



# Impact of military metallurgical plant wastes on the population's health risk



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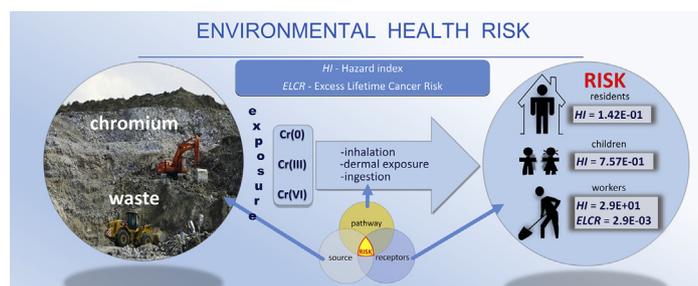
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## HIGHLIGHTS

- Assessment of exposure to Cr (III) and (VI) in environment is proposed.
- Estimation of environmental health risk on sites affected by waste dump is made.
- Mitigation of environmental health risk by improvement of waste processing is proposed.

## GRAPHICAL ABSTRACT



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## ABSTRACT

This paper presents the results of water, soil and air analyses taken in the vicinity of a former ferrochromium metallurgical plant. In the past, the area was used for the disposal of waste materials containing smelter slag, dust and other waste products from the manufacture of ferrochromium alloys for the army. Recently, production was abandoned and a project aimed at the liquidation of the dump has been initiated. The project concentrates on the recovery of chromium remains and the utilization of the leftover material as a road construction aggregate. Based on the analyses of ground water, soil and air, a health risk caused by environmental pollution with chromium, especially with Cr(VI), was determined for residential and occupational scenarios. It was found that the level of chromium emissions to the environment constitutes a potential danger of toxic and carcinogenic cases in humans exposed to the emission in the affected area. An increased level in the hazard quotient has been observed in the case of occupational activities. As far as the mutagenic effects are concerned, the occupational inhalation exposure was found to be very high, which may raise extreme concern about carcinogenic risk.

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## 1. Introduction

Metallurgical plants are a source of burdensome emissions of soil, water and air pollution. They can negatively affect the

environment even after the end of production. Accumulated waste materials, especially sludge, slag and dusts, have remained as environmental pollutants for years. The former ferrochromium works in Siechnice near Wrocław, Poland, which used to manufacture alloys for military purposes in the past, is such a case. The waste dump located near the works contains slag including, among others, iron and chromium in different chemical forms. The dump is a reason for concern for the local population and the

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water treatment company that draws water from the surrounding area for municipal purposes. Since the time when manufacturing in the Siechnice metallurgical works was closed down, a variety of plans have been proposed to solve the environmental problem (Swiat, 2012). The most feasible plan seems to be a recent project assuming the recovery of metallic components, mainly the ferrochromium alloy, by involvement of multiple operations such as ore extraction, transport, crushing, screening, magnetic separation, washing, etc. Some of these processes are accompanied by intensive dust generation, which may create environmental problems.

Chromium is a grey, hard metal most often classified as a heavy metal, commonly found in compounds in the trivalent state in nature. Trivalent chromium (Cr(III)) is recognized as an essential nutrient and is widely used as a nutritional supplement for humans and animals. Besides the trivalent Cr(III) form, under certain environmental conditions, chromium can also be found in the metallic zero-valent (Cr(0)) or the hexavalent (Cr(VI)) forms. The most common ore containing a significant amount of Cr(III) is chromite (FeOCr<sub>2</sub>O<sub>3</sub>). At the beginning of this century, approximately 13.5 million tons of chromite ore were produced and converted into about 5 million tons of ferrochromium (Papp, 2002).

Chromium in different forms can be found in water, soil and air. Natural sources of chromium are, for instance, rock strata rich in Cr(III)-bearing minerals (chromite in particular), which dissolve, and subsequently, Cr(III) can be oxidized to Cr(VI) (Oze et al., 2007).

Anthropogenic chromium sources are effluents from different technological processes like metallurgy, electroplating, leather tanning, textile dyeing, painting, inking, and aluminum manufacturing as well as a variety of niche uses (Časlavský et al., 2010). In the past, green-colored chromated copper arsenate (CCA) used for pressure-treated lumber was used, contributing to Cr(VI) in the environment. Since January 1, 2004, the US EPA banned the use of CCA-treated lumber for new residential purposes (Guertin et al., 2004). CCA-treated wood should not be used in raised vegetable beds or reused in other products such as mulch (EPA, 2015).

