applied sciences

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Is the Slag Heap of a Former Ferrochromium Plant a Significant Environmental Hazard?

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Highlights:

- The sediments from all water bodies near the landfill are heavily polluted with Cr;
- Ecotoxicological studies on the sediments and water demonstrated the highest toxicity to tested species came from the nearest site to the slag heap;
- Noncancer and cancer risk calculations indicate possible adverse health effects for all sediments taken from the three water bodies;
- There is a high risk of possible health problems for fish consumers.

Abstract: This study assessed the possible impact of a former ferrochromium plant in Siechnice (Lower Silesia, Poland) on water reservoirs and living organisms. The metal concentrations (Zn, Cu, Pb, Fe, and Cr) in the sediments were determined, along with ecotoxicological studies that were conducted on both the sediments and the surface water of three water bodies that border the slag heap. The samples of the sediments and water were taken at different distances from the landfill area. The studies also covered a human health risk assessment. The highest concentrations of all the studied elements were observed in the sediments taken from the water reservoir closest to the landfill. In the case of the sediments, a 30% death rate for *Heterocypris incongruens* (Ostracodtoxkit F) was recorded at the same site. Additionally, at this site, the ecotoxicological studies on the surface water revealed the highest mortality for *Daphnia magna* (Daphtoxkit F magna) and the lowest values of LC50 for algae (Algaltoxkit). The health risk assessment of the sediments was estimated by calculating the noncarcinogenic health risk using the hazard quotient (HQ) and hazard index (HI), and the carcinogenic risk was calculated using the excessive risk of cancer development (ECR) measurement. The hazard index (HIing) for Cr exceeded 1 for children, which suggests that possible adverse health effects might occur for humans. The ECR values calculated for Cr and Pb were above the range limit of 10^{-6}. The value for Cr was the highest for the sediments from the closest water reservoir to the landfill for both children and adults. Studies prove that the water reservoirs located near landfills pose potential ecological risks, and the risk is the highest where the distance is the shortest from the slag heap. In prospective human health risk assessments, the sediments from the closest water body pose a potential carcinogenic health risk to humans, especially to fish consumers, i.e., the residents of neighboring areas who might experience severe health problems from the intake of Cr and Pb through fish consumption. Significant steps should be taken to reduce Cr concentrations in the sediments to minimize the risk of human health adverse effects.

Keywords: Ostracodtoxkit F; Daphtoxkit F magna; Algaltoxkit F; health risk assessment; Siechnice; Wrocław; Lower Silesia

Citation: Wróbel, M.; Pieśniewska, A.; Zeynalli, F.; Kapelko, K.; Hanus-Lorenz, B.; Rybak, J. Is the Slag Heap of a Former Ferrochromium Plant a Significant Environmental Hazard? *Appl. Sci.* **2023**, *13*, 2001. https://doi.org/10.3390/app13032001

Academic Editors: Antonio Calisi, Tiziano Verri and Francesco Dondero

Received: 29 December 2022
Revised: 28 January 2023
Accepted: 2 February 2023
Published: 3 February 2023

1. Introduction

The constantly increasing standard of living requires the economy to adapt to its needs. Therefore, the amount of waste generated and the percentage of waste that remains inadequately managed is increasing [1]. That is the main reason for using and developing new instruments, tools, and methods [2,3], as well as conducting studies in association with health risks [4], which is supposed to minimize emissions and constantly monitor the changes in the environment caused by anthropogenically generated wastes. This is particularly relevant due to the hazards affecting the resilience of all environmental components, including soils [5], water [6], and air [7], for which the origin is industrial waste [8]. Living organisms can also suffer as a consequence of being exposed to the transmission of diseases [9] or the degradation of the environment and ecosystems [10] in which they live [11,12]. Predominantly, those wastes that contain metals and their compounds are the most hazardous [13,14]. Contaminants appear, inter alia, in the mining, smelting, and metallurgical industries, which often have significant metal concentrations [15]. In addition, postsmelter waste dump sites (particularly degraded sites) pose a risk to the environment and living organisms (with an emphasis on humans), as they are characterized by ubiquitous trace elements [16,17]. Different methods are proposed to deal with the hazards created by slag heaps [17,18], depending on the composition, texture, and environmental conditions found at the site. Nevertheless, in a number of cases, opportunities are being sought to reduce the formation of slag, which reduces the pollution associated with landfill sites [19–21].

The heap studied in this article is a remnant of a chromium steel smelter that operated in Siechnice (Lower Silesia, Poland) in the 20th century, which was constructed as a power plant and a carbide factory at the very beginning. The Siechnice smelter changed its areas of specialization from the production of calcium acetylene (carbide) to welding powders and ferroalloys, with a production capacity of up to 20,000 tons per year. Therefore, the smelter operations were associated with the generation of a significant amount of waste as byproducts of ferrochrome production in the form of solid slag (landfilled) and dust slag (formed in the solidification process as a result of allotropic transformations of dicalcium silicate). In the 1980s and 1990s, the ferrochrome steel plant in Siechnice produced about 220 t a^{-1} of Cr, 22 t a^{-1} of Fe, and 46 t a^{-1} of dust contaminated with As, Cu, Cd, Ni, Pb, and Mn [22–24]. The deposition of Cr into neighboring water infiltration fields was 0.3–6.92 t km^{-2} within the range of 10 km [25].

Due to the components used, the slag itself had chromium, iron, and aluminum compounds in its composition, as well as calcium and magnesium silicates. Efforts were therefore made to keep the slag as a coarse mass to reduce dust emissions. In order to do this, additives were added to stabilize the crystalline structures, but the chosen method proved ineffective due to the presence of high amounts of toxic metals in the slag, which was not conducive to the environment around the landfill [26]. The smelter was suspended in its operations and closed down in 1988 by the decision of the Polish Ministry, which was also undertaken after local society protests. The main allegations and concerns related to the general impact of the metals generated at the smelter on the surrounding environment and, in particular, on the drinkable water in the Wrocław area (due to the closeness of the water-bearing areas to the smelter in question and the heap formed) [26]. During the terminal years of the smelter's functioning, an area of 9 ha and a height of 30 m was covered by the heap [26], with slag as the main component, but municipal and sewage treatment plant waste or combustible materials were also present [27]. The closure of the smelter did not put an end to the environmental issues, as the waste has remained there until the present day. At the end of the activity in 1995, the heap was covered with earth as an insulating layer, over which vegetation was planted [28], all of which was intended to help reduce the negative impact on the environment. Since 2012, heap waste has been exploited to recover chromium. The closed smelter and the decommissioned heap seem to belong to history. However, studies confirm the presence of trace metals (e.g., Cr, Zn, Cu, Fe, Mn, and Cd) and postsmelter waste in the plant [29], soils [30], and groundwater area. After the closure of the plant, soil enrichment in Cr took place. Furthermore, the soil content of the following trace metals, Cd, Cu, Pb, and Zn, was higher than the geochemical background level [22,24,28,31]. High levels of Co, Cu, Fe, Ni, Pb, and Zn were recorded in aquatic macrophytes from reservoirs located in water infiltration fields [32,33] as well.

