

MASTER'S THESIS

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**STUDY OF MOBILE ELEMENT FRACTIONS IN SOIL AFFECTED BY
WASTE ROCK DEPOSIT**

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1. INTRODUCTION AND OBJECTIVES

1.1. Background of the study

Environmental pollution by toxic elements has become a serious problem in the world. The mobilization of toxic metals through extraction from ores and subsequent processing for different applications has led to the release of these elements into the environment. The problem of heavy metals' pollution is becoming more and more serious with increasing industrialization and disturbance of natural biogeochemical cycles. Unlike organic substances, heavy metals are essentially non-biodegradable and therefore accumulate in the environment. The accumulation of these toxic elements in soils and waters poses a risk to the environment and human health (Ali et al., 2013). Mining activities produce larger quantities of waste and have more adverse environmental impacts than waste from any other human activity (Bright, 2011).

The mining dump site serves as a source of potential toxic elements and poses danger to the downstream ecosystems like rivers, farms and resident communities (Opeña et al., 2022). Environmental pollution by heavy metals originated from abandoned mines can become a very important source of contamination both in soil and water. Therefore, the characterization of mining tailings' chemical and physical properties is important to assess the risk of potential environmental mobility of toxic trace metals that are contained in this kind of waste. Measurement of total metal concentrations is useful to evaluate the heavy metal burden but their mobility depends strongly on their specific chemical forms or ways of binding (Margui et al., 2004).

Extraction procedures by means of a single extractant are widely used in soil science. These procedures are designed to dissolve a phase whose element content is correlated with the availability of the element to the plants. This approach is well established for major elements and nutrients and it is commonly applied in studies of fertility and quality of crops, for predicting the uptake of essential elements, for diagnosis of deficiency or excess of one element in a soil, in studies of the physical-chemical behavior of elements in soils and for survey purposes (Rauret, 1998).

Environment is defined as the totality of circumstances surrounding an organism or group of organisms especially, the combination of external physical conditions that affect and influences the growth, development and survival of organisms (Raj et al., 2020).

1.2. Significance of the study

Environmental pollution by heavy metals originated from abandoned mines can become a very important source of contamination in soil, water and air. Therefore, the determination of heavy metals concentration in waste rock dumps is important to assess the risk of potential environmental mobility of toxic trace metals that are contained in that kind of waste.

1.3. Hypothesis

- The use of acetic acid and Lakanen-Erviö solution separately as extractants will offer complementary information on the mobility of potentially toxic elements in soil samples, facilitating a more comprehensive understanding of element dynamics in the environment;
- The targeted results from the extraction of the toxic elements by using acetic acid and Lakanen-Erviö solution separately will reveal differences in the magnitude and distribution of element fractions extracted.

1.4. The purpose of the study

The purpose of this study was to use alternative methods for assessing the environmental contamination level of toxic elements present in the waste rocks deposit by Gyöngyösoroszi mining, Hungary.

1.5. Specific objectives

This work was set to:

- Determine the concentration of heavy metals (Cd, Cu, Pb and Zn) and their mobility in the samples collected from the waste rocks deposit by Gyöngyösoroszi mining;
- To evaluate the extent and severity of heavy metal contamination in waste rocks dump
- To analyze the mobility of Cadmium, Copper, Lead and Zinc for identifying their contamination level;
- To provide valuable data for environmental monitoring and risk assessment programs;
- To contribute to scientific knowledge and innovation in environmental science and engineering.

2. LITERATURE REVIEW

2.1. Heavy metals

Heavy metals are defined as “naturally occurring metals having atomic number greater than 20 and an elemental density greater than 5 g/cm³ (Ali & Khan, 2018). Basically, heavy metals are unarguably the transition and post transition metals, and the examples which are common in various literatures are lead (Pb), cadmium (Cd), vanadium (v) cobalt (Co), chromium (Cr), copper (Cu), iron(Fe), arsenic (As), nickel (Ni), manganese (Mn), tin (Sn) zinc (Zn), and mercury (Hg.) (Ataikiru & Okieimen, 2021).

Metals are considered as the main constituent of the earth's crust from its time of creation and the early life has evolved in their presence in abundance. Thus, all living systems have evolved using some metals as essential constituents on the one hand and existed with the toxic metals as well on the other hand (Singh & Ambawat, 2020). The eight most common pollutant heavy metals listed by the Environment Protection Agency (EPA) are: As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn [4] (Khayatzadeh & Abbasi, 2010)

2.1.1. Binding of metals

Trace metals in soils and sediments may exist in different chemical forms or ways of binding. In unpolluted soils or sediments trace metals are mainly bound to silicates and primary minerals forming relatively immobile species, whereas in polluted ones trace metals are generally more mobile and bound to other soil or sediment phases. In environmental studies the determination of the different ways of binding gives more information on trace metal mobility, as well as on their availability or toxicity, in comparison with the total element content (Rauret, 1998).

2.1.2. Sources of heavy metals

Heavy metals are released into the environment from different natural/geological and anthropogenic sources. Natural sources of heavy metals include volcanic eruptions and weathering of metal-bearing rocks, while anthropogenic sources include mining and smelting operations, various industries, combustion of fossil fuels, manufacture and application of phosphate fertilizers and metallic pesticides in agriculture (Ali & Khan, 2018).

These metals (heavy metals) are released during mining and extraction of different elements from their respective ores. Heavy metals released to the atmosphere during mining, smelting, and other industrial processes return to the land through dry and wet deposition. Discharge of wastewaters such as industrial effluents and domestic sewage add heavy metals to the environment. Application of chemical fertilizers and combustion of fossil fuels also contribute to the anthropogenic input of heavy metals in the environment. Regarding contents of heavy metals in commercial chemical fertilizers, phosphate fertilizers are particularly important (Ali et al., 2019).

Wastes are the major source of soil pollution originating from mining, chemical, metal processing industries, and other allied industries. These wastes include varieties of chemicals like heavy metals, phenols and other organics, non-metals, etc. (Asati et al., 2016).

Table 1. Characteristics of Cd, Cu, Pb and Zn, their oxidation states, and human activities responsible for their environmental discharge

N	Metal type	Stable form	Metal release resources to the environment
1	Cadmium (Cd)	Cd (II)	Fertilizer industries, power generation, wastewater drainage, waste products, mining, battery industries, electroplating, dyes industry, metal plating, and the steel and plastics sectors.
2	Copper (Cu)	Cu (I), Cu (II)	Mining activities, tanning, metal plating and electronics manufacturing.
3	Lead (Pb)	Pb (II), Pb (IV)	Metal processing, mining, battery industry, electroplating, smelting, painting and dyes manufacturing, the plastics industry, fabrics, yachts manufacturing, printing industry, Pb-4contained tubes, preservative materials, the ceramics industry, cables and steel recovery, cathode radiation tubes, bearing manufacture, aviation fuel, nuclear reactor shielding, and radioactive substances vessel manufacturing.
4	Zinc (Zn)	Zn (II)	Brass coating, brass and Zn metals-related working activities, manufacturing of wood-related pulp, steel work activities related to pipe coating, paper manufacturing, painting industry, dyes manufacturing, and pharmaceutical and cosmetic products.

Source: (Jadaa & Mohammed, 2023).

2.1.3. Classification of heavy Metals

Heavy metals are the intrinsic component of the environment with essential and non-essential both types. Soils polluted with heavy metals have become common due to increase in geologic and anthropogenic activities (Asati et al., 2016). Metals, such as iron, copper, zinc and manganese, are essential metals since they play important roles in biological systems, whereas mercury, lead and cadmium are toxic, even in trace amounts. The essential metals can also produce toxic effects at high concentrations. Only a few metals with proven hazardous nature are to be completely excluded in food for human consumption (Türkmen et al., 2009).

Almost all heavy metals are serious toxicants as carcinogens. However, due to their chemical and physiological properties, heavy metals are useful in industrial areas including alloy, smelting and production of commercial products. Such applications increase the opportunity for heavy metal exposure. Waste from industrial processes is also a major source of environmental contamination and accumulation in the human body. Arsenic, cadmium, chromium, and nickel are classified as group 1 carcinogens by the International Agency for Research on Cancer, and are utilized commercially (Kim et al., 2015).

Heavy metals such as cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), zinc (Zn), selenium (Se), manganese (Mn), nickel (Ni) and molybdenum (Mo) are considered to be the essential trace elements for the biochemical and physiological functioning. Other than these metals all are considered as non-essential metals. But if these metals are present beyond their tolerance value, they can have deleterious effects on the environment and human health (Bhateria & Singh, 2019)

Figure 1 displays the categorization of metallic elements into various groups, along with some of their illustrative instances and locations within the periodic table (Jadaa & Mohammed, 2023).

N	Classification A	Classification B	Category examples
1	Non-essential metals	Extremely toxic heavy metals	As, Cd, Hg, Pb, Se, Sn, Tl
2		Precious heavy metals	Au, Ag, Pd, Pt, Ru
3		Radionuclides metals	Am, Pr, Ra, Th, U
4	Essential metals	Micronutrient metals	Co, Cr, Cu, Fe, Mn, Mo, Ni, Zn
5		Macronutrient metals	Ca, K, Mg

Extremely toxic
 Radionuclides
 Precious

Micronutrient
 Macronutrient

Figure 1. Classification of metals into different groups, their representative examples, and their distribution in the periodic table (Jadaa & Mohammed, 2023)

2.1.4. Contamination of environment by heavy metals

Heavy metal contamination refers to the excessive deposition of toxic heavy metals in the soil caused by human activities. Heavy metals in the soil include some significant metals of biological toxicity, such as mercury (Hg), cadmium (Cd), lead (Pb), chromium (Cr) and arsenic (As), etc. They also include other heavy metals of certain biological toxicity, such as zinc (Zn), copper (Cu), nickel (Ni), tin (Sn), vanadium (V), and so on (Su, 2014). Heavy metals are well-known environmental pollutants due to their toxicity, persistence in the environment, and bio accumulative nature. Their natural sources include weathering of metal-bearing rocks and volcanic eruptions, while anthropogenic sources include mining and various industrial and agricultural activities. Mining and industrial processing for extraction of mineral resources and their subsequent applications for industrial, agricultural, and economic development has led to an increase in the mobilization of these elements in the environment and disturbance of their biogeochemical cycles (Ali et al., 2019).