Chromium concentrations in soils vary from 0 to 1000 mg/kg. The average levels of chromium in the ambient air in Europe are reported to range between 20 and 70 ng/m<sup>3</sup> (WHO, 2000). The concentrations of chromium in ground water also differ substantially depending on the area concerned. Typically they are placed between 0.3 and 6 µg/L (Swietlik, 1998).

From the environment, people absorb chromium daily from food, beverages, and ambient air. The daily intake by humans is shown in Table 1 (WHO, 2000). In the case of highly polluted areas, the intake levels can significantly exceed the values shown on the table.

Chromium in the metallic form does not manifest any biological activity while the trivalent Cr(III) and hexavalent Cr(VI) forms biologically affect the human body. The two forms differ significantly in the effects produced. Chromium (III) is an important component of mammals' diet, whereas the latter is toxic and exhibits mutagenic effects (WHO, 2000; EPA, 2015b). Depending on the source of origin, Cr(VI) occurs in the form of chromate ion CrO<sub>4</sub><sup>2-</sup>, hydrochromate ion HCrO<sub>4</sub><sup>-</sup> or bichromate ion.

Hexavalent chromium is much less stable than the trivalent form. It easily undergoes reduction in the presence of some inorganic ions found in the environment.

The role of Cr(III) in living organisms consists of the control of lipid, peptide and glucose metabolism. The monitored Cr chemical forms are classified into different toxicity groups depending on the chemical state and exposure routes. According to the US EPA, Cr(VI) is classified as group A, (human carcinogen by the inhalation route of exposure). However, for oral and dermal routes of exposure, it is classified as group D (not classifiable as to human carcinogenicity). Cr(III) is also classified as the same group D (EPA, 2015b).

Cr(VI) is a thousand fold more toxic than Cr(III) because hexavalent chromium is capable of penetration through the cell membrane while trivalent chromium cannot get through the biological membranes. Cr(VI) reaching the cell interior may react with enzymes, DNA and RNA, which disturbs the proper functioning of these molecules. In further stages of the chemical transformations, destruction of the cells and formation of cancer cells can occur (Senczuk, 2005). Studies of workers in the chromate production, plating, and pigment industries consistently show increased rates of lung cancer. Exposure to Cr(VI) can also cause irritation of the lungs. Prolonged exposure to Cr(VI) can damage the mucous membranes of the nasal passages and result in ulcers. In severe cases, exposure may cause perforation of the wall separating the nasal passages. Exposure to hexavalent chromium can cause skin diseases like dermatitis and skin ulcers. Allergic reactions to chromium are also reported. The type and intensity of the adverse health effects strongly depend on the exposure pathway. The worst health effects resulting in a carcinogenic effect can be expected when Cr(VI) gets to the organisms with dust in the respiratory system (SAIF, 2009).

Because of the above mentioned adverse effects, governments set water, soil and airborne chromium concentration limits. For example, the Polish chromium occupational standards in the workplace in dusty air pollutants are as follows: for metallic chromium, Cr(II) and Cr(III), the maximal allowable concentration is 0.5 µg/L, and for Cr(VI), it is 0.1 µg/L of air. The maximum short-term exposure limit for Cr(VI) is 0.3 µg/L (MLSP, 2002). The Ministry of the Health Care established a standard for chromium in drinking water at 50 µg/L (MHC, 2010). The Cr(VI) level is not standardized. For soil classified to purity class A (intended for residential areas), the quality standards limit the maximal allowable chromium concentration to 50 mg/kg (ME, 2002).

In the USA, no separate limits of Cr(VI) levels were established in water. The law regulates only total Cr. The US EPA Drinking Water Maximum Contaminant Level (MCL) for total Cr is 100 µg/L, while California limits total Cr in drinking water to 50 µg/L (EPA, 2015a).

The presented health risk assessment was carried out at the Wrocław University of Technology, Poland, and at the University of Defence, Brno, Czech Republic, based on chromium concentration analyses in ground water, soil and air. The goal of this study was to investigate the environmental samples collected from the area affected by the former ferrochromium plant and the existing waste dump, after the termination of the manufacturing process in 1990. A further objective was to determine environmental hazards, particularly the toxic hazards and possible carcinogenic health risks in human populations exposed to Cr(VI).