The postsmelting heap legal issues are significant, which, due to the contamination shown by the studies mentioned below and the problematic composition of the slag, opt between permitting or prohibiting decommissioning and obtaining useful raw materials. The issue is the permeability of harmful elements into the surrounding groundwater and surface water, soil, or air and the possibility of securing the site according to environmental inspection guidelines. Current planning documents refer to the possibility of performing the above-mentioned activities or subjecting the slag heap to reclamation after unsuccessful decommissioning attempts by private owners [34].

Among the elements found in the Siechnice heap, the concentrations of chromium, which have generally been found to be carcinogenic [35], have been studied. This is the reason why its content in the environment should be continuously monitored. Studies of the areas in the vicinity of the heap to reveal the carcinogenic and noncarcinogenic risks to living organisms and their health detected, among other things, above normal (fourteenfold) concentrations of chromium [30]. This confirmed the conclusions about contamination from earlier studies, although they indicated that there was no risk of chromium leaching into the water [18,23]. These, and the other studies carried out, refer to the contamination of the slag heap itself and the consequences for the soil. However, research deficiencies have been observed for the water bodies and their sediments present in the area. Human health risk assessments of topsoils are typically used to measure the noncarcinogenic risk (NCR) to humans using three exposure pathways, i.e., ingestion, inhalation, and skin contact [36]. In this study, we identified the sediment-related indicators based on three main contact routes and provided risk assessments for adults and children. Studies of water quality and its impact on living organisms are important because there are more than a dozen artificially created water reservoirs within Siechnice and the surrounding areas. Furthermore, due to its location in the aquifer areas that supply Wrocław with drinkable water, it is crucial to ensure the appropriate standards in terms of water quality [26].

The historical presence of heavy industry still affects the quality of the environment. The research hypothesis assumes that the emissions related to the presence of the heap contribute to the deterioration of the environment because of the high presence of toxic metals in soil, water, and air and, therefore, may impact humans.

The presence and proximity of water bodies define a new quality of life for residents, as they have become strategically important for the urban development of the city. The emergence of bathing waters and fishing grounds, where different species of fish are observed, inspired a review of the safety of these water bodies for those who use them. It is therefore assumed that the elements observed in and around the heap area affect the living organisms present, thereby leading to negative alterations in terms of their health.

The purpose of the following article and accompanying research is to estimate the risks posed by heavy metal contaminations in the bottom sediments and water in the vicinity of the former Siechnice smelter. The health risk was inferred from the results of the toxicity tests and calculations. The results of the tests and their conclusions form the basis for the subsequent tests carried out at the site, as well as others performed in the vicinity of similar hazardous waste sites. Observing the changes will, therefore, be necessary not only for the soils and the heap itself but also for the surrounding water bodies. This is essential from a health point of view for all living organisms present at the site, but especially for people, including decision-makers, to take the necessary measures to ensure the safety of residents and other living organisms in the area.

2. Materials and Methods

2.1. Study Area

Siechnice has had city rights since 1997. Since 2000, a Municipal Economic Activity Zone has been established, which has favorable conditions for business, and there has been rapid growth in the city and a significant influx of people. The economic zone that attracts young inhabitants to the infrastructure of cultural, educational, and leisure services has been intensely developed. The green riverside recreational areas are attractive to young and active residents.

The study area was situated in the vicinity of postmetallurgical slag waste in Siechnice town, where the Siechnice smelter operated in the past.

The town's boundaries run roughly parallel to the course of the Oława River, with the Odra River forming the northern boundary and the Szalona River flowing through the southern part of the city. The oxbow lakes and floodplains are of various ages and show very different stages of succession. In Siechnice, we can find areas with numerous water reservoirs, both natural and artificial, which are willingly visited for recreational purposes despite their postindustrial pollution. The biggest reservoir, "Błekitna Laguna" (Blue Lagoon), has, since 2011, been made available to anglers as a fishery. With the regulations of the Polish Angling Association governing it, it is possible to fish for pike, zander, tench, carp, catfish, and eel [37]. Since 2017, it has been operated as a bathing beach. The other two reservoirs, "Huta" (Smelter) and "Mała Szwecja" (Little Sweden), are operated as fishing ponds.

2.2. Sampling (Water and Sediments)

Due to the characteristics of the area, the influence of emissions from the liquidated industry, and the dump before reclamation on the depositing environments in the catchment area of the water bodies, it was expected that higher concentrations of contaminants would be observed in the south-eastern part. Accordingly, the bottom sediment and water samples were collected and analyzed.

Surface water and bottom sediments were taken from 3 sites (S1, S2, and S3) in the vicinity of the slag heap in Siechnice on 23 September 2021. The distances from the sample sites were 1.81 km (S1), 0.5 km (S2), and 1.75 km (S3) from the center of the slag heap, respectively. Sediments were collected by grab-sampler. They were packed in bags and transported to the laboratory, and frozen until analysis. Then, the samples were air-dried and sieved using a 2 mm plastic sieve to remove detritus. Samples of surface water were taken as 10 L each; then, they were transferred into dark glass bottles (2.5 L) and stored at 4 °C until laboratory testing. A detailed description of the study sites is presented in Table 1 and Figure 1.

Table 1. Description of study areas.