The unplanned disposal of municipal waste, mining, use of extensive pesticides, insecticides, fungicides, and other agrochemicals uses were significant causes of environment pollution and causes of most concern. Heavy metals, such as cadmium, copper, lead, chromium, manganese, iron and mercury are major environmental pollutants, particularly in areas with high anthropogenic pressure (Asati et al., 2016). A heavy metal is toxic when relatively it is dense metal or metalloid that is noted for its potential toxicity, especially in environmental contexts. Heavy metal toxicity means excess of required concentration or it is unwanted which were found naturally on the earth, and become concentrated as a result of human caused activities, enter in plant, animal and human tissues via inhalation, diet and manual handling, and can bind to, and interfere with the functioning of vital cellular components (Asati et al., 2016).

Heavy metals enter natural waters through dry and wet deposition, industrial effluents, domestic sewage and agricultural runoff. Heavy metals are accumulated in sediments and biota. Retention of heavy metals in sediments depends on different physicochemical processes like adsorption/desorption, complexation and precipitation which in turn depend on different physical–chemical parameters, e.g., temperature, pH, particulate organic matter (POM), redox state, ion exchange capacity (CEC) and hydrodynamics (Ali & Khan, 2018). Pollutants may enter the ecosystem in various ways and can enter into the hydrosphere, lithosphere and atmosphere. Apart from entering through natural ways as mentioned earlier (through volcanic activity and weathering of rocks), anthropogenic activity is a big cause of pollutants entering the ecosystem. Heavy metals released into the atmosphere in volcanic eruptions and in different industrial emissions also ultimately return to the land and cause contamination of waters, soils and air. Since heavy metals are persistent in the environment, they either accumulate in biota or leach down into ground waters (MathuMitha et al., 2021).

With the rapid development of industries such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides, etc., heavy metals wastewaters are directly or indirectly discharged into the environment increasingly, especially in developing countries. Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or

carcinogenic. Toxic heavy metals of particular concern in treatment of industrial wastewaters include zinc, copper, nickel, mercury, cadmium, lead and chromium (Fu & Wang, 2011).

The presence of heavy metals in wastewater has been increasing with the growth of industry and human activities, e.g., plating and electroplating industry, batteries, pesticides, mining industry, rayon industry, metal rinse processes, tanning industry, fluidized bed bioreactors, textile industry, metal smelting, petrochemicals, paper manufacturing, and electrolysis applications. The heavy metal contaminated wastewater finds its way into the environment, threatening human health and the ecosystem (Qasem et al., 2021).

2.1.5. Effects of heavy metals in the hydrosphere

Water is the “life-blood of the biosphere.” Since water is a universal solvent, it dissolves different organic and inorganic chemicals and environmental pollutants. Aquatic ecosystems, both freshwater and marine, are vulnerable to pollution (MathuMitha et al., 2021). Heavy metals are diluted and affected by various surface water components (carbonate, sulphate, organic compounds - humic, fulvic, amino acids) that formed insoluble salts or complexes. These salts and complexes are predicted to be not harmful to aquatic organisms. Part of them sink and are accumulated in bottom sediments. However, when water pH has declined (during acidic rains or other acidic episodes) heavy metals can be mobilized and released into the water column and become toxic to aquatic biota. In addition, low concentrations of heavy metals can cause chronic stress which may not kill individual fish, but lead to a lower body weight and smaller size and thus reduce their ability to compete for food and habitat (Khayatzaadeh & Abbasi, 2010).

Anthropogenic Sources: Small amounts of heavy metals are released while mining and uncontrolled smelting of large quantities of metal ores in open fires. With the industrial revolution, metals were extracted from natural resources and processed in the industries from where heavy metals passed on into the atmosphere. Similarly traces of heavy metals get into the environment through discharge of waste - both domestic, agricultural and from auto exhausts (Sankhla et al., 2016)

2.1.6. Effects of heavy metals on Soil

Heavy metal affects physico-chemical properties of soil i.e. pH, organic matter, ion exchange capacity, texture, microbial growth, microbial density or metabolic processes. Heavy metals' accumulation badly deteriorates the soil quality and plant growth. Mainly heavy metals accumulate in soil through natural and anthropogenic processes. Generic processes mainly include parent material decomposition and atmospheric addition, while anthropogenic processes include industrial or sewage waste or sewage sludge and indiscriminate use of pesticides with fertilizers. Macronutrients unavailability and soil pH towards acidity are the major effects of heavy metals accumulations. Mainly accumulated metals rendered the seed germination, growth and production of plants. Heavy metals toxicity above the permissible limits is the main hindrances towards agriculture sustainability and crop production (Ali et al., 2022)

Since metals are non-biodegradable hence, remain persistent in the environment for a very long time. They cannot be broken down, moreover heavy metals present in soils and sediments remain present for an extended period until they are eluted to other compartments. They can also react with other elements in the soil or sediment and form or degrade to become more toxic (MathuMitha et al., 2021). Soils polluted with heavy metals have become common across the globe due to increase in geologic and anthropogenic activities. Plants growing on these soils show a reduction in growth, performance, and yield. Although heavy metals are naturally present in the soil, geologic and anthropogenic activities increase the concentration of these elements to amounts that are harmful to both plants and animals (Chibuike & Obiora, 2014).

2.1.7. Effect of heavy metals on plant

Heavy metals are found naturally from the earth's crust; they neither degrade nor destroy. Life has both organic and inorganic components, so without metal ions, life is not possible. Many metals such as Fe, Co, Cu, Se, Zn are essential metals. They are present in low concentrations in plants and maintain growth and metabolism. However, when metals present in higher concentrations than the requirements of plants, it causes toxic effects. Heavy metals from different natural and anthropogenic sources are released into the soils. Plant roots take up heavy metals from the soil and then pass them to different parts of plants which cause many harmful effects on the plants (Bharti & Sharma, 2022).

2.1.8. Effects of heavy metals on the atmosphere

Various metals produced from human activity are ubiquitously detected in ambient air. The metals may lead to induction and/or exacerbation of respiratory diseases, but the significant metals and factors contributing to such diseases have not been identified (Honda, 2015). Increased industrialization and urbanization have recently made air pollution a major environmental problem. The air pollution was reported to have been accelerated by dust and particulate matter (PMs), particularly fine particles such as PM_{2.5} and PM₁₀ which are released through natural and anthropogenic processes (MathuMitha et al., 2021).

Heavy metals are individual metals and metal compounds that can impact human health. Generally, humans are exposed to these metals by ingestion (drinking or eating) or inhalation (breathing). Working in or living near an industrial site which utilizes these metals and their compounds increases one's risk of exposure, as does living near a site where these metals have been improperly disposed. Subsistence lifestyles can also impose higher risks of exposure and health impacts because of hunting and gathering activities (Martin & Griswold, 2009).

2.2. Effects of Heavy Metals as toxic elements

2.2.1. Effects of Cadmium

Cadmium is a heavy metal that occurs as a natural constituent in earth's crust along with Copper, Lead, Nickel and Zinc. Cadmium is vastly used in batteries, coating, plating, alloys etc. in various industries. Humans are commonly exposed to cadmium by inhalation and ingestion. Cadmium enters in air and binds to small particles where it can combine with water or soil causing contamination of fish, plants and animals in nanoform. Spills at hazardous waste sites and improper waste disposal can cause cadmium leakages in nearby habitats. Sources of cadmium human exposures are fossil fuels, iron and steel production, cement nonferrous metals production, waste incineration, smoking, fertilizers, etc. Activities like volcanic eruption, mining and use of phosphate fertilizers provides cadmium exposures indirectly as toxins from earth crust. Plants take up cadmium from the soil and form the major source of cadmium intake in non-smoking, non-occupationally exposed populations (Sharma et al., 2015). Cadmium (Cd) is a toxic non-essential transition metal that poses a health risk for both humans and animals. It is naturally occurring in the environment as a pollutant that is derived from agricultural and industrial sources. Exposure to cadmium primarily occurs through the ingestion of contaminated food and water and, to a

significant extent, through inhalation and cigarette smoking. Cadmium accumulates in plants and animals with a long half-life of about 25–30 years. Epidemiological data suggest that occupational and environmental cadmium exposure may be related to various types of cancer, including breast, lung, prostate, nasopharynx, pancreas, and kidney cancers. It has been also demonstrated that environmental cadmium may be a risk factor for osteoporosis. The liver and kidneys are extremely sensitive to cadmium's toxic effects. This may be due to the ability of these tissues to synthesize metallothioneins (MT), which are Cd-inducible proteins that protect the cell by tightly binding the toxic cadmium ions (Genchi et al., 2020). Natural as well as anthropogenic sources of cadmium, including industrial emissions and the application of fertilizer and sewage sludge to farm land, may lead to contamination of soils, and to increased cadmium uptake by crops and vegetables grown for human consumption. The uptake process of soil cadmium by plants is enhanced at low pH. Cigarette smoking is a major source of cadmium exposure (Khanam, 2014).

2.2.2. Effects of Copper

Copper has a number of applications in industrial and agricultural processes and it can be released into the environment from many sources such as mining, metal piping, chemical industries and pesticides. Copper is needed by many enzymes to function normally and is thus classified as an essential element. The effects of high intake of copper in the human body are increased blood pressure and respiratory rates, damage to kidney and liver, convulsions, cramps, vomiting or even death. People with Wilson's disease are at greater risk for health effects from overexposure to copper (MathuMitha et al., 2021).

2.2.3. Effects of Lead

Lead is a non-essential element that occurs naturally in the environment. However, the highest concentrations found in nature are the result of human activities. Many of its physical and chemical properties such as softness, malleability, ductility, poor conductibility and resistance to corrosion, have favored that man uses lead and lead compounds since ancient times for a great variety of applications. Lead is a common environmental and occupational contaminant widely distributed around the world. Even though the toxic effects of lead and its compounds have been investigated for many years in a variety of systems, the data existing with regard to its mutagenic, clastogenic and carcinogenic properties are still contradictory. The International Agency for Research on

Cancer has classified lead as possible human carcinogen (group 2B) and its inorganic compounds as probable human carcinogens (group 2A) (García et al., 2010).