It should be noted that the chromium pollution in the environment results not only from the recent dump emissions but also from the past activity of the production plant. Reports estimate that during the last years of the plant's functioning (end of the 1980's), yearly emission of chromium from point sources was 95 t while the diffuse emission amounted to 126 t Cr/y (Bilyk and Kowal, 1993).

**Table 1**  
Daily chromium intake doses by humans from different exposure routes (WHO, 2000).

Route of exposure	Daily intake	Absorption
Foodstuff	<200 µg	<10 µg
Drinking water	0.8–16 µg	<1 µg
Ambient air	<1000 ng	<5 ng

## 2. Materials and methods

### 2.1. The site

The area affected by chromium emissions is located in the vicinity of a site used for many decades by the metallurgical works that manufactured alloys and other goods for military purposes. About 3.5 million tons of the ashes, slag and other waste materials had been accumulated till 1990 when production had been abandoned. The dump contains remains of the ferrochromium alloys as well as different solids with a relatively high concentration of heavy metals. Localization of the dump is shown in Fig. 1. It is situated in the neighborhood of a residential area and is about 300 m south-west from the aquifers composing water sources for the city of Wrocław.

Nowadays, the dump poses a big problem for the local community. It is a source of uncontrolled ground, water and air pollution affecting wells, gardens, the growing of vegetables and fruits and the general living conditions of the town population. The problem got worse when the local people started to extract waste ferrochromium pieces from the dump illegally. This kind of activity caused an additional emission to the environment (Nogaj, 2013).

### 2.2. Applied analytical methods

Total chromium and chromium (VI) were analyzed in the environmental samples collected from the waste dump, from its populated surroundings and from the vicinity of the processing plant.

Ground water sampling was carried out from three piezometers installed close to the residential zone, about 100 m north and northeast from the dump's edge, toward the aquiferous area. They were inserted 2 m deep into the ground (Fig. 1). The soil for the analyses was collected from the upper 10 cm ground layer at the same spots situated next to the piezometers. The ferrochromium waste material was taken directly from the dump.

Digging, loading and unloading the material generates a dusty fraction spread by the wind. Chromium, particularly Cr(VI)

included in the airborne particulate matter, may influence machine operators. Therefore, with the purpose of occupational risk determination, the analyses of ambient air were carried out. They were limited to the neighborhood of the processing plant. It had been assumed that the airborne dust does not reach the residential area, at least to a degree that could raise the concerns of the population. To evaluate an approximate occupational health risk, we had made repeated measurements, four times in two-week intervals, during working shifts, just in the closest neighborhood northwards.

The Polish Standard (PS, 1984) was adapted for sampling using a Quick Take 30 aspirator with an electronic flow control adjustment at the flow rate of 16.0 L/min and with 180 min sampling time applied. The air stream was filtered on Sartorius cellulose nitrate membrane filters with 25 mm diameter and 0.4  $\mu\text{m}$  pores. After sampling, the filters were protected in plastic boxes and delivered to the laboratory.

Analyses of chromium in the samples were carried out by the ICP method using an ICP-MS spectrometer Elan 9000 Perkin Elmer. For mineralization of the samples, pressure decomposition in nitric acid and hydrogen peroxide was applied by the use of a microwave mineralizer Anton-Paar PE Multiwave 3000.

For the analysis of hexavalent chromium, a procedure described in Ashley et al. (2003) was applied. Ion chromatography was used to separate Cr(VI). The equipment consisted of an HPLC PE series 200 with UV-Vis 785A and FD200, IC Dionex DX-120. The mobile phase flow rate was 1.0  $\text{cm}^3/\text{min}$ , a post-column reagent flow rate was 0.7  $\text{cm}^3/\text{min}$ , and a post-column tube length was 2.2 m. The extraction was made with a 2% NaOH and a 3%  $\text{Na}_2\text{CO}_3$  solution in deionized water. The mobile phase was 250 mM  $(\text{NH}_4)_2\text{SO}_4$  and 100 mM  $\text{NH}_4\text{OH}$ .

