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폐광산의 토양 중금속에 대한 생태 및 인체 위해성 평가

Identification of Soil Pollution and Human Health Risk Assessments of Soil Heavy Metals in Abandoned Mine Area in the Republic of Korea

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농생명공학부 응용생명화학전공

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A Dissertation for the Master of Science

Identification of Soil Pollution and Human Health Risk Assessments of Soil Heavy Metals in Abandoned Mine Area in the Republic of Korea

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지도교수 노 희 명

이 논문을 농학석사 학위논문으로 제출함
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ABSTRACT

Soil contamination by heavy metals is a severe environmental problem worldwide. Increases in toxic heavy metal levels in soil environments due to anthropogenic activities are major environmental concerns because this not only leads to a decrease in agricultural productivity but also to an increase in risks to terrestrial organisms. Despite efforts to remediate and stabilize mining areas, over 30% of the mines in the Republic of Korea have remained abandoned over the last century. Pollution identification and human health risk assessments were carried out in this study to evaluate risks associated with the soils at the Daeyang Yeongseong mine, which has been abandoned since 1980. Based on land use, the soils were classified as abandoned, agricultural, or forest soils. The Igeo values obtained from the ecological risk assessment indicated that the soils were extremely contaminated with respect to Cd, and the ERI results revealed that all sites were Cd-contaminated. As contamination was found in 34.8% of the total area, and Pb contamination was found in 18.6% of the total area, and most of the contamination occurred around the mine. The human health risk assessment indicated that in both children and adults, the noncancerous risk from As in the mine soils exceeded the limit (HI>1), and the noncancerous risk to children from Cd in the mine soils was high relative to the other regions. Other than Ni, all carcinogens exceeded the limit (1x10-4) for children in one section. In the case of adults, the As limit was exceeded in the soils surrounding the mine. The fields near the mine posed potential cancer risks to the local population because the As levels exceeded the allowable limit for cancer risk in children and adults. Observations revealed that the weathering of mine debris resulted in the release of heavy metals into the surrounding soils, and soil erosion accompanied by water movement accelerated the increase in the contamination levels and the total affected area. The contamination levels detected in this study were significantly higher than in a

previous study, implying the possibility of heavy metal release to nearby drinking water reservoirs. These findings can help scientists understand and prevent risks from heavy metals in abandoned areas, and it is critical to develop remediation and stabilization plans to reduce risks from heavy metals present in crops, soil, and water.

Key words : Soil heavy metals, Pollution identification, X-ray fluorescence, Leachability analysis, Spatial analysis, Health risk assessment

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I. INTRODUCTION

Soil is a key component of natural and human ecosystems because it supports life by providing habitats and regulating nutrients and water supply. However, significant accumulations of trace metals and metalloids in soils due to natural processes and/or human practices can pose severe environmental and health problems to human communities and the environment.

Recent global economic advances, fueled by high-tech industries, have resulted in widespread heavy metal and metalloid pollution due to an increased demand for valuable and critical metals, such as tungsten (W), which are required for high-tech functionalities. Mining wastes (waste rocks and tailings) that are left near mine sites after beneficiation processes are carried out invariably cause long-term environmental and health problems because metal mining and waste discharges result in local heavy metal and metalloid pollution. Acid mine drainage from tungsten tailings poses additional environmental and health hazards. Cadmium (Cd), copper (Cu), chromium (Cr), zinc (Zn), lead (Pb), mercury (Hg), and the most dangerous element, arsenic (As), are among the pollutants included (Liu et al., 2010). Therefore, the high As concentrations found in most tungsten deposits may be a significant source of environmental risk associated with tungsten mining (Fan et al., 2017). As a result, heavy metal exposure associated with tungsten mining is the primary concern for environmental and human safety.

Approximately 2,000 abandoned mines have been identified thus far in the Republic of Korea, and the most polluted locations show heavy metal contamination and pose safety problems. Environmental pollution and safety issues in abandoned

mine areas are major problems since they can severely endanger human health in rural regions.

The accumulation of heavy metals is harmful to human health. Exposure to arsenic over an extended period can result in skin lesions, skin cancer, peripheral nerve lesions, and peripheral vascular disorders (Fang et al., 2014). Chromium can cause a variety of illnesses, including kidney, thyroid, lung, larynx, bladder, testicle, and bone cancer. When consumed, lead can harm the body's skeletal, circulatory, nervous, enzyme, endocrine, and immune systems. Zinc is likely to cause human cancer and is neurotoxic; therefore, it is the most significant heavy metal toxin. High doses of this substance can result in dermatitis, skin irritation, neurological problems, and neuronal necrosis even though it is not considered a human carcinogen. Cadmium is an extremely hazardous element. In humans, it causes cancer and has a carcinogenic, mutagenic, genotoxic, and immunotoxin effect (Balali-Mood et al., 2021; Mahurpawar, 2015). Although copper has the potential to harm the liver, kidneys, digestive system, mucous membranes, and central nervous system, it is not considered to be a human carcinogen. Contact with nickel can have several negative health impacts on humans, including allergies, kidney and cardiovascular disease, and pulmonary fibrosis (Genchi et al., 2020)

Heavy metal accumulation also prevents plant growth. Withering, morphological alterations such as chlorosis, browning, dehydration, growth inhibition, and metabolic interferences such as enzyme or hereditary toxicity damage can occur (Nagajyoti et al., 2010). Arsenic interferes with plants' ability to harvest light because it reduces the amount of chlorophyll and photosynthetic activity (Bali & Sidhu, 2021). Additionally, it leads to a decrease in chlorophyll levels and an inhibition in CO2 fixation enzyme activity (Abbas et al., 2018). Cr(VI) is most toxic

to plants. By targeting proteins, DNA, and membrane lipids, it compromises the integrity of cells (Stambulska et al., 2018; Sharma et al., 2020). According to research on seed germination inhibition, it negatively impacts the shape, growth, and photosynthetic processes of plants. An increase in soil zinc levels prevents the use of iron in leaves for the synthesis of chlorophyll and allows manganese to be transported to the leaves for the production of chlorophyll. Cadmium inhibits water transport and the absorption of many elements by plants. Additionally, cadmium alters membrane functions by damaging the membranes through peroxidation. It also prevents the production of active oxygen and chlorophyll and inhibits the progress of reaction-oriented photochemistry. Excess copper causes oxidative stress in plants by increasing the generation of reactive oxygen species (ROS), which are necessary adjuncts to metal proteins (Shabbir et al., 2020). In addition to being a component of enzymes that facilitate the hydrolysis of elements in plant tissues, nickel is a crucial metal in plant metabolism (Rahman et al., 2005). Physiological changes, sulfur whitening, and necrosis are just a few of the toxic symptoms that high nickel concentrations in the environment cause in plants (Rajkumar & Freitas, 2008)

Because of the aforementioned factors, heavy metals may pose threats to people, animals, and the entire ecological system through the food chain (Eziz et al., 2018; Gall et al., 2015). Due to these characteristics, heavy metal-contaminated soils are considered a major issue in many countries. As a result, studies on the environmental distribution and pollution of heavy metals as well as the hazards they pose to the environment and human health have increased in recent years (Doabi et al., 2018; Wu et al., 2018).

To address these concerns, the ecological risks from heavy metals and the human health risks from soils surrounding abandoned mines were assessed in this

study. The agricultural land surrounding the abandoned mines were evaluated for human risks. The objectives of this study were (1) to assess pollution risk, (2) to evaluate leachability and mobility, (3) to assess the human health risk from soils near the abandoned mines, and (4) to provide essential information for further stabilization and remediation measures.

Ⅱ. MATERIALS AND METHODS

1. Study Area

The Daeyang Yeongseong Mine, one of the Republic of Korea waste metal mines, was chosen as the research site for this study. It is situated at 36.976969 N 128.17895E in Seogok-ri, Susan-myeon, Jecheon-si, Chungcheongbuk-do, Republic of Korea. The Daeyang Yeongseong Mine (DY)'s primary ore type is tungsten, and its geology is composed of granite and limestone. It is currently closed, and a sizable amount of leftover rock has been abandoned. A small farmers community is located near the study area. The study area has a tiny community with a population of 2017. Both the road and mine are directly across from the village. The average annual temperature is 10.3 °C, with an average temperature of 23.8 °C in August and -4.8 °C in January, and the annual precipitation amount is 1,359 mm. Most of the precipitation (59.2%, 804.4 mm) falls during the summer season between June and August. In the mine area, numerous mineral pollution sources exist, which contribute to soil pollution. The pollutants that remain from earlier mining operations at waste mines can enter Cheongpungho Lake during the summer when the rains are heavy, and this lake is connected to nearby agricultural lands and villages. As a result, the DY Mine is a suitable research area for assessing health risks to local residents from heavy metal soil contamination.

2. Sampling sites

Forty-three soil samples were taken in October 2020 in the vicinity of the mine using a random sampling strategy. A clean seedling shovel was used to collect the 43 point samples at a depth of 10 to 30 cm, and the samples were placed in labeled plastic bags. Using GPS, the sampling point locations were noted at the site. The sampling locations at the waste mine site are shown in Fig. 1. The soil samples were transported to the laboratory, air-dried, and sieved to a size of 2 mm. The sieved soil was stored for laboratory analysis in plastic containers.

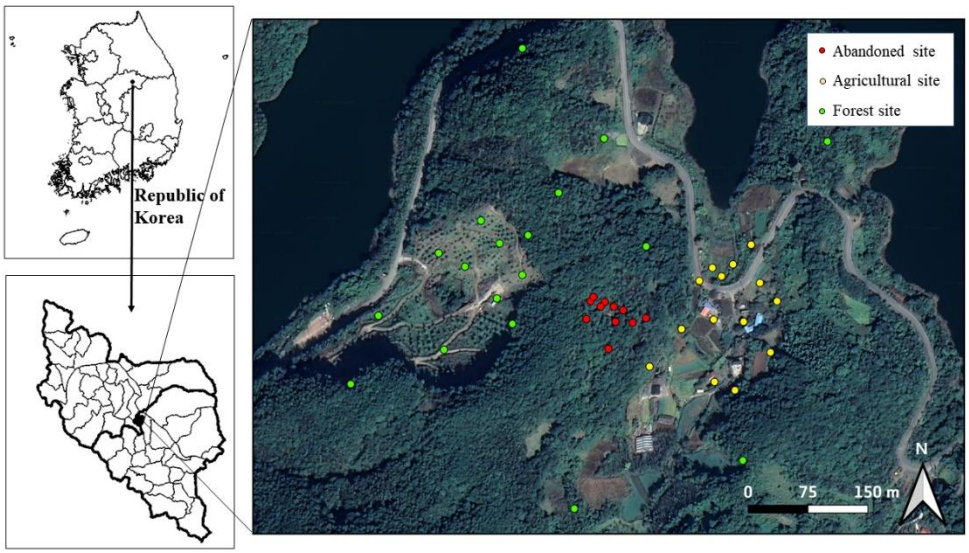

Figure 1. A map of the sampling site and study area. The colors red, yellow, and green represent abandoned, agricultural, and forest soils, respectively. In total, 43 samples were collected and plotted. Google Earth was used to create the satellite map.

3. Analysis of Soil Chemical Characteristics

A ratio of 1:5 soil to water was used to measure the pH and electrical conductivity (EC) of the soil in 50 ml polystyrene tubes. Twenty-five milliliters of water and 5 g of soil were combined and agitated well for 1 hour. The soil was precipitated and then measured (Orion versa star pro, Thermo Scientific Orion). The heat loss measurement method was used to calculate organic matter content (Heiri et al., 2001). The samples were placed in a crucible, heated to 550 °C for 4 hours, cooled in a drier, and weighed. The organic matter content was estimated by multiplying the initial sample weight by 100 and dividing the difference between the beginning sample weight and the final sample weight.

4. Analysis of Total Heavy Metal Concentration

X-ray-based spectroscopy is a nondestructive analysis method that can precisely identify the full chemical composition of elements in a sample. It provides both qualitative and quantitative information about samples by enhancing and automating workflow efficiency via rapid and accurate analysis and high throughput. The total metallic element content of the waste mine soil and the surrounding soil was examined using X-ray-based spectroscopy. By using XRF, the total amount of heavy metals in the soil was determined (ZSX Primus IV, Rigaku, Japan). Prior to measurement, all soil samples were ball-milled. All laboratory XRF analyses were conducted in triplicate. Excel was used to calculate each sample's mean and standard deviation. In this study, a total of 15 elements was evaluated, and these were

divided into 8 nutrients that are primarily used in field soils and 7 toxicologically important elements.

5. Extraction of Soil Water

Distilled water (DW) was used for extraction, which also resulted in conditions that resembled rainfall. Water extraction was used to assess element mobility, and the method used was adapted from a previous study (Cappuyns & Swennen, 2008). In the DW leaching test, a 1:1 ratio of soil to water was used, and after this mixture was left undisturbed for two weeks, the soil solution was filtered through a 0.45 micron filter. The filtrate was acidified with 1 ml of 10% HNO3, and inductively coupled plasma optical emission spectroscopy (ICP–OES, Thermoscientific icap 7200 ICP-OES duo) was used to assess the results. Triplicates were employed for measurements of all DW samples, which were diluted tenfold. The cadmium levels were typically below the detection limit in all samples; thus, they were not included in the comparison. The following equation was used to determine the ratio of water-soluble ions.

The percentage of water-soluble ions (%) = $\frac{C_{DW,i}}{C_{XRF,i}} \times 100$

where $C_{DW,i}$ is the element i concentration from the DW leaching test and $C_{XRF,i}$ is the element i concentration from the XRF.

