



Program: Environmental engineering

## **Bachelor Thesis**

Rehabilitation concept for Nalaikh Mining Licence Area (N-MLA): Monitoring of heavy metals in the soils in and around N-MLA.

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Date: 7<sup>th</sup> of May 2019

# Abstract

This thesis was focused on the investigation of environmental impacts of Nalaikh small-scale coal mining to identification and improve the mitigation measures and geotechnical recommendations for the rehabilitation concepts and further development of environmental management in Nalaikh district.

To evaluate the soil contamination levels, potential ecological risks, geo-accumulation index and pollution load indexes were estimated by determining and monitoring the concentrations of heavy metals particularly focused on the presence of arsenic in the soils, in and around Nalaikh mining area along the main wind direction from the northwest to southeast (NW-SE) and assessing the contaminated sites within the monitoring part of rehabilitation pyramid, Knippertz, 2005. An estimation of the arsenic content was used to make an interpolation of special distribution in Nalaikh basin, in which 19 sampling points on topsoil were investigated and based on that and the results were compared with the previous study (1). Moreover, by the request from Nalaikh government, 7 soil samples from 5 gardens in Nalaikh ger settlement area were examined and heavy metals content were measured by X-ray fluorescence spectrometry in the field.

In most cases, the content of elements did not exceed the maximum permissible values. However, the concentration of arsenic (As), cobalt (Co) and cadmium (Cd) were above the Mongolian guidelines as well as EU and WHO permissible levels for heavy metals in the soils in which the mean value of As 15.4 mg/kg, Co 138 mg/kg and Cd 11.5 mg/kg were measured. The highest concentration of arsenic (As) was detected in the nearest sampling point to the mining area with the value of 31.1 mg/kg.

The range of geo-accumulation index was ( $-0.595 < I_{geo} < 0.882$ ), indicating that some soils were not polluted and the others not to moderate contaminated by arsenic. In general, the accumulation of arsenic was high near to the mining area than the other areas which has less As when it goes far from the mine and the distribution of arsenic is entering into the settlement area from the mining region and the ash basin from the power plant.

**Keywords:** Soils, Arsenic, heavy metals, Nalaikh, mining, monitoring



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# 1. Introduction

This thesis was studied within a monitoring part of the project which investigates both environmental impacts and socio-economic conditions that influenced by mining activities. The purpose of the project is to identify and improve the mitigation measures and geotechnical recommendations based on the methodological approach of a rehabilitation pyramid as shown in (*Figure 1*), for the further development of environmental management in Nalaikh district and is supported by the German Corporation for International Cooperation (GIZ). Under the concept of monitoring part, and the aim of determining the geo-ecological impacts of the artisanal mining area, the presence of the heavy metals which released around the small-scale mining area along the main wind direction was investigated by X-ray fluorescence spectrometry. The field measurements were obtained from the 27<sup>th</sup> of March to 10<sup>th</sup> of April 2019.

In recent years, pollution of heavy metals has increased due to the anthropogenic activities such as an acceleration of industrialization, a growth of urbanization and mining operations, causing damages to the natural environment with a result of long-term cumulative health issues, even at very low concentration. However, most of these environmental-related diseases are not easy to detect and could be acquired for a long time inside a human body. Therefore, an estimation of the content and availability of heavy metals in the soils is of major importance to environmental health, crops and livestock production, food, water quality, and further use because trace elements might enter the human body via the consumption of contaminated drinking water or crops and vegetables grown on polluted soils. Hence the presence of heavy metals in garden soils were estimated, and chemical and physical properties of samples were analysed within the request from Nalaikh government. Emissions from the transport and ovens in the ger areas settle close to the ground for a long time, thus which is more problematic and harmful for the residents than the industrial emissions from high chimneys (1).

In this study several heavy metals were detected including antimony (Sb), arsenic (As), barium (Ba), cadmium (Cd), cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), lead (Pb), nickel (Ni), manganese (Mn), mercury (Hg), strontium (Sr), tin (Sn), rubidium (Rb), and zinc (Zn) of those, a few metals which have a content of below the detection limit has not been taken into account.

