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Environmental Health Hazards of the Demolition of the 'Siechnice' Smelter Slag Heap

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ABSTRACT

The activities of smelters are often responsible for emitting pollution, especially PTEs, which are known to have a negative impact on the environment. Hence, the areas with active or past smelter activities are now of great concern. Following this idea, the analysis of the soil samples from the area nearby post-metallurgic waste dump, which is a remnant of the smelter where ferrochrome was produced, was performed. The samples were analyzed in terms of metal concentrations (Zn, Cu, Pb, Fe, Cr) and only the concentrations of Pb did not exceed the limit value for soil. Calculations of the exposure doses for each of these metals were also presented, considering different routes of exposure. Additionally, Hazard Quotient (HQ), Hazard Index (HI), and excessive risk of cancer development (ECR) were calculated, which helped to estimate the health risk.

Keywords: potentially toxic elements, health risk assessment, smelter, Siechnice.

INTRODUCTION

Nowadays, the society and nature are struggling with a very serious problem of environmental pollution which is triggered by the rapid development of urbanization and industrialization. These two sectors are responsible for the production of many different pollutants which subsequently lead to the contamination of the environment and eventually can pose a serious threat to human health [e.g., Jiang, Ren, Hursthouse, & Deng, 2020]. Among these pollutants, potentially toxic elements (PTEs) are commonly studied in contaminated areas due to their high toxicity, persistence, concealment, and biological accumulation [Wang et al., 2019]. An important issue is to study the levels of PTEs in soils according to the fact that they are able to enter the human food chain via different pathways [Antoniadis et al., 2019; Edelstein & Ben-Hur, 2018; Rinklebe, Kumpiene, Du Laing, & Ok, 2017] and constitute a serious health risk, especially for children [e.g., Rinklebe et al., 2019]. However, it must be remembered that the negative consequences of pollution impact on human health do not always reveal themselves at a given moment, but the effects of toxicity may reveal after several years [Romanowska-Duda, n.d.]. The response of the organism to the contaminants taken up depends on the degree of exposure and the amount of substance intake as well as whether the person had any interdependent diseases that could contribute to the deterioration of health. Considering that the study focusing on the analyses of PTEs in the soil is a crucial issue nowadays and the limit values on the accumulation of heavy metals in the soil which are regulated by the Polish law cannot be exceeded. These values are presented in Table 1.

In the study area, during the years 1952-1990, ferrochrome was mined by the Siechnice

Table 1. The permissible concentrations of heavy metals that may occur in the soil were taken from Regulations of the Minister of Agriculture and Rural Development [Rozporządzenie Ministra Rolnictwa i Rozwoju Wsi, 2002]

Impurity Component	Concentration in mg/kg dry matter in any soil type		
Chemical element	Lightweight	Medium - heavy	Heavy
Pb	50	70	100
Cd	0.75	1	1.5
Cr	50	80	100
Cu	30	50	70
Zn	100	200	300

smelter. At first, the smelter produced chrome steel, but a few years later it also started the production of noble and seminoble ferroalloys. However, the inconvenient location of the smelter (300 m from the water-bearing areas of Wrocław) sparked many protests of the inhabitants of Siechnice and Wrocław [Gonda-Soroczyńska, 2007]. Moreover, due to the lack of specific equipment contributing to the reduction of emissions to air, the smelter was known as the main polluting and gas emitting factor. Considering that and the impossibility to modernize the smelter, in 1989 the Ministry of Industry issued a warrant to close the Siechnice smelter. After the closure, the smelter was partly disassembled; however, some residues were left behind and the main problem became the dump its dusting. The main component of the dump was the post-metallurgic slag, originating from the previous activity of the smelter. Apart from this, other wastes were stored next to the inactive smelter, i.e., used inflammable materials [Koszelnik-Leszek & Wall, 2005]. Firstly, the heap was not covered with vegetation and hence, dusting of the heap occurred, leading to the spread of contaminants and pollution of the air. This iron chromium heap was also known to have a negative impact on the ground water in the nearby area. This was due to leaching of PTEs from the heap, as well as from the soils directly below and adjacent to the heap [Gonda-Soroczyńska, 2007]. After many years, the negative impact of the dump was slightly reduced. Some basic reclamation actions were undertaken which helped to quickly solve the problem with F.E. dusting from the dump which was affecting residents before. The infiltration processes and leaching of the contamination into the lower parts of the waste dump were slowed down by the growing plants and hence better retention of water from precipitation. However, it must be emphasized that the waste dump was left too long without any plant cover, which could cause the accumulation of PTEs in the nearby areas [Roszak, 1991].

Presently, an American company called "Phoenix Services", which is the co-owner of the problematic area, is undertaking the actions aimed at the liquidation of the heap. The current situation, however, arouses much concern in the local community. The local residents complain about the onerous dustiness that arises during the current operations on the heap. The original plans for demolishment and protection solutions for the waste dump were different before focusing on minimalizing the dusting. However, the reality is more complicated. Additionally, the past activity of the smelter contributed to the accumulation of PTEs in the soil which may negatively influence the surrounding crops and hence pose a threat to human health. Even though the work on the heap began in 2012 and some steps were undertaken, the area of Siechnice is still under risk and constitutes a health hazard for the inhabitants. It has been already shown that the limit concentrations of PTEs in this area still can be exceeded [Borowczak & Hołtra, 2017].

