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EVALUATION OF CHROMIUM EXPOSURE IN ADULTS AND CHILDREN AROUND MAROS KARST IN INDONESIA

Annisa Utami RAUF[1,2*], Anwar MALLONGI[2], & Ratna Dwi Puji ASTUTI[2]

[1]*Department of Health Behavior, Environment and Social Medicine, Faculty of Medicine, Public Health and Nursing, Gadjah Mada University, Yogyakarta 55281, Indonesia. *corresponding author: annisaur@ugm.ac.id*

[2]*Department of Environmental Health, Faculty of Public Health, Hasanuddin University, Makassar 90245, Indonesia.*

Abstract: Chromium is a potentially toxic metal due to several acute and chronic effects on human. Chromium can accumulate in the soil and water as the result of weathering processes, industrial emissions, tanneries, and inorganic fertilizers. This study aimed to evaluate the potential threat from Cr exposure in adults and children of the community around Maros karst, Indonesia. The level of Cr was investigated on twenty soils and sixteen well water using Atomic Absorption Spectrophotometry (AAS). The integrated health risk assessment method from the United States Environmental Protection Agency (USEPA) and Monte Carlo simulation approach with 10,000 iterations were applied to assess non-cancer and cancer risk through combined pathways, ingestion and skin contact. The non-cancer risk with 95% confidence demonstrated that Cr exposure in adults and children was below the permissible limit (THI<1). The final prediction using human health risk assessment showed that the non-cancer risk for both receptors was considered acceptable. However, the total cancer risk (TCR) values exceeded the acceptable risk value of USEPA in children (2.33 x 10^{-4}) and adults (2.18 x 10^{-4}), indicating children have a greater risk for developing cancer than adults. Ingestion rate (IR) (26.0%) and Cr concentration in soil (26.4%) were the most important variables in determining cancer risk for adults and children, respectively. The findings could be valuable for managing well water consumption and soil remediation in residential areas.

Keywords: Health risk; chromium; dermal contact; oral intake; Monte Carlo simulation.

1. INTRODUCTION

Karst is a hill or mountain formation consisting of limestone, marble, dolomite, halite or gypsum. The karst region supplies approximately 25% of the world's water (Lucon et al., 2020). Naturally, the contamination of karstic rocks is relatively high due to mining exploration and non-karstic interbedding (Veress, 2016). The weathering of carbonate rocks influences groundwater quality in the karst system and increases the amount of released minerals (Kumar et al., 2018; Zhang et al., 2017). The karst area provides many sources of raw materials for the processing of cement products, coal mines, and smelting activities (Astuti et al., 2023). Anthropogenic activities and natural contamination in this area will release high concentrations of potentially toxic elements such as cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb), nickel (Ni), copper (Cu), and arsenic (As), which are harmful to the environment and human health (Genç, 2021; Xiao et al., 2019; Zhang et al., 2019).

Chromium is one of the dominant elements that commonly found in karst areas (Astuti et al., 2021a; Rohani et al., 2023; Rauf et al., 2021a). Usually, this element is produced from fly ash, geochemical processes, fuel combustion and mining. Anthropogenic activities will increase high level of chromium compounds and affect the quality of groundwater, air and the land (Hausladen et al., 2018; Tiwari et al., 2019). Chromium is one of the most hazardous metals that classified as a carcinogen by the International Agency for Research on Cancer (IARC). Chromium has two oxidation states, hexavalent chromium and trivalent chromium. Hexavalent chromium (Cr(VI)) possibly damages human cells, leads to metabolic problems, and induces mutations by its direct reaction to DNA (IARC, 1990; Nordberg et al., 2015). Trivalent chromium (Cr(III)) is less toxic than Cr(VI). The general population is exposed to

Cr(III) by eating food, drinking water, and inhaling air-containing chemicals (ATSDR, 2008).

Workers and residents around mines or factories are populations that are vulnerable to Cr exposure in the environment. High levels of chromium in drinking water are associated with adverse health effects (Ray, 2016; Zhu & Costa, 2020). Previous evidence shows that Cr (VI) poses a severe threat to rat livers and chronic Cr poisoning (Yang et al., 2021). Mucous membranes may experience burns, irritation, and allergies because of Cr (VI) contact to the skin. After entering the bloodstream, Cr can distribute into the body (kidney, liver, and GI tract), causing protein signalling changes and genomic instability (Ge et al., 2018).