The detection limit of chromium (VI) in the case of air samples was 0.004  $\mu\text{g}$  per sample. For the ground water, it was about 1  $\mu\text{g}/\text{L}$ , and for soil, it was about 5  $\mu\text{g}/\text{kg}$ .

### 2.3. Health risk assessment

The aim of this step of the work was to quantify both the workers' and residents' health risk based on the exposure of both

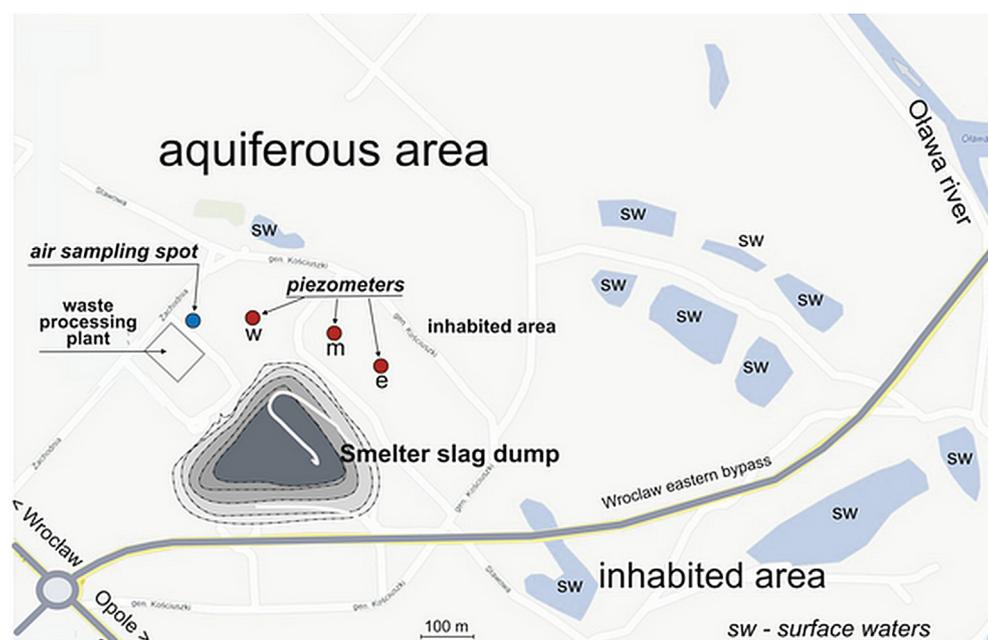


Fig. 1. Map of the area affected by the chromium waste dump with the indicated water sampling spots.

population groups to chromium in water, soil and air. The taken-in doses were determined in compliance with the assumed scenarios and the facts recommended by the EPA (Moya et al., 2011). As the chromium demonstrates both toxic and carcinogenic effects, quantification was conducted separately for these effects.

For the purpose of the health effects assessment, methodological principles of the risk assessment related to polluted areas have been adapted based on the US EPA guidelines for the “Superfund” project (EPA, 1991) with certain modifications. Also, guidelines for the chromium exposure assessment and possible exposure scenarios published by the EPA (1992) have been taken into account. Specific conditions and constraints of the area in question required the construction of adequate procedures and exposure scenarios. The health risk assessment was carried out on the basis of the developed scenarios, analyses of different chromium forms and the chromium toxicity data.

According to EPA recommendations, a conservative approach to risk assessment was applied, and thus the greatest potential risk was addressed. For instance, in this approach, it is assumed that all chromium in the water samples exists in the most harmful forms, that is in the form of Cr(VI) or Cr(III). This is because these two forms of chromium undergo conversions from one form to another in water and in the human body, depending on environmental conditions. Measuring just one form may not capture these changeable chromium forms.

The following exposure scenarios have been taken into account:

- occupational exposure of workers involved in the waste material processing. The staff activities comprised mechanical operations at the work site (extracting the material, loading, transport and unloading, etc.). For this scenario, the non-carcinogenic hazard level as well as the carcinogenic risk were determined.
- exposure of adult residents comprising lifelong habitation and recreational garden activities in the affected zone. For this exposure scenario, just the intensity of non-carcinogenic effects, expressed by hazard quotients, was determined because based on the measurements of the air contaminants, it was assumed that the residents were not affected by the airborne Cr(VI) form. Gardening and recreation, however, are associated with accidental soil and ground water ingestion, which is different for the adults and children.
- Exposure of children in the above mentioned residential zone. There were similar conditions but different accidental soil and water ingestion doses. The most affected age population was taken into account was the 0–6 year children's group.