Lead is a naturally occurring metal present in small amounts in the earth's crust. It is used in the production of lead-acid batteries, ammunition, metal products (solder and pipes), and devices to shield X-rays. In humans, exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. Lead is distributed mostly to the bones and can cause osteoporosis (MathuMitha et al., 2021). Occupational exposure to inorganic lead occurs in mines and smelters as well as welding of lead painted metal, and in battery plants. Low or moderate exposure may take place in the glass industry. High levels of air emissions may pollute areas near lead mines and smelters. Airborne lead can be deposited on soil and water, thus reaching humans via the food chain (Khanam, 2014).

2.2.4. Effects of Zinc

Zinc is highly toxic and could be damaging to human health. Industries discharging waste streams that contain significant levels of zinc include steel works with galvanizing lines, zinc and brass metal works, zinc and brass plating, viscose rayon yarn and fiber production, ground wood pulp production and newsprint paper production. Zinc salts are also used in the inorganic pigments industry (e.g. zinc chromate) and high zinc levels have been reported in acid mine drainage. Considering the harmful effects of heavy metals, it is necessary to remove them from liquid wastes at least to a limit accepted by national and international regulatory agencies before their discharge to the environment. Treatment processes employed for zinc removal from wastewater may involve precipitation with disposal of the resultant sludge or recovery, membrane processes, ion exchange resins, although these are often expensive and ineffective at low metal concentrations. Therefore, there is a need for a cost effective treatment method that is capable of removing low concentrations of zinc from solution (Deliyanni et al., 2006). Zinc (Zn) is one of the most important trace elements in the body and it is essential as a catalytic, structural and regulatory ion. It is involved in homeostasis, in immune responses, in oxidative stress, in apoptosis and in ageing. Zinc-binding proteins (metallothioneins, MTs), are protective in situations of stress and in situations of exposure to toxic metals, infections and low Zn nutrition (Stefanidou et al., 2006).

2.3. Mobility and bioavailability of heavy metals

The mobility/availability of trace metals is studied by the so-called partial dissolution techniques that use chemical extractants to define the fractionation of trace metals in sediment and soil samples. The basis of these methods is on the bonding ability of metals to different solid phases and the degree of selectivity of the extractants. Therefore, metal speciation will depend on the experimental conditions (reagent concentration, pH, ratio extractant volume/solid mass, time and extent of contact between extractant and solid phase). Heavy metals interact with the environment depending on the different geochemical phases to which they are linked (clays, organic matter, Fe and Mn oxides and hydroxides, carbonates, sulphides and residual silicates) and, also, on the way in which they are associated to the sediments (chemical or physical sorption, precipitation, flocculation, complexation, etc.). Thus, the environmental impact of the pollution is related to the availability of the heavy metals, i.e. to the reversibility of the process by which metals are incorporated to the solid matrix (Alvarez et al., 2011).

The potential toxicity of heavy metals in soil is a function of their mobility and bioavailability. Metal mobility is dependent on the phase in which the metal occurs as well as physical and chemical processes that control transformations between phases. The mobility and bioavailability of trace metals are highly dependent on their specific chemical forms or behavior of binding to each soil phase (Asmoay et al., 2019).

In environmental studies, the total metals' concentration is not the actual total value but refers to the fraction of metals in the soil, which is removed by strong extractants such as nitric acid and perchloric acid. It includes readily exchangeable ions along with more strongly bound forms within the solid phase of the soil that is not bioavailable (Gupta & Sinha, 2006). In the case of plants, the level of free metal ions in the soil solution may be the most important parameter in view of the toxicity as free ions are more toxic than complex metals. Further, the importance of metal in soil solutions is emphasized due to the mobility of metals (Gupta & Sinha, 2006). Soil properties such as pH and organic matter content are known to influence the bioavailability of metals in soils. The total metal present in the soil is not available to the plant grown therein (Gupta & Sinha, 2006)

Bioavailability of heavy metals depends greatly on the characteristics of the particle surface, on the kind of strength of the bond and on the properties of the solution in contact with the solid

samples. Thus, the exchangeable fraction corresponds to the form of metals that is most available for plant uptake and can be released by merely changing the ionic strength of the medium. The metal content bound to carbonates is sensitive to pH changes and can become mobilisable when pH is lowered. The metal fraction bound to Fe–Mn oxides and organic matter can be mobilized with increasing reducing or oxidizing conditions in the environment. Finally, the metal fraction associated with the residual fraction (e.g. silicate) can only be mobilized as a result of weathering, which can only cause long-term effects. Solid wastes generated through the mining and processing of mineral ores are also a potential source of heavy metals. Improper disposal can cause wind and water erosion, which can result in transport of contaminants. Additionally, leakage generated from waste piles could pollute nearby groundwater systems and surface streams (Filgueiras et al 2002).

Abandoned mining sites contain residues from ore processing operations that are characterized by high concentrations of heavy metals. The form in which a metal exists strongly influences its mobility and, thus, the effects on the environment. Measurement of total metal concentrations is useful to evaluate the heavy metal burden but their mobility depends strongly on their specific chemical forms or ways of binding (Margui et al., 2004). In an impacted ecosystem, the potential risks of Trace Elements (TEs) to ecological and human receptors largely depends on several factors, which primarily include site and waste characteristics, source term and chemical properties of the contaminants including chemical speciation, geo-hydrological characteristics of the site, diversity of ecological receptors, and climate. These factors, to a large extent, influence the magnitude and intensity of solubility, mobility, and bioavailability of TEs. Thus predicting mobility and bioavailability of TEs in the soil environment is critical yet quite complicated. Generally, a TE in soil has to be mobile before it can become bioavailable to plants and other soil biota. As indicated earlier, contaminants, such as TEs, need to be mobile and bio accessible to organisms to be beneficial or detrimental, they would also need to be mobilized to eventually reach a surface body of water or to be leached to underlying ground water (Carrillo et al., 2006).

The metals that are separated in the exchangeable fraction are those metals that are retained on the soil surface by relatively weak electrostatic interactions and which can be released by an ion exchange process. The heavy metal fractions that are extracted in the Fe-Mn oxide, organic and

residual fractions can be bioavailable to plants when the pH and redox conditions of the soil changes (Ataikiru & Okieimen, 2021).

2.4. Mining Activities

Mining, though brings several socio-economic benefits, is considered to be one of the most dangerous anthropogenic activities in the world (Arunakumara et al., 2013). Heavy metals occur in the earth's geological structures, and can therefore enter water resources through natural processes. For example, heavy rains or flowing water can leach heavy metals out of geological formations. Such processes are exacerbated when this geology is disturbed by economic activities such as mining. These processes expose the mined-out area to water and air, and can lead to consequences such as acid mine drainage (AMD). The low pH conditions associated with AMD mobilize toxic elements (Sankhla et al., 2016).

Mine waste may arise in a number of forms: as stripped soil and coarse, broken, partly weathered rock overburden in open cast or strip-mining operations; as unweathered development waste rock in underground mining; and as fine-grained tailings, the residuum of the process of comminution and mineral-extraction from ores. The various wastes are usually stored separately. The top-soil is stock-piled for eventual use in environmentally rehabilitating the dumps of coarse wastes, or the surfaces of backfilled surface-mining voids. The coarse broken rock is usually stored in dumps, either with or without compaction, or is used to progressively backfill opencast or strip-mining voids (Bright, 2011).

Human activities, such as mining and smelting, induce release of potentially toxic elements (PTE) into soils. This may cause accumulation of PTE in the food chain and further harm to human health. On the other hand, PTE are naturally present in soils as a result of weathering of PTE rich parent materials (e.g. geochemical anomalies in mining or volcanic contexts) (Kierczak et al., 2008).

2.5. Single and sequential extraction procedures

Single and sequential extraction methods are used in more fundamental studies such as: to elucidate the soil chemistry, to assess the structure and composition of soil components and to improve understanding of the processes in the soil that control the mobilization and retention of nutrient and toxic elements as well as to illuminate their transport mechanisms (Rao et al., 2008).

Both single and sequential extraction methods are of major interest to the environmental scientist particularly in the study of the fate of environmental pollutants. Many of the extractants intended to target particular phases are also used in functional studies. The specificity of many of these reagents can be improved by combining a series of them in a sequential extraction scheme in which the residue from a first extraction is used as the material for a second extraction and so on through a number of stages. The soil phase attacked by each extracting reagent is thus restricted by the preceding extraction in the series and is thereby made more specific. Even if all these procedures are operationally defined, they provide useful information (Rao et al., 2008).

There are numerous methods with various types of single extractants, they generally fall into three groups: (1) Unbuffered mild extractants such as NaNO_3 , CaCl_2 , NH_4NO_3 which extract the exchangeable fraction of the elements (2) Complexing agents such as DTPA and EDTA which release the fraction of the elements mobilized by the complexation process (3) Acid reagents such as CH_3COOH and HCl which allow the fraction of the elements remobilized by an acidification process (Rao et al., 2010).

2.5.1. Single step extractions

The use of single step extractions to ascertain chemically distinguishable pools of metals within the soil matrix has been investigated since the early 1970's. Since then, the number of extraction procedures has grown exponentially. A clear need arises towards standardization and assessment of the interrelationships between these protocols. The different chemical forms in which metals occur within the soil matrix determine their mobility and bioavailability (Meers et al., 2007).

In recent years the assessment of the mobile fractions of heavy metals in soils, as an indication of potential risk of toxic species entering the biosphere and the possible negative effects on ground water quality and their availability to plants and the need to evaluate the environmental impact has been a major topic of investigation all over the world as the number of contamination sites are increasing. One of the approaches most widely used to study metal mobility in soils is the use of single extraction procedures using unbuffered salt solutions that can be considered as good models for simulating raining and flooding events. Single extractants can also be considered in their role of releasing elements from particular soil phases with which they are bound or associated (Rao et al., 2008).