Health risk examination is a vital proxy to assess the hazard of a few contaminants (Li et al., 2018; Mallongi et al., 2022a; USEPA, 1989a). Therefore, knowing pollutant sources and their potential contamination is an essential tool for managing human health risks (Wang et al., 2022). This method helps to track the potential risks of toxic substances in the environment as a reference for policymaking and mitigation strategies in the future (Mallongi et al., 2022b; Jiang et al., 2021).

Located on the west side of Makassar City, Maros region is known as one of the largest karst areas in the world. Maros has archaeological sources from prehistoric caves from thousands of years ago. The prehistoric cave sites in Maros-Pangkep comprise a karst landscape. There are hundreds of caves with stalactites and stalagmites. Few decades ago, some locations in this area are used to be stone quarries and cement factories (Mallongi et al., 2022a; Rauf et al., 2021b). Due to geological conditions, changes in land use, and the rise of anthropogenic activity in the area, pollution can occur and increase the accumulation of harmful substances in environmental media. Previous studies have shown a severe condition where Hg and Cr accumulate in soil and well water (Midula et al., 2023; Astuti et al., 2021a; Rohani et al., 2023). Dust generated from the dry processing of raw materials and involving high temperatures will be released into the environment and reach nearby settlements.

Chromium accumulation in soil and water may derive from industrial activity and natural weathering from soil parent materials (Wang et al., 2022). However, there is a lack of information about the health effects possibility from Cr accumulation and the most influential variable related to cancer and non- cancer risk. The study aimed to evaluate the health risk of Cr exposure through dermal and oral pathways, identify the dominant route, assess the most influential factor, and possible health effect on adults and children in the nearest population.

2. METHODS

2.1. Study Area

Maros regency is in an altitude range of 0 to 1000 m above sea level. There are several inactive mountains in this region, where almost all villages in Maros are on sloped land and hills. The minimum temperature of the study area is 23°C in July, and the maximum temperature is 34°C in October. Maros and Pangkep Regency have some of the most extensive karst resources in the world. However, this area is vulnerable and prone to environmental degradation due to human activities and the natural weathering process (Astuti et al, 2021b). The sites are surrounded by exploration activities such as mining marble, limestone and cement.

2.2. Sampling Collection

Soil and groundwater wells were collected on April 20, 2022. Each specific location was recorded using GPS Garmin ETrex 10. About 800-1000 g of samples took from 20 surface soils (0-25 cm), placed into a zip-lock plastic bag, and labelled. All soil samples were placed on a tray and dried after being separated from roots, stones, and other unneeded components. Samples digested with the mixture of HNO_3:$HClO_4$ added 5 mL H_2SO_4. Crisis were measured using the PinAAcle 900H Atomic Absorbance Spectroscopy (AAS) PerkinElmer at 357.9 nm.

Groundwater wells were placed at High-Density Polyethylene (HDPE) and stored in the icebox. The concentrated HNO_3 (69%) was added until it reached pH 2. Then, dissolve the sample with 2 mL H_2SO_4, two drops of H_3PO_4, 0.5 mL diphenylcarbazide, and 25 mL aquabidest. The absorbance of the samples was measured using a UV-VIS instrument. Quality control of the instrument was performed using a Standard Reference Material (SRM1646a estuarine sediment) from the Department of Commerce, NIST, Gaithersburg, MD 20899 with three replications.

2.3. Health Risk Assessment

Human health risk assessment for calculating chemical intake from various media was formulated by the United States Environmental Protection Agency (USEPA). The guidance provides the estimation of toxicity values from ingestion and skin contact derived by the EPA Integrated Risk Information System (IRIS) called the reference dose

(RfD) (USEPA, 1989b).