### 3. Results

#### 3.1. Exposure assessment

The level of chromium in the examined materials differed substantially depending on the sample type and sampling spot. Sampling of the waste was repeated in 10 different spots of the dump and from different depths, then each sample was averaged. Contents of Cr in the furnace slag ranged between  $0.67E + 03$  and  $47.12E + 03$  mg/kg of the dry matter. Except for the slag, other materials like sand, soil, bricks and pieces of ferrochromium alloy were also found in the waste. The Cr(VI) level ranged between 12.7 and 116.2 mg/kg. For the risk evaluation, the upper value was applied.

Ground water for the analyses was collected from the three piezometers labeled with letters “w”, “m” and “e.” The sampling was repeated consecutively four times in the two-week intervals. The results are presented in Table 2.

**Table 2**

Contents of total and Cr(VI) in ground water collected from the piezometers (mg/L).

Piezometer	Sampling							
	1		2		3		4	
	Cr	Cr(VI)	Cr	Cr(VI)	Cr	Cr(VI)	Cr	Cr(VI)
“e”	1.02	0.02	0.08	0.01	0.91	0.04	1.07	0.02
“m”	1.43	0.01	1.22	0.01	1.73	0.03	1.57	0.04
“w”	1.09	0.01	0.99	0.00	1.23	0.02	1.18	0.02

The average concentration of total chromium in the ground water within the sampling period was 1.13 mg/L. The analyses carried out showed that the level of Cr(VI) in the water was between 0.00 and 0.04 mg/L, and it underwent substantial changes with time and location. The average Cr(VI) concentration was 0.02 mg/L.

The total chromium level in the soil taken near the piezometers from the depth of 10 cm was between 92 and 186.4 mg/kg with its average value 133.6 mg/kg. The average Cr(VI) level was relatively low. It ranged from 2.56 to 5.07 mg/kg, and its average concentration was 4.13 mg/kg Table 3 presents the concentration of total and hexavalent chromium in the soil.

The measurements of airborne dust released from the waste handling area proved that Cr(VI) was present in the air (Table 4). The average amount of Cr(VI) in the ambient air was 0.04 mg/m<sup>3</sup>. It dropped considerably along with increasing the distance from the waste processing plant area. The average total Cr contents in the air was 0.36 mg/m<sup>3</sup>.

#### 3.1.1. Exposure assessment for non-carcinogenic effects

For calculations of Chronic Daily Intakes (CDI) the formulas mentioned below were applied, determining the chromium doses absorbed by accidental soil and water ingestion as well as inhalation of airborne dust (Čáslavský et al., 2010):

- Cr by accidental soil (or waste material) ingestion [mg kg<sup>-1</sup> d<sup>-1</sup>]

$$CDI_{ING, S} = c_S \times IR_{ING, S} \times FI \times EF \times ED \times BW^{-1} \times AT^{-1} \times 10^{-6} \quad (1)$$

- Cr by accidental water ingestion [mg kg<sup>-1</sup> d<sup>-1</sup>]

$$CDI_{ING, W} = c_W \times IR_{ING, W} \times FI \times EF \times ED \times BW^{-1} \times AT^{-1} \times 10^{-6} \quad (2)$$

- Cr by inhalation of chromium with airborne dust [mg kg<sup>-1</sup> d<sup>-1</sup>]

$$CDI_{INH} = c_A \times IR_{INH} \times ET \times EF \times ED \times BW^{-1} \times AT^{-1} \quad (3)$$

where:

**Table 3**

Contents of total and hexavalent chromium in the soil collected near the piezometers (mg/kg).

Piezometer	Sampling							
	1		2		3		4	
	Cr	Cr(VI)	Cr	Cr(VI)	Cr	Cr(VI)	Cr	Cr(VI)
“e”	104.2	2.65	92.6	4.60	99.3	3.98	108.5	4.05
“m”	134.4	3.80	118.6	4.76	128.1	4.43	127.3	2.56
“w”	156.9	4.71	169.0	4.28	186.4	5.07	177.7	4.70

**Table 4**

Contents of total and hexavalent chromium in the air collected from near the waste processing plant (mg/m<sup>3</sup>).