6. Spatial Distribution Analysis

Spatial distribution analysis is a type of geographic analysis in which the spatial patterns of human behavior or environmental events are analyzed analytically and geometrically. Because of recent advances in remote sensing and geographic information systems, the results of this type of analysis are now clearer, easier to understand, and contain more spatial information than they did before. Thus, the spatial distribution of heavy metals in soils can be communicated to the public and government in a straightforward manner. For the spatial study, free and open source QGIS3.8.2 software was employed. The inverse distance weight interpolation method, which gives a neighboring site more weight, was employed to gauge the degree of contamination.

Sigmaplot 10.0 (Systat Software Inc.) was used to create box plots and scatter plots.

7. Index of Geological Accumulation (Igeo)

It is generally recognized that the geochemical fractions of heavy metals in soil have an important role in determining their environmental toxicity. A geological index was proposed to assess the possible geological danger of heavy metals. Soil environmental risk was assessed using an environmental index (the geological accumulation index). The degree of elemental contamination in the soil was calculated using the geological accumulation index (Igeo) as a guide. The geological accumulation index was first introduced by Muller (1969). It can be described using the equation below.

$$I_{geo} = \log_2 \left(\frac{Ci}{1.5 \times Cib}\right)$$

In this study, the heavy metal Cib values were collected from Korea (Ministry of Environment), and the global background soil median concentrations were employed. Ci and Cib are the concentrations measured for all heavy metals and the local geochemical background concentrations (Bowen, 1979). The soil contamination levels can be categorized as lightly contaminated (0< Igeo <1), moderately contaminated (1< Igeo <3), heavily contaminated (3 < Igeo<5), or extremely contaminated (5< Igeo) depending on the Igeo value (Table 1).

Table 1. The relationship between contamination level and geoaccumulation index (Igeo).

Contamination level	Value
Geoaccumulation index	
Uncontaminated	≤ 0
lightly contaminated	$0 < I_{geo} \leq 1$
Moderately contaminated	$1 < I_{geo} \leq 3$
heavily contaminated	$3 < I_{geo} \leq 5$
Extremely contaminated	$I_{geo} > 5$

8. Ecological Risk Index (ERI)

The ecological risk index (ERI) was used to assess the extent of soil heavy metal contamination based on the environment's reaction to heavy metal contamination factors (CF) and toxic response (Tr). To assess the potential ecological effects of heavy metals, Hakanson (1980) proposed an ecological index. The equation is as follows:

$$CF = \frac{Cn}{Bn}$$

$$ERI = CF \times Tr$$

Tr is 10, 30, 2, 5, 5, 5 and 1 for As, Cd, Cr, Cu, Ni, Pb, and Zn, respectively. CF is the ratio of the concentrations of each metal in the samples to the baseline or background concentration. Cn is the measured concentration of the metal in the sample, and Bn is the geochemical background concentration of the metal. The levels of certain harmful effects are categorized based on the Eri scores as low risk (Eri<40), moderate risk (40< Eri <80), considerable risk (80< Eri <160), high risk (160 < Eri <320), and extremely high risk (320< Eri) (Table 2).

Table 2. The relationship between contamination level and value of the ecological risk index.

Contamination level	Value
Ecological risk index	
Low risk	$E_r^i < 40$
Moderate risk	$40 \leqslant E_r^i < 80$
Considerable risk	$80 \leqslant E_r^i < 160$
High risk	$160 \leqslant E_r^i < 320$
Extremely high risk	$E_r^i \geqslant 320$

9. Evaluation of Soil Ecological Toxicity

The OECD 208 Chemical Substance Test Guidelines are intended to identify and characterize potential chemical hazards. The OECE 208 test uses land plant types and standard seeds from selected plants to evaluate seed germination and growth, as well as the impact of substances on the early growth of higher plants.

The seeds of two agricultural plants were chosen based on their common use in phytotoxicity experiments: Indian mustard (Brassica juncea) and radish (Raphanus sativus). Brassica juncea and Rapanus sativus, two double-leaved plants with high heavy metal tolerance and germination rates, were used in a prior study to test plant toxicity (Bamgbose & Anderson, 2015; Kebrom et al., 2019; Manesh et al., 2018; Sinha et al., 2010). A Petri dish with a diameter of 90 mm was filled with 30 g of soil and 15 mL of DW. Ten seeds were planted in moist soil and incubated for 14 days at a temperature of 25±1 °C. Sixteen hours of light and 8 hours of darkness were provided.

Bagur-González et al. (2011) used the following index to evaluate acute phytotoxicity: root elongation as determined by the equation for RE.

$$RE = \frac{\text{Elong.sample} - \text{Elong.control}}{\text{Elong.control}}$$

where Elong.control is the average length of the seed roots in the empty control, and Elong.sample is the average length of the seed roots in the saturation extract (cm).

In this case, the soil utilized as the control had an Igeo value of less than 1 for all values except Cd. High Igeo values for Cd were present in all soil types and were therefore not further evaluated. L is the average root length, and N is the average number of seeds that germinate. The index values vary from -1 (maximum phytotoxicity) to > 1 (stimulation of seed germination or root growth). Negative RE values indicate phytotoxicity, while positive values indicate radicle lengthening or seed germination stimulation. Phytotoxicity levels are classified into four categories based on RE values: low (0>RE>-0.25), moderate (-0.25>RE>-0.5), high (-0.5>RE>-0.75), and very high (-0.75>RE>-1) (Bagur-González et al., 2011).

10. Human Health Risk Assessment

Some agricultural land in Republic of Korea is distributed around waste metal mining areas in forested areas. Mine erosion due to wind and rainfall, from metal-containing leachate infiltration to the surface during dispersion and rainfall loss, and from subsequent infiltration into groundwater are the main ways metals enter ecosystems (Okereafor et al., 2020; Sherene, 2010). These routes provide pathways for humans to be exposed to harmful heavy metal, and the health of both adults and children who live nearby can be endangered. Therefore, in this study, the negative effects of heavy metals on residents living in agricultural areas near waste metal mines was evaluated.

Moya et al. (2011) indicated that the health risk assessment (HRA) approach can be utilized to evaluate possible health risks from heavy metals (Yuswir et al., 2015). The model guidelines categorize the dangers to the human health posed by numerous exogenous substances into two categories. Noncancer risk (NCR) and cancer risk (CR). According to Bello et al. (2019), CR is generally defined as the likelihood for developing cancer for the rest of one's life as a result of exposure to particular contaminants or contaminant mixtures in the environment, while NCR is more closely related to chronic exposure, including genetic and malformation effects (USEPA, 1989).

Three routes of exposure to soil heavy metals were investigated in this study: oral consumption, skin contact, and inhalation. The study participants were divided into two age groups: adults and children. Equations (1), (2), and (3) were used to compute the average daily dose (ADD) of heavy metals (Adimalla et al., 2020;

Ahmad et al., 2021; Huang et al., 2021; Kumar et al., 2019).

(1) $$\text{ADDing} = Cs \times \frac{\text{IngR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \times \text{CF}$$

(2) $$\text{ADDderm} = Cs \times \frac{\text{SA} \times \text{AF} \times \text{ABF} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \times \text{CF}$$

(3) $$\text{ADDinh} = Cs \times \frac{\text{InhR} \times \text{EF} \times \text{ED}}{\text{PEF} \times \text{BW} \times \text{AT}}$$

In (1), (2), and (3), ADDing, ADDderm, and ADDinh are the average daily doses (mg/kg/day) due to ingestion, contact with skin, and inhalation, respectively. Cs is the concentration in grams per kilogram of soil, IngR is the rate of ingestion in milligrams per day, ED is the exposure duration in years, EF is the frequency in days per day, and CF is the conversion factor (10 E^{-6} kg mg^{-1}). BW stands for body weight (kg), AT for average dose period (days), SA for surface area of exposed skin (cm^2), AF for adhesion factor (mg/cm^2), ABF for skin absorption factor (no units), and PEF for emission factor (m^3/kg). In Table 3, the specific parameter values are displayed.

The probability of acquiring cancer in one's lifetime as a result of exposure to carcinogens is known as the cancer risk (CR) and is calculated as follows (Adimalla et al., 2020; Ahmad et al., 2021).

$$CR = ADD \times CSF$$

$$TCR = \sum CR$$

The cancer slope factor for each metal in this context (mg/kg/day; Table 4) is called CSF. The CSF value is a toxicity value that shows the relationship between received dose and response numerically. TCR is the total carcinogenic risk indexes. In general, risk values between 1×10-4 and 1×10-6 are regarded as reasonable.

Table 3. Calculation parameters and values used in the health risk assessment model to evaluate exposure risk.

Parameter	Description	Unit	Children	Adult	Reference
ABF	dermal adsorption factor	-	0.03（As） 0.001（other metlas）		Khan et al. 2020
AT	exposure to contaminated	day	365× ED		Khan et al. 2020 US EPA, 2002
AF	skin adherence factor	mg/cm^2	0.2	0.07	Khan et al. 2020
BW	average body weight	kg	15	70	Khan et al. 2020
ED	exposure duration	years	6	24	US EPA, 2011 Khan et al. 2020
EF	exposure frequency	day/year	180	180	Khan et al. 2020
PEF	particle emission factor	m^3/kg	1.36×10^9	1.36×10^9	Khan et al. 2020
R_{ing}	ingestion rate of soil	mg/day	200	100	US EPA, 2011 Khan et al. 2020
R_{inh}	Inhalation rate	m^3/day	7.6	20	Franklin Obiri Nyarko et al. 2021, Narsimha Adimalla et al 2020
SA	exposed skin area	cm^2	1150	2145	Khan et al. 2020

The equation for proposed risk index (HQ) calculates and evaluates noncancer risk (Adimalla et al., 2020; Ahmad et al., 2021).

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

RfD refers to the reference dose of each metal under various exposure pathways (mg/kg/day, Table 4).

The risk index (HI) was derived from the equation for the total noncancer risk from various chemicals and/or exposure pathways (Adimalla et al., 2020; Ahmad et al., 2021). An HI value > 1 indicates a potential noncancer effect, whereas an HI value < 1 indicates no danger unrelated to cancer.

Table 4. Reference dose for noncancer effects (RfD) and cancer slope factors for cancer effect (CSF) values of metals in soils by different exposure pathways used in the health risk assessment model in this study.

elements	*RfD*（mg/(kg · d)）			*CSF*（(kg · d)/mg）		
	ingestion	dermal contact	inhalation	ingestion	dermal contact	Inhalation
As	3.00E-04[a]	1.23E-04[a]	3.00E-04[a]	1.50E+00[a]	3.66E+00[b]	1.51E+01[b]
Cd	1.00E-04[a]	1.00E-05[a]	1.00E-04[a]	3.80E-01[a]	n/a	6.30E+00[a]
Cr	3.00E-03[a]	6.00E-05[a]	2.86E-05[a]	5.00E-01[a]	n/a	4.20E+01[b]
Cu	4.00E-02[a]	1.20E-02[a]	4.02E-02[a]	n/a	n/a	n/a
Ni	2.00E-02[b]	5.40E-03[b]	2.06E-02[b]	n/a	n/a	8.40E-01[b]
Pb	3.50E-03[a]	5.25E-04[a]	3.25E-03[a]	8.50E-03[a]	n/a	4.20E-02[a]
Zn	3.00E-01[b]	6.00E-02[b]	3.00E-01[b]	n/a	n/a	n/a

n/a, data not available. [a] Ahmad et al. (2021), [b] Huang et al. (2021)

Ⅲ. RESULTS AND DISCUSSION

1. pH, EC, and Soil Organic Matter

The values of the descriptive statistics (means, standard deviations, maximum, and median) for soil physicochemical parameters at the DY sites are shown in Table 5. One of the key factors that affect how readily available, retained, and mobile nutrients and heavy metals are in soil is pH. Heavy metal contamination, high pH, limited cation exchange capacity, low concentrations of organic matter, and low nutrient concentrations are important challenges that mine soils from metal mining areas present to the survival of living organisms (Akala & Lal, 2001; Asensio et al., 2011; Barrutia et al., 2011; Mourinha et al., 2022). Acid mine drainage occurs when sulfides in rock fragments oxidize (Johnson & Hallberg, 2005; Lin et al., 2007). The low pH of the mine soil leads to problems associated with enhanced metal solubility (Lombi et al., 2002; McBride et al., 1997). To prevent pollution and ecological risk due to these environmental issues, mine soil quality must be improved.

For the soils in this study, the average pH and EC were 6.9 and 208.24, respectively. The average pH of mine soil is 4.75 EC at 422μS/cm, and the average pH of agricultural soil at 7.63 EC at 149μS/cm. The waste soil had a lower pH and a higher EC value than the agricultural soil, as shown in Table 5. The alkaline pH values were found a distance of approximately 95 m from the pit entrance. This is supported by the pH distribution for the area shown in Fig. 2. Additionally, the figure

shows soil pH tends to increase with distance from the waste mines. This suggests that the farther the distance is, the lower the impact of the waste mine.