Oral ingestion of water

$$ADD_{w-ing} = \frac{C\ x\ IR_{ing}\ x\ EF\ x\ ED\ x\ CF}{AT\ x\ BW} ..\ Eq. 1$$

Oral ingestion of soil

$$ADD_{s-ing} = \frac{C\ x\ IR\ x\ EF\ x\ ED\ x\ CF}{AT\ x\ BW} \ldots..\ Eq. 2$$

Dermal contact with water

$$ADD_{w-der} = \frac{C\ x\ SA\ x\ Kp\ x\ ET\ x\ EF\ x\ ED\ x\ ABS_d\ x\ CF}{AT\ x\ BW} ..Eq. 3$$

Dermal contact with soil

$$ADD_{s-der} = \frac{C\ x\ ED\ x\ EF\ x\ SL\ x\ SA\ x\ ABS_d\ x\ CF}{AT\ x\ BW} \ldots Eq. 4$$

To calculate the non-cancer risk, we applied the hazard quotient (HQ). Both exposure pathways are estimated with the following expression.

$$HQ = \frac{ADD}{RfD} \ldots\ldots\ldots\ldots\ldots. Eq. 5$$

An assessment of the non-carcinogenic risk posed by multiple routes was conducted using a total hazard index (THI). RfD is the reference dosage of Cr in each route. This ratio represents the non-cancer risk from oral and dermal exposure. THI< 1 indicates that risk is negligible, but if THI>1, the non-cancer risk possibly exists.

$$THI = \Sigma\ HQ \ldots\ldots\ldots\ldots\ldots. Eq. 6$$

Cancer risk (CR) is the probability of chronic effects or developing cancer in humans that exposed to carcinogens (USEPA, 1989b). The cancer risk through oral and dermal was calculated using the following equation.

$$CR = ADD\ x\ CSF \ldots\ldots. Eq. 7$$

Where CR is the cancer risk and CSF stands for cancer slope factor. Slope factors were obtained from animal studies or previous epidemiological studies of adult populations. The existing animal results support the conclusion of the mutagenic actions and development of tumors as a result of chemical exposure (USEPA, 1989a). If the cancer risk values exceed 1x 10^{-4}- 1x10^{-6}, the risk is considered to be unacceptable. While values ≤1x10^{-4} are acceptable risk levels, one person per 10,000 will develop cancer due to the exposure.

2.4. Monte Carlo Simulation (MCS)

Risk assessment involves several activities, including building a mathematical model to relate exposure to a toxicant to the likelihood of an adverse effect. In this probabilistic risk approach, all the parameters used to assess the risk are considered distributions to achieve a wide range of outcomes (a risk or hazard quotient) after repeated simulations, usually 10,000 or more (Saha et al., 2016; Yang et al., 2019). In MCS, cancer or non-cancer risk estimation is classified as Y. The variables of interest in this study were Cr concentration (C), ingestion rate (IR), absorption factor (ABS_d), exposure duration (ED), exposure frequency (EF), body weight (BW), skin adherence (SA), defined as $\underline{X}$ (input parameters).

$$Y = h(\underline{X}) = h(X_1, X_2, \ldots, X_k) \ldots\ldots\ldots Eq. 8$$

These variables were obtained directly from the standard values (secondary data), interviews, and questionnaires from the exposure events that experienced by the residents. Monte-Carlo method was carried on to establish the simulation model, and the Crystal Ball software was used to calculate the risk.

3. RESULT AND DISCUSSION

Maros is an area surrounded by karst hills. This limestone karst area sits at the southern part of the Tonasa Formation. The karst landscape covers about 450 km^2 between 4°7′S and 5°1′S and is situated on an alluvial plain. This area also has prehistoric sites in the form of rock art in several caves as evidence of prehistoric art that has existed for thousands of years (Gagan et al., 2022). Limestone sources at Maros-Pangkep karst areas are used as raw materials for cement and gypsum production (Astuti et al., 2021b). In environmental media, the presence of toxic metals, including Cr, is caused by anthropogenic activities and natural erosion from geogenic rocks weathering (Zissimos et al., 2020). Mineral matters from the rocks released a low concentration of trace elements to soil and groundwater (Valencia et al., 2022; Demir, 2022). The majority of cement factories in Indonesia still use fossil fuel, which lead to distributed and transported of particulate matter more than 5 Km from emission sources.