Considering the fact that exceedings of some PTEs still appear in this area, the possibility of potential risk occurrence is assumed. Hence, the aim of this work was to determine how the activities connected with the demolition of the slag heap affect the local community and its surroundings and assess the health risk. Therefore, the soil samples were subjected to analysis which provided the information about the concentration of selected PTEs (Zn, Cu, Pb, Fe, Cr). On the basis of these results, the exposure doses for children and adults were calculated, considering three different routes of exposure such as inhalation, ingestion, and dermal contact. Additionally, Hazard Quotient (HQ), Hazard Index (HI), and excessive risk of cancer development (ECR) were determined.

MATERIALS AND METHODS

Study area

Siechnice is a town of 8000 habitants [demografia.stat.gov.pl], located in the Lower Silesian voivodship, in the south-western part of Poland (Fig. 1). Until 1990, a ferrochrome smelter operated in this area; however, it had to be closed due decision of the Polish Ministry of Industry from 1989. The previous activity of the smelter resulted in the creation of a slag heap. The heap is located in the north-western part of the city, between the eastern ring road of Wrocław and the path through the wasteland. Apart from the wastelands in the immediate vicinity of the slag heap, there are also meadows and fields. The cubic capacity of the heap is estimated to reach over 1.5 million m^3 [Karczewska & Bortniak, 2008]. The heap has a shape of the triangle with the edge length of 550 m. Due to its characteristics and the fact that it contains large amounts of harmful substances, it is called an environmental bomb. In 2009, it was included in the program of the ecological bomb disposal [http://www.sejm.gov.pl/sejm7.nsf]. As a result, the actions aiming at the elimination of the heap started in 2012 and continue to this day. However, the elimination is performed in a way which does not prevent from dusting of the material collected in the heap. Hence, it is raising concerns among the local residents.

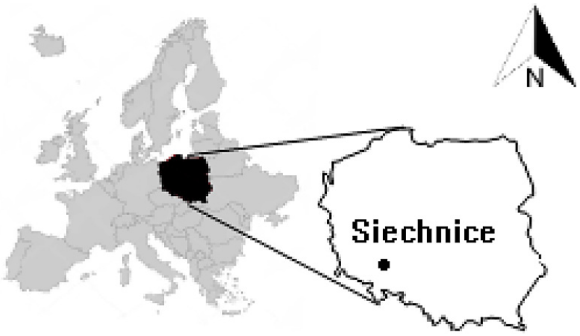

Fig. 1. Location of the study area

Sampling and location of sampling points

Soil sampling occurred on 30th January 2020. The samples were obtained from the area near the Siechnice slag heap, about 15 km away from Wrocław. Four samples (No. 2-5) were taken within the slag heap (Fig. 2) while the sample no. 1 was collected far from the place of the main sampling (about 700 m from the heap on the windward side), and it was marked as zero soil sample (geochemical background). A spade was used in the soil collection from the top layer down and the samples were placed in 250ml-containers. The containers were marked with their exact locations and numbered from 1 to 5.

Sample treatment and analysis

The soil samples were delivered to the laboratory and dried at room temperature. Rests of plants and stones were removed from samples No. 5 and No. 2. Then, the soil was sifted with a 0.15 mm mesh, milled to obtain a dusty form, and specific portions were weighted using an electronic calibration scale. The samples prepared in

