15\cdot10^{-8}$	$1.23\cdot10^{-7}$	$3.34\cdot10^{-7}$	$7.57\cdot10^{-8}$
HQ_{derm}	$4.47\cdot10^{-7}$	$1.56\cdot10^{-5}$	$5.98\cdot10^{-7}$	$2.27\cdot10^{-5}$	$1.08\cdot10^{-5}$	$4.18\cdot10^{-5}$	$1.14\cdot10^{-4}$	$2.58\cdot10^{-5}$
HI	$2.44\cdot10^{-5}$	$8.53\cdot10^{-4}$	$3.27\cdot10^{-5}$	$1.24\cdot10^{-3}$	$5.88\cdot10^{-4}$	$2.28\cdot10^{-3}$	$6.22\cdot10^{-3}$	$1.41\cdot10^{-3}$

Table 13

ADD values for all elements for site 3 [ng/(kg·day)]

ADD	Hg	Fe	Cd	Cr	Ni[a]	Pb	Zn	Cu
	Adults							
ADD_{ing}	$1.89\cdot10^{-2}$	8.30	$4.6\cdot10^{1}$	8.57	–	$1.46\cdot10^{1}$	$5.42\cdot10^{1}$	$1.25\cdot10^{1}$
ADD_{inh}	$1.36\cdot10^{-6}$	$5.97\cdot10^{-4}$	$3.35\cdot10^{-5}$	$6.16\cdot10^{-4}$	–	$1.05\cdot10^{-3}$	$3.90\cdot10^{-3}$	$8.98\cdot10^{-4}$
ADD_{derm}	$3.77\cdot10^{-4}$	$1.66\cdot10^{-1}$	$9.28\cdot10^{-3}$	$1.71\cdot10^{-1}$	–	$2.91\cdot10^{-1}$	1.08	$2.49\cdot10^{-1}$
	Children							
ADD_{ing}	$4.41\cdot10^{-2}$	$1.94\cdot10^{1}$	1.08	$2.0\cdot10^{1}$	–	$3.4\cdot10^{1}$	$1.27\cdot10^{2}$	$2.91\cdot10^{1}$
ADD_{inh}	$2.41\cdot10^{-6}$	$1.06\cdot10^{-3}$	$5.93\cdot10^{-5}$	$1.09\cdot10^{-3}$	–	$1.86\cdot10^{-3}$	$6.92\cdot10^{-3}$	$1.59\cdot10^{-3}$
ADD_{derm}	$2.47\cdot10^{-4}$	$1.08\cdot10^{-1}$	$6.08\cdot10^{-3}$	$1.12\cdot10^{-1}$	–	$1.90\cdot10^{-1}$	$7.08\cdot10^{-1}$	$1.63\cdot10^{-1}$

[a]Concentrations of Ni below the limit of determination using the ASA (FAAS) technique.

The *ADD* value for site 3 was the highest for oral exposure, both for adults and children. The highest dose was recorded again for Zn, both for adults and children, 54.2 ng/(kg·day) and 127 ng/(kg·day), respectively. In the case of other elements, no high oral exposure was found.

Table 14

HQ and *HI* values for all elements for site 3

Parameter	Hg	Fe	Cd	Cr	Ni[a]	Pb	Zn	Cu
	Adults							
HQ_{ing}	$4.73\cdot10^{-7}$	$2.07\cdot10^{-4}$	$1.16\cdot10^{-5}$	$2.14\cdot10^{-4}$	–	$3.64\cdot10^{-4}$	$1.36\cdot10^{-3}$	$3.12\cdot10^{-4}$
HQ_{inh}	$3.40\cdot10^{-11}$	$1.49\cdot10^{-8}$	$8.36\cdot10^{-10}$	$1.54\cdot10^{-8}$	–	$2.62\cdot10^{-8}$	$9.75\cdot10^{-8}$	$2.25\cdot10^{-8}$
HQ_{derm}	$3.14\cdot10^{-8}$	$1.38\cdot10^{-5}$	$7.73\cdot10^{-7}$	$1.42\cdot10^{-5}$	–	$2.42\cdot10^{-5}$	$9.01\cdot10^{-5}$	$2.08\cdot10^{-5}$
HI	$5.04\cdot10^{-7}$	$2.21\cdot10^{-4}$	$1.24\cdot10^{-5}$	$2.28\cdot10^{-4}$	–	$3.88\cdot10^{-4}$	$1.45\cdot10^{-3}$	$3.33\cdot10^{-4}$
	Children							
HQ_{ing}	$1.10\cdot10^{-6}$	$4.84\cdot10^{-4}$	$2.71\cdot10^{-5}$	$5.00\cdot10^{-4}$	–	$8.50\cdot10^{-4}$	$3.16\cdot10^{-3}$	$7.28\cdot10^{-4}$
HQ_{inh}	$6.03\cdot10^{-11}$	$2.65\cdot10^{-8}$	$1.48\cdot10^{-9}$	$2.73\cdot10^{-8}$	–	$4.65\cdot10^{-8}$	$1.73\cdot10^{-7}$	$3.98\cdot10^{-8}$
HQ_{derm}	$2.06\cdot10^{-8}$	$9.03\cdot10^{-6}$	$5.06\cdot10^{-7}$	$9.33\cdot10^{-6}$	–	$1.59\cdot10^{-5}$	$5.90\cdot10^{-5}$	$1.36\cdot10^{-5}$
HI	$1.12\cdot10^{-6}$	$4.93\cdot10^{-4}$	$2.76\cdot10^{-5}$	$5.09\cdot10^{-4}$	–	$8.66\cdot10^{-4}$	$3.22\cdot10^{-3}$	$7.42\cdot10^{-4}$