The industrial activities may increase Cr levels due to the explosion of the karst mountains and the coal combustion process of cement-making materials. In groundwater wells, Cr(VI) standard is covered under the total chromium drinking water because these forms, with Cr(III), can convert back depending on environmental conditions. Hexavalent chromium in groundwater is also related to geogenic factors (Zissimos et al., 2020). Weathering of rocks that enter water bodies will produce some Cr ions in groundwater. In Aosta, Italy, industrial areas contribute to the high level and accumulation of Cr from superficial slag deposits from the nearest steel company. The Cr(VI) is also secondary contamination in unsaturated soil (Tiwari et al., 2019).

Table 1. Exposure factors and reference values

Parameters	Unit	Value	Definition
$\mathbf{ADD_{w-ing}}$	mg/(kg.d)	Calculated data	The average daily dose of water-ingestion
$\mathbf{ADD_{s-ing}}$	mg/(kg.d)	Calculated data	The average daily dose of soil-ingestion
$\mathbf{ADD_{w-der}}$	mg/(kg.d)	Calculated data	The average daily dose of water-skin contact
$\mathbf{ADD_{s-der}}$	mg/(kg.d)	Calculated data	Average daily dose of soil-skin contact
C	mg/(kg.d)	Site-specific	The concentration of an element in environmental media
$\boldsymbol{IR_{ing}}$	mg/d	100 (child), 200 (adult)	Ingestion intake rate
$\boldsymbol{RfD_{ing}}$	-	0.003	Benchmark dose/ estimate daily exposure
$\boldsymbol{RfD_{derm}}$	-	0.0006	Benchmark dose/ estimate daily exposure
SA	cm^2	Site-specific	Skin contact area
Kp	cm/h	0.002 (Cr)	The dermal permeability coefficient of a compound in water
$\boldsymbol{ABS_d}$	-	0.001	Dermal adsorption factor
SL	mg/cm^2	0.07 (child), 0.2 (adult)	Skin adherence factor
ET	hour(s)	2 (child), 8 (adult)	Exposure time
EF	day	Site-specific	Exposure frequency
ED	year	6 (child), 30 (adult)	Exposure duration
AT	day	ED x 365 (non-carcinogenic), 70 x 365 (carcinogenic)	Average exposure time
BW	kg	Site-specific	Body weight
CF	kg/mg	10^{-6}	Conversion factor

Concentrations of Cr in soil and groundwater wells at study area and various references are shown in Table 2. The data shows that the level of Cr(VI) in drinking water from groundwater wells is safe and below the maximum level according to several established standards. The National Standard of Indonesia, WHO (2011) and China were retrieved and recorded from the literature accessed. The average concentration of Cr(VI) in the present study indicates the quality of the groundwater wells is lower than Indonesian and WHO (2011) standards. Most of the well holes in this area are covered for preventing the dust or aerosols from emission and surrounding activities. This condition shows that Cr(VI) might come from natural geogenic factors. Kazakis et al., (2015) found the concentration of Cr(VI) in karst and deeper porous aquifers (Kazakis et al., 2015). A prior study in Pangkajene, Indonesia, showed the upstream area near the karst has a high presence of Cr(VI) and experienced an ecological risk in consumed well water (Astuti et al., 2021a).

Table 2. Chromium concentration and minimum level of contamination.

Organization/ Country	Standard Parameters	Cr (ppm)	References
Average concentration in present study	Drinking water (Cr^{6+})	0.0013	Site-specific
	Soil	48.551	
Indonesia (Ministry of Health; Ministry of Environment and Forestry)	Drinking water (Cr^{6+})	0.05	(PERMENKES, 2017).
	Outdoor soil	≤6300	(PERMENKES, 2017)
WHO	Drinking water	0.1	(WHO, 2011)
	Soil	0.1	(Kinuthia et al., 2020)
	Wastewater	0.05	(Chiroma et al., 2014)
	Soil	11	(Kinuthia et al., 2020)
	Wastewater	0.1	(USEPA, 1989a)
China	Soil	90 150 300	Grade I Grade II Grade III (Duzgoren-Aydin et al., 2006)

The high concentration of Cr total in the soil indicates the region may be experiencing an enrichment process and dry deposition from fly ash (Kinuthia et al., 2020; Rauf et al., 2020). Cr topsoil levels were associated with cancer, female mortality, Non-Hodgkin lymphoma (NHL), and gastrointestinal problems (Núñez et al., 2016). Another study in Moa City found that Cr enrichment in a residential area is higher as the distance increases from the industrial area (Zissimos et al., 2020).