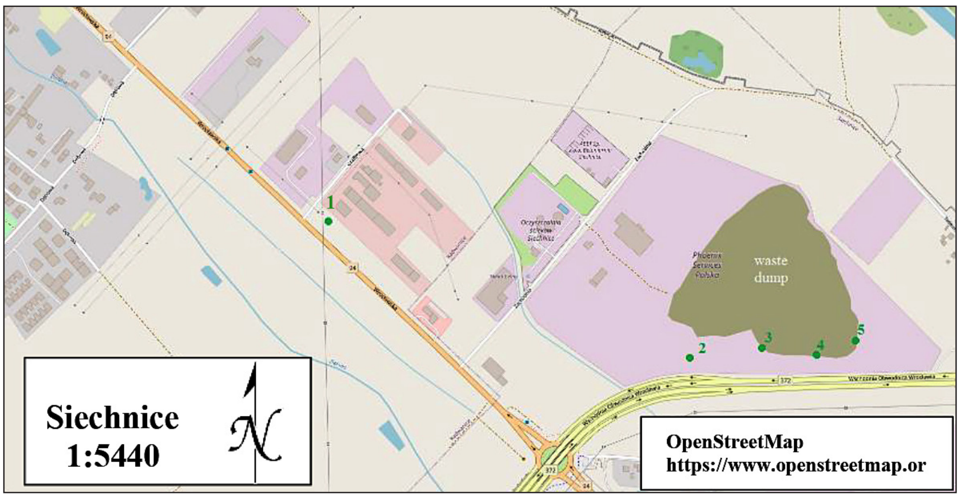

Fig. 2. Location of sampling points

such a way were then subjected to mineralization. The amount of soil did not exceed 0.200 g. For the digestion process, 8 ml of 65% high purity nitric acid was introduced into each sample. Moreover, a blank sample, containing only 8 ml of nitric acid, was prepared. The laboratory dishes were closed and placed in housing and later in the miner rotor. The digestion was performed with the use of "MILESTONE START D Microwave Mineraliser". The mineralization process was consisted of four stages with 4 different times and the whole process took 32 minutes followed by 30 minutes of ventilation and cooling. Then, the unit was switched off. The dishes were removed, opened, and rinsed with deionized water. The samples were then filtered into 50 ml graduated flasks with a hard quantitative paper filter and were subjected to further determination of metal concentration by iCE 3500 AAS Atomic Absorption Spectrometer. During the determination of metal concentrations, no radiation was emitted in its basic state. Electrodeless Discharge Lamp (EDL) contained a metal cathode and a closed anode in the cylinder. The lamp was filled with noble gas. The nebulizer was used to spray the previously prepared mineralized soil samples. In the presence of the aerosol and air, which directed the aerosol towards the burner, it was possible to spray a mixture of acetylene and air in the flame. The separation process of the element to be determined was carried out by a monochromator and then the radiation was directed to the detector where the intensity of radiation was measured. Before starting the measurements, a calibration curve was prepared. The curve was drawn through sample No. 1. A benchmark curve was prepared from previously prepared solutions. The determinations were made in three repetitions. Data processing was performed in Excel.

Health risk calculation

The environmental risk assessment in Siechnice is necessary due to the toxic compounds that float in the air. The exposure of residents may occur through dermal contact, inhalation of air and during consumption of cultivated vegetables and fruits by residents. The EPA defines the environmental risk assessment as the danger posed to people as well as to the environment in which people use to live [EPA, 2004]. The risk assessment for the agglomeration near Wrocław was conducted on the basis of the indicators used by the EPA. After the determination of Cr, Cu, Fe, Pb and Zn metals from the soil samples taken. Calculations had to be performed on the indicators used for the risk assessment and certain assumptions or fixed values had to be made, e.g., exposure period or inhalation risk unit, which are reported by IRAC and EPA. Calculation of indicators such as:

1. Exposure dose: average daily dose (ADD) from three routes: (ingestion, inhalation, and dermal contact).
2. Non-cancerogenic health risk assessment: hazard quotient (HQ) and hazard index (HI)
3. Cancerogenic health risk assessment: total excess cancer risk (ECR).

Elements such as Zn, Cu, Cr, Pb and Fe were selected for analysis. The selection of these elements was not accidental because for the production of ferrochrome in the former Siechnice Steelworks, high chromium exceedances were expected. The second justification for the choice of these elements is their action, mostly carcinogenic but also contributing to many diseases. The assessment of health risk can allow determining which group is most exposed to toxic substances, and which pathway is the most onerous exposure. In addition, it will also determine what systemic effects can occur during different degrees of exposure to metals.

Exposure dose

The model, called Average Daily Dose (ADD), allows calculating the exposure of a person who is in contact with heavy metals at the level of three potential routes of contact with a toxic substance. The model was developed by EPA. The exposure dose was calculated in mg/kg per day [EPA, 2004].

This is the so-called taken dose, which was determined according to the following formulas:

$$ADDing = \mathrm{C} \cdot \frac{\mathrm{IngR} \cdot \mathrm{EF} \cdot \mathrm{ED}}{BW \cdot AT} \tag{1}$$

$$ADDinh = \mathrm{C} \cdot \frac{\mathrm{InhR} \cdot \mathrm{EF} \cdot \mathrm{ED}}{PEF \cdot BW \cdot AT} \cdot 10^6 \tag{2}$$

$$ADDderm = \mathrm{C} \cdot \frac{\mathrm{SL} \cdot \mathrm{SA} \cdot \mathrm{ABS} \cdot \mathrm{EF} \cdot \mathrm{ED}}{BW \cdot AT} \tag{3}$$

where: C – average metal concentration in road dust [mg/kg]; $IngR$ – value of daily accidental dust intake [mg/d]; $InhR$ – daily lung ventilation [m^3/d]; EF – contact frequency [d/year]; ED – duration of contact [year]; BW – average body weight [kg]; AT – averaging period [d]; PEF – particle emission factor [m^3/kg]; SL – coefficient of dust adherence to the skin [$mg/cm^2 \cdot d$]; *SA* – skin surface exposed to dust [cm^2]; *ABS* – percutaneous absorption coefficient, unnamed quantity. These parameters are shown in Table 2.

The calculation of Hazard Quotient (HQ) and Hazard Index (HI)

HQ is a formula that allows calculating a hazard that does not cause a cancer risk. In order to proceed with the calculation, it is important to define the RfD reference dose which is given from Integrated Information Risk System (IRIS). The HI is the sum of the HQ for the three exposure routes ingestion, inhalation, and dermal. It is worth noting that if HI<1, then the health exposure is considered low; if HI>1, then there is the possibility of symptoms and pathogenic effects [Aluko and others, 2018].