[a]Concentrations of Ni below the limit of determination using the ASA (FAAS) technique.

Table 15 presents the results of the *ECR* index of human exposure to carcinogenic effects of elements. The *ECR* was calculated for Ni, Pb, Cr and Cd because these elements are carcinogenic.

Table 15

ECR index for the metals in the soil

Metal	Age group	Sample		
		1	2	3
Ni	adults	$1.05\cdot10^{-3}$	$1.80\cdot10^{-4}$	below the limit by ASA technique
	children	$2.80\cdot10^{-3}$	$4.80\cdot10^{-4}$	
Pb	adults	$4.80\cdot10^{-4}$	$3.00\cdot10^{-5}$	$1.00\cdot10^{-5}$
	children	$1.27\cdot10^{-3}$	$9.00\cdot10^{-5}$	$3.00\cdot10^{-5}$
Cr	adults	$4.62\cdot10^{-2}$	$1.75\cdot10^{-2}$	$7.20\cdot10^{-3}$
	children	$1.23\cdot10^{-1}$	$4.68\cdot10^{-2}$	$1.92\cdot10^{-2}$
Cd	adults	$1.90\cdot10^{-4}$	$7.00\cdot10^{-5}$	$6.00\cdot10^{-5}$
	children	$5.00\cdot10^{-4}$	$1.80\cdot10^{-4}$	$1.60\cdot10^{-4}$

The *ECR* values for soil samples from site 1 indicate the risk of cancer as all elements exceeded the recommended values for both groups (if the *ECR* ranges between 10^{-6} and 10^{-4}, the risk of cancer is low [4]). The highest *ECR* values occur in the case of Cr for children ($1.23\cdot10^{-1}$), for adults the value is $4.62\cdot10^{-2}$. The lowest values were recorded for Cd (adults $1.90 \cdot 10^{-4}$), and Pb (adults $4.80 \cdot 10^{-4}$). *ECR* values for soil samples from site 2 indicate carcinogenic exposure to Ni, Cr, and Cd. The highest values were recorded for Cr (adults $1.75 \cdot 10^{-2}$ and children $4.68 \cdot 10^{-2}$). For Ni, it was also for both age groups, for Cd an exceedance was recorded only in the case of children. The values of *ECR* for samples taken from site 3 indicate carcinogenic effects for Cr (both age groups) and Cd (children). The highest value was recorded for children in the case of Cd ($1.92 \cdot 10^{-2}$). *ECR* values for Pb do not exceed the safe limit. The *ECR* index was not calculated for Ni due to the too low concentration of this element in the soil samples.

3.3. SOIL POLLUTION ASSESSMENT

The *PI* index was calculated for all elements in Table 16. The highest *PI* values were recorded for Zn, Cu, and Pb. For these elements, exceedances of the permissible values in the soil were also recorded. Although, based on other elements soil can be classified into class I and II (low soil contamination), only a few elements allow us to classify for III or IV because of the greater soil enrichment in these elements. The highest enrichment was recorded for Cu, Zn, and Pb at site 1 (class V of soil enrichment), at site 2 it was Hg (class V). Such enrichment was not recorded at site 3.

Table 16

PI and *PLI* indices for the elements in soil

Sample	*PI* Hg	*PI* Fe	*PI* Cd	*PI* Cr	*PI* Ni	*PI* Pb	*PI* Zn	*PI* Cu	*PLI* Li
1	4.2	0.03	2.1	2.78	4.09	22.31	15.30	97.43	5.39
2	7.28	0.01	0.78	1.05	0.70	1.51	1.48	2.10	0.85
3	0.33	0.01	0.66	0.43	–	0.57	0.76	1.10	0.42

Concentration of Ni in sample 3 is below the limit of determination by the ASA (FAAS) technique.

To assess the degree of accumulation of heavy metals of anthropogenic origin in the soil, the I_{geo} index was calculated. The results are summarized in Table 17.