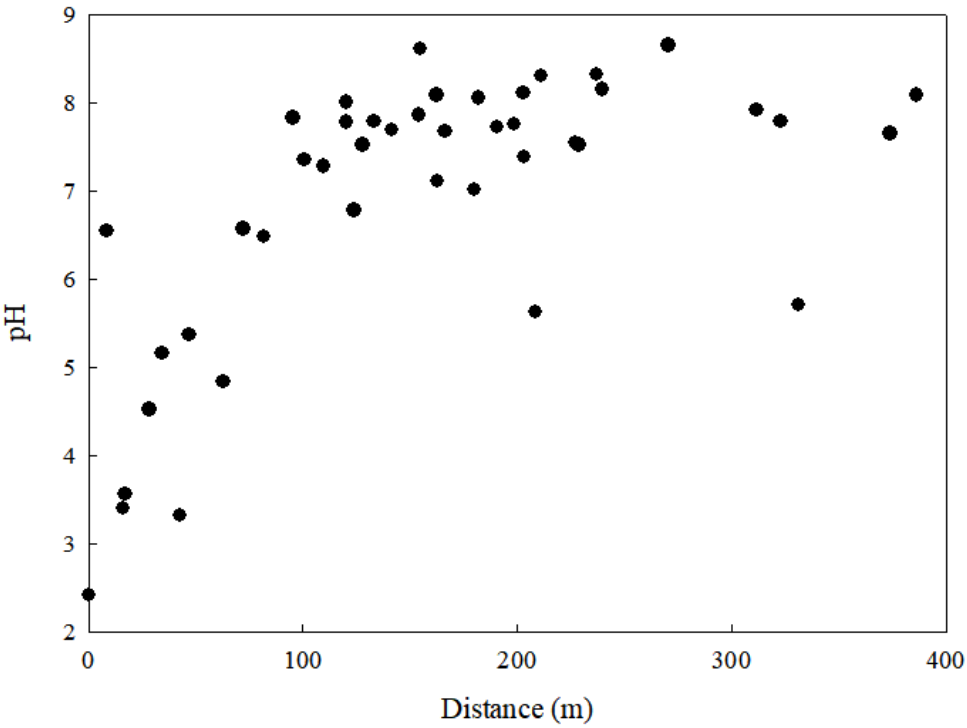

Figure 2. The relationship between distance from mine pit and pH.

The average EC value in this study was below the recommended EC value for irrigation water, which is less than 0.7-0.75 dS/m (700-750 μS/cm), as per the FAO report (Ayers & Westcot, 1985; Bauder et al., 2011). However, the waste mine soil currently has a high EC value, and issues could arise if the EC value of the soil were to decrease, bringing about adverse effects.

The average soil organic matter (SOM) content of the soil was 5.29%. In the soil, organic matter can interact with heavy metals to create stable metal-organic complexes, which can decompose via oxidation to make metals biosoluble. This is a factor that needs to be examined.

Table 5. pH, EC, and SOM descriptive statistics.

Region	Elements	Maximum	Minimum	Mean	Std.	C.V
All soil	pH	8.65	2.43	6.91	1.55	22.5
(N=43)	EC(dS/m)	2356	21.7	208	356	170
	SOM (%)	16.9	0.98	5.29	2.86	53.9
Abandoned	pH	6.57	2.43	4.75	1.38	29.0
Soils	EC(μS/cm)	2356	21.7	422	651	154
(N=11)	SOM (%)	16.9	4.02	8.02	3.82	47.7
Agricultural	pH	8.61	5.64	7.63	0.70	9.14
Soils	EC(μS/cm)	305	38.1	149	78.6	52.8
(N=14)	SOM (%)	8.00	0.98	4.26	1.66	38.8
Forest	pH	8.65	5.71	7.67	0.62	8.10
Soils	EC(μS/cm)	222	80.5	124	33.2	26.7
(N=18)	SOM (%)	7.60	2.50	4.43	1.53	34.5

2. Total Heavy Metals Concentration

The elemental content and concentration of all soils, as determined by XRF, are listed in Table 6. Reference values are also provided for the global and Republic of Korean soil allowable limits. Clearly, the overall concentration of metals determined in this study had a higher average value than both the international and Korean soil quality criteria. However, only a portion of the soil that was near the abandoned mine showed these high values. Other than the value for As and Cd, the median values were lower than the reference values when compared with the global reference value. Arsenic had the greatest average concentration among the metals, followed by Pb and Zn.

Table 6. Summarize the mean, median, minimum, maximum of soil, and allowable contaminated soil limits.

Parameters	Heavy metals (mg kg^{-1})						
	As	Cd	Cr	Cu	Ni	Pb	Zn
Mean	3661	53	79	85	41	1055	817
Median	66	43	69	44	38	94	138
Minimum	1	10	13	4	8	0	29
Maximum	71585	160	263	567	115	12451	6136
Standard deviation	12152	36	43	109	21	2508	1426
Coefficient of Variance	332	68	55	129	51	238	175
WHO/FAO [a]	20	3	100	100	50	100	300
Republic Of Korea [b]	25	4	5(VI)	150	100	200	300

.[a] Khalid et al. (2017), [b] RKME. (2016)

3. Geological Accumulation Index (Igeo)

The spatial accumulation of individual metals is vital to thoroughly investigate to comprehend the severity of heavy metal environmental contamination and assess its potential risk. Table 7 provides a summary of the geological accumulation index (Igeo) evaluation values. According to Korean background soil calculations, the average value of heavy metals increased in the following order: Ni (-1.07), Cr (-0.61), Cu (0.22), Zn (0.84), Pb (1.50), As (3.34), and Cd. In particular, the average Igeo values of As and Cd exceeded 3 and 6, respectively, classifying them as pollutants of concern. The values for zinc and copper were only mildly affected, whereas that of lead belonged to the moderate contamination category. The accumulation of heavy metals in the soil plainly posed a threat to the environmental conditions of the soil in the area. However, some metals (Ni, Cr) in the soil showed low Igeo values, indicating nonsignificant contamination. The distribution of Igeo values is shown in Figs. 3 and 4. Nutrient elements other than magnesium (Mg) showed negative Igeo values, indicating that these soils were not contaminated and that these elements were primarily produced by natural processes and did not originate from the mines.

Kriging interpolation was applied to all samples using a digital mapping method to obtain visual data on the spatial distribution of Igeo. Fig. 6 reveals the heavy metal distribution pattern from the mining tailing ponds to the agricultural land. An examination of the map reveals that Pb and Zn contamination in the field soil was mostly concentrated in two locations along the mountain range, while Cd pollution was most widespread, and As pollution was found in most field areas where people reside. This can be explained by pollution deposition along with transport caused

by wind or water. Therefore, heavy metal contaminants from waste mining have the potential to significantly enhance environmental risks. To elucidate the trend more clearly, distance and the values of Igeo were compared (Fig. 6). Less heavy metal pollution was found in soils farther away from the waste mines; soils close to the mines were most polluted. As a result, as the distance from the waste mine increased, the pollution levels tended to decrease. Similarly, as the distance from the waste mine increased, the concentration of heavy metals (Cu, Zn, As, and Pb) steadily decreased in the field soil (Fig. 5). This finding also suggests that a common source of pollution was responsible for the contamination.

Table 7. Summary of the mean, median, minimum, maximum, and percentile geoaccumulation index values. The background levels were derived from the median concentration of world soils by Bowne (1979) and RKME (2016). The contamination levels were categorized based on the Igeo values: uncontaminated (Igeo≦0); slight contaminated (0< Igeo<1); moderately contaminated (1< Igeo<3); heavily contaminated (3<Igeo<5); and extremely contaminated (Igeo>5).

Parameters	Nutrient elements (%)								Heavy metals (mg kg^{-1})						
	C	Ca	Fe	K	Mg	N	P	S	As	Cd	Cr	Cu	Ni	Pb	Zn
Background level	3.48	1.5	4	1.4	0.5	0.5	0.08	0.07	6.83	0.3	25.4	15.3	17.7	18.4	54.3
Mean	-0.17	0.11	-0.58	-1.65	2.47	-0.14	-1.02	-0.47	3.15	6.63	0.85	1.19	0.43	2.43	1.57
Median	-0.26	0.69	-0.94	-1.40	2.69	-0.18	-1.12	-1.14	2.69	6.58	0.86	0.94	0.52	1.78	0.76
Minimum	-0.89	-5.73	-2.28	-4.32	0.33	-0.77	-2.72	-2.32	-3.36	4.47	-1.55	-2.52	-1.73	-3.79	-1.49
Maximum	1.84	2.86	2.46	-0.04	3.61	1.18	3.57	4.97	12.77	8.47	2.79	4.63	2.11	8.82	6.24
Standard deviation	0.50	1.88	1.14	1.03	0.78	0.37	1.13	1.90	3.62	0.83	0.78	1.32	0.76	2.72	2.10
Coefficient of Variance	-297	1722	-195	-62.3	31.6	-272	-111	-408	114	12.5	91.66	111	177	112	134
10th percentile	-0.71	-1.72	-1.21	-3.49	1.36	-0.58	-2.18	-1.92	-0.01	5.39	-0.22	0.15	-0.53	0.15	-0.33

25th percentile	-0.49	-0.74	-1.07	-2.00	2.06	-0.35	-1.87	-1.70	0.59	6.17	0.69	0.54	0.2	0.83	0.03
75th percentile	0.11	1.23	-0.72	-0.88	3.06	0.07	-0.52	-0.33	3.70	6.96	1.25	1.52	0.76	2.74	2.50
90th percentile	0.34	1.82	1.57	-0.60	3.22	0.31	0.05	3.30	9.76	7.95	1.63	3.39	1.440	7.01	4.97
Uncontaminated	28	15	36	43	0	29	38	36	5	0	5	3	7	2	10
Slight contaminated	14	11	1	0	3	13	4	0	8	0	21	20	30	11	14
Moderate contaminated	1	17	6	0	27	1	0	2	11	0	17	14	6	19	10
Heavy contaminated	0	0	0	0	13	0	1	5	11	1	0	6	0	2	5
Extremely contaminated	0	0	0	0	0	0	0	0	8	42	0	0	0	8	4

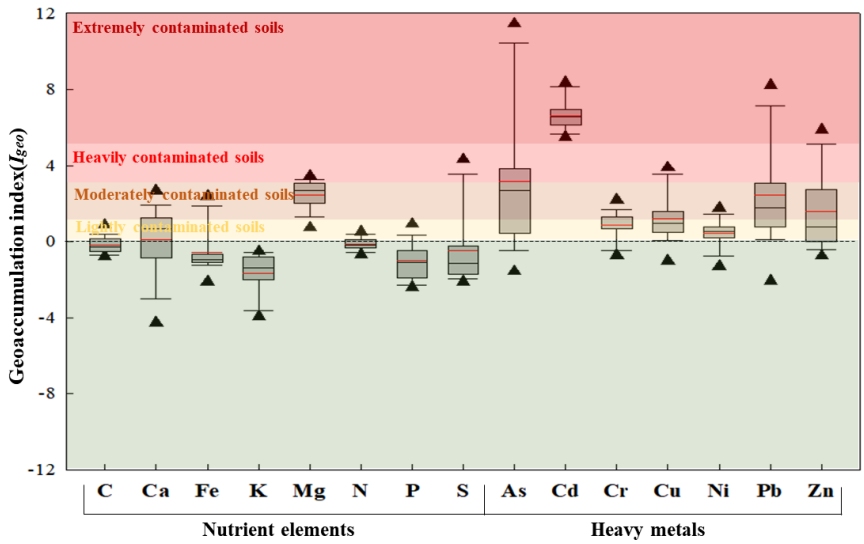

Figure 3. Box plot of the geoaccumulation indexes (Igeo). The median and mean are represented by the black and red horizontal lines, respectively. The box represents the 25th-75th percentiles, while the whiskers represent the 10th-90th percentiles. Uncontaminated, lightly contaminated, moderately contaminated, heavily contaminated, and extremely contaminated soils are represented by the green, yellow, brown, pink, and red colored areas, respectively.

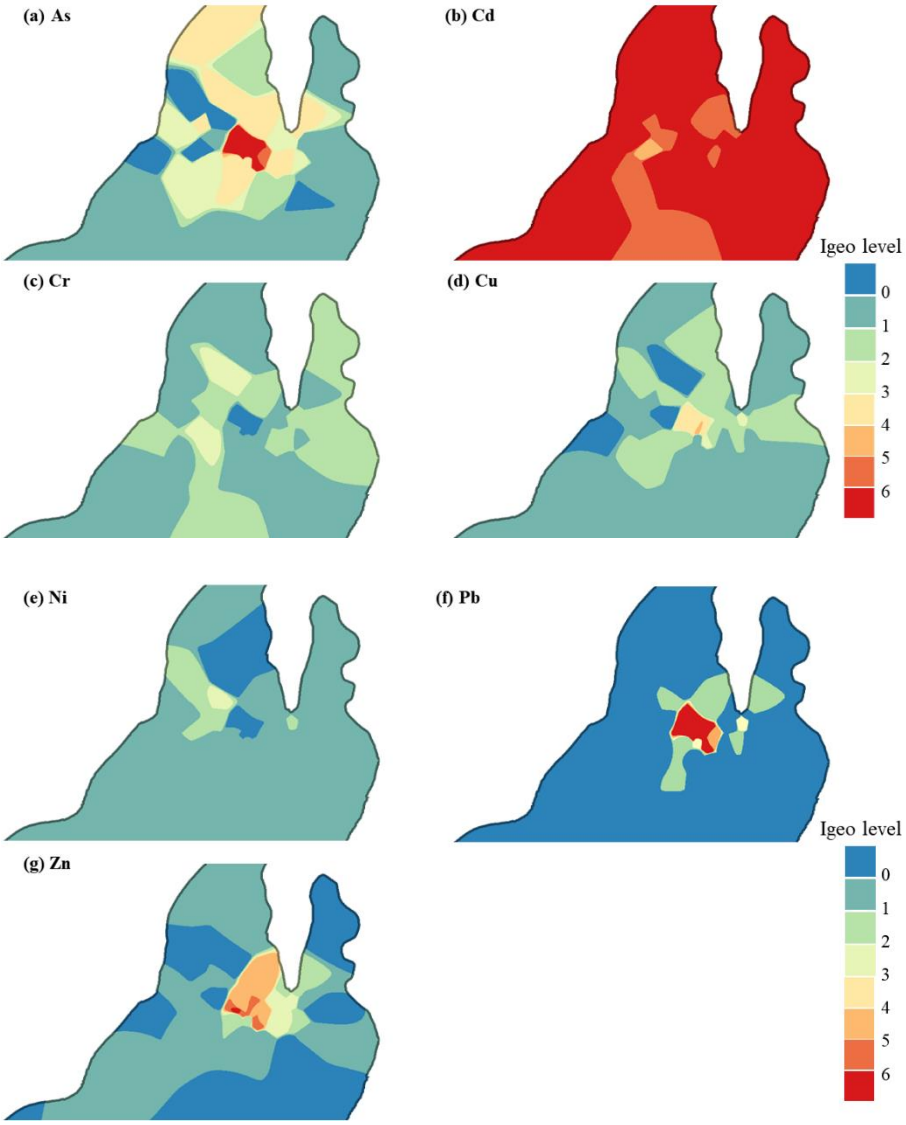

Figure 4. Spatial distribution maps of the geoaccumulation index of heavy metals.