Sampling							
1		2		3		4	
Cr	Cr(VI)	Cr	Cr(VI)	Cr	Cr(VI)	Cr	Cr(VI)
0.44	0.012	0.36	0.022	0.41	0.007	0.21	0.014

$c_s$  [mg/kg] is the average concentration of chromium in soil/waste material,

$c_w$  [mg/L] is the concentration of chromium in water,

$c_A$  [mg/m<sup>3</sup>] is the concentration of chromium in the air,

$IR_{ING,S}$  [mg/d] is the amount of accidentally ingested soil or waste material per day—50 mg/d for adults (soil for resident or waste for occupational activity) and 100 mg/d for children (soil) (Moya et al., 2011; EPA, 2011),

$IR_{ING,W}$  [mL/d] is the daily amount of accidentally ingested groundwater per day—0.075 mL/d for adults and 0.150 mL/d for children applied,

$IR_{INH}$  [m<sup>3</sup>/h] is the inhaled air rate,

$FI \in (0; 1)$  is a fraction of the contaminated source (0.3 applied),

$EF$  [d/y] is the exposure frequency,

$ED$  [y] is the exposure duration — 30 years was applied for residents (EPA, 1991) and 6 years for the scheduled time of the dump liquidation for the occupational scenario,

$ET$  [h/d] is the exposure time,

$BW$  [kg] is the average body weight,

$AT$  [d] is the time of exposure during which the concentrations of contaminants  $c_s$ ,  $c_w$  and  $c_A$  are assumed to be constant,

$1 \times 10^{-6}$  = conversion factor (kg/mg) or (L/mL).

It should be stressed that the above listed parameters have different values depending on the exposure scenario (occupational, adult residents, children). The chronic daily intakes were determined separately for Cr(III) and Cr(VI) where the concentration of Cr(III) was intentionally applied as the difference between total Cr and Cr(VI). That means the conservative assumption of hazard estimation was used.

### 3.1.2. Exposure assessment for carcinogenic effects

To determine the carcinogenic risk within the occupational scenario, the inhalation unit risk  $IUR$  was used and the Cr(VI) chronic exposure concentrations ( $EC$ ) were calculated using the following formula (Braun, 2005; Lytle and Woo, 2007; EPA, 2009):

$$EC = c_A \times ET \times CF \times EF \times \frac{ED}{AT} \quad (4)$$

where:

$EC$  [mg/m<sup>3</sup>] is the chronic exposure concentration (averaged over a 70-year lifetime)

$c_A$  [mg/m<sup>3</sup>] is Cr(VI) concentration in the air

$ET$  [h/d] is the exposure time. It is 8 h a day in the occupational scenario,

$CF$  is a conversion factor = 1/24 (h → d)

$EF$  is exposure frequency in d/y. In the occupational scenario it is 220 days a year,

$ED$  [y] is the exposure duration.  $ED$  was assumed 6 years as the scheduled time of the dump liquidation is 6 years.

$AT$  is the averaging time of = 24 h/d × 365 d/y × 70 y (lifetime) = 613,200 h.

## 3.2. Dose – response relation

The dose – response relation was conducted on the basis of the calculated daily intakes, chronic exposure concentration and toxicity data (EPA, 1992) presented in Table 5.

The determination of the dose-response relation was conducted separately for carcinogenic and non-carcinogenic effects.

### 3.2.1. Dose-non-carcinogenic response relation

In the case of the toxic, non-carcinogenic effects caused by the chromium present in the environment, the hazard quotient  $HQ$  was determined. It was calculated by comparing the daily doses of a pollutant taken in with the reference doses  $RfD$  or reference concentrations  $RfC$  (in the case of the inhalation route). Due to the lack of a relevant toxicity study addressing the respiratory effects of Cr(III), it was assumed, based on literature data, that Cr(III) is much less toxic than Cr(VI) and its  $RfC$  is 1000 times higher than for the latter (Dianyi, 2008; Dayan and Payne, 2001; EPA, 1998).