No	Designation on the Map	Geographical Coordinates	Location	Description	Distance from the Middle of the Heap
S1	S1	51°02′10.3″ N 17°09′35.7″ E	Bathing beach "Błękitna Laguna"	The bathing beach, which is an artificial reservoir, was created as a side-effect of the construction of the Wrocław motorway bypass, for which significant amounts of land were required. The bathing beach has been in operation since 2017 and serves as an entertainment area for residents and tourists.	1.82 km depth: 0.5 m distance from the shore: 50 m
S2	S2	51°02′24.9″ N 17°08′34.6″ E	Fishing pond "Huta"	Fishing in the area is only possible for persons with a valid permit issued by authorized persons.	0.50 km depth: 0.5 m distance from the shore: 50 m
S3	S3	51°03′19.8″ N 17°09′00.9″ E	Fishing pond "Mała Szwecja"	A fishery pond intended for holders of fishing cards, where fishing is possible after purchasing a license.	1.75 km depth: 0.5 m distance from the shore: 50 m

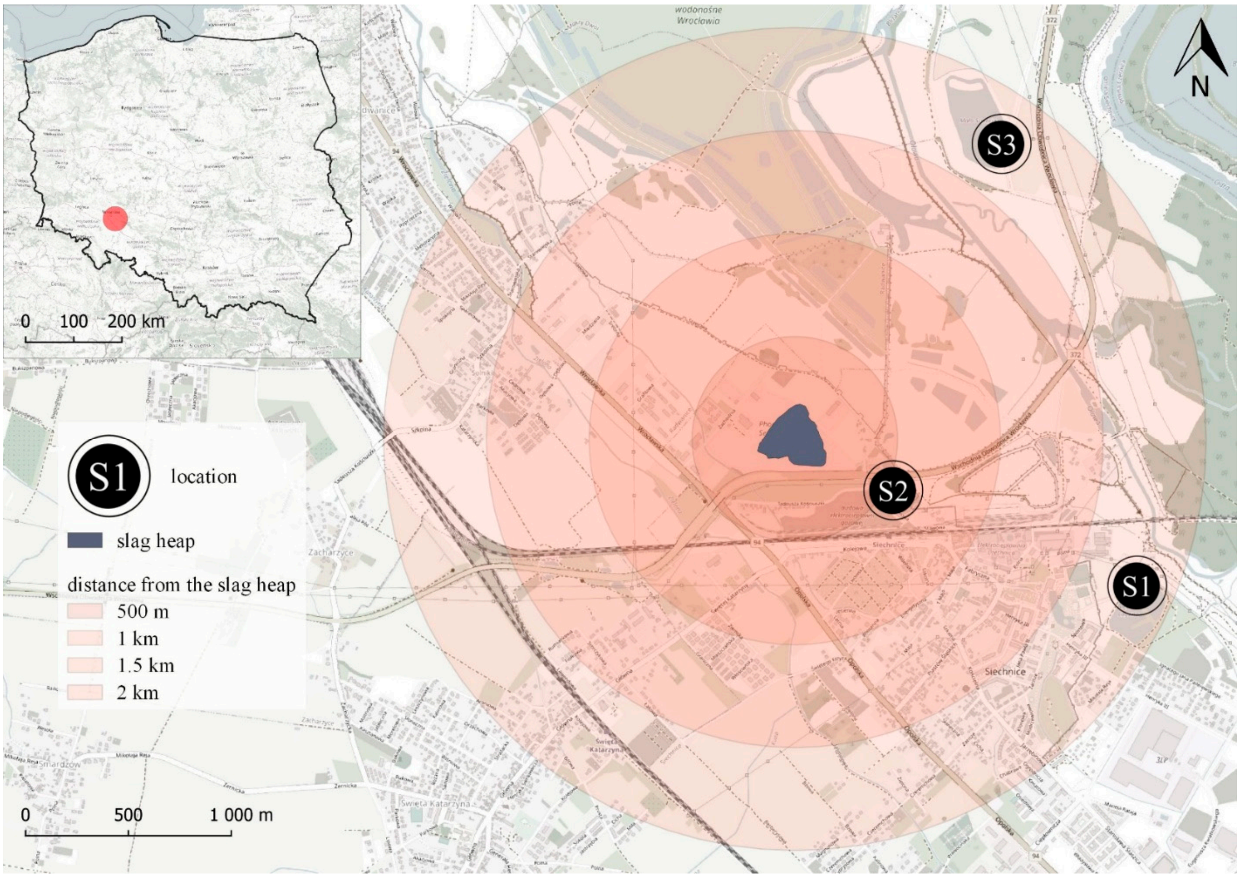

Figure 1. Location of postmetallurgical slag heap and sample sites (S1, S2, S3). Source: https://www.openstreetmap.org/ (accessed on 27 September 2022). S1–S3: sample sites.

2.3. Ecotoxicological Tests on Sediments

Ostracodtoxkit F

Ostracodtoxkit F^{TM} testing was performed in accordance with the protocol (Ostracodtoxkit F, MicroBioTests Inc., Gent, Belgium) and ISO14371 [38]. After the preparation of standard freshwater, the hatching of ostracod cysts (*H. incongruens*), and the length measurements of the hatchlings, an algal suspension was prepared. A total of 1000 µL sediment pods, 2 mL of standard freshwater, 2 mL of algal suspension, and 10 ostracods were added to the test plates. There were 6 replicates for each test, which were filled with the reference sediments and the test sediments, covered with parafilm and a lid, and incubated in the dark for 6 days. At the end of this period, the percentage of mortality rate and growth inhibition were calculated with the following formulas:

$$\text{mortality\%} = \frac{\text{the number of dead organisms}}{60}$$

where 60–total number of studied organisms.

$$\%\text{growth inhibition} = 100 - \left[\frac{\text{growth in test sediment}}{\text{growth in reference sediment}}\right]$$

2.4. Ecotoxicological Tests on Surface Water

2.4.1. Algaltoxkit F™

The growth inhibition test Algaltoxkit F™ was performed according to OECD Guideline 201 [39] and suitable protocol (Algaltoxkit F, MicroBioTests Inc., Gent, Belgium). Algae culture medium and algal inoculum were prepared. The algae suspension was poured into

25 mL calibrated flasks, and then algae culture medium was added up to the 25 mL mark and shaken. The dilution series of the studied surface water samples (%) were as follows: C0—0%, C1—100%, C2—50%, C3—25%, C4—12.5%, and C5—6.25%. The test vials were incubated at 23 °C +/− 2 °C for satisfactory algae growth. Three measurements were made after 24, 48 and 72 h of algae exposure to the water collected with a spectrophotometer for a wavelength of 670 nm. A standard curve (Figure 2) was also prepared, from which the calculations of the number of algae cells per ml of the tested solution were made.