Parameters such as Hazard quotient (HQ) and hazard index (HI) can be used to assess health risk. These equations are as follows:

$$HQ = \frac{\mathrm{ADD}}{\mathrm{RfD}} \tag{4}$$

$$HI = \sum HQ \tag{5}$$

Table 2. Formulas required for ADD calculation proposed by Narsimha Adimalla [Adimalla, 2020]

Parameter	Adults	Children
ingR	200	100
EF	180	180
ED	70	6
AT	70 · 365d	6 · 365d
BW	70	15
inhR	20	7,6
PEF	$1.39 \cdot 10^9$	$1.39 \cdot 10^9$
ABS	0.001	0.001
SL	0.7	0.2
SA	5700	2800
ET	14	8

Table 3. Reference dose – values in mg/kg per day needed for the following calculations proposed by EPA [EPA, 1989]

Mg/kg	RfDing	RfDinh	RfDderm
Cr	$3 \cdot 10^{-3}$	$2.86 \cdot 10^{-5}$	$3 \cdot 10^{-3}$
Cu	$4 \cdot 10^{-2}$	$4 \cdot 10^{-2}$	$1.2 \cdot 10^{-2}$
Fe	$7 \cdot 10^{-1}$	$7 \cdot 10^{-1}$	$7.38 \cdot 10^{1}$
Pb	$1.4 \cdot 10^{-3}$	$3.52 \cdot 10^{-3}$	$5.24 \cdot 10^{-4}$
Zn	$3 \cdot 10^{-1}$	0.3	$6 \cdot 10^{-2}$

Table 4. IUR values for Cr and Pb according to Liu, Shang and Wan [Liu, Shang, and Wan, 2018]

Heavy metals [mg/kg]	Inhalation Unit Risk [IUR] $\mu g/m^3$
Cr	$1.2 \cdot 10^{-2}$
Pb	$8 \cdot 10^{-5}$

where: *ADD* – has to be calculated in 3 factors ingestion, inhalation, and dermal; *RfD* – reference dose for the calculated metals, the data given in Table 2. The values given in the table have been converted during the calculation process to a nanogram unit.

$$1mg = 1 \cdot 10^6\ ng \tag{6}$$

The excessive risk of cancer development (ECR) calculation

ECR is a parameter used to assess the possibility of a carcinogenic substance to penetrate the human body through the airways. In order to calculate this parameter, an Inhalation Unit Risk (IUR) should be used for the individual elements showing carcinogenic properties. Inhalation Unit Risk is defined as a behavioral agent which cause cancer while a person inhales it, as a result of a toxic element which is in airborne. The Risk-Screening Environmental Indicators (RSEI) give IUR values in units $\mu g/m^3$ [EPA, 2004].

The range of values that indicate no exposure to cancer are between 10^{-6} – 10^{-4} [Rybak and others, 2020].

$$ECR = \frac{\mathrm{C \cdot ET \cdot EF \cdot ED \cdot IUR}}{BW \cdot AT} \tag{7}$$

where: *C* – average concentration of metals [mg/kg]; *ET* – exposure time [h/d]; *EF* – contact frequency [d/year]; *ED* – duration of contact [year]; *IUR* – inhalation risk [$\mu g/m^3$]; *BW* – average body weight [kg]; *AT* – averaging period [d] [Rybak and others, 2020].

RESULTS

Metal concentration

The obtained concentrations of selected heavy metals are presented in Table 5. The interpretation of these results is based on Table 1, which contains the values of permissible concentrations of elements in the soil, according to the Regulation [Rozporządzenie Ministra, 2002]. During the analysis of the results, only light soil was taken into consideration, as it is present in Siechnice area.

Table 5. Heavy metal content at sampling sites

No.	Zn [mg/kg]	Cu [mg/kg]	Pb [mg/kg]	Fe [mg/kg]	Cr [mg/kg]
0	84.84	77.56	17.32	9539.59	696.30
2	80.29	73.01	13.10	9973.82	222.03
3	68.91	81.34	25.76	13440.62	31.19
4	44.49	76.58	22.11	6411.24	153.15
5	81.09	88.48	44.30	8940.15	705.30

The results of the study indicate an elevated level of studied elements in the soil, which is shown in Table 5. While analyzing the results, it can be concluded that 60% of the 1 studied sites exceeded the permissible element concentrations. Exceedances for Cu and Fe occurred at 1-5 sampling sites. In the case of Cr, the exceedance did not occur only at site 3.

It was recorded that Zn does not exceed the limit value of 100 mg/kg, as it shows Figure 3. The highest concentration was recorded at sample site 1, i.e., in sample zero and was 84.84 mg/kg. The lowest value of this element was found in the sampling site 4 and it is 44.49 mg/kg (Fig. 3). Figure 4 shows that Cu at each of the five sampling sites exceeds the limit value of 30 mg/kg in soil and the highest exceedance was at site number 5 - 88.48 mg/kg, it is 2.9 times higher above the permissible values. Site number 2 had 73.01 mg/kg of Cu and this is the site with the lowest possible exceedance, and it was 2.43 higher than the admissible value (Fig. 4).