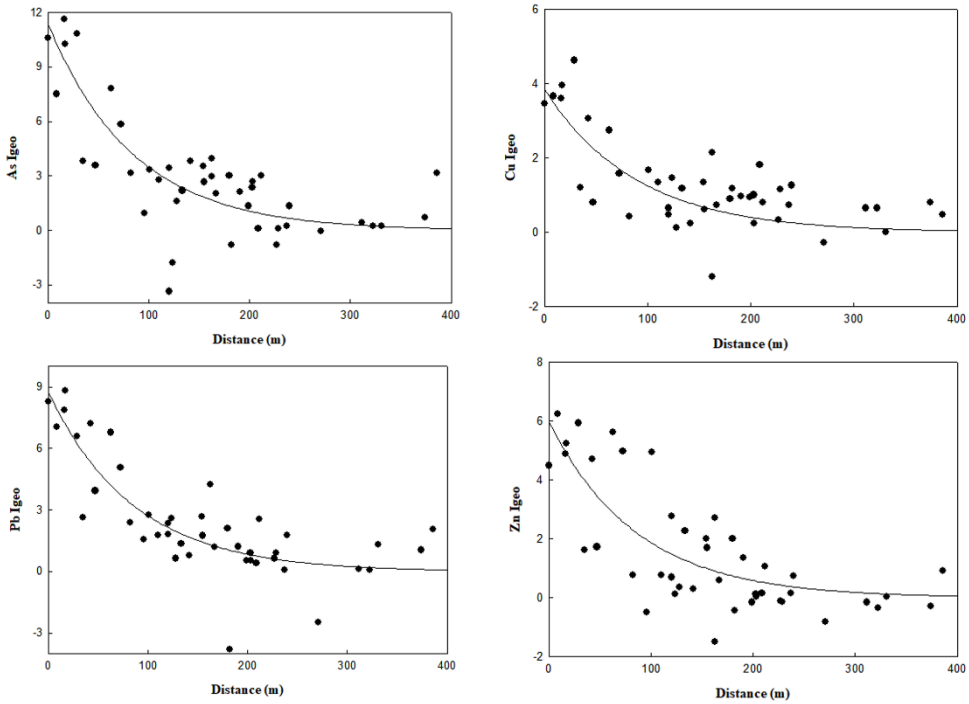

Figure 5. The relationship between distance from mine pit and Igeo of As, Cu, Pb, Zn

4. Regional Ecological Risk Index (ERI)

The ERI is frequently utilized to assess the possible ecological risk posed by pollutants such as heavy metals and their effects on an ecological system (Diami et al., 2016). Table 8 lists the specific findings of the potential ecological risk factor (ERI) for individual heavy metals. A distribution pattern resembling that of the Igeo values was found in the spatial distribution map (Fig. 6) of the ERI. Waste mine sites containing Cu, Pb, and Zn and sites contaminated with As and Cd were the sampling locations with the highest potential risk for each heavy metal. The soils around the mining and mineral resource areas in the fields had very high ecological risks due to the Eri values of As and Cd, which were determined to be above >320. In the study region, the individual ecological risk indexes of soil heavy metals decreased in the following order: Cd > As > Pb > Zn > Cu > Cr > Ni. A total of 34.8% of the total sites demonstrated a high risk for As, while 18.6% of the total sites demonstrated a significant risk for Pb. Other than Cd, As, and Pb, the soil heavy metal concentrations were not found to be environmentally hazardous. Eri is the individual heavy metal potential ecological risk index; bold type indicates sample sites with high or very high ecological risk.

When the individual ecotoxicity index of each heavy metal was compared with root growth from plant toxicity trials, a correlation was found between root growth length and heavy metals with high ERI values, such as cadmium, arsenic, lead, and zinc, which is shown in Fig. 7. Plants do not grow well in soil with high ERI values for each heavy metal. This enabled us to establish a connection between the plant toxicity experiments and the ecotoxicity index.

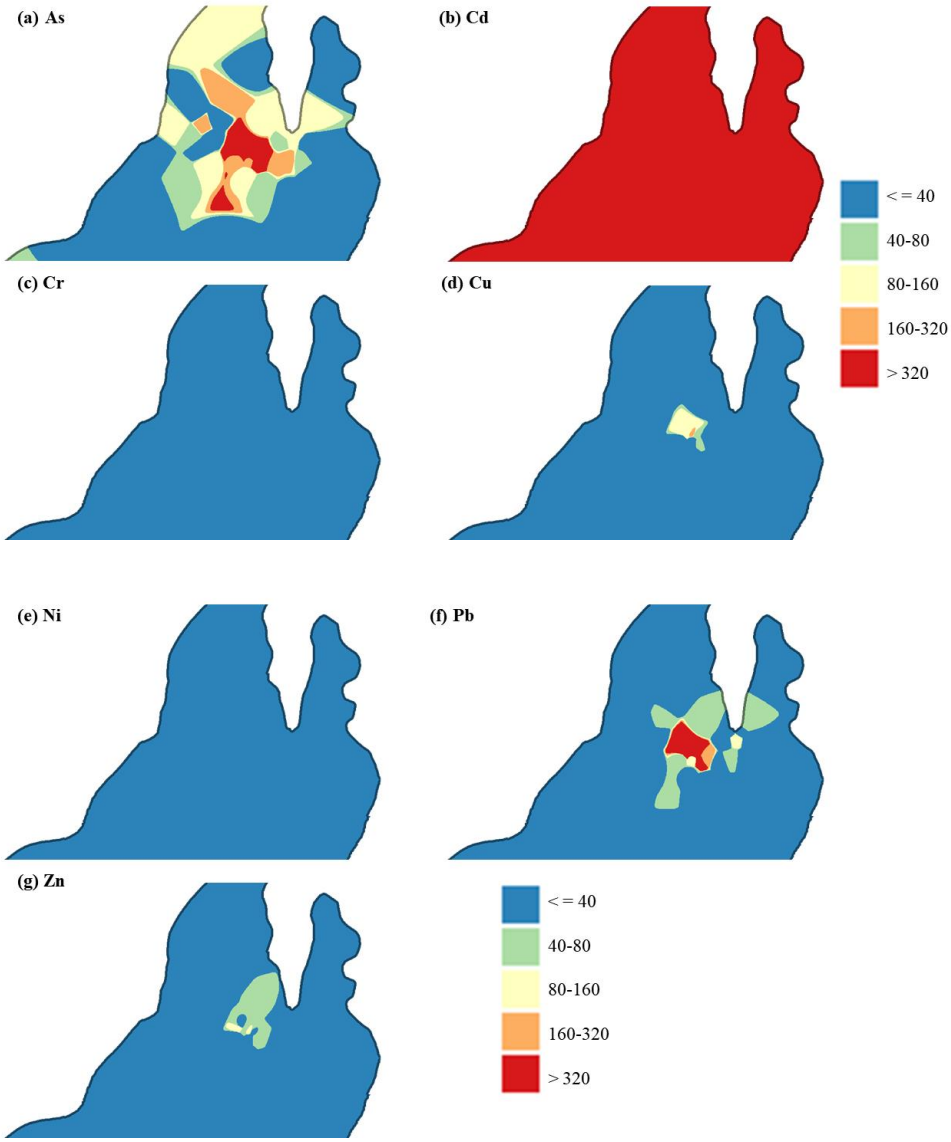

Figure 6. Spatial distribution maps of the ecological risk index for heavy metals.

Table 8. Potential ecological risk indexes for heavy metals at the potential ecological risk indexes of sampling sites.

Sample site	As	Cd	Cr	Cu	Ni	Pb	Zn
DY01	136.2	**3600**	5.04	10.46	8.76	31.25	2.85
DY02	38.07	**4000**	3.15	17.97	5.93	25.54	2.52
DY03	24.89	**4300**	6.77	13.07	13.28	15.49	1.23
DY04	**235.7**	**9400**	20.71	3.27	3.95	0.00	0.53
DY05	123	**4700**	5.43	13.07	9.32	44.57	3.11
DY06	8.78	**6200**	4.33	16.99	21.47	0.54	1.10
DY07	**212.3**	**2000**	8.35	8.82	17.80	13.04	1.84
DY08	4.39	**11600**	8.19	20.59	32.49	45.92	1.64
DY09	**152.3**	**2700**	8.35	23.86	13.28	50.82	46.26
DY10	68.81	**3300**	4.72	16.99	10.17	19.29	7.29
DY11	95.17	**2400**	5.51	11.44	11.58	25.27	4.86
DY12	117.1	**5200**	8.19	33.33	20.34	142.1	9.85
DY13	121.5	**3000**	6.38	14.05	11.30	32.07	5.99
DY14	16.11	**5800**	7.48	26.47	12.71	10.05	1.68
DY15	16.11	**5100**	6.38	16.67	11.58	14.13	1.36
DY16	96.63	**5100**	5.12	8.82	9.89	10.87	1.53
DY17	61.49	**4600**	5.51	12.42	11.30	17.12	2.27
DY18	1.46	**1000**	14.09	11.76	20.62	38.04	2.43
DY19	29.28	**2300**	9.53	1.31	26.84	22.01	1.07
DY20	**2737**	**7100**	4.96	95.10	12.15	**986.4**	113.00
DY21	**23108**	**13500**	1.81	83.01	2.26	**2352**	33.68
DY22	**47210**	**16000**	1.02	91.18	5.08	**173**	44.36

DY23	**18244**	**14900**	2.44	116.67	3.95	**338**	56.70
DY24	**27316**	**5600**	1.89	**185.29**	5.65	**715.2**	91.60
DY25	**104809**	**14900**	1.97	63.07	2.82	**1104**	39.34
DY26	**215.2**	**3800**	5.12	17.32	10.45	46.20	4.64
DY27	**178.6**	**4300**	5.28	13.07	11.02	114.7	4.95
DY28	**3401**	**6900**	3.46	50.33	7.91	**823.9**	74.18
DY29	**866.8**	**2400**	4.09	22.55	10.73	**253.8**	47.18
DY30	**164**	**5000**	9.53	10.46	11.86	26.36	10.22
DY31	**175.7**	**5000**	6.54	18.95	14.41	48.10	6.02
DY32	65.89	**4000**	5.91	14.71	10.17	17.39	3.81
DY33	17.57	**3300**	6.54	12.42	13.56	7.88	1.66
DY34	14.64	**5600**	8.27	6.21	8.19	1.36	0.85
DY35	76.13	**2300**	5.98	15.03	12.71	14.13	1.62
DY36	102.5	**5600**	12.44	18.95	7.63	25.82	2.58
DY37	133.2	**3500**	5.04	10.13	9.04	39.67	2.54
DY38	45.39	**3800**	5.35	8.17	9.32	11.68	1.92
DY39	38.07	**3000**	4.65	14.38	9.60	10.87	1.34
DY40	8.78	**3500**	5.12	9.48	12.43	11.68	1.38
DY41	17.57	**3700**	5.28	7.52	8.76	18.75	1.53
DY42	20.50	**4300**	5.35	11.76	12.15	8.15	1.34
DY43	17.57	**2300**	6.06	11.76	8.47	7.88	1.18

E_r^i is the individual heavy metal potential ecological risk index; bold type indicates the sample sites with high or very high ecological risk.

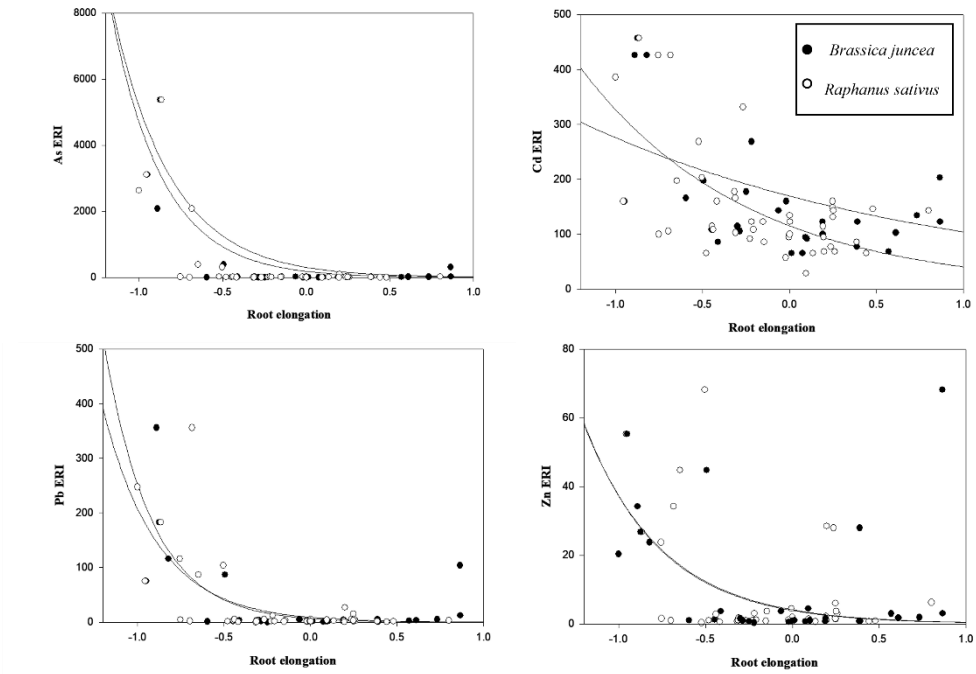

Figure 7. The relationship between root elongation and ERI (As, Cd, Pb, Zn).