2.6. Leachability

The MSZ-21470-50 Hungarian standard is the most common test used in environmental protection for heavy metals in soil in Hungary. It contains 4 different batch extractions, including aqua regia and $\text{HNO}_3 + \text{H}_2\text{O}_2$, which are necessary to give the total content of the material as a base of reference. It should be kept in mind that while these methods are called ‘total digestion methods’, true total digestion would require additional reagents, such as HF and HClO_4 . The distilled water test is for simulating availability to rainwater (very similar to other common standards such as EN 12457-2, DIN 38414-S4 or the ASTM D 3987-85), while the Lakanen-Erviö solution is used for the estimation of availability for plants. Further advantages of the MSZ-21470-50 are: small amount of sample is necessary, it takes little time, and has a low cost compared to other methods (Hegedűs et al., 2016).

2.6.1. MSZ-21470-50:2006 Hungarian standard

MSZ-21470-50:2006 is the Hungarian standard (Hungarian Standards Institution) for the measurement of toxic elements, heavy metals and Chromium(VI) in soil for environmental protection purposes. It consists of 4 separate single-step batch processes (Fig. 2):

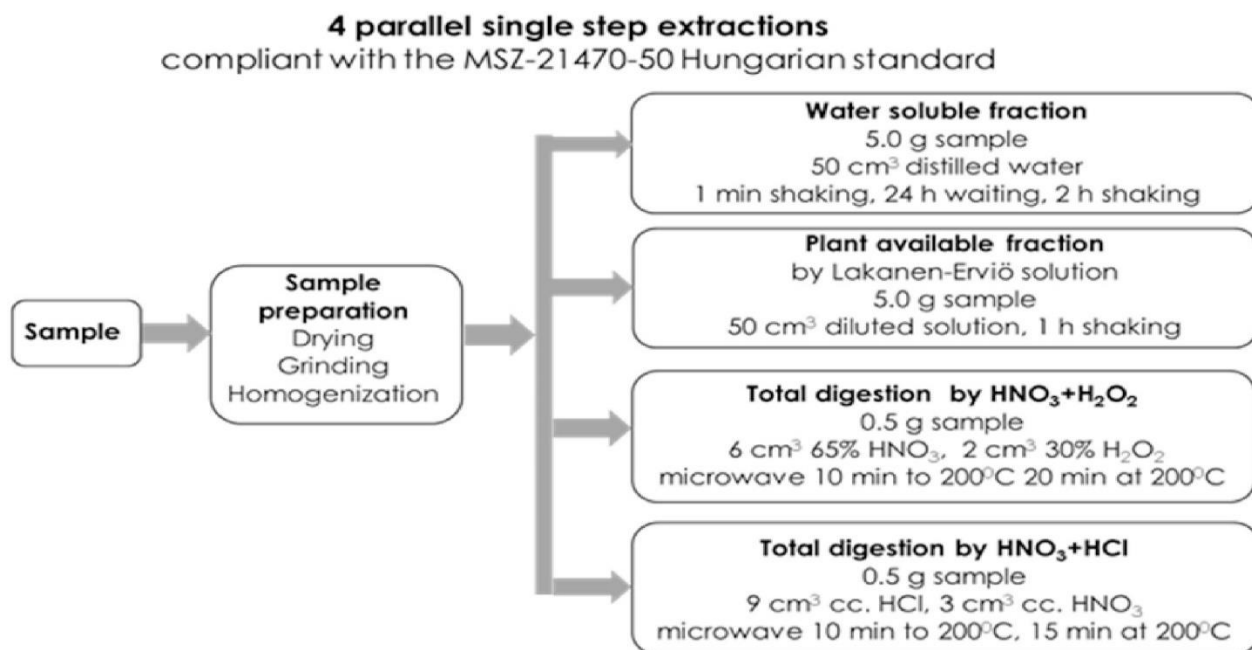


Figure 2. Flowchart of the four parallel single-step extractions compliant with MSZ-21470-50:2006 (Hegedűs et al., 2017).

3. MATERIALS AND METHODS

3.1. Materials

3.1.1. Study area

This research work was conducted in the abandoned mined spoil dumping site located in Mátraszentimre, Heves county, Hungary.

The mean annual temperature in the city of Gyöngyös, near the study area, it is 10.7°C and at the top of the Mátra Mountains (highest elevation 1014 m) it is 5.9°C. The annual average rainfall at an elevation of 300 m in the Mátra Mts. is 600 mm, while it is 750 mm at 900 m elevation. The wettest part of the year is at the end of the fall and the beginning of winter. The higher parts of the medium range mountains, above 700 to 800 m, consist of mixed beech and evergreen forests, while oak forests interspersed with bushy and grassy areas cover the lower regions. Pine trees are only found in plantations (Odor et al. 1998).

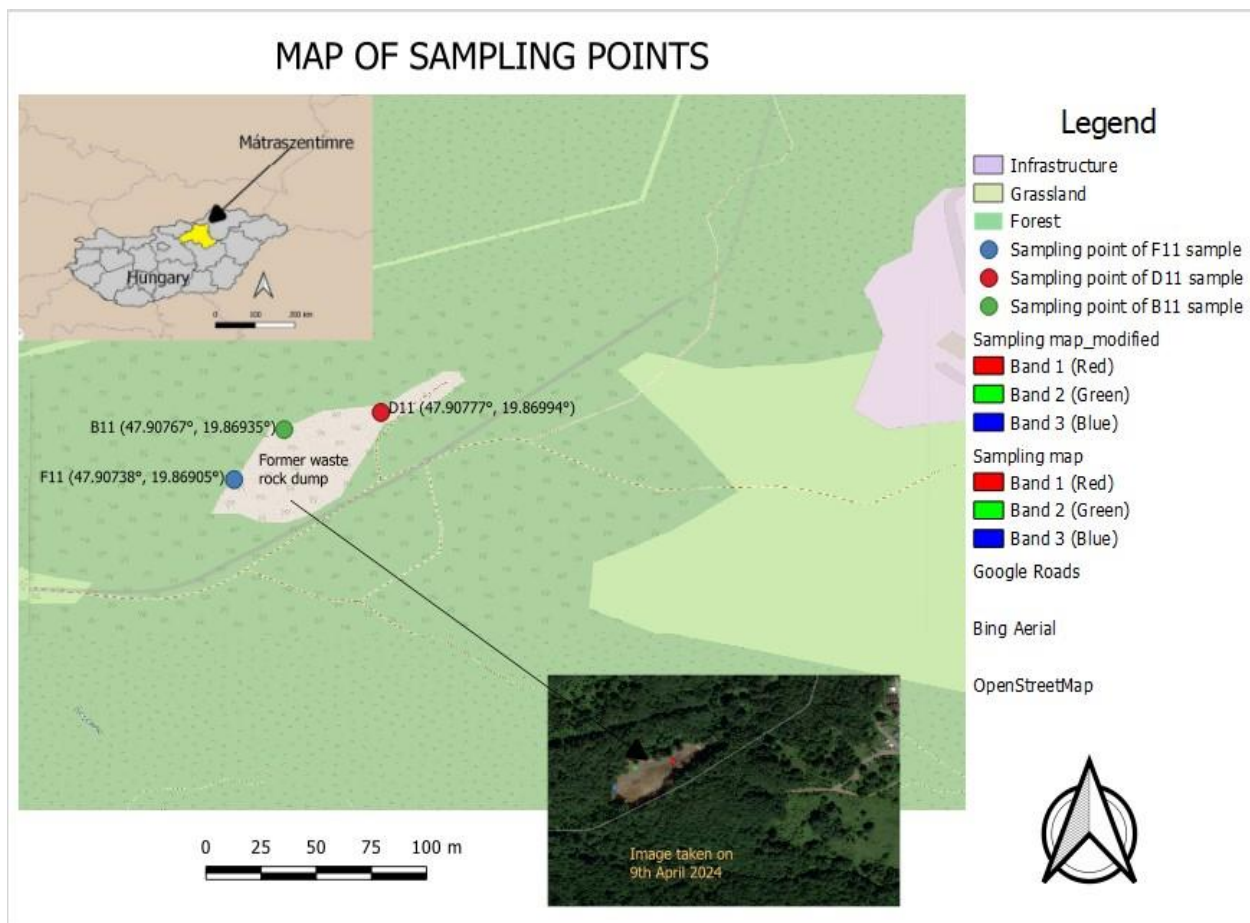


Figure 3. Map of the sampling area, made using Quantum Geographic Information System (QGIS)

Mine waste dumps of various ages were left over at the exit of the exploration and access adits within the studied abandoned mining area. The bare surface of the waste dumps is prone to erosion. The mine was abandoned in 1985 but mine closure and remediation activities started only in 2005 and have been in progress since then (Vaszita & Gruiz, 2010).

3.1.2. Sampling site

The samples were taken from the waste rock deposit by the mining site located near the village Mátraszentimre in Heves County, Hungary.

3.1.3. Apparatus

The following apparatus were used: Automatic pipette, Erlenmeyer flasks, plastic Graduated cylinders of 50 ml and 15 ml, funnel, analytical balance, filter papers, beaker, laboratory plastic spatulas spoon, mortar and pestle, filter papers.

3.1.4. Reagents

Acetic acid (0.11 mol L^{-1}) was used to extract the acid soluble element content. Lakanen-Erviö method (0.5 mol L^{-1} ammonium acetate + 0.02 mol L^{-1} EDTA, pH = 4.65) was used to extract the plant available element content. (Lakanen & Erviö, 1971).

3.1.5. Instrument

Leaching of the soil samples with the two extractants was assisted by two different methods. Multi-rotator for homogenizing samples by rotating them; Digital lab Orbital shaker for homogenizing samples by shaking them; Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) for quantitative analysis of heavy metal elements in samples (Jobin Yvon Activa M, analytical lines of detection: Cd 228.802 nm, Cu 324.754 nm, Pb 220.353 nm, Zn 213.857 nm).