The permissible Pb concentration in the soil is 50 mg/kg and none of the samples exceeded this value (Fig. 5). At site number 5, the highest concentration of this element was reached: 44.30 mg/kg and the lowest concentration was at site number 2 – 13.10 mg/kg. Figure 6 presents the

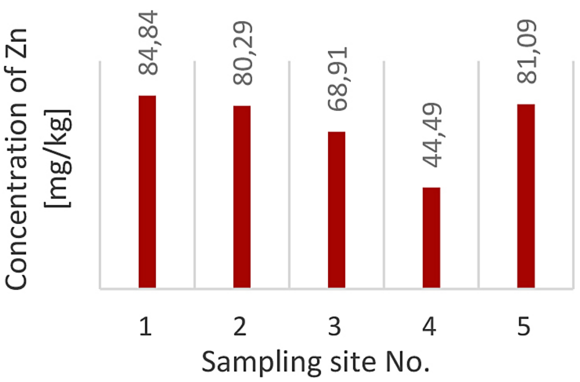

Fig. 3. Concentration of Zn in the soil in mg/kg

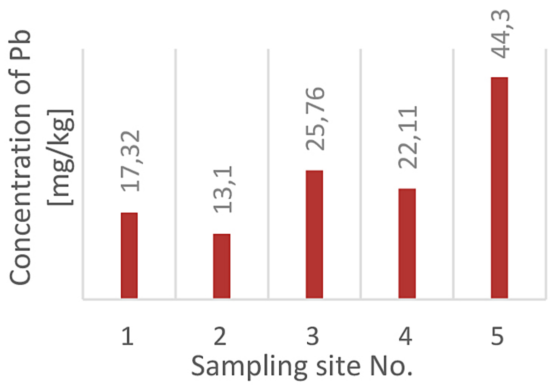

Fig. 5. Concentration of Pb in the soil in mg/kg

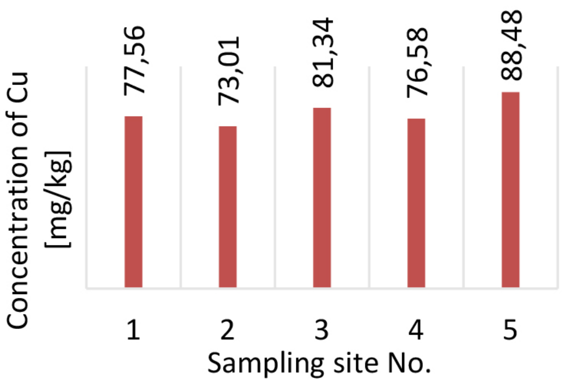

Fig. 4. Concentration of Cu in the soil in mg/kg

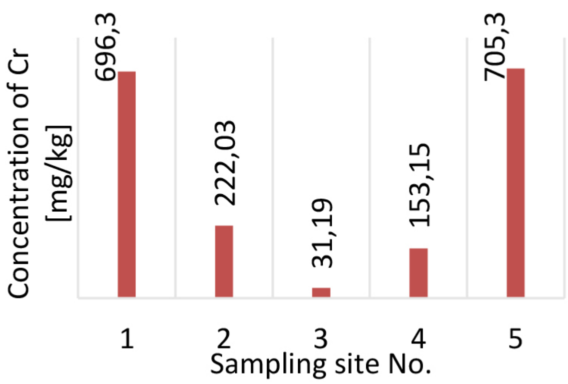

Fig. 6. Concentration of Cr in the soil in mg/kg

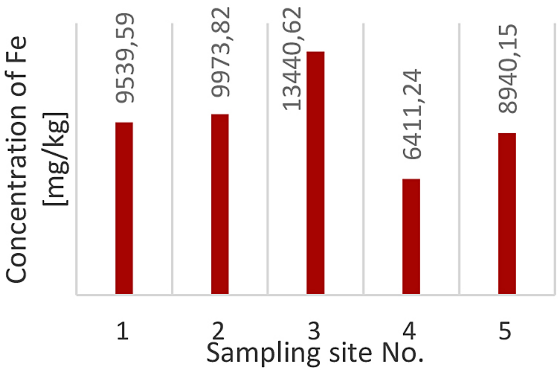

Fig. 7. Concentration of Fe in the soil in mg/kg

concentration of Cr in soil samples. The limit value for Cr – 50 mg/kg was not exceeded only at one site number 3 - 31.19 mg/kg. The highest exceedance was recorded at sampling site number 5 - 705.30 mg/kg, it was 14 times higher than the permissible value. Soil zero reached the concentration of Cr 696.30 mg.kg which is almost 14 times higher than the permissible value (Fig. 6).

The concentration of Fe present in Figure 7 should be interpreted as a high value if it exceeds >3800 mg/kg of soil, and the highest value was recorded at site number 3 -13440.62 mg/kg. The lowest value of this element was at site number 4 Fe-6411.24 mg/kg.

Exposure dose

Table 6 presents the results of the ADD exposure doses for children and adults, which have been calculated for three different routes of exposure such as inhalation, ingestion, and dermal contact and for four different metals. They were divided into 2 groups (children and adults) and 3 categories of exposure (inhalation, ingestion, and dermal).