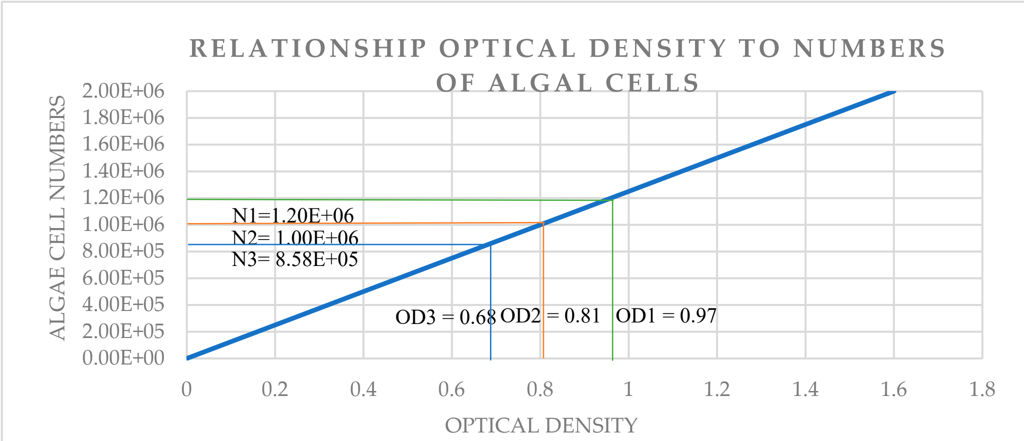

Figure 2. Standard curve based on r: the relationship of optical density to numbers of algal cells (linear regression). N1—number of cells after 24 h, N2—number of cells after 48 h, N3—number of cells after 72 h, OD1—optical density after 24 h, OD2—optical density after 48h, OD3—optical density after 72 h.

Optical density was used as a recommended indirect measurement of biomass concentration in algal cell suspensions. The absorbance of light by a suspension is directly related to cell density using a standard curve [40].

The LC50 (%) was then calculated by comparing the algal cell counts of the control and test samples.

2.4.2. Daphtoxkit F Magna

This assay followed the protocol (Daphtoxkit F magna, MicroBioTests Inc., Belgium) and the OECD 202 [41] guidelines. Five half-dilutions of surface water samples (mixed with the solvent, which was distilled water) were prepared (100%, 50%, 25%, 12.5%, and 6.25%) and marked C1–C5 (the highest concentration was C1; the lowest concentration was C5). A total of 10 mL of standard fresh water was added to each well in the control row. A total of 10 mL of the obtained substance was transferred into the test rows, starting from the lowest concentration (C5). A total of 20 organisms were transferred into the wells, and then 5 crustaceans were transferred to each of the 4 wells in the appropriate rows for a given toxic concentration. A parafilm strip was placed on the plate and covered with a lid, and the samples were incubated at 20 °C. Later, the percentage mortality of *D. magna* was calculated after 24 and 48 h of exposure to the toxic substance.

2.5. The Assessment of Metal Concentrations in the Sediments

The iCE 3500 AAS Atomic Absorption Spectrometer was used to determine the concentrations of the selected metals (Cr, Pb, Zn, Cu, and Fe) in the bottom sediment samples obtained from S1, S2, and S3. The test sediments were dried and then sieved with a mesh diameter of 1 mm. Weights of approximately 0.2 g were prepared on an analytical balance. Subsequently, the samples were poured with 8 mL of 65% nitric acid and subjected to the mineralization process. The filtrate obtained was then used to determine the content of the above-mentioned metals in the tested material for the measurement point. The measurement methodology was in accordance with the standard [42]. To verify the quality, certified reference materials (CRM) from Sigma Aldrich were applied in the analyses of the elements. For instrument readings, the reagent blank samples were used. The detection limits for the digestion blanks were calculated using three times the standard deviation. Detection limits: 0.151 g/L for Zn; 0.013 g/L for Cr; 0.022 g/L; 0.048 g/L for Cu. The procedure of standard addition was applied to ensure that the determination was accurate.

2.6. The Health Risk Assessment of the Sediments

For both children and adults, the average daily doses (ADD) (mg/kg per day) of HMs were determined by ingestion (ADDing) and dermal contact (ADDder), where ADDing, ADDinh, and ADDder denote the daily dose of exposure to metals (mg/kg per day) via ingestion, inhalation, and dermal contact, respectively. In this study, the NCR for the metal compounds was assessed by using the hazard quotient (HQ) and hazard index (HI), and excessive cancer risk (ECR) as well.

2.6.1. Exposure Dose

The formula to calculate the average daily dose (ADD) [mg/kg] was taken from the Environmental Protection Agency [36]. ADD is a method for measuring exposure to elements through 3 possible pathways (ingestion, inhalation, and dermal contact).

$$\mathrm{ADD}ing = C \times \frac{IngR \times EF \times ED}{BW \times AT}$$

$$\mathrm{ADD}inh = C \times \frac{InhR \times EF \times ED}{PEF \times BW \times AT} \times 10^6$$

$$\mathrm{ADD}derm = C \times \frac{SL \times SA \times ABS \times EF \times ED}{BW \times AT}$$

where C—average concentration of elements [mg/kg]; $IngR$—the daily accidental 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—dust adhesion coefficient to the skin [mg/cm^2 × d]; SA—skin surface exposed to dust [cm^2], and ABS—percutaneous absorption coefficient, unnamed amount. These parameters are shown in Table 2.

Table 2. Parameters for ADD.

Parameters	Adults	Children
IngR	200	100
EF	180	180
ED	70	6
AT	25,550	2190
BW	70	15
InhR	20	7.6
PEF	1.39×10^9	1.39×10^9
ABS	0.001	0.001
SL	0.7	0.2
SA	5700	2800

2.6.2. Hazard Quotient (HQ) and Hazard Index (HI)

A hazard quotient (HQ) of less than (or equal to) 1 indicates that no adverse effects are likely to occur. To calculate the hazard quotient (HQ), we needed the reference doses

[RfD] of the studied elements taken from [36], which is shown in Table 3 and the average daily doses (ADD).

$$HQ = \frac{ADD}{RfD}$$

Table 3. Reference doses (RfD) for the selected elements.

Toxic Metals	Reference Doses [RfD] (ng/kg × d)		
	RfDing	**RfDinh**	**RfDderm**
Cr	3×10^3	2.86×10^1	3×10^3
Pb	1.4×10^3	3.52×10^3	5.24×10^4
Zn	3×10^5	3×10^5	6×10^4
Fe	7×10^5	7×10^5	7.38×10^5
Cu	4×10^4	4×10^4	1.2×10^4

Hazard index (HI) is the sum of all hazard quotients (HQ).

$$HI = \sum HQ \quad (1)$$

2.6.3. Excessive Risk for Cancer (ECR)

The excessive risk of developing cancer (ECR) is calculated using the formula

$$ECR = \frac{C \times ET \times EF \times ED \times IUR}{BW \times AT}$$

where C—average metal concentration in road dust (water soluble) (mg/kg); ET—exposure time (h/d); EF—contact frequency (d/year); ED—duration of contact (year); IUR—slope factor (g/m^3); BW—average body weight (kg), and AT—averaging period (d).