5. Concentration of Potentially Leachable Heavy Metals

Heavy metal transport is a significant issue, in addition to the effects of heavy metal deposition in the soil. Rainfall causes soil from closed mines to be carried to areas where people dwell. The waste mines may be the source of heavy metals in the fields below the mines. Long-term heavy metal pollution released from abandoned mines can inevitably impact people's homes and the ecological environment of fields.

XRF measures total concentration but does not identify bioavailable fractions in soils. The ability to identify these components is required to estimate their impacts on plants and other organisms in the soil. Absorption mechanisms control biological availability, so measuring how these ions are absorbed in the soil is critical for determining how heavy metals affect plants. Additionally, water flow can be used to measure the mobility of heavy metals and is crucial for determining the extent to which residents may be impacted. The concentration of Cr was not included in the ICP–OES measurements because it was rarely detected. Through DW extraction, the average concentrations of As, Cd, Cu, Ni, Pb, and Zn in all soils were found to be 0.06, 0.04, 0.13, 0.01, 0.03 and 3.86, respectively. When compared with agricultural soil, the waste soil had a greater total concentration of heavy metals as well as a larger overall fraction that could be easily dissolved (Table 9). However, the order of different heavy metals percentages varied. Zn, at 0.5%, had the highest percentage of water extractable ions in the abandoned mine soil, followed by Cu and Cd, at 0.16 and 0.072, respectively. Although the values for the other metals were below 0.05%, that of arsenic was highest in soils that were inhabited and used in the fields, at 0.14%. As has strong solubility and human absorption at high pH conditions, while most

heavy metals do not have this property (Masscheleyn et al., 1991). The higher the pH is, the higher the ratio of arsenate (Hughes, 2002; Masscheleyn et al., 1991). As a result, the field soil near the mine may have more arsenic, which could be harmful to humans. These results for water extractable ions show that arsenic was more readily mobilized in the agricultural land. Arsenic can rapidly accumulate in organisms throughout the food chain and eventually have an impact on human health. Most heavy metals other than arsenic tend to have a high leaching rate at low pH (Reddy et al., 1995). With an increase in pH, cadmium produces cadmium precipitates such cadmium hydroxide and cadmium carbonate. High leaching levels are evident in mining soils, which have low pH values, since adsorption to the soils increases at pH 8 (Kubier et al., 2019). Additionally, zinc mobility is very low at pH values of 7 and higher and improves as pH decreases, intensifying at pH values less than 5 (Scokart et al., 1983). These traits explain why zinc levels are high in leachates near waste mines. Copper shows similar trends. When pH is lower than 6.5, copper solubility is particularly high (Fan et al., 2011). Additionally, nickel is highly extractable at low pH values. However, the pollution level of nickel was lower than that of the other types of heavy metals; thus, there was no significant difference between the regions overall. In other words, arsenic is likely to have a greater impact than the other heavy metals in the field soils where people live and cultivate crops.

Fig. 8 shows the extent to which leachate affects the development of plants. Cadmium and zinc led to a substantial amount of damage. These two species posed severe serious ecological risk because were present in the leachate and are soluble at low pH levels. The Igeo and ERI values also show that cadmium had a high overall concentration, and actual investigations have demonstrated that abandoned mines

are primarily responsible for this environmentally hazardous effect.

Table 9. Comparison and leachability assessment of distilled water extracts and XRF using ICP–OES, categorized into all, abandoned, and agricultural soils. The mean, standard deviation (Std.), coefficient of variance (C.V.), minimum (Min.), and maximum (Max.) elemental concentrations determined using ICP–OES. The ratio was calculated using the mean values from distilled water extraction and XRF.

Categories		Parameters	Heavy metals (mg kg^{-1})						
			As	Cd	Cr	Cu	Ni	Pb	Zn
Distilled water extraction	All soils (N=43)	Mean	0.06	0.04	0	0.13	0.01	0.03	3.86
		Std.	0.09	0.12	0	0.57	0.02	0.02	11.3
		C.V.	151	303	-	441	192	57.8	292
		Min.	0.002	0	0	0	0.0003	0.004	0
		Max.	0.57	0.61	0	3.75	0.11	0.13	49.4
	Abandoned soils	Mean	0.08	0.15	0	0.44	0.01	0.04	15.1
	(N=11)	Std.	0.16	0.19	0	1.06	0.005	0.04	18.1
		C.V.	181	130	-	242	67.6	86.0	120
		Min.	0.002	0	0	0.0002	0.0003	0.005	0.02
		Max.	0.57	0.61	0	3.75	0.02	0.13	49.4

	Agricultural soils	Mean	0.07	0.0007	0	0.02	0.01	0.03	0.01
	(N=14)	Std.	0.08	0.0005	0	0.01	0.03	0.009	0.005
		C.V.	83.8	74.78	-	49.38	225.1	26.63	63.46
		Min.	0.004	0	0	0	0.001	0.004	0.002
		Max.	0.21	0.002	0	0.04	0.11	0.04	0.02
	Forest soils	Mean	0.04	0.001	0	0.02	0.006	0.3	0.007
	(N=18)	Std.	0.04	0.0007	0	0.02	0.002	0.004	0.006
		C.V.	95.8	66.1	-	76.8	43.2	13.4	95.1
		Min.	0.02	0	0	0	0.001	0.02	0
		Max.	0.19	0.003	0	0.06	0.01	0.04	0.02
XRF	All soils (N=43)	Mean	3662	53.2	79.0	84.6	40.6	1055	817
		Std.	12152	36.0	43.1	108	20.7	2508	1426
		C.V.	332	67.6	54.6	129	51.0	238	175
		Min.	1	10	13	4	8	0	29
		Max.	71585	160	263	567	115	12451	6136
	Abandoned soils	Mean	14171	84.5	42.8	208	26.1	3866	2528

	(N=11)	Std.	20708	50.3	19.3	157	12.0	3733	1864
		C.V.	146	59.5	45.2	75.5	46.0	96.6	73.7
		Min.	91	24	13	31	8	146	138
		Max.	71585	160	67	567	43	12451	6136
	Agricultural soils	Mean	52.4	40.8	79.6	48.2	42.6	111	235
	(N=14)	Std.	38.9	9.90	16.8	20.1	9.74	123	164
		C.V.	79.0	25.0	21.1	41.7	22.9	110	70
		Min.	11	23	59	25	33	29	73
		Max.	120	58	121	102	72	523	555
	Forest soils	Mean	47.4	43.7	98.7	37.5	47.9	70.9	224
	(N=18)	Std.	48.1	25.7	51.5	17.7	26.0	53.1	556
		C.V.	101.3	58.9	52.1	47.1	54.3	74.9	247.8
		Min.	1	10	40	4	14	0	29
		Max.	161	116	263	73	115	187	2512
Leachability (%)	All soils		0.002	0.075	0	0.154	0.025	0.003	0.472
	Abandoned soils		0.001	0.178	0	0.212	0.038	0.001	0.597

Agricultural soils	0.134	0.002	0	0.041	0.023	0.027	0.004
Forest soils	0.084	0.002	0	0.053	0.013	0.423	0.003

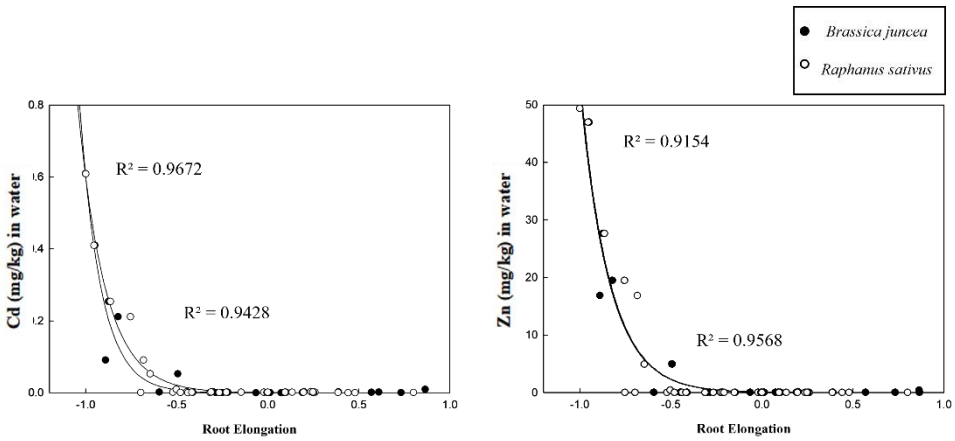

Figure 8. The relationship between root elongation and Cd and Zn in water.

6. Evaluating Human Risk

Skin absorption and unintentional ingestion pose risks to humans who are exposed to deposits tainted with metals (Luo et al., 2012). Due to unintentional contact between hands and clothing, ingestion may take place through the mouth. In contrast, the amount of exposed skin, the concentration of metals in sediments, the quantity of sediments, and the likelihood of metal absorption through the skin affect the amount of metal that is absorbed into the blood through the skin.

Table 10 displays the CR and HQ values calculated based on ADDderm, ADDinh, and ADDing. The findings revealed that the values of ADD in children and adults for soil were in the following order: ADDing, ADDderm, and ADDinh. As a result, the prevalence of ADD in children was higher than in adults, as the current study shows that ingestion is the primary route of exposure that results in negative impacts on human health.

Table 10. Average daily dose (ADD) measured in mg/kg/day for three modes of soil exposure.

Element		ADD_{ing}		ADD_{derm}		ADD_{inh}	
		Children	**Adults**	**Children**	**Adults**	**Children**	**Adults**
As	Min	6.58E-06	7.05E-07	2.27E-07	3.17E-08	1.84E-10	1.04E-10
	Max	4.71E-01	5.04E-02	1.62E-02	2.27E-03	1.32E-05	7.42E-06
	Mean	2.41E-02	2.58E-03	8.31E-04	1.16E-04	6.73E-07	3.79E-07
Cd	Min	6.58E-05	7.05E-06	7.56E-08	1.06E-08	1.84E-09	1.04E-09
	Max	1.05E-03	1.13E-04	1.21E-06	1.69E-07	2.94E-08	1.66E-08
	Mean	3.50E-04	3.75E-05	4.02E-07	5.63E-08	9.77E-09	5.51E-09
Cr	Min	8.55E-05	9.16E-06	9.83E-08	1.38E-08	2.39E-09	1.35E-09
	Max	1.73E-03	1.85E-04	1.99E-06	2.78E-07	4.83E-08	2.72E-08
	Mean	5.19E-04	5.56E-05	5.97E-07	8.35E-08	1.45E-08	8.18E-09
Cu	Min	2.63E-05	2.82E-06	3.02E-08	4.23E-09	7.35E-10	4.14E-10
	Max	3.73E-03	3.99E-04	4.29E-06	6.00E-07	1.04E-07	5.87E-08
	Mean	5.56E-04	5.96E-05	6.40E-07	8.95E-08	1.55E-08	8.77E-09
Ni	Min	5.26E-05	5.64E-06	6.05E-08	8.46E-09	1.47E-09	8.29E-10
	Max	7.56E-04	8.10E-05	8.70E-07	1.22E-07	2.11E-08	1.19E-08
	Mean	2.67E-04	2.86E-05	3.07E-07	4.29E-08	7.46E-09	4.20E-09
Pb	Min	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Max	8.19E-02	8.77E-03	9.42E-05	1.32E-05	2.29E-06	1.29E-06
	Mean	6.94E-03	7.43E-04	7.98-06	1.12E-06	1.94E-07	1.09E-07
Zn	Min	1.91E-04	2.004E-05	2.19E-07	3.07E-08	5.33E-09	3.00E-09
	Max	4.03E-02	4.32E-03	4.64E-05	6.49E-06	1.13E-06	6.36E-07
	Mean	5.37E-03	5.76E-04	6.18E-06	8.64E-07	1.50E-07	8.47E-08

6.1 Risk of Carcinogens

Among the metals investigated, Cd, Cr, Ni, and Pb are thought to be carcinogens that potentially increase the risk of human carcinogenesis (CR) (Raja et al., 2021). These heavy metals are known to cause CR through a variety of exposure pathways, including ingestion, inhalation, and absorption from soil particles through the skin (Hamad et al., 2014; Saddique et al., 2018). A number of variables, including exposure duration, dose, age, weight, and the cancer-inducing ability of contaminated substances, affect CR. A crucial risk assessment index that quantifies the relationship between response and exposure is the USEPA's recommended cancer gradient coefficient (CSF) (Farris & Ray, 2014). The tolerable cancer risk level (CR/TCR) range, according to the USEPA, is between 1 10-6 and 10-4. Cu and Zn were excluded from the analysis because no determined values were available for them.

As, Cr, Cd, and Pb had high TCR values, as indicated by Table 11. Few soils showed concentrations that were completely safe for children, and most of the soils were very carcinogenic. Ingestion is the most dangerous exposure route in children, and dermal contact is also very harmful. Notably, field soils were among the soils that exhibited high risks for childhood cancer. The risk to adults was also high in the field soils, which were field soils near the mountains. Other than the soils at these sites, the others showed moderate values, but adults could be impacted if the contamination is left untreated. Additionally, children are likely to be affected by Cr, Cd, and Pb, in that order. Similar to As, Cr and Cd were found to be at tolerable levels for adults in the field soils but posed a risk to children. In most soils, Pb did

not show values that were likely to significantly result in CR in the exposed population. The area surrounding the abandoned mine had soils that posed Pb risks to children, but the field soil and the soil in the areas where people reside were all within the permitted limits. Except for As, no other heavy metal exceeded the permissible levels in adults. Nickel was the only heavy metal that showed an CR value below the USEPA-recommended threshold of 1 10-4. Thus, the CR of the residual heavy metals was high on slopes opposite to the abandoned mines, which are not inhabited.