For adults, the highest exposure to Cr occurs by ingestion. The highest exposure occurs at site 0 (981.09) and 5 (993.77). The lowest risk occurs through dermal contact at site 1. The highest exposure occurs at points 0 and 5 and is equal to 0.07 in both cases. As far as the route of dermal exposure is concerned, a high exposure occurs at sites 0 (19.57) and 5 (19.83). The lowest risk to humans occurs at site 3 as the ADD is 0.88. The highest risk of daily exposure to chromium for children occurs at sample sites 0 and 5 for each route of exposure. The highest exposure to this element occurs by ingestion. In sample zero it is 2289.21 and in sample 5 it is 2318.79. The smallest factor is at site 3. Dermal contact is the second possibility with a high exposure factor for children. At site 0 it is 12.82 and at site 5 it is 12.99. Again, the third point has the lowest exposure rate – 0.01. The inhalation route has the lowest exposure for children. At both sites it is the same 0.13 and this is the highest exposure risk. At site 3, it is 0.01, which is the lowest value. The highest daily risk of children being exposed to Cu is found in sample sites 5 and 3 for the two routes of exposure – dermal contact and ingestion. The highest exposure to Cu occurs through ingestion. In sample 5 it is 290.89 and in sample 3 it is 267.43. The smallest factor is at site 2 (240.04). Dermal contact is the second possibility with a high exposure factor for children. At site 5 it is 1.63 and at site 3 it is 1.50. The lowest exposure is 1.34 and occurs at site 2. The lowest exposure for children is the inhalation route. At four sites (0-4) it is 0.01. The ADD for site 5 is 0.02 For adults, the highest exposure to Cu occurs by ingestion. The highest exposure were found at sites 5 (124.67) and 3 (114.61). The lowest risk is via the inhalation route, at all sites, the ADD is 0.01. The dermal route is the highest exposure at sites 5 (2.49) and 3 (2.29). The lowest ADD is found at point 2 (2.05). While analyzing the data from Table No. 6, it can be stated that the highest ADD exposure to Fe in children occurs by ingestion, followed by the dermal route and the smallest concern is for inhalation exposure. The exposure by ingestion is highest at site 3 (44188.33) and site 2 (32790.65) and the smallest at site 4 (21078.06). For the dermal route, sites 3(247.45, and 2 (183.630 had the highest exposure values. The lowest dermal exposure is at site 4 (118.04). Sites 3 (2.42) and 2 (1.79) had the highest exposure factor during the inhalation exposure. The lowest ADD is at site 4 (1,61). For adults, the daily exposure at the ingestion route level is also highest at sites 3 (44188.33) and 2 (32790.65). The lowest ADD value is in site 4, the exposure via dermal contact is highest at site 3 (377.81) and 2 (280.36), while the lowest value is 180.22, and it is at site 4. The same sites are also associated with the inhalation route exposure. The highest ADD values belong to sites 3 (1.36) and 2 (1.01). Daily health exposure, with respect to the Pb element in ingestion, is highest in children and adults at sites 5 and 3 (Table 5). For both groups, there is no inhalation exposure at all sites, ADD are 0. For dermal contact, the daily highest exposure may be at sites 5 and 3 for children and adults (Table 6). The health exposure for Zn via ingestion in

Table 6. Results of exposure dose ADD for children and adults

Heavy metals [mg/kg]	ADDing [mg/kg]		ADDinh [mg/kg]		ADDderm [mg/kg]	
Cr	Children	Adult	Children	Adult	Children	Adult
Sample number						
0	2289.21	981.09	0.13	0.07	12.82	19.57
2	729.96	312.84	0.04	0.02	4.09	6.24
3	102.55	43.95	0.01	0.00	0.57	0.88
4	503.49	215.78	0.03	0.02	2.82	4.3
5	2318.79	993.77	0.13	0.07	12.99	19.83
Cu						
0	254.99	109.28	0.01	0.01	1.43	2.18
2	240.04	102.88	0.01	0.01	1.34	2.05
3	267.43	114.61	0.01	0.01	1.5	2.29
4	251.78	107.90	0.01	0.01	1.41	2.15
5	290.89	124.67	0.02	0.01	1.63	2.49
Fe						
0	31363.04	13441.30	1.71	0.97	175.63	268.15
2	32790.65	14053.14	1.79	1.01	183.63	280.36
3	44188.33	18937.85	2.42	1.36	247.45	377.81
4	21078.06	9033.46	1.15	0.65	118.04	180.22
5	29392.29	12596.70	1.61	0.91	164.60	251.30
Pb						
0	56.96	24.41	0.00	0.00	0.32	0.49
2	43,.07	18.46	0.00	0.00	0.24	0.37
3	84.70	36.30	0.00	0.00	0.47	0.72
4	72.69	31.15	0.00	0.00	0.41	0.62
5	145.65	62.42	0.01	0.00	0.82	1.25
Zn						
0	278.93	119.54	0.02	0.01	1.56	2.38
2	263.96	113.13	0.01	0.01	1.48	2.26
3	226.54	97.09	0.01	0.01	1.27	1.94
4	146.26	62.68	0.01	0.00	0.82	1.25
5	266.60	114.26	0.01	0.01	1.49	2.28

children and adults at highest at sites 0 and 5 = 0. ADD by inhalation in children is highest at site 0 – 0.02 followed by a constant value of 0.01. The calculated value is 0.01 for adults at sites 0, 2, 3, 5. Site 4 was characterized by no risk, as ADD is 0. For the dermal contact, the highest exposure can be fairly high at sites 0 and 5 in children and adults and their ADD is 0.

Hazard Quotient (HQ) and HI Hazard Index

Hazard Quotient (HQ)

The determination of the risk factor is intended to determine the likelihood of exposure to the health of residents, but this will not have adverse effects on their health. According to HQ <1 , HQ>1 [70]. It is possible to determine which element, depending on the exposure route, will or will not show a health hazard. The results are presented in Table 7.