The IUR values of Cr and Pb are 1.2×10^{-2} and 8×10^{-5}, respectively [EPA]. The values of the parameters described in the formula are given in Table 2, and the values for ET are 14 h/d for adults and 8 h/d for children, respectively. If the ECR ranges between 10^{-6}–10^{-4}, there is a low risk of cancer [36].

2.7. Statistical Analysis

The concentrations of the elements were analyzed by STATISTICA®. All data were checked for normal distribution (Shapiro–Wilk W test) and homogeneity of variance (Levene's test). Then tests of significance were performed at a 95% confidence level. The significance of the differences between the three sites S1, S2, and S3, regarding the concentration of the selected metals, were carried out with one-way ANOVA.

Ecotoxicological studies with Algaltoxkit F and Daphtoxkit F magna were designed to assess the LC50 (lethal concentration). This means the concentration that causes the death of 50% of the tested species, i.e., algae and crustaceans, in studied dilutions of the surface water. The higher value of LC50, the less toxicity to the studied species. The *logistic* regression model was applied to establish the LC50. In the case of the sediments, Ostracodtoxkit F was applied, although we did not calculate the LC50, as we followed the procedure of the test and, therefore, we did not prepare the dilutions of the sediments; instead of this, the percentage of mortality rate and growth inhibition was simply calculated according to the test protocol.

3. Results and Discussion

3.1. Heavy Metal Concentrations in the Sediments

The mean concentrations of the studied metals (Cr, Cu, Pb, Zn, and Fe) for the sediment samples taken from S1, S2, and S3 are shown in Table 4. The significant differences (p values < 0.05) among the samples collected at the three sites are presented in Table S1 (Supplementary Material). Additionally, the estimates of the trace element compositions of the upper continental crust (UCC) were presented as well [43]. LAWA classification [44] was applied to assess the level of contamination of studied sites. The highest values were reached for Cr (705.3 ± 12.9 mg/kg) and Fe (13442.4 ± 67.10 mg/kg) at S2 ("Huta"), which was the nearest sampling site to the slag heap, and it was classified as moderately polluted/heavily polluted with Cr (class II–III). The highest concentrations of Pb, Zn, and Cu were also recorded at S2. This site showed significantly higher concentration levels compared to the other studied sites ($p < 0.05$). The results also revealed moderate contamination (class II) of S2 with Cu and uncontaminated/moderate contamination (class I, II) with Cu at S1 and S3. The Zn content was low, with all sites not contaminated with Zn. The order of the accumulation of the metals is Fe > Cr > Cu > Zn > Pb at S1 and S2, and Fe > Cu > Zn > Cr > Pb at S3. Previously, a high concentration of Cr was found in the water bodies in this area [24]. It is not surprising that the concentrations of Cr and Fe were elevated, although Fe is one of the major elements of the upper-continental crust; therefore, its high concentration is not astonishing [43]. The slag heap contains the remains of the ferrochromium alloys, which can easily enter the water bodies. Other toxic metals can also be present as a result of the previous activity of the former ferrochromium plant. The studies of Pawełczyk [45] also confirmed the existence of Cr contamination in this area. Based on the groundwater, soil, and dust samples, the authors assessed the possible health risk caused by chromium, especially with Cr(VI), in the former ferrochromium plant area. The metal concentrations in the soil were also assessed in this area [46]. According to the authors, the permissible concentrations of Cu, Zn, Ni, and Cr in the studied samples of soil exceeded the geochemical background level in the uncontaminated soil in Poland. Additionally, in the studies by Borowczak and Hołtra [46], it was found that the Cr in the soil of this area exceeded polish regulations (maximum value = 276.49 mg Cr/kg d.m.) which was probably connected (according to authors) with the ongoing works on the heap. The Cu and Zn content was also in excess compared to the geochemical background. There was no exceedance of Pb content in these studies. Studies on the sediments in this area have never been performed before, even though sediments play a key role in the quality of aquatic ecosystems, as they are reservoirs for contaminants. The concentrations of the metals assessed in this study suggest that the bioaccumulation of elements in fish could occur. According to Gwimbi et al. [47], sediments can be long-term sources of contamination to higher trophic levels; therefore, the bioaccumulation of toxicants is highly possible; the level Cr was relatively high compared to the other findings. For example, in a study focused on the heavy metal assessment of sediments conducted in an urban aquaculture pond in the coal-based city of Dhanbad, India, the neighboring traffic roads and industrial and residential areas were found to have high concentrations of Cr, Pb, and Zn, as well as Cd and Mn [48]. The chromium concentrations in the sediments in these studies were 99.71 ± 9.71 mg/kg during the premonsoon season and 84.4 ± 10.49 mg/kg during the postmonsoon season, respectively, which is more than two–seven times lower than in our studies. An ecological risk assessment and heavy metal analysis of sediments carried out at Chagan Lake in Northeast China showed that the concentration of Cr was 57.6 mg/kg, Zn: 66.83 mg/kg, Cu: 20.73 mg/kg, and Pb–26.56 mg/kg [49]. The contamination of this lake is due to tourism development; the negative impact on the lake is also connected with chemical fertilizer and thermal power plants. Additionally, some irrigation water from rice production enters the lake. Despite this, the concentrations of Cr are significantly lower than those presented in our study. All the sampling sites in Siechnice are heavily polluted with Cr. The concentrations of Fe are also very high, although this element is usually not perceived as a contaminant, as it is a major component of UCC. Furthermore, studies on

Wigry Lake situated in north-eastern Poland (the area of Suwałki Lakeland, which is one of the most valuable Polish lakes) revealed that total chromium concentration in the sediments ranged from 0.2 to 22.61 mg/kg [50], which is more than 30 times lower than in our studies.

Table 4. The mean concentrations of the selected toxic metals in the sediments ±SD for sites: S1 "Błękitna Laguna", S2 "Huta", and S3 "Mała Szwecja" [mg/kg]. * The content of Fe was expressed as FeO in weight percent oxide, as this is one of the major elements.