The potential health effects of Cr are determined by the amount of intake (ADD), non-cancer risk (THI), and cancer risk (TCR) (Cocârţă et al., 2016; USEPA, 1989a; Xiao et al., 2017). The obtained intake data were summarized using simple descriptive statistics, including range, average, and standard deviation in Table 3. As shown in Figure 1, the THI values of Cr in both pathways were lower than the acceptable limit (THI<1) (17), indicating no adverse health effects to residences around the karst area.

The THI values of both groups were lower than the USEPA regulatory limit of non-cancer risk (THI<1), indicating the possibility to experience the non-cancer disease is low, and the risk is acceptable. However, it should be noted that regular consumption of Cr(VI) over a long period can cause digestive problems (ATSDR, 2008). This is also related to the level of Cr toxicity which can cause cell damage and inflammation in the digestive system even though there are no symptoms in short term exposure. Figure 2 showed the TCR values in both pathways from adults and children were exceeded the acceptable limit of 1.0 x 10^{-6} (USEPA, 1989a). The TCR values of adults and children in the 95th percentile was 2.18 x 10^{-4} and 2.33 x 10^{-4}, respectively. The presence of Cr(VI) as a carcinogen must be considered because all heavy metals are highly toxic, even at low concentrations (Ali et al., 2019; USEPA, 1989b; Plohák et al., 2022). Ingestion exposure of Cr(VI) is harmful to children due to its association with health problems including neurological inflammations and intellectual disability (FSCJ, 2019). The cancer risk is mainly caused by oral exposure, which 100 times higher than dermal exposure (Zhang et al., 2019; Gaurav & Sharma, 2020). Previous research found that children are significantly at risk of cancer than adults through ingestion, while dermal contact does not pose any severe threat (Rauf et al., 2021a). However, the combined risk of the two pathways will significantly increase cancer risk.

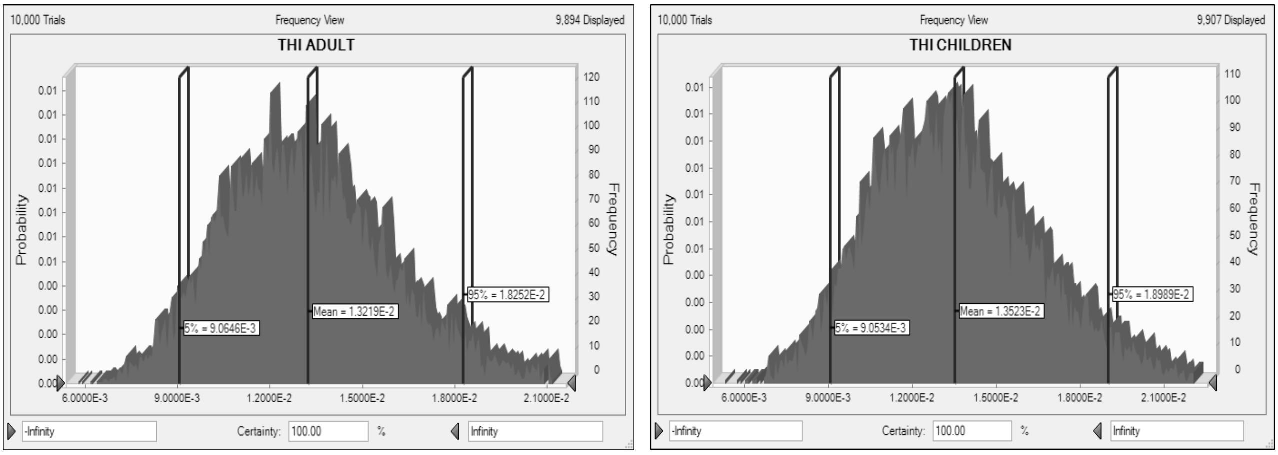

Figure 1. Total Hazard Index (THI) of adults and children.