The results obtained in Table 7 indicate that for all metals via the three possible routes of exposure, the HQ factor is <1. This means that above-mentioned elements will not pose a risk due to negative effects on the health of the locals. The values that exceed 0 occur in children and adults by ingestion. In the case of children, the HQ coefficient for the element Cr, s at site 5 is 0.77 and this is the highest value, the lowest value occurs at site 3 (0.03). For the sample, zero HQ is 0.76. For adults, the HQ at sites 1 and 5 is 0.33 and the

Table 7. Results of HQ for children and adults

Heavy metals [mg/kg]	HQing [mg/kg]		HQinh [mg/kg]		HQderm [mg/kg]	
Cr	Children	Adult	Children	Adult	Children	Adult
Sample number						
0	0.76	0.33	0.00	0.00	0.00	0.01
2	0.24	0.10	0.00	0.00	0.00	0.00
3	0.03	0.01	0.00	0.00	0.00	0.00
4	0.17	0.07	0.00	0.00	0.00	0.00
5	0.77	0.33	0.00	0.00	0.00	0.01
Cu						
0	0.01	0.00	0.00	0.00	0.00	0.00
2	0.01	0.00	0.00	0.00	0.00	0.00
3	0.01	0.00	0.00	0.00	0.00	0.00
4	0.01	0.00	0.00	0.00	0.00	0.00
5	0.01	0.00	0.00	0.00	0.00	0.00
Fe						
0	0.04	0.02	0.00	0.00	0.00	0.00
2	0.05	0.02	0.00	0.00	0.00	0.00
3	0.06	0.03	0.00	0.00	0.00	0.00
4	0.03	0.01	0.00	0.00	0.00	0.00
5	0.04	0.02	0.00	0.00	0.00	0.00
Pb						
0	0.04	0.02	0.00	0.00	0.00	0.00
2	0.03	0.01	0.00	0.00	0.00	0.00
3	0.06	0.03	0.00	0.00	0.00	0.00
4	0.05	0.02	0.00	0.00	0.00	0.00
5	0.10	0.04	0.00	0.00	0.00	0.00
Zn						
0	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00	0.00	0.00

lowest value is at site 3 (0.01). The dermal HQ factor at sites 1 and 5 for adults is 0.01. For Cu, sites 0 to 5 via the route of ingestion in children have HQ of 0.01. For Fe, via the route of ingestion in children, site 3 has the highest HQ of 0.06 and the lowest at site 4 (0.03) for adults which are the same sites, but with other values of 3 (0.03) and 4 (0.01). In spite of this, HQ did not show an exceedance of 1 in the soil, which would indicate a potential threat to the local people (Table 7).

Hazard Index (HI)

The results, which are shown in Table 8, are related to HI, which is an indicator that indicates a hazard for more than one substance. Despite the previous results obtained from HQ, the determination of HI shows whether there are health hazards in the mixtures of elements. HI [70] having >1 caused visible health effects in inhabitants, <1 to none.

The results indicate that the HI<1 content for all metals in children and adults will not cause health exposure, because the results are not higher than 1. The largest HI occurs in children and adults in sample number 5, in the case of Cr. HI value in children is 0.78 and in adults 0.34.

ECR

The highest rate, ECR for children in the case of Cr is at site 5 (2.23) and 0 (2.20), and the lowest value is at site 3 (0.10). In the case of adults, the highest rate is 0.83 and is at site 5. The lowest

Table 8. Results of HI for children and adults

No.	Health risk hazard index	
	Children	Adult
Cr		
0	0.77	0.34
2	0.25	0.11
3	0.03	0.02
4	0.17	0.07
5	0.78	0.34
Cu		
0	0.01	0.00
2	0.01	0.00
3	0.01	0.00
4	0.01	0.00
5	0.01	0.00
Fe		
0	0.05	0.02
2	0.05	0.02
3	0.06	0.03
4	0.03	0.01
5	0.04	0.02
Pb		
0	0.04	0.02
2	0.03	0.01
3	0.06	0.03
4	0.05	0.02
5	0.10	0.05
Zn		
0	0.00	0.00
2	0.00	0.00
3	0.00	0.00
4	0.00	0.00
5	0.00	0.00

Table 9. Results of ECR for children and adults

No.	Health risk hazard index	
	Children	Adult
Cr		
0	2.20	0.82
2	0.70	0.26
3	0.10	0.04
4	0.48	0.18
5	2.23	0.83
Pb		
0	1748.33	89237.45
2	1322.16	67485.28
3	2599.95	132705.73
4	2231.27	113887.50
5	4470.69	228191.71

rate is 0.04 and occurs at site 3. In the case of Pb, the highest ECR for children is at site 5 (4470.96) and for adults is the same site with different values (228191.71). The lowest value in both cases was reached for site 2 and ECR for children is 67485.28 and for adults is 1322.161 (Table 9).

As indicated by the EPA (Environmental Protection Agency), the elements that belong to the group that cause cancer are Cr and Pb. The exposure to cancer is considered when the ECR is > 10^{-6}.