3.1.6. Recent research studies

Pseudo-total element content (mg/kg dry weight) of the samples (after microwave assisted digestion with Nitric acid and Hydrogen peroxide) from the recent research studies were used to determine the mobility of heavy metals. The samples used for determining Pseudo-total element content in the recent research studies were the same as the samples also used in this current research studies.

3.2. Methods

3.2.1. Sampling method

Soil samples were collected in three sampling points along the main dump sites. In each sampling point, surface soils were collected using soil auger from 10 cm depth. Soil samples were mixed thoroughly in each sampling point to make composite samples. Around 1 kg composite sample from each sampling point was taken and brought for laboratory analysis in the Hungarian University of Agriculture and Life Sciences, Institute of Environmental Sciences, Gödöllő, Hungary.

3.2.2. Preparation of drying sample

Some amount of sieved powder was started to be add into the tube (50 mL plastic centrifuge tube) until an approximately of 1 g; After measuring 1 g of each sample powder, they were moved to the table where acetic acid or Lakanen-Erviö extractant was added.

3.2.3. One-step batch extraction of samples using Acetic acid

The acetic acid of 0.11 M was used; 5 ml of acetic acid was taken twice using automatic pipette and mixing it with each sample of approximately 1 g prepared soil sample; After adding 10 ml of acetic acid to each prepared sample, the homogeneous mixture of solute and solvent was done by using two types of instruments: (a) Multi-rotator for homogenizing samples by rotating them at different times. The first batch was rotated in the period of 30 minutes; The second one was rotated in the period of 45 minutes; The last one was rotated in the period of 60 minutes. (b) Digital lab orbital shaker for homogenizing samples by shaking them at the time of 60 minutes.

3.2.4. One-step batch extraction of samples using Lakanen-Erviö extractant

5 ml of Lakanen-Erviö extractant was taken twice using automatic pipette and mixing it with each sample of approximately 1 g of prepared waste rock; After adding 10 ml of Lakanen-Erviö extractant to each prepared sample, the homogenization of solution was performed by using two types of instruments: (a) Multi-rotator for homogenizing samples by rotating them in the period of 60minutes. (b) Digital lab Orbital shaker for homogenizing samples by shaking them at the time of 60 minutes.

3.2.5. Filtration of sample solution

The tubes (Plastic Graduated cylinders) of 15 ml supported by flasks were taken, then after the filter papers were appropriately folded; The filter papers were put on the funnels and then put funnels on the tubes of 15 ml supported by flask for each; The homogeneous solution was poured on the filter paper laid on each funnel; The filtered solutions had started to flow from the filter papers through the funnels to the tubes.

3.2.6. Quantitative analysis

Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) were used for the quantitative analysis of elements in samples. The ICP-OES has high capacity to detect elements at very low concentrations, typically down to parts per billion or even parts per trillion levels. It can analyze multiple elements simultaneously, making it efficient for complex samples and relatively quickly.

3.2.7. Statistical Analysis

The statistical analysis was carried out by means using SPSS software. Treatment effects were determined by analysis of variance (ANOVA). Differences were considered significant if $p < 0.05$.

3.2.8. Mobility Factor (MF)

The heavy metal mobility was determined as Mobility Factor (MF) by comparing the concentration (mg/kg dry weight) of samples obtained from the use of Acetic acid and Lakanen Erviö solution separately to the Pseudo-total element content (mg/kg dry weight) of the samples after microwave assisted digestion with Nitric acid and Hydrogen peroxide ($\text{HNO}_3/\text{H}_2\text{O}_2$).

3.2.9. Hierarchy for preparing solutions

The Figure (4) below shows the methodology used in this study work for getting 32 subsamples from 3 main samples.

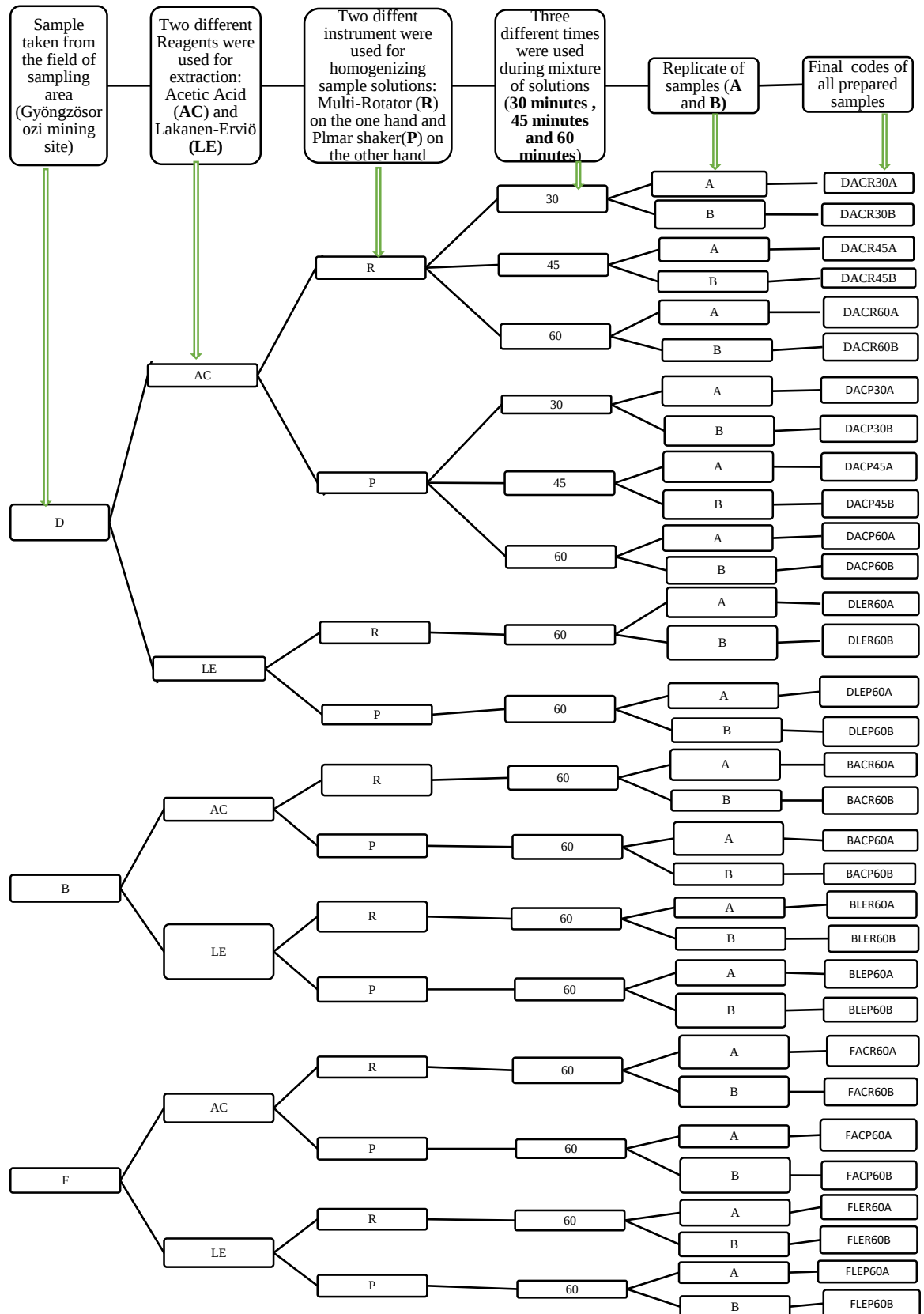


Figure 4. Shows the performed methodology used for preparing 32 solutions

4. RESULTS AND DISCUSSION

With reference to the methodology located in Figure 2, each code of prepared sample was linked with its result in concentration (mg/kg dry weight) gotten after quantitative analysis using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The output was figured out in Table 2.

Table 2. Codes of prepared samples linked with their concentration in solid samples

Code of prepared samples	Concentration in solid samples (mg/kg dry weight)			
	Cd	Cu	Pb	Zn
DACR30A	0.304	0.782	201.8	47.58
DACR30B	0.281	0.762	178.1	46.50
DACR45A	0.352	0.741	176.4	46.23
DACR45B	0.356	0.733	203.5	53.03
DACR60A	0.378	0.706	191.6	52.07
DACR60B	0.317	0.748	189.0	49.65
DACP30A	0.338	0.766	180.2	52.26
DACP30B	0.296	0.890	162.1	47.80
DACP45A	0.337	0.698	187.9	52.47
DACP45B	0.342	0.732	198.8	54.76
DACP60A	0.324	0.726	187.0	50.80
DACP60B	0.351	0.729	169.7	50.02
BACR60A	0.022	0.359	6.913	11.91
BACR60B	0.036	0.411	6.799	12.75
BACP60A	0.025	0.409	7.055	12.52
BACP60B	0.019	0.359	6.416	11.36
FACR60A	bdl	0.619	413.2	12.59
FACR60B	bdl	0.701	423.2	12.21
FACP60A	bdl	0.650	431.6	12.84
FACP60B	bdl	0.641	419.1	12.79
DLER60A	0.678	7.236	1837	86.06
DLER60B	0.692	7.440	2010	85.01
DLEP60A	0.739	7.556	1909	91.60
DLEP60B	0.676	6.929	1894	90.96
BLER60A	0.204	3.630	165.1	26.33
BLER60B	0.174	3.555	173.5	26.57
BLEP60A	0.152	3.641	157.2	25.15
BLEP60B	0.170	3.438	145.9	24.95
FLER60A	0.105	2.003	5100	18.98
FLER60B	0.107	1.985	5086	18.73
FLEP60A	0.095	1.793	3464	17.45
FLEP60B	0.070	1.760	3148	15.98

Overall results of 4 targeted heavy metal elements (Cadmium, Copper, Lead and Zinc) in three main samples were showed in the Table 3, according to the used extractants which were acetic acid and Lakanen Erviö extractant.