Table 17

I_{geo} indices for the analyzed elements

Sample	Hg	Fe	Cd	Cr	Ni	Pb	Zn	Cu	Hg
1	1.48	4.69	–5.59	0.48	0.89	1.44	3.89	3.35	6.02
2	2.27	–0.24	–6.68	–0.94	–0.50	–1.10	0.01	–0.01	0.49
3	–2.16	–0.44	–7.47	–1.18	–1.78		–1.38	–0.96	–0.43

Concentration of Pb in sample 3 is below the limit of determination by the ASA (FAAS) technique.

The highest contamination according to I_{geo} was recorded for Cu at site 1, and strong contamination was found for Pb and Zn at the same site. For soil taken at site 3, no contamination was recorded for all elements. Moderately soil pollution was found at site 2 for Hg. The obtained results are consistent with the *PI* index, indicating the highest soil pollution at site 1.

4. DISCUSSION

Exceeding the permissible concentrations of the analyzed metals in the soil occurred only at site 1 for Cu: 5 times higher, and Zn 2.5 times higher, respectively. High concentrations were also recorded for Fe. Although, this element does not harm the soil environment as it is necessary for plants and animals [11]. High Cu content in the soil may cause the accumulation of this element in plants that are then consumed by people and animals. In the case of Cu, intoxication includes vomiting, abdominal pain, damage to the digestive system, and kidneys, and liver failure, which may result in death. Zn is an element very easily absorbed and accumulated by plants [12]. High consumption of this element by humans may lead to digestive system disorders, long-term exposure may cause cancer. On the other hand, however, both of these elements are necessary for the proper functioning of living organisms and they are usually resistant to their high concentrations in the body [13]. High concentrations of these elements result from the production of agricultural fertilizers by the Złotniki Works. The additional contribution to the highest contamination of site 1 is its proximity to the emitter, wind direction, and the surrounding of a railway line, and the presence of an access road to the plant.

Metals can travel on dust particles, and then during production, the Złotniki Works emits trace amounts of dust on which metal particles could settle. The deposition of dust particles also depends on atmospheric factors, such as wind strength and direction or air humidity.

According to soil pollution indices, it was also proved that site 1 is the most contaminated. At this site, based on I_{geo}, strong and very strong soil contamination with Zn and Cu was found. Pb also heavily pollutes the soil at this site. Based on the I_{geo} index, soil contamination at site 2 was also found with elements such as Pb, Cu, and Hg, but the contamination was moderate. At site 3, no soil contamination was found. Similar conclusions were obtained based on soil pollution indices (*PI* and *PLI*).

In 2014, Musztyfaga et al. [14] showed the impact of the activities of Złotniki Works on the soil environment around the company. Zn and Cu were also identified as the elements most polluting the soil in the studied area. The conducted research confirmed these results. Even though a lot of time has passed since the studies Musztyfaga et al. [14], contaminants from the plant's former activities are still present.

According to *ADD*, *HQ*, and *HI* for heavy metals in the soil, there was no risk of negative health effects. The value of the *HQ* hazard quotient for all sites and both age groups is reduced according to the formula: $HQ_{ing} > HQ_{derm} > HQ_{inh}$. The value never exceeds 1 signifying no risk of negative health effects.

The *ECR* shows human exposure to the carcinogenic effects of elements found in the environment. For site 1, the safe limit of the *ECR* index (1×10^{-4}) was exceeded for Ni, Pb, Cr and Cd. The highest values were obtained for Cr. At site 2, the safe limit was exceeded for Ni, Cr, and Cd, and at site 3, it was in the case of Cr and Cd. These results indicate the risk of cancer for people living in the vicinity of the Złotniki Works, the highest near site 1. Such contamination is probably the result of the historical accumulation of these elements in the soil due to the industrial use of these areas in the 19th and 20th centuries.

Therefore, the soil in the vicinity of the Złotniki Works pose a risk of cancer among people living in the surrounding areas due to the carcinogenic metals they contain.

5. CONCLUSION

It was found that the Złotniki Works still has an impact on the surrounding environment, causing health threats to residents in the immediate vicinity. This thesis is confirmed by the results obtained – exceeding the permissible concentrations of metals in the soil for Pb, Zn, and Cu. All exceedances were found in soil samples taken at site 1 (located east of the plant, close to the truck parking, access road, and a railway line). Increased Fe content was also found there. Based on the calculations of the I_{geo} geoaccumulation index, it was found that the most heavily polluted soil is also from site 1 as the very strong soil contamination with Pb, Cu, and Zn was recorded. This is also confirmed by other soil pollution indices such as the single pollution index (*PI*) and pollution load index (*PLI*).

The pollution results from historical industrial activity in the area as well as the proximity of railway, road, and wind direction. According to the *ECR* index, there is a risk of cancer for people from the surrounding areas. The research shows that it is still necessary to examine the surroundings because, despite the improvement of standards in workplaces, there are still sites where there are a lot of pollutants deriving from earlier periods of industrial activity.

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