Discussion

Siechnice is a city that has been exposed to the elements deposited in the soil for many years. This is due to the old steelworks and the problem persists to this day. Despite the fact that the heap is not exploited, the deposition of metals in the soil is still a great problem [Biłyk and Kowal, 1993]. While analyzing the results, it can be concluded that 60% of the studied sites exceeded the permissible element concentrations. The exceedances for Cu and Fe were at sites 1–5. In the case of Cr, the exceedance did not occur only at site 3. The obtained values for the control site (site 1) were high: it should have much lower values than the soil located near the slag heap. The high values of the elements in the control soil may result from the fact that this sample was taken near the main road from/to Wrocław and from the possible influence of industries located there, which deal with laser cutting, electro-technical industry and service of French cars etc. In the publication of Borowczak and Hołtra [Borowczak, Hołtra, 2017], the control sample was taken at three sites from a cultivated field in Siechnice, where the concentration of Cu was 10.14 mg/kg, which indicates that the concentration in the control sample is 7.6 times higher. For Zn, the concentration is 47.65, which is 1.78 times higher than our results for the control sample. The highest exceedance occurs in the Pb concentration, as the difference between the control sample obtained in this study and the samples from the study Borowczak and Hołtra [Borowczak, Hołtra, 2017] is 6.67 times higher. This suggests that taking a zero sample should be restricted to the areas far away from any industries and roads, as they also affect soil contamination. The impact of air mass distribution, according to the wind rose, should also be taken into account. The recorded high concentrations of elements should be a cause for residents' concerns. Siechnice is the place where tomatoes are currently grown for trade. Consumption of the fruit or vegetables grown on this land with high concentrations of metals may have consequences related to human health, which may be associated, for example, abdominal pain, emesis, impaired vitamin D metabolism, gastrointestinal problems, and stomach cramps. Notoriously, protests and complaints about the operation of the heap occurred in these areas. Residents do not accept the current situation of exploitation slag heap. This process causes excessive dust rise during the work on the heap. This is another reason why the society is exposed to heavy metals. Absorption of heavy metals can occur by inhalation and by contact with the skin. The children living in Siechnice are the most vulnerable because they have different susceptibility to substances that are in the environment [WHO, 2011] and the people who work for the operation of the slag heap are in the first risk group that is most likely to become ill. The consumption of crops on which dust settles from the heap, the inhalation of air from floating dust, the accumulation of heavy metals in the soil, transferred to the plants, highly contributes to health risk. This may result in cough, breathing problems defined as dyspnea, alveolar murmur within the lungs, anosmia, and other diseases. On the basis of the calculation of the health risk in Siechnice, resulting from the studied heavy metals (Zn, Pb, Fe, Cu, and Cr), it was found that the highest exposure by ingestion corresponds to Fe and Pb. It is important to note that according to the standards, the concentration of Pb in the soil does not exceed the acceptable standard. The highest exposure in the case of counterattack of the element Fe while dermal contact.

However, HQ and HI indices did not exceed <1, in the case of children and adults, which proves that there is no probability of health exposure by a mixture of elements compared to separate elements. The obtained results indicate that the health exposure of the Siechnice residents occurs through the route of consumption. The highest index in children is 0.77 and 0.76 (Table 7), for adults 0.33. In the publication of EPA [www.epa.gov], the HQ index for Cr in Wrocław is lower than for Siechnice. In the case of Zn, the HQ index for Wrocław (0.0022) is higher than in Siechnice (0.00) for each route of exposure. The values for HI in the case of Siechnice as well as in Wrocław are low, which will not show harmfulness for inhabitants. In the case of ECR, which is an indicator associated with cancer in Siechnice, high values were found for Pb (Table 9). This is the element that poses a risk of the disease, both in adults and children. As far as the Cr values are concerned, they are low and do not constitute a cancer risk for children and adults living in Siechnice.

The occurrence of numerous exceedances of acceptable metal values in the soil near the heap located in Siechnice should encourage taking the actions which will reduce the health exposure of the inhabitants aimed at reducing dust from the heap, by installing water sprays that will reduce the dust rise, together with covering the slag heap with foil. It is also important to control the chemical composition of the soils in the area, so a solution would be to carry out cyclic monitoring of the soil composition.

CONCLUSIONS

The samples that were taken from the Siechnice slag heap area showed high concentrations of such heavy metals as Cu, Cr, Pb, Zn, and Fe in soil. The concentration of some metals (mg/kg) exceeds the limit value. In this case of Cr (which is classified by EPA as a carcinogenic element), the limit value in soil was exceeded 14 times and this is the highest exceedance compared to the rest of studied elements. The only element that did not exceed the limit value in soil is Pb, although the excessive risk of cancer development Cr in a case of Pb is higher than for other elements, which proves that there is a possible risk of cancer for adults and children by ingestion. In Siechnice, the possible exposure and health risk of the inhabitants exist. Health problems can be caused by high Pb contents, both in the soil and in the air. Long-term contact with both elements can cause cancer. The highest daily exposure for children and adults occurs via the ingestion route, and these two groups are mostly exposed to Fe, which an element that is essential in the human body. However, as for all microelements, the maximum level could be also harmful. The dermal exposure to this element is also possible and the lowest risk occurs by the inhalation route. Referring to the results, it is therefore necessary to protect the slag heap by covering it and using water sprays to minimize dust distribution.

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