Table 3. The concentration results (mg/kg) of Cadmium, Copper, Lead and Zinc

Samples	Targeted heavy metal elements	Concentration of heavy metal elements (mg/kg of weight) by using Acetic acid as extractant	Concentration of heavy metal elements (mg/kg of weight) by using Lakanen Erviö as extractant
B11	Cd	0.026 ± 0.007	0.175 ± 0.022
	Cu	0.384 ± 0.029	3.566 ± 0.093
	Pb	6.796± 0.274	160.4 ± 11.72
	Zn	12.14 ± 0.629	25.75 ± 0.817
D11	Cd	0.331 ± 0.028	0.696 ± 0.029
	Cu	0.751 ± 0.050	7.290 ± 0.275
	Pb	185.5 ± 12.76	1913± 72.19
	Zn	50.27 ± 2.770	88.41 ± 3.356
F11	Cd	bdl	0.094 ± 0.017
	Cu	0.653 ± 0.035	1.885 ± 0.127
	Pb	421.8 ± 7.730	4200 ± 1040
	Zn	12.61 ± 0.286	17.79 ± 1.379

4.1.The statistical analysis of samples on the impact of results found

Table 4. Analysis of variance among samples

		ANOVA					
		Sum of Squares	df	Mean Square	F	Sig.	
Cadmium	Between Groups	.985	2	.493	30.004	<.001	
	Within Groups	.476	29	.016			
	Total	1.461	31				
Copper	Between Groups	6.664	2	3.332	.636	.537	
	Within Groups	151.900	29	5.238			
	Total	158.564	31				
Lead	Between Groups	22530766.243	2	11265383.121	8.006	.002	
	Within Groups	40804286.864	29	1407044.375			
	Total	63335053.106	31				
Zinc	Between Groups	14665.413	2	7332.706	43.250	<.001	
	Within Groups	4916.752	29	169.543			
	Total	19582.165	31				

With reference to the Table 4, the F-statistics of 30.004, 8.006 and 43.25 for Cadmium, Lead and Zinc, respectively are greater than the critical value for F-distribution [$F_{\alpha, (v_1, v_2)} = F_{0.05, (2, 29)} = 3.31$]; This means that there was a significant difference between the mean concentration (mg/kg dry weight) of Cadmium, Lead and Zinc in samples. With reference also to the Table 4 at the last column, the significant levels of <0.001, 0.002 and <0.001 for Cadmium, Lead and Zinc, respectively were lower than significant value (0.05); This means that there was a significant difference between the mean concentration (mg/kg dry weight) of Cd, Pb and Zn in samples.

Where

V1: Numerator degrees of freedom or treatment between groups; V2: Denominator degrees of freedom or Error within groups; α : Significant value of 0.05.

The F-statistics of 0.636 for Copper was low than the critical value for F-distribution [$F_{\alpha, (v_1, v_2)} = F_{0.05, (2, 29)} = 3.31$]; This means that there was no significant difference between the mean concentration (mg/kg dry weight) of Copper in samples. The significant levels of 0.537 for Copper was greater than significant value (0.05); This means that there was no significant difference between the mean concentration (mg/kg dry weight) of Cu in samples.

4.2.The statistical analysis of extractants on the impact of results found

Table 5. Analysis of variance between extractants

		ANOVA				
		Sum of Squares	df	Mean Square	F	Sig.
Cadmium	Between Groups	.105	1	.105	2.312	.139
	Within Groups	1.357	30	.045		
	Total	1.461	31			
Copper	Between Groups	96.607	1	96.607	46.777	<.001
	Within Groups	61.958	30	2.065		
	Total	158.564	31			
Lead	Between Groups	26901849.158	1	26901849.158	22.152	<.001
	Within Groups	36433203.949	30	1214440.132		
	Total	63335053.106	31			
Zinc	Between Groups	590.560	1	590.560	.933	.342
	Within Groups	18991.605	30	633.054		
	Total	19582.165	31			

With reference to the Table 5, the F-statistics of 46.777 and 22.152 for Copper and Lead respectively were greater than the critical value for F-distribution [$F_{\alpha, (v_1, v_2)} = F_{0.05, (1, 30)} = 4.17$]; This means that there was a significant difference between the use of acetic acid and Lakanen Erviö extractant, separately in the extraction of Copper and Lead. With reference also to the Table 5 at the last column, the significant levels of <0.001 and <0.001 for Copper and Lead, respectively were lower than significant value (0.05); This also means that there was a significant difference between the use of acetic acid and Lakanen Erviö extractant separately in the extraction of Copper and Lead.

With reference to the Table 5, the F-statistics of 2.312 and 0.933 for Cadmium and Zinc, respectively were lower than the critical value for F-distribution [$F_{\alpha, (v_1, v_2)} = F_{0.05, (1, 30)} = 4.17$]; This means that there was no significant difference between the use of acetic acid and Lakanen Erviö separately in the extraction of Copper and Lead. With reference also to the Table 5 at the last column, the significant levels of 0.139 and 0.342 for Cadmium and Zinc respectively were greater than significant value (0.05); This also means that there was no significant difference between the use of acetic acid and Lakanen Erviö separately in the extraction of Copper and Lead.

4.3. The statistical analysis of matrix between samples and extractants

Table 6. The statistical analysis of matrix between samples and extractants

Tests of Between-Subjects Effects							
Source	Dependent Variable	Type III Sum of Squares	df	Mean Square	F	Sig.	Partial Eta Squared
Corrected Model	Cadmium	1.447 ^a	5	.289	553.079	<.001	.991
	Copper	158.230 ^b	5	31.646	2459.717	<.001	.998
	Lead	60073267.450 ^c	5	12014653.490	95.770	<.001	.948
	Zinc	19454.835 ^d	5	3890.967	794.513	<.001	.993
Intercept	Cadmium	1.313	1	1.313	2509.039	<.001	.990
	Copper	158.352	1	158.352	12308.041	<.001	.998
	Lead	35572079.826	1	35572079.826	283.548	<.001	.916
	Zinc	32122.764	1	32122.764	6559.285	<.001	.996
Samples	Cadmium	1.340	2	.670	1279.812	<.001	.990
	Copper	41.451	2	20.726	1610.921	<.001	.992
	Lead	19991112.911	2	9995556.455	79.676	<.001	.860
	Zinc	18790.825	2	9395.412	1918.490	<.001	.993
Extractants	Cadmium	.278	1	.278	531.535	<.001	.953
	Copper	89.978	1	89.978	6993.626	<.001	.996
	Lead	24016012.925	1	24016012.925	191.434	<.001	.880
	Zinc	2431.376	1	2431.376	496.473	<.001	.950
Samples * Extractants	Cadmium	.104	2	.052	99.678	<.001	.885
	Copper	35.974	2	17.987	1398.060	<.001	.991
	Lead	13233662.722	2	6616831.361	52.743	<.001	.802
	Zinc	1488.006	2	744.003	151.921	<.001	.921
Error	Cadmium	.014	26	.001			
	Copper	.335	26	.013			
	Lead	3261785.656	26	125453.294			
	Zinc	127.330	26	4.897			
Total	Cadmium	3.433	32				
	Copper	287.095	32				
	Lead	89673987.890	32				
	Zinc	66856.584	32				
Corrected Total	Cadmium	1.461	31				
	Copper	158.564	31				
	Lead	63335053.106	31				
	Zinc	19582.165	31				

a. R Squared = .991 (Adjusted R Squared = .989)

b. R Squared = .998 (Adjusted R Squared = .997)

c. R Squared = .948 (Adjusted R Squared = .939)

d. R Squared = .993 (Adjusted R Squared = .992)

The matrix was formed by two independent variables which are samples (D₁₁, B₁₁ and F₁₁) and extractants (acetic acid and Lakanen Erviö). The matrix was constituted by 3 main columns of samples with 4 sub main columns of heavy metal elements (Cd, Cu, Pb and Zn) and two main rows of extractants (acetic acid and Lakanen Erviö).

4.3.1. Matrix between samples and extractants with results of Cd, Cu, Pb and Zn elements in concentration (mg/kg)

Table 7. Matrix between samples and extractants

Samples Extractants	B11				D11				F11			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
Acetic acid	0.025	0.384	6.795	12.13	0.331	0.751	185.5	50.26	bdl	0.652	421.7	12.60
Lakanen Erviö	0.175	3.566	160.4	25.74	0.696	7.290	1912	88.41	0.094	1.885	4199	17.78

The statistical analysis in the Table 6 showed that there was a significant difference between the matrix of samples and extractants where the F-statistics of 99.678, 1398.060, 52.743 and 151.921 for Cadmium, Copper, Lead and Zinc, respectively were greater than the critical value for F-distribution [$F_{\alpha, (v_1, v_2)} = F_{0.05, (2, 26)} = 3.37$]. The significant levels of 0.001, 0.001, 0.001 and 0.001 for Cadmium, Copper, Lead and Zinc, respectively were lower than significant value (0.05); This also means that there was a significant difference between the matrix of samples and extractants.

Cadmium

The Figure 5 shows that Lakanen Erviö was a stronger extractant than Acetic acid among all samples for extracting Cadmium element.

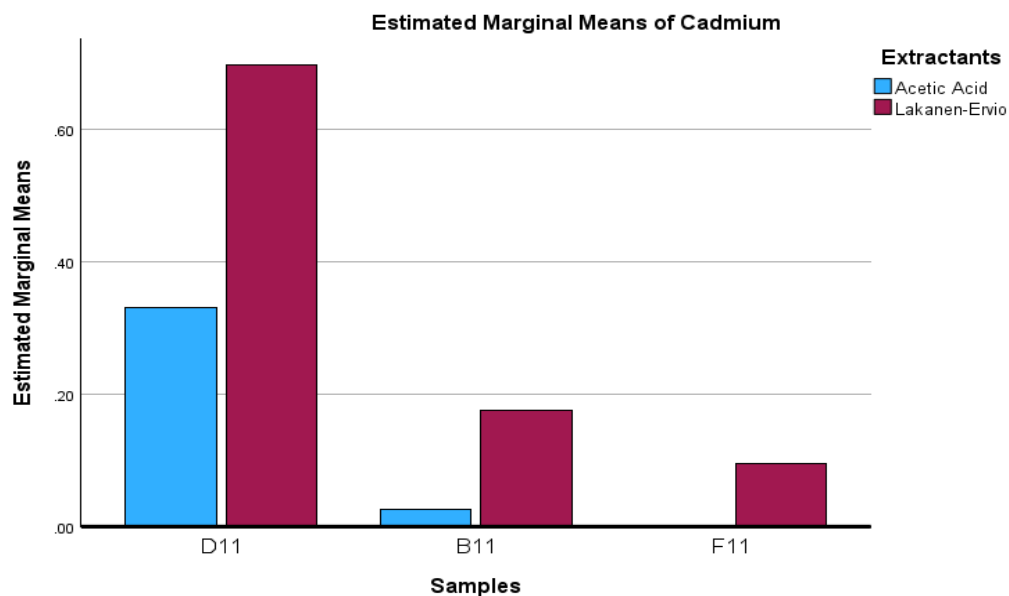


Figure 5. The concentration level of Cadmium among samples and the capability of extractants for extracting it from samples

Copper

The Figure 6 shows that Lakanen Erviö was a stronger extractant than Acetic acid among all samples for extracting Copper element.