The results for cancer risk indicated that for the heavy metals investigated in this study, children had higher TCR values than adults. This is because children are more heavily exposed to heavy metals than adults due to their use of handheld devices and due to exposure to contaminated environmental media during play and other similar activities (Wang et al., 2010). The TCR value of As in the abandoned mine region and in its surroundings was significantly higher than the limit, and the majority of values were very close to the limit. In particular, the cancer risk arising from the agricultural soils that were closest to the mountain were confirmed. This type of contamination can eventually harm human health if they are not specifically addressed in the future. Fig. 9 shows the results discussed in this section.

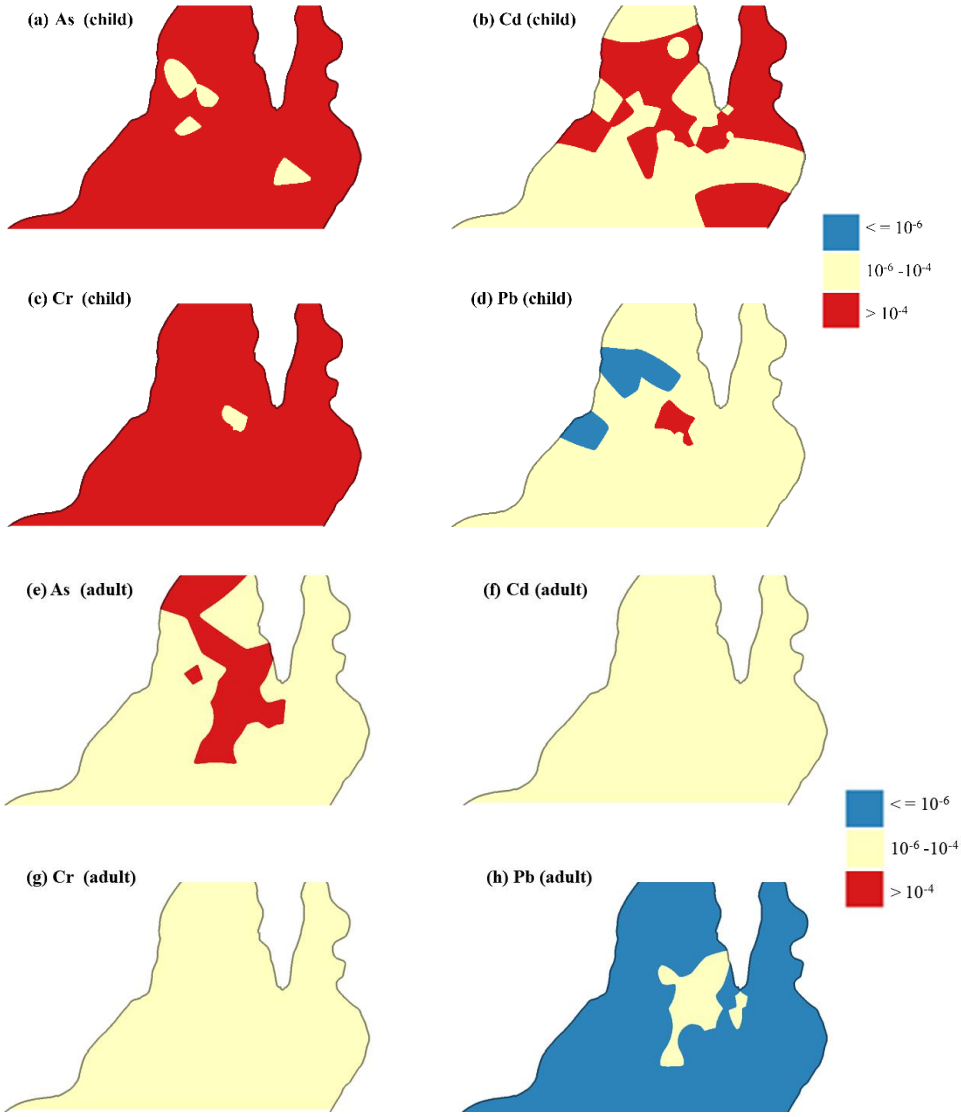

Figure 9. For the heavy metal contaminants, the spatial distribution of carcinogenic risk was in the following order: (a) As, (b) Cd, (c) Cr, and (d) Pb (if TCR > 10^{-4}, exposure to heavy metals may result in noncarcinogenic disorders; (a-d) show results for children, while (e-h) show results for adults)

Table 11. CR from heavy metals in the soil samples collected from the study area.

Element		Cring		Crderm		Crinh		LCR	
		Children	**Adults**	**Children**	**Adults**	**Children**	**Adults**	**Children**	**Adults**
As	Min	9.86E-06	1.06E-06	8.30E-07	1.16E-07	2.77E-09	1.56E-09	1.07E-05	1.17E-06
	Max	7.06E-01	7.56E-02	5.94E-02	8.31E-03	1.99E-04	1.12E-04	7.66E-01	8.41E-02
	Mean	3.61E-02	3.87E-03	3.04E-03	4.25E-04	1.02E-05	5.73E-06	3.92E-02	4.30E-03
Cd	Min	2.50E-05	2.68E-06			1.16E-08	6.53E-09	2.50E-05	2.68E-06
	Max	4.00E-04	4.28E-05			1.85E-07	1.04E-07	4.00E-04	4.29E-05
	Mean	1.33E-01	1.42E-05			6.16E-08	3.47E-08	1.33E-04	1.43E-05
Cr	Min	4.27E-05	4.58E-06			1.00E-07	5.66E-08	4.28E-08	4.64E-06
	Max	8.65E-04	9.26E-05			2.03E-06	1.14E-06	8.67E-04	9.38E-05
	Mean	2.60E-04	2.78E-05			6.09E-07	3.44E-07	2.60E-04	2.82E-05
Ni	Min					1.23E-09	6.96E-10	1.23E-09	6.69E-10
	Max					1.77E-08	1.00E-08	1.77E-08	1.00E-08

	Mean			6.26E-09	3.53E-09	6.26E-09	3.53E-09
Pb	Min	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Max	6.96E-04	7.46E-05	9.61E-08	5.42E-08	6.96E-04	7.46E-05
	Mean	5.90E-05	6.32E-06	8.14E-09	4.59E-09	5.90E-05	6.32E-06

6.2 Risk of Non-carcinogens

With respect to noncancer risk, an HI value of less than 1 indicates that a substance has no negative effects on health, and an HI value of more than 1 indicates that noncancer risk is present. As, Pb, and Cd exposure risk for both adults and children existed in and around the waste mine soils based on the HI values of the metals investigated in this study. As and Cd as well as waste mine soils demonstrated risks, especially for children. While Cr, Cu, Ni, and Zn had low HIs, showing that they did not have an impact on adults and children, As contributed to the most to the highest HI value observed in both adults and children. Only Cd showed high HI values for children in nearly all soils, including the soils on the opposite slope, and all sites that showed high levels of noncancer risk were close to the abandoned mines. This is because Cd displayed high concentrations overall and because children consume more Cd than adults do. Other than heavy metals, the concentrations of other metals at the sites were not hazardous people and did not pose cancer risks. Locally, higher levels of noncancer risk were found in comparison to cancer risk; therefore, the current level of contamination is anticipated to have a low level of direct impact, but if the abandoned mine soils are left untreated, they could eventually have negative impacts. Table 12 provides specific data, and Fig. 10 provides the results discussed in the preceding paragraphs.

The potential health risk associated with intake by children was higher than that associated with adult intake, similar to the trends in carcinogenic hazards. Additionally, children are more vulnerable to heavy metal exposure because they place their hands in their mouths more frequently (Rasmussen et al., 2001). Many

studies have found that children face more health risks than adults because children have greater rates of metabolism and absorption and display hemoglobin sensitivity to toxic metals (Bacigalupo & Hale, 2012; Kormoker et al., 2021; Zheng et al., 2020).

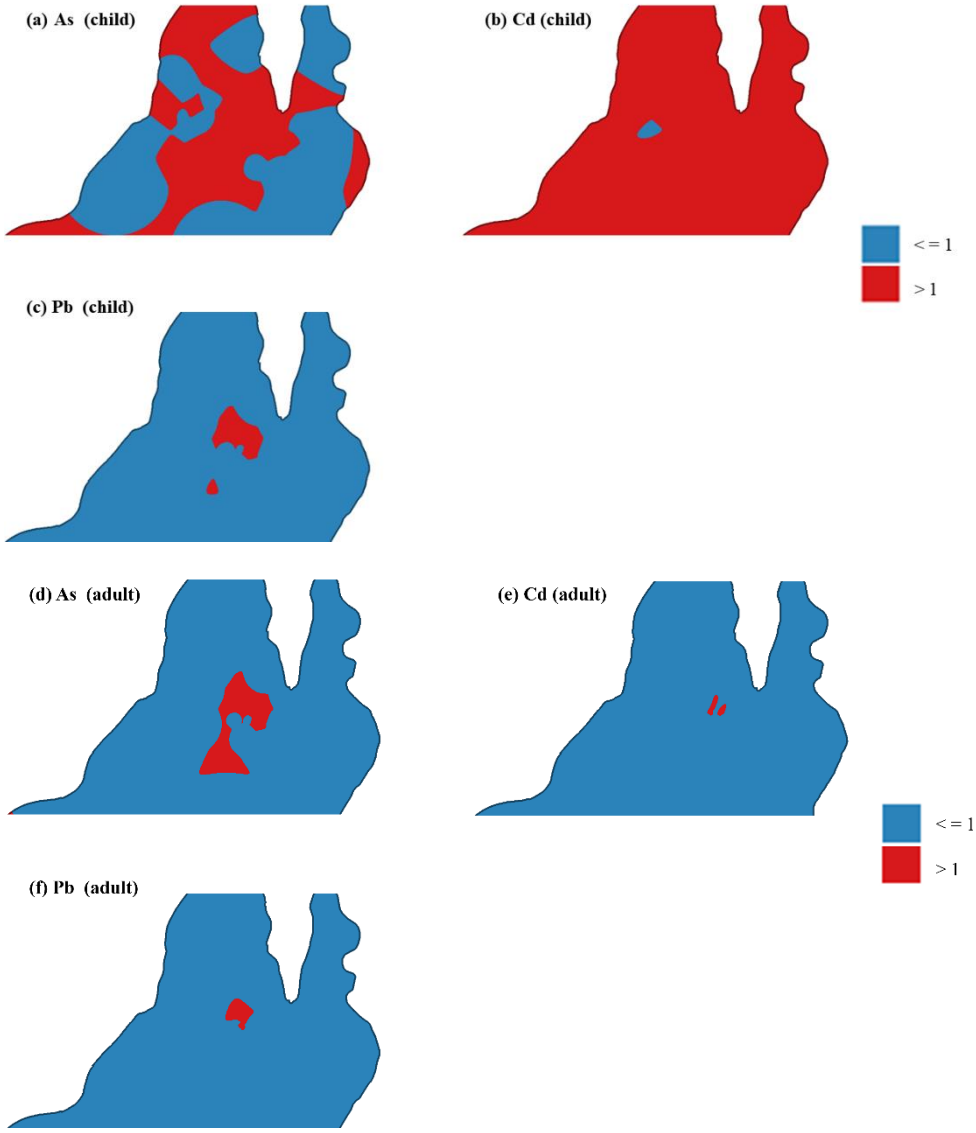

Figure 10. For the heavy metal contaminants, the spatial distribution of noncarcinogenic risk was in the following order: (a) As, (b) Cd, and (c) Pb (if HI > 1, exposure to heavy metals may result in noncarcinogenic disorders; (a-c) show the result for children, while (d-f) show the results for adults)

Table 12. HQ resulting from heavy metals in the soil samples collected from the study area.

Element		HQing		HQderm		HQinh		HI	
		Children	**Adults**	**Children**	**Adults**	**Children**	**Adults**	**Children**	**Adults**
As	Min	2.19E-02	2.35E-03	1.84E-03	2.58E-04	6.12E-07	3.45E-07	2.38E-02	2.61E-03
	Max	1.57E+03	1.68E+02	1.32E+02	1.58E+01	4.38E-02	2.47E-02	1.70E+03	1.87E+02
	Mean	8.03E+01	8.60E+00	6.75E+00	9.45E-01	2.24E-03	1.26E-03	8.70E+01	9.55E+00
Cd	Min	6.58E-01	7.05E-02	7.56E-03	1.06E-03	1.84E-05	1.04E-05	6.65E-01	7.15E-02
	Max	1.05E+01	1.13E+00	1.21E-01	1.69E-02	2.94E-04	1.66E-04	1.06E+01	1.14E+00
	Mean	3.50E+00	3.75-01	4.02E-02	5.63E-03	9.77E-05	5.51E-05	3.54E+00	3.80E-01
Cr	Min	2.85E-02	3.05E-03	1.64E-03	2.29E-04	8.35E-05	4.71E-05	3.02E-02	3.33E-03
	Max	5.76E-01	6.18E-02	3.31E-02	4.64E-03	1.69E-03	9.53E-04	6.11E-01	6.74E-02
	Mean	1.73E-01	1.85E-02	9.95E-03	1.39E-03	5.07E-04	2.83E-04	1.84E-01	2.02E-02
Cu	Min	6.58E-04	7.05E-05	2.52E-06	3.53E-07	1.83E-08	1.03E-08	6.60E-04	7.08E-05
	Max	9.32E-02	9.99E-03	3.57E-04	5.00E-05	2.59E-06	1.49E-06	9.36E-02	1.00E-02

	Mean	1.39E-02	1.49E-03	5.33E-05	7.46E-06	3.87E-07	2.18E-07	1.40E-02	1.50E-03
Ni	Min	2.63E-03	2.82E-04	1.12E-05	1.57E-06	7.13E-08	4.02E-08	2.64E-03	2.83E-04
	Max	3.78E-02	4.05E-03	1.61E-04	2.25E-05	1.03E-06	5.78E-07	3.80E-02	4.07E-03
	Mean	1.33E-02	1.43E-03	5.68E-05	7.95E-06	3.62E-07	2.04E-07	1.34E-02	1.44E-03
Pb	Min	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Max	2.34E+01	2.51E+00	1.79E-01	2.51E-02	7.04E-04	3.97E-04	2.36E+01	2.53E+00
	Mean	1.98E+00	2.12E-01	1.52E-02	2.13E-03	5.96E-05	3.36E-05	2.00E+00	2.14E-01
Zn	Min	6.36E-04	6.84E-05	3.65E-06	5.11E-07	1.78E-08	1.00E-08	6.39E-04	6.86E-05
	Max	1.34E-01	1.44E-02	7.73E-04	1.08E-04	3.76E-06	2.12E-06	1.35E-01	1.45E-02
	Mean	1.79E-02	1.92E-03	1.03E-04	1.44E-05	5.00E-07	2.82E-07	1.80E-02	1.93E-03

Table 13. The number of samples showing noncarcinogenic and carcinogenic risks to children and adults in each region of this study.