	Sampling Site			
Concentration of Trace Elements [mg/kg]	**S1**	**S2**	**S3**	**UCC Values [43]**
Cr	222.03 ± 3.56	705.3 ± 12.9	31.19 ± 1.5	35–112
Pb	17.32 ± 4.37	44.3 ± 5.08	13.10 ± 1.88	17–18
Zn	68.91 ± 5.88	84.84 ± 7.1	44.49 ± 6.21	52–71
Cu	77.56 ± 6.61	88.48 ± 9.17	73.01 ± 6.25	14–32
Fe	9971.4 ± 17.02	13442.4 ± 67.1	6411.3 ± 24.2	4.09–7.26 * in weight percent oxide

3.2. Ecotoxicological Studies

3.2.1. Ostracodtoxkit F-Sediments

The mortality rate [%] of *H. incongruens* is presented in Table 5. In the protocol of the test, there is no recommendation for LC50 calculation; therefore, the studies were restricted to the two nondiluted samples taken from the three sites. In the case of sediments, a 30% mortality rate for ostracods was observed for site S2, which is the only observation in line with the observed heavy metal concentrations. The highest values of the selected elements were obtained for this site. The growth inhibition of *H. incongruens* ranged from 29% (S3) to 88% (S1). The recorded growth inhibition for S1 and S3 with no mortality is probably connected to the presence of toxic metals in the sediments, although the concentrations were lower than those recorded at S2, where a relatively higher percentage of ostracod growth inhibition (88%) was also recorded, which is connected to the highest content of all the studied elements found in the sediment. Ostracodtoxkit F was applied in different but similar studies, where *H. incongruens* showed sensitivity due to the presence of trace elements in the bottom sediment of the water reservoirs [51]. Although, studies on the sediments in the area of the former ferrochromium plant have never been conducted.

Table 5. The percentage of mortality via Ostracodtoxkit F for the studied sediments from sites S1 "Błękitna Laguna", S2 "Huta", and S3 "Mała Szwecja" [%].

Sampling Sites	The Average Length of the Body Day 0	The Average Length of the Body Day 6	Percentage Mortality [%]	Percentage Growth Inhibition [%]
Control	195	532	-	-
S1	190	395	-	39
S2	185	227	30%	88
S3	200	440	-	29

3.2.2. Daphtoxkit F Magna–Surface Water

D. magna is used in the toxicity assessment of water bodies [52,53] and is proven to be effective in environmental monitoring studies [54]. The percentage mortality of *D. magna* after 24 and 48 h of exposure to the dilution series of the surface water samples from the S1, S2, and S3 sites is shown in Table 6. Mortality increased as the exposure time increased. The impact on the organisms was not noticed after 24 h of exposure. The mortality rate was 35% at S1 and 40% at S2 (nondiluted samples: 100%) after 48 h of exposure. No mortality of *D.magna* was observed at S3 in all the dilution series. Although, in all the analyzed samples, the mortality of the organisms did not exceed 50% of the population; therefore, it was not possible to calculate LC50.

Table 6. The average mortality rate of *D. magna* for the studied surface water from sites S1 "Błękitna Laguna", S2 "Huta", and S3 "Mała Szwecja" [%].

Sampling Sites	Dilution [%]	Mortality Rate [%]	
		24 h	48 h
S1	control	0	0
	6.25	5	5
	12.5	0	0
	25	0	0
	50	5	20
	100	0	35
S2	control	0	0
	6.25	5	15
	12.5	0	25
	25	0	35
	50	0	35
	100	0	40
S3	control	0	0
	6.25	0	0
	12.5	0	0
	25	0	0
	50	0	0
	100	0	0

3.2.3. Algaltoxkit F-Surface Water

Algaltoxkit F is commonly used in ecotoxicological research [54,55] and can be used in the evaluation of water toxicity in water bodies. The calculation of LC50 was possible in the case of algae over 24, 48, and 72 h (Table 7). According to the rule, the higher the value of LC50, the less toxic the sample (to the tested algae) is. In all samples, the toxicity was slightly higher with time, although the lowest values were obtained for S2, which is in line with other studies; the LC50 [%] value for both site S1 and site S3 was around 30% for the diluted sample, which suggest that these samples are not highly toxic in comparison with S2. Studies on the toxicity towards water organisms have not been conducted here before, although the assessment of health risks based on the metal concentrations in the water and soil in the former plant has been performed before [45,56]. Both studies suggest that there is an impact on health. In both studies, the level of chromium was found to be dangerous and carcinogenic in humans in the affected area.

Table 7. The results of LC50 [%] for Algaltoxkit F for the studied surface water from sites S1 "Błękitna Laguna", S2 "Huta", and S3 "Mała Szwecja".

LC50 [%]	24 h	48 h	72 h
S1	33%	25%	16%
S2	3%	0.03%	-
S3	30%	-	29%

3.3. The Assessment of Health Risk–Sediments

3.3.1. Average Daily Dose (ADD)

Table 8 shows all the calculations for the ADDing, ADDinh, and ADDderm values for the sediments taken from three studied sites. The highest ADD value was recorded at S2, which is in line with other findings. Exposure to Fe through ingestion was 4.41×10^4 mg/kg for children and 1.9×10^4 mg/kg for adults. Our calculations showed that the lowest exposure was for Pb via inhalation at all sites; it was below 1×10^{-2} mg/kg. Only at S2 was the ADDinh for Pb for children 1×10^{-2} mg/kg. We also found high exposure to Cr through ingestion (2.32×10^3 mg/kg for children; 9.93×10^2 mg/kg for adults) at S2. Cr is one of the worst toxic elements present in the studied area; therefore, the exposure to Cr through ingestion, inhalation, or dermal contact might cause minor health problems, such as skin irritation, allergic reactions, or severe problems, i.e., respiratory and cancerous diseases [57].

Table 8. ADD values [mg/kg] for the sediments at all the studied sites: S1 "Błękitna Laguna", S2 "Huta", and S3 "Mała Szwecja".