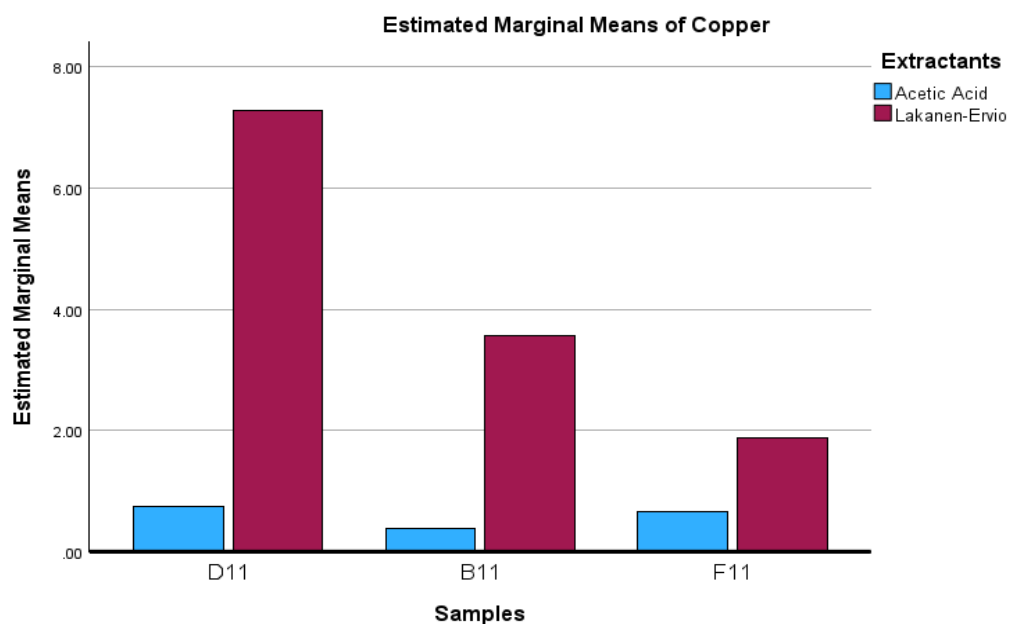


Figure 6. The concentration of Copper among samples and the capability of extractants for extracting it from samples

Lead

The Figure 7 shows that Lakanen Erviö was a stronger extractant than Acetic acid among all waste rock samples for extracting Lead element.

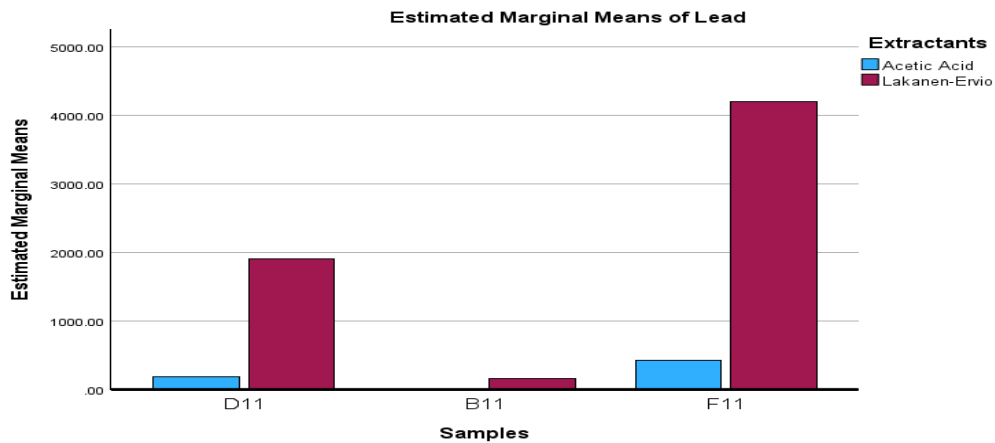


Figure 7. The concentration of lead among samples and the capability of extractants for extracting it from the samples

Zinc

The Figure 8 shows that Lakanen Erviö was a stronger extractant than Acetic acid among all samples for extracting Zinc element.

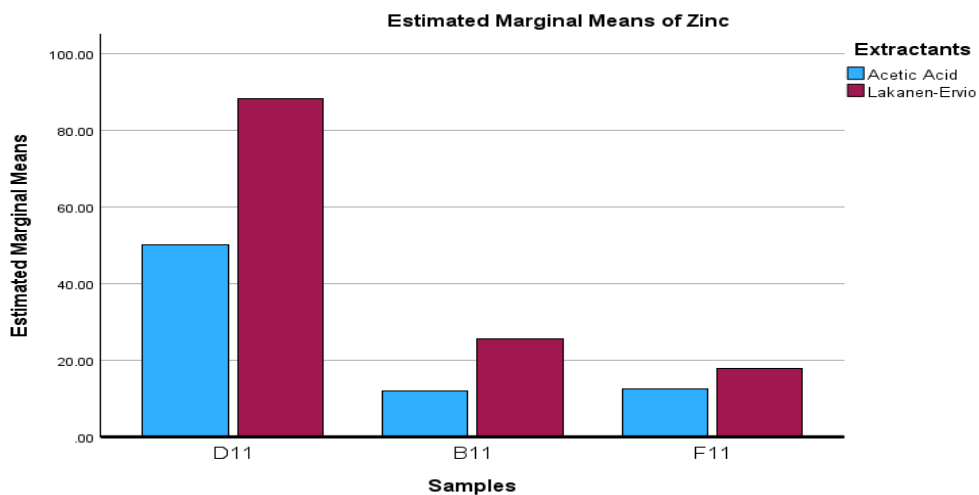


Figure 8. The concentration level of Zinc among samples and the capability of extractants for extracting it from the samples

4.4. The statistical analysis of mixers on the impact of results found

Table 8. Analysis of variance between mixers

		ANOVA				
		Sum of Squares	df	Mean Square	F	Sig.
Cadmium	Between Groups	.000	1	.000	.003	.953
	Within Groups	1.461	30	.049		
	Total	1.461	31			
Copper	Between Groups	.015	1	.015	.003	.958
	Within Groups	158.549	30	5.285		
	Total	158.564	31			
Lead	Between Groups	426442.428	1	426442.428	.203	.655
	Within Groups	62908610.678	30	2096953.689		
	Total	63335053.106	31			
Zinc	Between Groups	9.613	1	9.613	.015	.904
	Within Groups	19572.552	30	652.418		
	Total	19582.165	31			

With reference to the statistical analysis located in Table 8, the F-statistics of 0.003, 0.003, 0.203 and 0.015 for Cadmium, Copper, Lead and Zinc, respectively were lower than the critical value for F-distribution [$F_{\alpha, (v_1, v_2)} = F_{0.05, (1, 30)} = 4.17$]; This means that there was no significant difference between the use of Multi-rotator and Palmer shaker separately during mixing. The calculated significant levels of 0.953, 0.958, 0.655 and 0.904 for Cadmium, Copper, Lead and Zinc, respectively were greater than significant value (0.05); This also means that there was no significant difference between the use of Multi-rotator and Palmer shaker separately during mixing.

4.5. The statistical analysis of time periods used for mixing solutions

Table 9. Analysis of variance between time period used for mixing

		ANOVA				
		Sum of Squares	df	Mean Square	F	Sig.
Cadmium	Between Groups	.068	2	.034	.706	.502
	Within Groups	1.393	29	.048		
	Total	1.461	31			
Copper	Between Groups	16.437	2	8.218	1.677	.205
	Within Groups	142.128	29	4.901		
	Total	158.564	31			
Lead	Between Groups	5547285.110	2	2773642.555	1.392	.265
	Within Groups	57787767.997	29	1992681.655		
	Total	63335053.106	31			
Zinc	Between Groups	1465.532	2	732.766	1.173	.324
	Within Groups	18116.633	29	624.711		
	Total	19582.165	31			

The statistical analysis located in the Table 9 shows that there was no significant difference between the 3 time periods (30 minutes, 45 minutes and 60 minutes) used for mixing solutions, where the F-statistics of 0.706, 1.677, 1.392 and 1.173 for Cadmium, Copper, Lead and Zinc, respectively were lower than the critical value for F-distribution [$F_{\alpha, (v_1, v_2)} = F_{0.05, (2, 29)} = 3.33$].

The significant levels of 0.502, 0.205, 0.265 and 0.324 for Cadmium, Copper, Lead and Zinc, respectively were greater than significant value (0.05); This also means that there was no significant difference between those 3 time periods used for mixing.