Categories			Parameters	Heavy metals (mg kg^{-1})						
				As	Cd	Cr	Cu	Ni	Pb	Zn
LCR	Abandoned soils	Child	Acceptable	0	0	0	-	11	0	-
	(N=11)		Tolerable	0	3	4	-	0	4	-
			Unacceptable	11	8	7	-	0	7	-
		Adult	Acceptable	0	0	0	-	11	1	-
			Tolerable	0	11	11	-	0	10	-
			Unacceptable	11	0	0	-	0	0	-
	Agricultural soils	Child	Acceptable	0	0	0	-	14	0	-
	(N=14)		Tolerable	1	8	0	-	0	14	-
			Unacceptable	13	6	14	-	0	0	-
		Adult	Acceptable	0	0	0	-	14	12	-
			Tolerable	12	14	14	-	0	2	-
			Unacceptable	2	0	0	-	0	0	-
	Forest soils	Child	Acceptable	0	0	0	-	18	3	-
	(N=18)		Tolerable	3	10	0	-	0	15	-
			Unacceptable	15	8	18	-	0	0	-
		Adult	Acceptable	0	0	0	-	18	16	-
			Tolerable	14	18	18	-	0	2	-

			Unacceptable	4	0	0	-	0	0	-
HI	Abandoned soils (N=11)	Child	No risk	0	0	11	11	11	3	11
			Non-carcinogenic risk	11	11	0	0	0	8	0
		Adult	No risk	3	8	11	11	11	8	11
			Non-carcinogenic risk	9	3	0	0	0	3	0
	Agricultural soils (N=14)	Child	No risk	6	0	14	14	14	14	14
			Non-carcinogenic risk	8	14	0	0	0	0	0
		Adult	No risk	14	14	14	14	14	14	14
			Non-carcinogenic risk	0	0	0	0	0	0	0
	Forest soils (N=18)	Child	No risk	11	1	18	18	18	18	18
			Non-carcinogenic risk	7	16	0	0	0	0	0
		Adult	No risk	18	18	18	18	18	18	18
			Non-carcinogenic risk	0	0	0	0	0	0	0

Table 13 shows the number of noncarcinogenic and carcinogenic areas in each zone for both children and adults. Arsenic displayed a high cancer risk even in the agricultural soils. More attention should be given to the high As levels in these areas because people live in and around these areas. Pb and Cd presented risks in some agricultural and forest soils, although their concentrations were lower than those of As.

According to the population report compiled in Jecheon-si in June 2022, 4.29% of the residents of Susan-myeon, Jecheon-si, are under the age of 18, 50.05% of the adults are between the ages of 19 and 64, and 45.66% of the resides are over the age of 64 (KOSAT, 2022).

Although people who are elderly are also susceptible to heavy metals, in this study, cancer risk and noncancer risk were assessed by splitting the residents into only two categories: adults and children. Therefore, from these data, we cannot conclude that heavy metals have little impact on most residents. The people who live next to the abandoned mines are farmers. They are exposed to heavy metals through a variety of means, including through soil contact or through the consumption of crops cultivated in soils contaminated with heavy metals. In other words, the risks that residents face should not be neglected by ignoring the existing situation. Steps should be taken to prevent ongoing exposure to heavy metal hazards in the soil.

IV. CONCLUSIONS

Soil contamination and its effect on soil quality, plant growth, and public health is becoming a growing concern. As, Cd, Cu, and Pb are all present in various amounts in soils near mining sites. In the current study, soils from a waste mine in Jecheon-si, Chungcheongbuk-do, Republic of Korea, were used to identify and describe heavy metal spatial distribution, environmental risks, ecological effects, and human health risks. Higher levels of Igeo and ERI were found in soils that were near the waste mine, and these soils also showed greater heavy metal contamination. The As and Cd concentrations in the current study were above the WHO/FAO and RKME (2016) maximum permissible limits for selected heavy metals. However, these soils are thought to pose high ecological risks due to the incorporation of Cd in the integrated index (ERI). According to the research on contamination, in the field areas where people live, Cd pollution was found to be most common, and As was the main cause of pollution. A relationship was found when the root growth and ERI of Brassica juncea and Raphanus sativus were compared. The higher the ERI was, the smaller the root growth of the plants. This suggests that the ERI of Cd and As in the research area was influential. Arsenic in particular had a high rate of leaching into field soils. This is because, unlike other heavy metals, arsenic has high mobility at high pH levels. Additionally, the sampling areas that showed the greatest potential risks for each heavy metal were sites contaminated with As and Cd. Heavy metals in the soil and their bioaccumulation in Indian mustard and radish had an impact on plant growth and output. Furthermore, acute toxicity plant tests performed via

environmental toxicity assessment revealed the lowest pH, a high concentration of heavy metals, and slow plant growth in nearby soils, which contained more water-soluble heavy metals than other locations at the mine site. According to the water extraction experimental results for evaluating element mobility, the main elements in the abandoned soils not only displayed higher concentrations but were also more easily mobilized by DW extraction. In particular, Cd and Zn had a large influence on plants. The lower the pH was, the more mobile the elements and the more affected the plants.

Due to As and Cd ingestion, the HI values were the highest level in children, and TCR demonstrated that all heavy metals affected human health risk except Ni. According to the study's findings, excessive heavy metal exposure can cause noncancerous health issues in addition to cancer in humans. Children are more susceptible to heavy metal consumption than adults, making them more vulnerable to their hazards. The noncancerous risk from As via soil exposure was higher in both adults and children than from other heavy metals. Given that the As cancer risk in children and adults exceeded the permitted levels, the fields next to the mines may potentially pose cancer hazards to the local people. This means that the people in these areas could be at high risk for developing harmful effects if they continue to ingest these metals through the crops, groundwater, and soil. Similarly, the TCR values (for both adults and children) were found to be above the threshold ranges. Therefore, appropriately monitoring and remediation might be necessary to prevent future chronic health concerns.

According to these findings, the erosion of ore and abandoned waste ore around the mine in Susan-myeon, Jecheon-si, Chungcheongbuk-do, affects the concentration of most heavy metals that cause pollution around the waste mines, and

plant growth is inhibited due to the low pH values and the high heavy metal concentration. The abandoned mine's soil showed a high risk for carcinogenesis, as well as noncancerous and potential ecological risks, even though mining activities have ceased. The agricultural land around the mine, however, showed low values that did not significantly harm adults, although periodic evaluation is advised. However, it should be noted that young children remain vulnerable. Furthermore, because there are many elderly people who are 65 years of age or older in Jecheon-si, thorough risk identification and health risk assessments should be performed on a regular basis. By examining heavy metal spatial distribution and suggesting appropriate management directions to minimize potential pollution effects, this study serves to facilitate the identification of the environmental impact of heavy metal pollutants. Additional research is required on strategies for toxic pollutant remediation that can support environmental sustainability.

V. REFERENCES

Abbas, G., Murtaza, B., Bibi, I., Shahid, M., Niazi, N. K., Khan, M. I., Amjad, M., Hussain, M., & Natasha. (2018). Arsenic uptake, toxicity, detoxification, and speciation in plants: Physiological, biochemical, and molecular aspects. International Journal of Environmental Research and Public Health, 15(1), 59.

Adimalla, N., Chen, J., & Qian, H. (2020). Spatial characteristics of heavy metal contamination and potential human health risk assessment of urban soils: A case study from an urban region of South India. Ecotoxicology and Environmental Safety, 194, 110406.

Ahmad, W., Alharthy, R. D., Zubair, M., Ahmed, M., Hameed, A., & Rafique, S. (2021). Toxic and heavy metals contamination assessment in soil and water to evaluate human health risk. Scientific Reports, 11(1), 17006.

Akala, V. A., & Lal, R. (2001). Soil organic carbon pools and sequestration rates in reclaimed minesoils in Ohio. Journal of Environmental Quality, 30(6), 2098–2104.

Asensio, V., Vega, F. A., Andrade, M. L., & Covelo, E. F. (2011). Tree vegetation to improve physico-chemical properties in bare mine soils. Fresenius Environmental Bulletin, 20(12a), 3295–3303.

Ayers, R. S., & Westcot, D. W. (1985). Water quality for agriculture. FAO irrigation and drainage paper 29. Revision 1. Food and Agriculture Organization.

Bacigalupo, C., & Hale, B. (2012). Human health risks of Pb and As exposure via consumption of home garden vegetables and incidental soil and dust ingestion: A probabilistic screening tool. Science of The Total Environment, 423, 27–38.

Bagur-González, M. G., Estepa-Molina, C., Martín-Peinado, F., & Morales-Ruano, S. (2011). Toxicity assessment using Lactuca sativa L. bioassay of the metal(loid)s As, Cu, Mn, Pb and Zn in soluble-in-water saturated soil extracts from an abandoned mining site. Journal of Soils and Sediments, 11(2), 281–289.

Balali-Mood, M., Naseri, K., Tahergorabi, Z., Khazdair, M. R., & Sadeghi, M. (2021). Toxic mechanisms of five heavy metals: Mercury, lead, chromium, cadmium, and arsenic. Frontiers in Pharmacology, 12, 643972.

Bali, A. S., & Sidhu, G. P. S. (2021). Arsenic acquisition, toxicity and tolerance in plants - From physiology to remediation: A review. Chemosphere, 283, 131050.

Bamgbose, I., & Anderson, T. A. (2015). Phytotoxicity of three plant-based biodiesels, unmodified castor oil, and Diesel fuel to alfalfa (Medicago sativa L.), lettuce (Lactuca sativa L.), radish (Raphanus sativus), and wheatgrass (Triticum aestivum). Ecotoxicology and Environmental Safety, 122, 268–274.

Barrutia, O., Artetxe, U., Hernández, A., Olano, J. M., García-Plazaola, J. I., Garbisu, C., & Becerril, J. M. (2011). Native plant communities in an abandoned Pb-Zn mining area of northern spain: Implications for phytoremediation and germplasm preservation. International Journal of Phytoremediation, 13(3), 256–270.

Bauder, T. A., Waskom, R. M., Sutherland, P. L., Davis, J. G., Follett, R. H., & Soltanpour, P. N. (2011). Irrigation water quality criteria. Service in action; no. 0.506. Colorado State University

Bello, S., Nasiru, R., Garba, N. N., & Adeyemo, D. J. (2019). Carcinogenic and non-carcinogenic health risk assessment of heavy metals exposure from Shanono and Bagwai artisanal gold mines, Kano state, Nigeria. Scientific African, 6, e00197.

Bowen, H. J. M. (1979). Environmental chemistry of the elements. Academic Press.

Cappuyns, V., & Swennen, R. (2008). The use of leaching tests to study the potential mobilization of heavy metals from soils and sediments: A comparison. Water, Air, and Soil Pollution, 191(1-4), 95–111.

Diami, S. M., Kusin, F. M., & Madzin, Z. (2016). Potential ecological and human health risks of heavy metals in surface soils associated with iron ore mining in Pahang, Malaysia. Environmental Science and Pollution Research, 23(20), 21086–21097.

Doabi, S. A., Karami, M., Afyuni, M., & Yeganeh, M. (2018). Pollution and health risk assessment of heavy metals in agricultural soil, atmospheric dust and major food crops in Kermanshah province, Iran. Ecotoxicology and Environmental Safety, 163, 153–164.

Eziz, M., Mohammad, A., Mamut, A., & Hini, G. (2018). A human health risk assessment of heavy metals in agricultural soils of Yanqi Basin, Silk Road Economic Belt, China. Human and Ecological Risk Assessment: An International Journal, 24(5), 1352–1366.

Fan, J., He, Z., Ma, L. Q., & Stoffella, P. J. (2011). Accumulation and availability of copper in citrus grove soils as affected by fungicide application. Journal of Soils and Sediments, 11(4), 639–648.

Fan, Y., Zhu, T., Li, M., He, J., & Huang, R. (2017). Heavy metal contamination in soil and brown rice and human health risk assessment near three mining areas in Central China. Journal of Healthcare Engineering, 2017, 4124302.

Fang, Z., Zhao, M., Zhen, H., Chen, L., Shi, P., & Huang, Z. (2014). Genotoxicity of tri- and hexavalent chromium compounds in vivo and their modes of action on DNA damage in vitro. PLoS One, 9(8), e103194.

Farris, F. F., & Ray, S. D. (2014). Cancer potency factor. In P. Wexler (Ed.), Encyclopedia of toxicology (pp. 5220). Elsevier.

Gall, J. E., Boyd, R. S., & Rajakaruna, N. (2015). Transfer of heavy metals through terrestrial food webs: a review. Environmental monitoring and assessment, 187(4), 1-21.