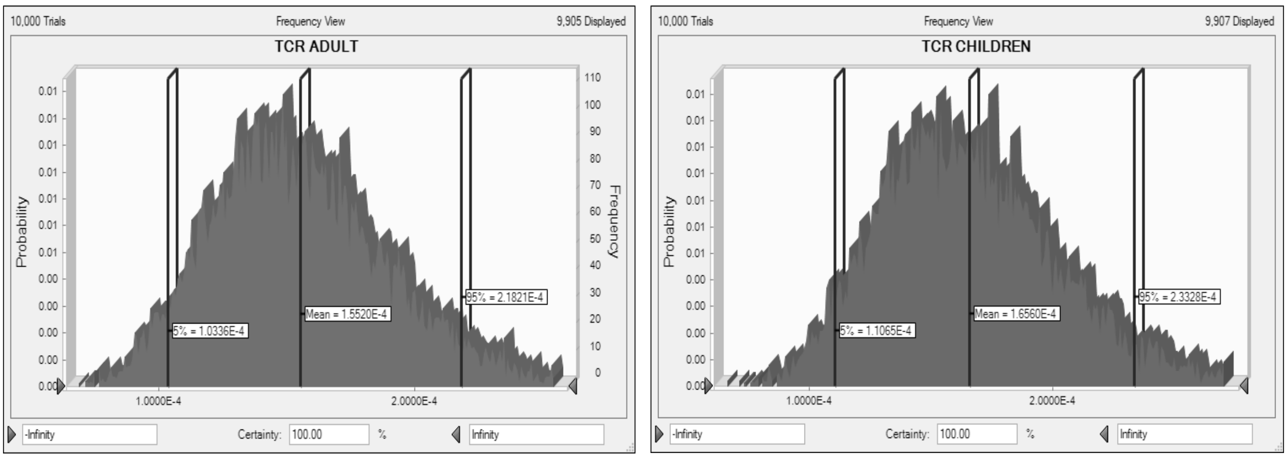

Figure 2. Total cancer risk (TCR) of adults and children.