The hazard quotients are expressed by the following formulas (EPA, 1992):

$$HQ = \frac{CDI}{RfD} \text{ for the oral intake} \quad (5)$$

$$HQ = \frac{EC}{RfC} \text{ for inhalation exposure route.} \quad (6)$$

The reference doses  $RfD$  and concentrations  $RfC$  have to be consistent within the exposure duration which means that the reference values used should be determined for appropriate exposure periods. For exposure to multiple non-carcinogenic factors, the aggregate potential for the non-carcinogenic health effects (the hazard index  $HI$ ) is calculated from the following formula:

$$HI = \sum HQ_i \quad (7)$$

where  $HQ_i$  is a hazard quotient for the  $i$ -th factor.

### 3.2.2. Dose-carcinogenic response relation

The excess lifetime cancer risk  $ELCR$  has been determined using chronic exposure concentrations  $EC$  calculated from Equation (4). It amounted to 2.4E-04 mg/m<sup>3</sup>. Such an approach determines the probability of developing cancer over a person's lifetime at a given exposure level.  $ELCR$  is expressed by a value representing the number of extra cancer cases expected in a given number of people, based on exposure to a carcinogen at a stated dose. The formula is shown below:

$$ELCR = EC \times IUR \quad (8)$$

The hazard quotients and excess lifetime cancer risks that were calculated for the different scenarios are presented in Table 6.

According to Table 6, the hazard indices  $HI$  for both children and adults in the residential scenario have values less than one. Thus, it can be concluded that the pollutants should not cause harmful toxic effects in the population. On the other hand, the  $HI$  value for the occupational scenario exceeds the safe level almost 30 times. The main harmful factor contributing to such a high hazard is exposure to the Cr(VI) present in the dust. Such a value is absolutely not acceptable; therefore, some protective measures are necessary for hazard reduction.

Regarding the carcinogenic hazard, the calculated risk in the occupational scenario amounts to 2.9E-03. According to the accepted standards, such a risk level is also unacceptable. A risk level approaching  $10^{-3}$  absolutely requires protective measures. In general, the US EPA considers excess cancer risks that are below 1

**Table 5**  
Carcinogenic and toxicity values of chromium (EPA, 1992).

Cr form	Carcinogen classification	NOAEL mg/(kg·d)	Reference dose RfD mg/(kg·d)	Reference concentration RfC mg/m <sup>3</sup>	Inhalation unit risk IUR m <sup>3</sup> /μg
Cr(III)	Group D - by the oral route of exposure (carcinogenicity cannot be determined)	1.468E + 03	1.5 E+00	–	–
Cr(VI)	Group A - human carcinogen by the inhalation route of exposure. Group D - by the oral route of exposure (carcinogenicity cannot be determined)	2.5E + 00	3.0E – 03	1.0E – 04	1.2E – 02

**Table 6**  
Hazard quotient HQ<sub>i</sub>, hazard index HI and excess lifetime cancer risk ELCR.

Exposure type	Workers	Residents	
		Adults	Children
<i>HQ</i> – Residential activity			
<i>ground water ingestion Cr(III)</i>	–	6.8E – 10	3.6E – 09
<i>soil ingestion Cr(III)</i>	–	5.3E – 05	2.8E – 04
<i>ground water ingestion Cr(VI)</i>	–	6.2E – 09	3.3E – 08
<i>soil ingestion Cr(VI)</i>	–	8.5E – 04	4.5E – 03
<i>HI</i> – Residential activity	–	0.142	0.757
<i>HQ</i> – Occupational activity			
<i>inhalation Cr(III)</i>	7.0E – 01	–	–
<i>inhalation Cr(VI)</i>	2.8E + 01	–	–
<i>waste ingestion Cr(III)</i>	6.0E – 03	–	–
<i>waste ingestion Cr(VI)</i>	1.5E – 02	–	–
<i>HI</i> – Occupational activity	<b>2.9E + 01</b>	–	–
<i>ELCR</i> – Occupational activity <i>inhalation</i>	<b>2.9E – 03</b>	–	–

chance in 1,000,000 ( $1 \cdot 10^{-6}$  or  $1E-06$ ) to be small enough for regarding them as negligible and risks above  $1E-04$  to be sufficiently large that some sort of remediation is desirable.