Genchi, G., Carocci, A., Lauria, G., Sinicropi, M. S., & Catalano, A. (2020). Nickel: Human health and environmental toxicology. International Journal of Environmental Research and Public Health, 17(3), 679.

Hakanson, L. (1980). An ecological risk index for aquatic pollution control. A sedimentological approach. Water Research, 14(8), 975–1001.

Hamad, S. H., Schauer, J. J., Shafer, M. M., Al-Rheem, E. A., Skaar, P. S., Heo, J., & Tejedor-Tejedor, I. (2014). Risk assessment of total and bioavailable potentially toxic elements (PTEs) in urban soils of Baghdad–Iraq. Science of The Total Environment, 494-495, 39–48.

Heiri, O., Lotter, A. F., & Lemcke, G. (2001). Loss on ignition as a method for estimating organic and carbonate content in sediments: Reproducibility and comparability of results. Journal of Paleolimnology, 25(1), 101–110.

Huang, J., Wu, Y., Sun, J., Li, X., Geng, X., Zhao, M., Sun, T., & Fan, Z. (2021). Health risk assessment of heavy metal(loid)s in park soils of the largest megacity in China by using Monte Carlo simulation coupled with Positive matrix factorization model. Journal of Hazardous Materials, 415, 125629.

Hughes, M. F. (2002). Arsenic toxicity and potential mechanisms of action. Toxicology Letters, 133(1), 1–16.

Johnson, D. B., & Hallberg, K. B. (2005). Acid mine drainage remediation options: A review. Science of The Total Environment, 338(1-2), 3–14.

Kebrom, T. H., Woldesenbet, S., Bayabil, H. K., Garcia, M., Gao, M., Ampim, P., Awal, R., & Fares, A. (2019). Evaluation of phytotoxicity of three organic amendments to collard greens using the seed germination bioassay. Environmental Science and Pollution Research International, 26(6), 5454–5462.

Khalid, S., Shahid, M., Niazi, N. K., Murtaza, B., Bibi, I., & Dumat, C. (2017). A comparison of technologies for remediation of heavy metal contaminated soils. Journal of Geochemical Exploration, 182, 247–268.

Kormoker, T., Proshad, R., Islam, S., Ahmed, S., Chandra, K., Uddin, M., & Rahman, M. (2021). Toxic metals in agricultural soils near the industrial areas of Bangladesh: Ecological and human health risk assessment. Toxin Reviews, 40(4), 1135–1154.

KOSAT. (2022). Age and gender census - cities, counties and districts. Statistics Korea.
Kubier, A., Wilkin, R. T., & Pichler, T. (2019). Cadmium in soils and groundwater: A review. Applied Geochemistry: Journal of the International Association of Geochemistry and Cosmochemistry, 108, 1–16.

Kumar, V., Sharma, A., Kaur, P., Singh Sidhu, G. P., Bali, A. S., Bhardwaj, R., Thukral, A. K., & Cerda, A. (2019). Pollution assessment of heavy metals in soils of India and ecological risk assessment: A state-of-the-art. Chemosphere, 216, 449–462.

Lin, C., Wu, Y., Lu, W., Chen, A., & Liu, Y. (2007). Water chemistry and ecotoxicity of an acid mine drainage-affected stream in subtropical China during a major flood event. Journal of Hazardous Materials, 142(1-2), 199–207.

Liu, C. P., Luo, C. L., Gao, Y., Li, F. B., Lin, L. W., Wu, C. A., & Li, X. D. (2010). Arsenic contamination and potential health risk implications at an abandoned tungsten mine, southern China. Environmental Pollution, 158(3), 820–826.

Lombi, E., Zhao, F. J., Zhang, G., Sun, B., Fitz, W., Zhang, H., & McGrath, S. P. (2002). In situ fixation of metals in soils using bauxite residue: Chemical assessment. Environmental Pollution, 118(3), 435–443.

Luo, X. S., Ding, J., Xu, B., Wang, Y. J., Li, H. B., & Yu, S. (2012). Incorporating bioaccessibility into human health risk assessments of heavy metals in urban park soils. Science of The Total Environment, 424, 88–96.
Mahurpawar, M. (2015). Effects of heavy metals on human healtheffects of heavy metals on

human health. International Journal of Research-Granthaalayah, 3(9SE), 1–7.

Manesh, R. R., Grassi, G., Bergami, E., Marques-Santos, L. F., Faleri, C., Liberatori, G., & Corsi, I. (2018). Co-exposure to titanium dioxide nanoparticles does not affect cadmium toxicity in radish seeds (Raphanus sativus). Ecotoxicology and Environmental Safety, 148, 359–366.

Masscheleyn, P. H., Delaune, R. D., & Patrick, W. H. (1991). Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. Environmental Science & Technology, 25(8), 1414–1419.

McBride, M., Sauve, S., & Hendershot, W. (1997). Solubility control of Cu, Zn, Cd and Pb in contaminated soils. European Journal of Soil Science, 48(2), 337–346.

Mourinha, C., Palma, P., Alexandre, C., Cruz, N., Rodrigues, S. M., & Alvarenga, P. (2022). Potentially toxic elements' contamination of soils affected by mining activities in the Portuguese Sector of the Iberian Pyrite Belt and optional remediation actions: a review. Environments, 9(1), 11.

Moya, J., Phillips, L., Schuda, L., Wood, P., Diaz, A., Lee, R., Clickner, R., Birch, R. J., Adjei, N., Blood, P., Chapman, K., Castro, R., & Mahaffey, K. (2011). Exposure factors handbook: 2011 edition. US Environmental Protection Agency.

Muller, G. (1969). Index of geoaccumulation in sediments of the Rhine River. Geojournal, 2, 108–118.

Nagajyoti, P. C., Lee, K. D., & Sreekanth, T. V. M. (2010). Heavy metals, occurrence and toxicity for plants: A review. Environmental Chemistry Letters, 8(3), 199–216.

Obiri-Nyarko, F., Duah, A. A., Karikari, A. Y., Agyekum, W. A., Manu, E., & Tagoe, R. (2021). Assessment of heavy metal contamination in soils at the Kpone landfill site, Ghana: Implication for ecological and health risk assessment. Chemosphere, 282, 131007.

OECD. (2006). Test No. 208: Terrestrial plant test: Seedling emergence and seedling growth test. OECD.

Okereafor, U., Makhatha, M., Mekuto, L., Uche-Okereafor, N., Sebola, T., & Mavumengwana, V. (2020). Toxic metal implications on agricultural soils, plants, animals, aquatic life and human health. International Journal of Environmental Research and Public Health, 17(7), 2204.

Rahman, H., Sabreen, S., Alam, S., & Kawai, S. (2005). Effects of nickel on growth and composition of metal micronutrients in barley plants grown in nutrient solution. Journal of Plant Nutrition, 28(3), 393–404.

Raja, V., Lakshmi, R. V., Sekar, C. P., Chidambaram, S., & Neelakantan, M. A. (2021). Health risk assessment of heavy metals in groundwater of industrial township Virudhunagar, Tamil Nadu, India. Archives of Environmental Contamination and Toxicology, 80(1), 144–163.

Rajkumar, M., & Freitas, H. (2008). Effects of inoculation of plant-growth promoting bacteria on Ni uptake by Indian mustard. Bioresource Technology, 99(9), 3491–3498.

Rasmussen, P. E., Subramanian, K. S., & Jessiman, B. J. (2001). A multi-element profile of house dust in relation to exterior dust and soils in the city of Ottawa, Canada. Science of The

Total Environment, 267(1-3), 125–140.

Reddy, K. J., Wang, L., & Gloss, S. P. (1995). Solubility and mobility of copper, zinc and lead in acidic environments. Plant and Soil, 171(1), 53–58.

RKME. (2016). The Korean soil environmental conservation act. Ministry of Environment, Korean Ministry of Environment.

Saddique, U., Muhammad, S., Tariq, M., Zhang, H., Arif, M., Jadoon, I. A. K., & Khattak, N. U. (2018). Potentially toxic elements in soil of the Khyber Pakhtunkhwa province and Tribal areas, Pakistan: Evaluation for human and ecological risk assessment. Environmental Geochemistry and Health, 40(5), 2177–2190.

Scokart, P. O., Meeus-Verdinne, K., & De Borger, R. (1983). Mobility of heavy metals in polluted soils near zinc smelters. Water, Air, & Soil Pollution, 20(4), 451–463.

Shabbir, Z., Sardar, A., Shabbir, A., Abbas, G., Shamshad, S., Khalid, S., Natasha, Murtaza, G., Dumat, C., & Shahid, M. (2020). Copper uptake, essentiality, toxicity, detoxification and risk assessment in soil-plant environment. Chemosphere, 259, 127436.

Sharma, A., Kapoor, D., Wang, J., Shahzad, B., Kumar, V., Bali, A. S., Jasrotia, S., Zheng, B. & Yan, D. (2020). Chromium bioaccumulation and its impacts on plants: an overview. Plants, 9(1), 100.

Sherene, T. (2010). Mobility and transport of heavy metals in polluted soil environment. Biological Forum—An International Journal, 2(2), 112–121.

Sinha, S., Sinam, G., Mishra, R. K., & Mallick, S. (2010). Metal accumulation, growth, antioxidants and oil yield of Brassica juncea L. exposed to different metals. Ecotoxicology and Environmental Safety, 73(6), 1352–1361.

Stambulska, U. Y., Bayliak, M. M., & Lushchak, V. I. (2018). Chromium(VI) toxicity in legume plants: Modulation effects of rhizobial symbiosis. BioMed Research International, 2018, 8031213.

Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K., & Sutton, D. J. (2012). Heavy metal toxicity and the environment. Experientia Supplementum, 101, 133–164.

US Environmental Protection Agency (USEPA) (1989) Risk Assessment Guidance for Superfund. Volume I: Human Health Evaluation Manual (Part A), Washington, DC, USA: EPA/540/1-89/002. Office of Emergency and Remedial Response

US Environmental Protection Agency (USEPA) (2002) Supplemental guidance for developing soil screening levels for superfund sites, OSWER 9355. Office of Emergency and Remedial Response, Washingston

US Environmental Protection Agency (USEPA) (2011) Exposure factors handbook. National Center for Environmental Assessment, Washington, DC (EPA/600/R-09/052F)

Wang, Z., Chai, L., Yang, Z., Wang, Y., & Wang, H. (2010). Identifying sources and assessing potential risk of heavy metals in soils from direct exposure to children in a mine-impacted city, Changsha, China.Journal of environmental quality, 39(5), 1616-1623.

Wu, W., Wu, P., Yang, F., Sun, D. L., Zhang, D. X., & Zhou, Y. K. (2018). Assessment of heavy metal pollution and human health risks in urban soils around an electronics

manufacturing facility. Science of The Total Environment, 630, 53–61.

Yuswir, N. S., Praveena, S. M., Aris, A. Z., Ismail, S. N. S., & Hashim, Z. (2015). Health risk assessment of heavy metal in urban surface soil (Klang District, Malaysia). Bulletin of Environmental Contamination and Toxicology, 95(1), 80–89.

Zheng, N., Hou, S., Wang, S., Sun, S., An, Q., Li, P., & Li, X. (2020). Health risk assessment of heavy metals in street dust around a zinc smelting plant in China based on bioavailability and bioaccessibility. Ecotoxicology and Environmental Safety, 197, 110617.

초 록

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중금속의 토양 오염은 전 세계적으로 심각한 환경 문제이다. 인위적인 활동에 의한 토양 환경의 독성 중금속 농도의 증가는 오염이 농업 생산성의 감소뿐만 아니라 육지 생물의 위험 증가를 초래하기 때문에 주요한 환경 문제 중 하나이다. 광구의 교정조치와 안정화를 위한 노력에도 불구하고, 대한민국의 광산의 30% 이상이 지난 세기 동안 버려져 있었다. 본 연구에서는 1980년 이후 방치된 대양영성광산의 토양위험도를 평가하기 위해 오염도 파악과 인체건강위험도 평가를 수행하였다. 따라서 토지이용에 따라 토양은 폐광산 토양, 농업 토양, 산림 토양으로 구분되었다. 생태위험도 결과에 따르면, Igeo 값은 Cd가 극도로 오염되었음을 나타낸다. ERI 결과에 따르면 Cd는 전체 면적의 34.8%에서, As는 전체 면적의 18.6%에서 오염되었으며, 대부분의 오염은 광산 주변에서 발생하였다. 인간건강위험평가는 어린이와 성인 모두 광산토양의 비소로 인한 암 발생 위험이 한계치(HI>1)보다 높았으며, Cd로 인한 암 발생 위험이 다른 모든 지역보다 어린이에서 더 높은 것으로 나타났다. Ni을 제외한 모든 발암물질은 어린이

기준치($1x10^{-4}$)를 초과하는 구간이 있었다. 성인의 경우 광산을 둘러싼 토양과 마찬가지로 As 한계를 초과했다. 광산 근처 밭에서의 비소가 어린이와 성인의 암 위험 허용 한도를 초과하기 때문에 광산 근처의 밭에 사는 지역 주민들 역시 암 위험을 초래할 가능성이 높다. 광산 잔해의 풍화로 중금속이 주변 토양으로 방출되고, 물 이동에 따른 토양 침식으로 오염 수준의 증가가 가속화한 걸로 관측되었다. 오염도는 이전 연구보다 상당히 높아 인근 식수 저수지로 중금속이 방출될 가능성이 있음을 시사했다. 이러한 연구결과는 과학자들이 폐광산 지역의 중금속 위험을 이해하고 예방하는 데 도움이 될 수 있으며, 농작물, 토양, 물의 중금속 위험을 줄이기 위한 교정조치 및 안정화 계획을 개발하는 것이 중요하다는 것을 시사한다.

주요어 : 토양 중금속, 토양 오염식별, X선 형광분석, 침출수 분석, 공간 분석, 건강 위험 평가

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