Sampling Sites	Toxic Metals [mg/kg]	ADDing [mg/kg]		ADDinh [mg/kg]		ADDderm [mg/kg]	
		Children	Adults	Children	Adults	Children	Adults
S1	Cr	7.30×10^2	3.13×10^2	5.25×10^{-1}	2.25×10^{-1}	4.09×10^0	6.24×10^0
	Pb	5.69×10^1	2.44×10^1	4.10×10^{-2}	1.76×10^{-2}	3.19×10^{-1}	4.87×10^{-1}
	Zn	2.27×10^2	9.71×10^1	1.63×10^{-1}	6.99×10^{-2}	1.27×10^0	1.94×10^0
	Cu	2.55×10^2	1.09×10^2	1.83×10^{-1}	7.86×10^{-2}	1.43×10^0	2.18×10^0
	Fe	3.28×10^4	1.40×10^4	2.36×10^1	1.01×10^1	1.84×10^2	2.80×10^2
S2	Cr	2.32×103	9.94×10^2	1.67×10^0	7.15×10^{-1}	1.30×10^1	1.98×10^1
	Pb	1.46×10^2	6.24×10^1	1.05×10^{-1}	4.49×10^{-2}	8.16×10^{-1}	1.25×10^0
	Zn	2.79×10^2	1.20×10^2	2.01×10^{-1}	8.60×10^{-2}	1.56×10^0	2.38×10^0
	Cu	2.91×10^2	1.25×10^2	2.09×10^{-1}	8.97×10^{-2}	1.63×10^0	2.49×10^0
	Fe	4.42×10^4	1.89×10^4	3.18×10^1	1.36×10^1	2.47×10^2	3.78×10^2
S3	Cr	1.03×10^2	4.39×10^1	7.38×10^{-2}	3.16×10^{-2}	5.74×10^{-1}	8.77×10^{-1}
	Pb	4.31×10^1	1.85×10^1	3.10×10^{-2}	1.33×10^{-2}	2.41×10^{-1}	3.68×10^{-1}
	Zn	1.46×10^2	6.27×10^1	1.05×10^{-1}	4.51×10^{-2}	8.19×10^{-1}	1.25×10^0
	Cu	2.40×10^2	1.03×10^2	1.73×10^{-1}	7.40×10^{-2}	1.34×10^0	2.05×10^0
	Fe	2.11×10^4	9.03×10^3	1.52×10^1	6.50×10^0	1.18×10^2	1.80×10^2

3.3.2. Hazard Quotient (HQ) and Hazard Index (HI)

There are many studies concerning metal presence in the sediments of lakes and ponds [58–60], and it is possible to calculate hazard quotient (HQ) and hazard index (HI) based on them. The noncarcinogenic health risk was assessed in the samples of the sediments taken from the water reservoirs (S1, S2, and S3) by calculating HQ, whereby, in most cases, this parameter was less than 1. According to EPA, if the HQ ≤ 1, adverse effects on human health are unlikely. Only at S2 was the HQ 1.1 for children (oral route) for Fe. Similar results were recorded for the HI, where a possible health risk was also observed only at S2 (HI greater than 1) for Fe (Tables 9 and 10). Both HQ and HI have not been calculated in these sediments before, although they were assessed in the soil samples near the slag heap in Siechnice, where the HQing and HI for Cr for children were close to 1 [30]. In the work of Pawełczyk et al. [45], an increased HQ level for Cr (based on groundwater, soil, and dust samples) was recorded for occupational activities. On the other hand, in the work of Wróbel et al. [56], the highest values for HQ and HI were recorded in soil for Cr, but they were not greater than 1, which is also the case in our studies.

Table 9. HQ for ingestion, inhalation, and dermal contact for the sediments at all the studied sites: S1 "Błękitna Laguna", S2 "Huta", and S3 "Mała Szwecja" [mg/kg].

Sampling Sites	Toxic Metals [mg/kg]	HQing		HQinh		HQderm	
		Children	Adults	Children	Adults	Children	Adults
S1	Cr	2.43×10^{-1}	1.04×10^{-1}	1.84×10^{-2}	7.87×10^{-3}	1.23×10^{-2}	2.08×10^{-3}
	Pb	4.07×10^{-2}	1.74×10^{-2}	1.16×10^{-5}	4.99×10^{-6}	6.09×10^{-4}	9.29×10^{-4}
	Zn	7.55×10^{-4}	3.24×10^{-4}	5.43×10^{-7}	2.33×10^{-7}	2.11×10^{-5}	3.23×10^{-5}
	Cu	3.64×10^{-4}	1.56×10^{-4}	2.62×10^{-8}	1.12×10^{-8}	1.93×10^{-6}	2.95×10^{-6}
	Fe	8.19×10^{-1}	3.51×10^{-1}	5.90×10^{-4}	2.53×10^{-4}	1.53×10^{-2}	2.34×10^{-2}
S2	Cr	7.73×10^{-1}	3.31×10^{-1}	5.83×10^{-2}	2.50×10^{-2}	3.90×10^{-2}	6.61×10^{-3}
	Pb	1.04×10^{-1}	4.46×10^{-2}	2.98×10^{-5}	1.28×10^{-5}	1.56×10^{-3}	2.38×10^{-3}
	Zn	9.30×10^{-4}	3.98×10^{-4}	6.69×10^{-7}	2.87×10^{-7}	2.60×10^{-5}	3.97×10^{-5}
	Cu	4.16×10^{-4}	1.78×10^{-4}	2.99×10^{-8}	1.28×10^{-8}	2.21×10^{-6}	3.37×10^{-6}
	Fe	1.10×10^{0}	4.73×10^{-1}	7.95×10^{-4}	3.41×10^{-4}	2.06×10^{-2}	3.15×10^{-2}
S3	Cr	3.42×10^{-2}	1.46×10^{-2}	2.58×10^{-3}	1.11×10^{-3}	1.72×10^{-3}	2.92×10^{-4}
	Pb	3.08×10^{-2}	1.32×10^{-2}	8.80×10^{-6}	3.77×10^{-6}	4.60×10^{-4}	7.03×10^{-4}
	Zn	4.88×10^{-4}	2.09×10^{-4}	3.51×10^{-7}	1.50×10^{-7}	1.37×10^{-5}	2.08×10^{-5}
	Cu	3.43×10^{-4}	1.47×10^{-4}	2.47×10^{-8}	1.06×10^{-8}	1.82×10^{-6}	2.78×10^{-6}
	Fe	5.27×10^{-1}	2.26×10^{-1}	3.79×10^{-4}	1.62×10^{-4}	9.83×10^{-3}	1.50×10^{-2}

Table 10. HI for the sediments at all the studied sites: S1 "Błękitna Laguna", S2 "Huta", and S3 "Mała Szwecja" [mg/kg].