Estimation of the risk associated with chromium exposure is a complex issue and the obtained results require the application of the precautionary approach in order not to underestimate the health hazard. Cr(VI) is not as stable as Cr(III) because it is a strong oxidizing agent. It is fast reacting, and forms complexes. The oxidation number of Cr in groundwater is governed by pH and redox potential Eh (Jacobs and Testa, 2004). Therefore it was not possible in this study to apply the so called “best justified” scenario. Instead of it the “most conservative” approach was applied as described by Frangos (2011). The study carried out demonstrated that the main risk factor for people is dust emission and airborne chromium associated with occupational activity. On the other hand, concentration of Cr(VI) and Cr(III) in the soil and water does not pose a real risk to human health. Similar conclusions are presented by Paustenbach et al. (2003) which reported results of studies involving human volunteers.

Concentrations of Cr(VI) found in ground water should not have a major impact upon the health risk even in the event of accidental consumption. Cr(VI) contents in the ground water oscillates around 0.01–0.04 mg/L. In his research Finley et al. (1996) concluded that even about 2 mg/L should not be clearly damaging to people's health.

The ELCR values similar to the authors results were obtained by NIOSH (National Institute for Occupational Safety and Health, USA). The estimates of excess lifetime risk of cancer resulting from occupational exposure to Cr(VI)-containing mists and dusts in a cohort of Baltimore, MD chromate chemical production workers at  $1 \mu\text{g}/\text{m}^3$  was 0.00205 (Proctor et al., 2016). On the other hand, the estimated ELCRs for residents at Stockton in Australia where an incident occurred at the Orica plant located at Kooragang Island on 8 August 2011 were very low. They ranged between  $4.0E-07$  and  $2.0E-06$  (Frangos, 2011).

In order to lower the occupational non-carcinogenic hazards as

well as the carcinogenic risk, it is necessary to apply some effective measures to reduce dust emission and protect the workers. We would recommend developing, if possible, wet operations and wet processing of the waste material. Sprinkling the waste material with water could be advisable. Also dust extraction attachments, dust filters and particularly individual protection accessories like dust masks, dust protective cabins, etc. should be prescribed.

As far as the residents are concerned, the waste dump does not arouse any reservations related to the health standards. The calculated HQ values do not exceed unity, both for adults and children.

#### 4. Uncertainty analysis and discussion

It should be emphasized that the obtained results have to be interpreted cautiously, taking into account numerous conscious uncertainties and simplifications made during the risk considerations. They could not be avoided because of certain inevitable assumptions. Nevertheless, the obtained results made it possible to evaluate the hazard and health risk levels expected at the sites affected by the chromium waste dump.

The ambiguities result from the imperfection of the chemical analyses, the simplifying assumptions and the incompleteness of some toxicological data on chromium toxicity. The procedure presented here is based on the conservative approach to risk assessment, which tends rather to overestimate than underestimate the risk. The main factors contributing to assessment uncertainty are:

- The lack of routine and systematic data from monitoring of the environmental samples collected at the area concerned. It is not known whether the concentrations of chromium in groundwater, soil and especially in the air will remain at a constant level over the longer period of exposure time.
- The concentration of dust in the air strongly depends on weather conditions, air humidity, wind direction and speed, etc. This implies severe fluctuations in the measured values affecting the risk calculations.
- Because of the lack of data on the absorption coefficients of chromium in the human body, the coefficient was assumed to be equal to 1 for all the chromium forms.
- There was no distinction made between different chromium forms for the hazard quotients calculations. For that purpose, for the Cr(III) hazard calculations, the total chromium contents reduced by Cr(VI) contents was applied, which could involve an overestimation of the hazard posed by trivalent chromium. In fact, such an approach did not have a significant contribution to the Cr(III) hazard quotients.

#### 5. Conclusions

The investigations of the chromium emissions from the waste dump showed quite high concentrations of its trivalent and hexavalent forms in the environment. The level of non-carcinogenic

hazards determined for the residents' scenario does not arouse any concern both for adults and children. The situation is completely different in the case of the occupational exposure scenario related to waste dump processing. The calculated carcinogenic risk is extremely high, which implies the necessity of careful revision of all unit operations included in the waste processing line in respect to hazard reduction. The major hazard is connected to dust emissions to the environment. The same remarks concern the non-carcinogenic hazards and calculated hazard quotients, which strongly exceed the acceptable standards.

Under the current toxicity standards, the investigated occupational activity requires protective measures in order to reduce the workers' exposure to dust emissions. There are relatively simple methods of exposure reduction available, which certainly should be implemented by the contractor during the industrial processing of the waste.

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