4.6. The statistical analysis of replicate on the impact of results found

Table 10. Analysis of variance for replicate

		ANOVA				
		Sum of Squares	df	Mean Square	F	Sig.
Cadmium	Between Groups	.001	1	.001	.018	.895
	Within Groups	1.460	30	.049		
	Total	1.461	31			
Copper	Between Groups	.008	1	.008	.001	.969
	Within Groups	158.557	30	5.285		
	Total	158.564	31			
Lead	Between Groups	1260.824	1	1260.824	.001	.981
	Within Groups	63333792.282	30	2111126.409		
	Total	63335053.106	31			
Zinc	Between Groups	.448	1	.448	.001	.979
	Within Groups	19581.717	30	652.724		
	Total	19582.165	31			

The statistical analysis located in the Table 10 showed that there was no significant difference between the replicated samples, where the F-statistics of 0.018, 0.001, 0.001 and 0.001 for Cadmium, Copper, Lead and Zinc, respectively were lower than the critical value for F-distribution [$F_{\alpha, (v_1, v_2)} = F_{0.05, (1, 30)} = 4.17$]. The significant levels of 0.895, 0.969, 0.981 and 0.979 for Cadmium, Copper, Lead and Zinc, respectively were greater than significant value (0.05); This also means that there was no significant difference between the replicated samples.

4.7. Determination of heavy metal mobility

Mobility factors were used to assess and compare the relative mobility of 4 heavy metals (Cadmium, Copper, Lead and Zinc) under D11, B11 and F11 waste rock samples.

With this research study, the mobility factor was determined by comparing the concentration of a heavy metal in the potentially mobile fractions extracted by acetic acid and Lakanen Erviö, separately to the Pseudototal concentration of that metal in the waste rock sample.

A simplified formula for estimating the mobility factor (MF) could be:

$$\text{MF} = (\text{C mobile} / \text{C total}) * 100$$

Where: **MF** = Mobility factor of the heavy metal; **C mobile** = Concentration of the heavy metal in the mobile fractions; **C total** = Total concentration of the heavy metal in the waste rock sample

The mobility factor calculated using this formula provided insight into the relative mobility or bioavailability of the heavy metal in the sample. A higher mobility factor suggested a higher proportion of the metal was potentially mobile or bioavailable, while a lower mobility factor indicated a lower proportion of the metal was likely to be mobile or bioavailable.

Table 11. Reveals the calculation of mobility factor of Cd, Cu, Pb and Zn by comparing the potentially mobile fractions extracted by acetic acid and Lakanen Erviö separately to the Pseudototal concentration of these metals

Samples	Targeted heavy metal elements	Concentration of heavy metal elements (mg/kg of weight) by using Acetic acid as extractant	Concentration of heavy metal elements (mg/kg of weight) by using Lakanen Erviö as extractant	Pseudototal element content (mg/kg dry weight) of the samples (after microwave assisted digestion with HNO ₃ /H ₂ O ₂)	Mobility factor (%)	
					Comparing the concentration obtained by using acetic acid as extractant to the Pseudototal concentration	Comparing the concentration obtained by using Lakanen Erviö as extractant to the Pseudototal concentration
B11	Cd	0.025± 0.007	0.1752 ± 0.022	bdl	<i>No data found</i>	<i>No data found</i>
	Cu	0.384± 0.029	3.566 ± 0.093	40.09 ± 0.026	1.0	8.9
	Pb	6.79 ± 0.274	160.4 ± 11.72	797.3 ± 4.025	0.9	20.1
	Zn	12.13 ± 0.629	25.74 ± 0.817	162.6 ± 0.388	7.5	15.8
D11	Cd	0.331 ± 0.028	0.696 ± 0.029	7.894 ± 0.055	4.2	8.8
	Cu	0.751 ± 0.050	7.290 ± 0.275	62.22 ± 0.168	1.2	11.7
	Pb	185.5± 12.75	1912 ± 72.18	4348±10.20	4.3	44.0
	Zn	50.26 ± 2.770	88.41 ± 3.356	1239± 0.638	4.1	7.1
F11	Cd	bdl	0.094 ± 0.017	5.909 ± 0.064	<i>No data found</i>	1.6
	Cu	0.652 ± 0.035	1.885 ± 0.126	36.98 ± 0.123	1.8	5.1
	Pb	421.7 ± 7.730	4199±1039	6043±23.49	7.0	69.5
	Zn	12.60 ± 0.286	17.78 ± 1.379	1044± 2.777	1.2	1.7

The high mobility of heavy metals was shown by the use of Lakanen Erviö as an extractant more than using Acetic acid. The mobility of Cadmium by using Acetic Acid as extractant was 4.3% in D11 sample; The mobility of Cadmium by using Lakanen Erviö as extractant ranged from 1.6% in F11 sample to 8.8% in D11 sample. The mobility of Copper by using Acetic Acid as extractant ranged from 1.0% in B11 sample to 1.8% in F11 sample; The mobility of Copper by using Lakanen Erviö as extractant ranged from 5.1% in F11 sample to 11.7% in D11 sample. The mobility of

Lead by using Acetic Acid as extractant ranged from 0.9% in B11 sample to 7.0% in F11 sample; The mobility of Lead by using Lakanen Erviö as extractant ranged from 20.1% in B11 sample to 69.5% in F11 sample. The mobility of Zinc by using Acetic Acid as extractant ranged from 1.2% in F11 sample to 7.5% in B11 sample; The mobility of Zinc by using Lakanen Erviö as extractant ranged from 1.7% in F11 sample to 69.5% in B11 sample

4.8. Assessment of heavy metal contamination

Comparing the measured concentrations obtained by using Acetic Acid as extractant on the one hand and Lakanen Erviö on the other hand to the regulatory guidelines or standards or thresholds for heavy metal concentrations in Hungary. With reference to the Hungarian regulations related to the limit of heavy metals in soil, sediment, water and air shows that the Cadmium, Copper, Lead and Zinc elements should be at most 1 mg/kg, 75 mg/kg, 100 mg/kg and 200 mg/kg, respectively.

Cadmium element found in all samples by using acetic acid and Lakanen Erviö separately revealed that it was lower than the standard limit of 1 mg/kg; Its highest concentration was 0.69 mg/kg obtained in D11 sample by using Lakanen Erviö as extractant. This means that It was below the limit. Copper element found in all samples by using acetic acid and Lakanen Erviö separately revealed that it was lower than the standard limit of 75 mg/kg; Its highest concentration was 7.29 mg/ kg obtained in D11 sample by using Lakanen Erviö as extractant. This means that It was below the limit.

Lead element found in all samples except B11 sample (extracted using acetic acid) were extremely high than the standard limit of 100 mg/kg; The extraction of Lead with Acetic acid showed high concentration in D11 and F11 samples for 185 mg/kg and 422 mg/kg, respectively; The extraction of Lead with Lakanen Erviö revealed a high concentration in B11 sample for 160 mg/kg and also showed an extremely high concentration in D11 and F11 samples for 1912 mg/kg and 4199 mg/kg, respectively. This means that there were negative effects caused by lead in the environment of the study area.

Zinc element found in all samples by using acetic acid and Lakanen Erviö separately revealed that it was lower than the standard limit of 200 mg/kg. Its highest concentration was 88.8 mg/ kg obtained in D11 sample by using Lakanen Erviö as extractant; This means that It was below the limit.

5. CONCLUSIONS AND PROPOALS

The determination of heavy metals in waste rock dump released out valuable information which are useful for better management of mining site and its surrounding area. The mining dump site serves as source of potential toxic elements and poses danger to the downstream ecosystems like rivers, farms and resident communities; However, the gotten results provide data required for taking action of reducing the negative impact of heavy metals on the environment and human health of the surrounding area.

The waste rock dump should be protected in the way that their effects on the natural environment and human health are minimized for an unlimited period of time. The controls and statutory regulations for waste rock dump should be tightened in all countries, and the engineering skills related to the protection and the safety of waste rock dump from mining activities should also be improved.

This research study revealed that the waste rock dump located in Mátraszentimre, Northern Hungary has lower concentrations of Cd, Cu and Zn with reference to the standards limit of heavy metal in Hungary. The concentration of Pb is extremely high than the acceptable limit in Hungarian standards. The use of acetic acid and Lakanen Erviö separately during extraction showed that there is a significant difference between the results provided by them. The samples used in this research study revealed that there was a significant difference among them according to the concentration of Cd, Cu, Pb and Zn obtained in each sample. The mixers, time periods and replication of samples used for preparing the final homogeneity solutions showed that there were no significances different among them (the use of different mixers, use of different time periods for mixing, and replicated samples did not affect the results of this research study).

Phytoremediation activity is needed in the area to lessen the downward mobility of heavy metals (like Pb which is extremely high in waste rock deposited by Gyöngyösoroszi mining) and to protect the soil ecosystems and water sources.

6. SUMMARY

The aim of this research was to study the mobility and availability of potentially toxic elements in waste rocks deposited by the Gyöngyösoroszi mining, Hungary. A rapid diagnosis about toxic element behavior has been performed using two single-step extraction procedures, two different laboratory mixers and three different time periods of mixing. Single-step extraction by Lakanen & Erviö and with acetic acid are two common methods used for extracting easily mobilisable toxic elements simultaneously. The elements studied were Cd, Cu, Pb and Zn due to their hazardous potential and related abundance in the waste rock dump of mining activities. The waste rock samples were collected in the field and analyzed using Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-OES). The statistical analysis was carried out by means using SPSS software. Treatment effects were determined by analysis of variance (ANOVA). Differences were considered significant if $p < 0.05$. The grand mean of concentration (mg/kg) in all waste rock samples extracted by using acetic acid were 0.204, 0.658, 197 and 35.1 mg kg⁻¹ for Cd, Cu, Pb and Zn, respectively. On the other hand, the grand mean of heavy metal content extracted by using Lakanen & Erviö method were 0.322, 4.25, 2091 and 43.98, respectively. The concentration of Cd, Cu, Pb and Zn extracted in all waste rock samples by using acetic acid were lower compared to the use of Lakanen & Erviö as extractant. Lead (Pb) had a high mobility and was in critical category due to its concentration which was extremely high than the Hungarian standards of potentially toxic element limit. The combination of single-step extraction methods and multivariate techniques provided useful information about the waste rock dump samples and a better understanding about heavy metal mobility, availability and hazardousness.

Keywords: Single step extractions, potentially toxic elements, mining, acetic acid, Lakanen-Erviö, mobility, ICP-OES

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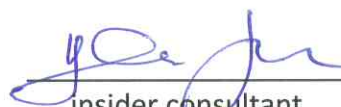
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