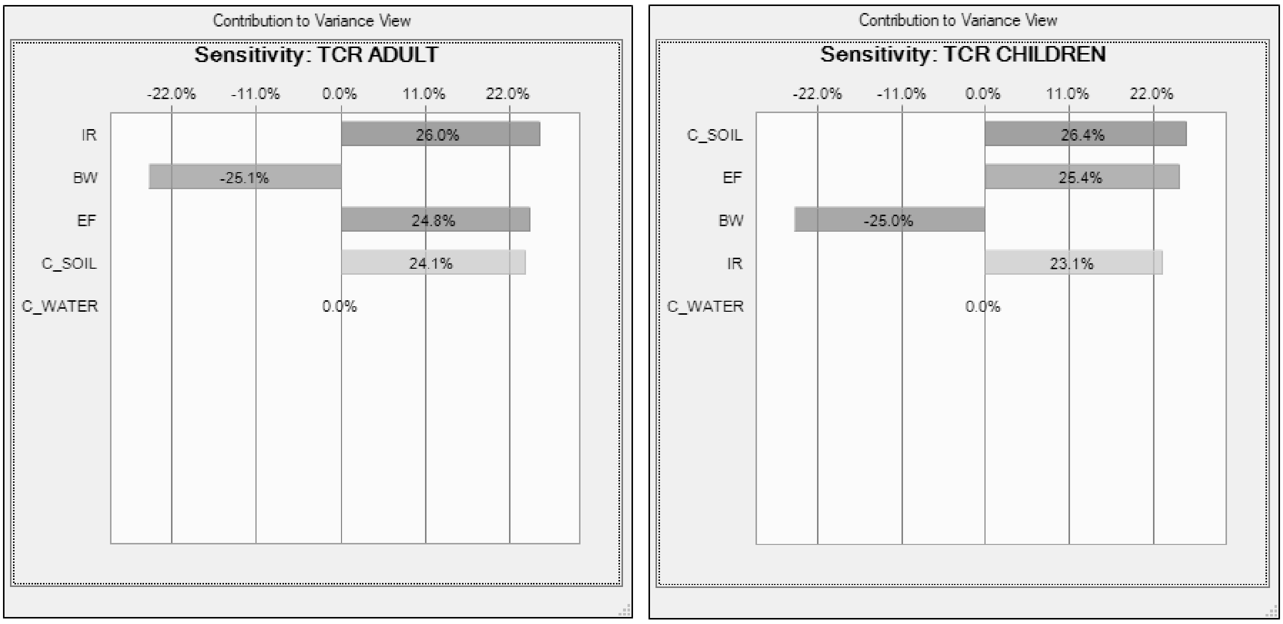

Figure 3. Sensitivity analysis of cancer risk in adults and children.

Increasing chromium (in the form of Cr(VI)) concentration and its accumulation around industrial area can significantly reduce the quality of drinking water and may pose high cancer risk for the local population (Astuti et al., 2023). In Odisha, India, the risk of skin cancer was lower than ingestion related-risk (Naz et al., 2016). Adults have a high potential for dermal exposure due to their outdoor activities and longer duration of working hours. This condition allows them to be exposed during the cultivating activity in agricultural land, fertilizer pollution, industrial emissions, dust, and soil resuspension. The skin may frequently contact to Cr in the soil before they wash their hands and bathe. Most people are exposed to Cr on the skin through resuspension from dust carried by fly ash and contaminated surfaces. Exposure to Cr in the skin can cause symptoms of itching, burning sensations, allergic reactions, skin ulcers, and redness (Langård, & Costa, 2015; Rauf et al., 2020).

The sensitivity analysis is shown in Figure 3. In adults, the IR of soil, EF, and Cr concentrations significantly contribute with 26.0 %, 24.8 %, and 24.1% cancer risk, respectively. IR had the most significant impact on elevating the cancer risk for the adult group. It is following a study conducted in Iran, where the consumption of drinking water contaminated with hazardous substances is affected by IR, followed by C and EF (Kalantary et al., 2022). In children, the most influential variable is Cr concentration in soil (26.4%), which indicated that high toxicity and long-term exposure to Cr through dermal contact and ingestion in soil media could increase the likelihood of cancer risk and adverse effects (Wang et al., 2022; Astuti et al., 2023).

Table 3. Average daily intake of Cr through ingestion and dermal pathways.

Media		Adult		Children	
		ADDingestion	ADDdermal	ADDingestion	ADDdermal
Soil	Range	2.3E-05 – 5.3E-05	2.5E-07 – 5.8E-07	2.3E-05– 5.8E-05	2.2E-08 – 5.5E-08
	Average	3.8E-05	4.2E-07	4.1E-05	3.9E-08
	CI 95%	8.6E-07	9.4E-09	2.4E-06	2.3E-09
	STD	6.8E-06	7.5E-08	8.4E-06	7.8E-09
Water	Range	6.2E-10 – 1.4E-09	5.5E-13 – 1.2E-12	6.2E-10 – 1.5E-09	3.3E-14 – 8.4E-14
	Average	1.1E-09	9.0E-13	1.1E-09	6.0E-14
	CI 95%	2.3E-11	2.0E-14	6.6E-11	3.5E-15
	STD	1.8 E-10	1,6E-13	2.2E-10	1.2E-14

4. CONCLUSION

Predictive models using MCS simulations can be used to predict cancer and non-cancer risks in human. This study observed the implications of long-term exposure that influence the health risk in local communities that exposed to Cr through combined pathways, skin contact and ingestion. It was found that the non-cancer risk was still within safe limits for adults and children (THI<1), while in contrast, the cancer risk in adults and children were exceeded the applicable standards from USEPA. High level of Cr in the environment are strongly associated with ecological and health problems. Toxicity and persistence of toxic metals in the environment must be a major concern, even though the concentrations are still within safe standards. The sensitivity model revealed that the most dominant factor in the cancer risk for adults and children were ingestion rate (IR) and Cr concentration. Periodic monitoring and removal of Cr ions from drinking water and topsoil must be the main focus of the government and researchers to prevent adverse health effects in local communities around karst area.

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