Sampling Sites	Toxic Metals [mg/kg]	HI	
		Children	Adults
S1	Cr	1.14×10^{-1}	2.74×10^{-1}
	Pb	1.84×10^{-2}	4.13×10^{-2}
	Zn	3.56×10^{-4}	7.77×10^{-4}
	Cu	1.59×10^{-4}	3.66×10^{-4}
	Fe	3.75×10^{-1}	8.35×10^{-1}
S2	Cr	3.63×10^{-1}	8.70×10^{-1}
	Pb	4.70×10^{-2}	1.06×10^{-1}
	Zn	4.38×10^{-4}	9.56×10^{-4}
	Cu	1.81×10^{-4}	4.18×10^{-4}
	Fe	5.05×10^{-1}	1.13×10^{0}
S3	Cr	1.60×10^{-2}	3.85×10^{-2}
	Pb	1.39×10^{-2}	3.12×10^{-2}
	Zn	2.30×10^{-4}	5.02×10^{-4}
	Cu	1.50×10^{-4}	3.45×10^{-4}
	Fe	2.41×10^{-1}	5.37×10^{-1}

3.3.3. Excessive Risk for Cancer (ECR)

It is possible to calculate the ECR values for toxic metals, such as Cr and Pb, in sediments, and there are many studies focusing on the concentrations of metals in the sediments of water reservoirs [61–63]. If the ECR ranges between 10^{-6}–10^{-4}, there is a low risk of cancer. Carcinogenic risk is considered to occur when ECR > 10^{-6}. For the studied elements that are recognized by EPA as carcinogenic, the risk of cancer development related to the sediments was calculated, and the results are summarized in Table 11. An apparent carcinogenic health risk was observed at all the sampling sites. In our study, the highest ECR values for Cr were found in S2 (for children (2.23×10^{0}) and adults (8.3×10^{0})), as the highest Cr concentration was found at this site. In other studies, the sediments in the former area of the slag heap have never been studied, although soil samples were assessed in terms of their cancer risk. It was found that the ECR values for Pb in the soil samples near the slag heap were high; however, for Cr, the risk was negligible [30]. The situation is completely different in the studies of Pawełczyk et al. [45], wherein the carcinogenic risk was extremely high for Cr for occupational exposure scenarios. In the studies of Wróbel et al. [56], the high ECR values for Cr for children were obtained from the soil samples taken from the former ferrochromium plant area. Surprisingly, lower values for Pb were obtained in these studies.

Table 11. ECR values for children and adults for the sediments at all the studied sites: S1 "Błękitna Laguna", S2 "Huta", and S3 "Mała Szwecja" [mg/kg].

Site	Toxic Metals [mg/kg]	ECR	
		Children	Adults
S1	Cr	7×10^{-1}	2.6×10^{-1}
	Pb	3.6×10^{-4}	1.36×10^{-4}
S2	Cr	2.23×10^{0}	8.3×10^{-1}
	Pb	9.3×10^{-4}	3.5×10^{-4}
S3	Cr	1×10^{-1}	4×10^{-2}
	Pb	2.8×10^{-4}	1.03×10^{-4}

The obtained results for ECR prove that the former ferrochromium plant is still a significant environmental hazard and could have a critical impact on the surrounding environment. Old environmental practices and outdated technologies can still have a key role in maintaining the good health of the whole ecosystem as they could serve as a reservoir for pollutants that can be dangerous to all living organisms, and they can be released again into the environment. Therefore, it is extremely important to assess past environmental burdens to protect the environment. Future studies should track the possible changes in the Cr and Pb concentrations, as these elements pose a carcinogenic risk to humans and other living organisms.

4. Conclusions

This study gives a comprehensive assessment of the metal contamination and the associated environmental health risk of the following metals: Cu, Zn, Pb, Fe, and Cr in the sediments of the water bodies surrounding the area of the former ferrochromium plant. The metal concentrations in the sediments could be attributed to the former plant's activity. The Cr level at all sites exceeded the permissible limit. The highest values were reached for Cr and Fe at site 2 (S2, "Huta"), which is located closest to the slag heap. The concentrations of the metals were relatively lower at the other sampling sites where the distance from the heap was greater. The toxicity towards living organisms was tested via the application of commercial tests: Ostracodtoxkit F for assessing the toxicity of the sediments and Daphtoxkit F magna and Algaltoxkit F for the water toxicity studies. In the case of sediments, a 30% death rate for *H. incongruens* was recorded in the sediments at the closest site to the landfill (S2, "Huta"). The highest mortality of *D. magna* (40% after 48 h) was observed in the water taken at this site (S2, "Huta"), and for algae, the lowest values of LC50 were calculated at S2 also, proving that the water in this reservoir still poses a health risk to living organisms, which also corresponds to the highest concentrations of studied elements recorded at this site. The results calculated from the sediments generally showed that the former ferrochromium plant poses the highest risk. The health exposure expressed by the health risk hazard quotient decreases as follows: HQing > HQderm > HQinh. The HI value for Cr for children was above 1, which indicates the high health impact of this metal when ingested by children. ECR was determined for Cr and Pb. All the values were above the range limit of 10^{-6}. The ECR value for Cr was the highest in the sediments at the site closest to the landfill for both children and adults. Therefore, the cancer risk from Cr and Pb for both children and adults was found to be very high. Pb and Cr were determined to have extremely high environmental risks due to their high concentrations. Thus, the former ferrochromium plant can be harmful to health when considering Cr and Pb contamination, and it is possible that potential danger to humans consuming fish from this water reservoir, as well as to other living organisms, currently exists in the water reservoir. In other studied water bodies, even though the risk is lower, it still exists. In conclusion, because of the potential risk of toxic metal contamination, efforts to control this area should be made, especially when considering the proven Cr contamination. Therefore, further research is needed in this area, particularly focusing on the bioaccumulation of metals in fish and assessing the change in metal content in the bottom sediments as a function of depth, which will give precise information about the potential health risk. This comprehensive risk assessment is essential for the risk assessment of the sediments from these studied water reservoirs.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app13032001/s1, Table S1: Results of one-way ANOVA for studied sites in Siechnice.

Author Contributions: Conceptualization, M.W. and J.R.; data curation, M.W.; formal analysis, M.W. and F.Z.; funding acquisition, J.R.; investigation, M.W., F.Z. and K.K.; methodology, M.W.; project administration, J.R.; resources, M.W.; supervision, J.R.; validation, M.W., A.P. and F.Z.; visualization, A.P. and J.R.; writing—original draft, M.W., A.P., J.R., B.H.-L. and F.Z.; writing—review and editing, M.W., A.P. and J.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data related to this study are included in this article and its Supplementary Materials File.

Acknowledgments: Map data copyrighted OpenStreetMap contributors and available from https://www.openstreetmap.org/ (accessed on 27 September 2022).

Conflicts of Interest: The authors declare no conflict of interest.

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