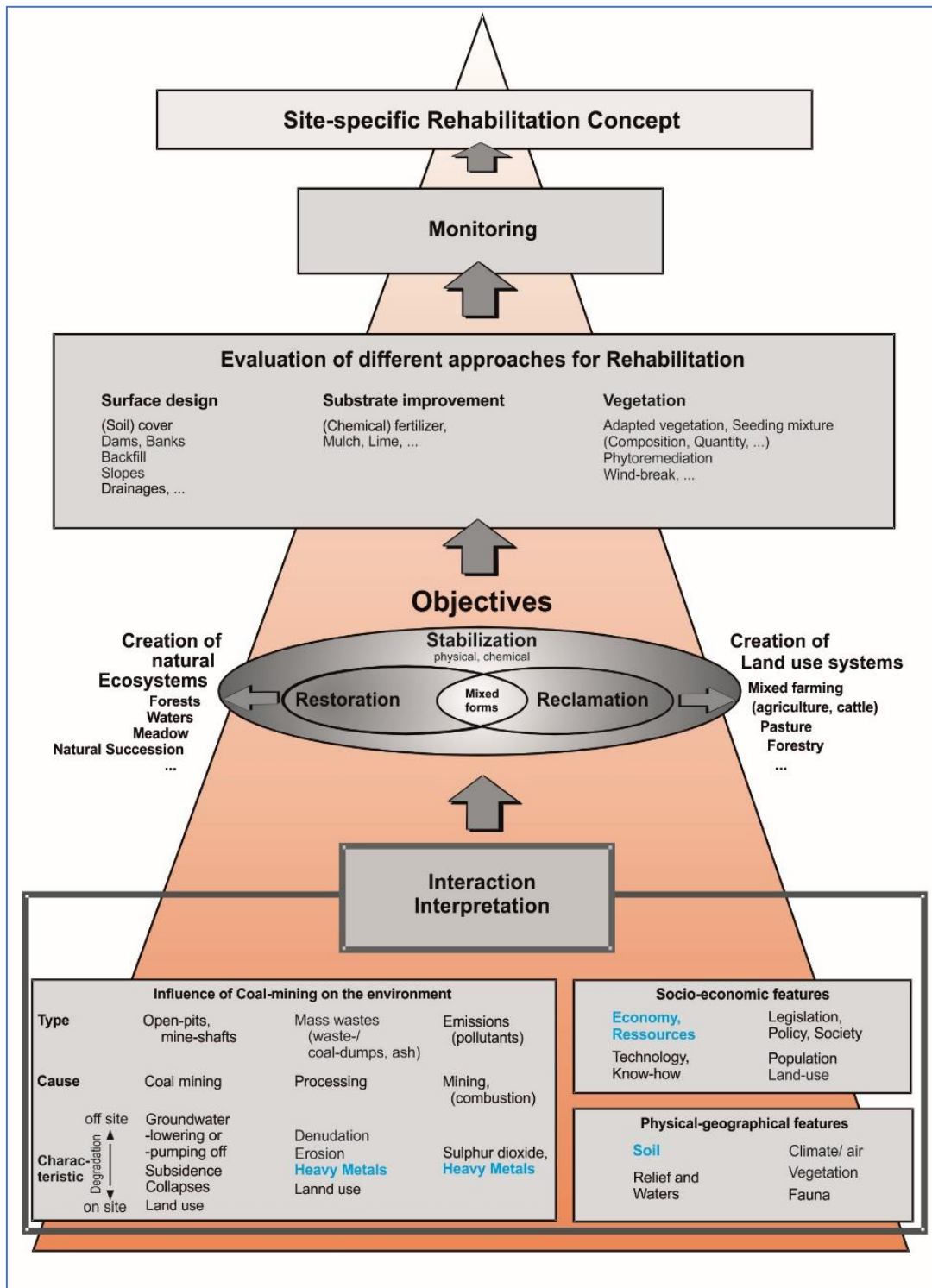


Figure 1 Rehabilitation Pyramid proposed by Knippertz,2005 (2).

A rehabilitation concept is an important part of every mining activities and the identification of possibilities and perspectives for rehabilitation, mitigation measures and derivation of recommendation and improvements on affected mining areas are dependent on various factors that are modelled in a rehabilitation concept pyramid in which the method's transferability to other products besides coal or to different ecozones has been proved in the study (2). As shown in (*Figure 1*), at the bottom of the pyramid the influencing factors are classified in three groups as the influence of coal mining on the environment, socio-economic features and physical-geographical features which must be taken into account and analysed within the first step. The interpretation of interactions between these influencing factors determine the objectives of the rehabilitation process in which reclamation refers to the creation of land use systems, whereas restoration leads to the creation of natural ecosystems. The physical or chemical stabilization of objectives describes the stability and security of the whole process. Depending on the objectives, different approaches for rehabilitation are evaluated. The regular monitoring regarding the main objectives is an essential part of any rehabilitation concept and is important for determining the negative tendency of environmental parameters and helps to establish appropriate countermeasures.

Accumulation of arsenic in the soils and water bodies were presented in many studies in Mongolia such as elevated levels of arsenic in drinking, surface, and groundwater in northern parts of Mongolia have found (3 & 4). According to the previous studies (1 & 5), the concentration of arsenic was elevated in the soils and some water surfaces in and around Nalaikh mining area particularly, the concentration of arsenic in Bus lake was constantly exceeding the WHO guideline (0.01 mg/L) due to the natural presence of arsenic and requires remediation (1 & 5).

Since arsenic is a widely distributed nonessential trace element in nature and is one of the most toxic heavy metals in the world, it is studied more in detail, and the pollution load index, mobility, and geo-accumulation index were calculated based on its measured values via the atmospheric pathway.

## 2. Research Question and Hypothesis

### **The objective of the thesis:**

The main aim of this study is to evaluate the potential ecological risks, geo-accumulation index and pollution load indexes by determining and monitoring the concentrations of heavy metals particularly focused on the presence of arsenic in the soils, in and around Nalaikh mining area along the main wind direction from the northwest to southeast (NW-SE) and assessing the contaminated sites within the monitoring part of rehabilitation pyramid.

Additionally, to determine and investigate the aforementioned parameters and qualities in garden soils where vegetables and fruits are grown within the Nalaikh district area. The purpose is to assess whether it is harmful to human health and meets the heavy metal's guideline for agricultural soils or not.

### **Research Questions:**

**RQ1:** What is the concentration of heavy metals in the soils in and around the Nalaikh mining license area?

**RQ2:** Is there any change on heavy metals (arsenic) concentration along the main wind direction?

**RQ3:** Is the presence of heavy metals accumulated by human activities including mining activity, operation of the power plant, or agricultural use?

**RQ4:** What is the concentration of heavy metals in garden soils?

**RQ5:** Are there any remediation technologies required in Nalaikh basin?

### **Hypothesis:**

**H<sub>1</sub>:** There is a positive correlation between wind direction and the concentration of heavy metals in the soils in which the presence of metals increases along wind direction due to the wind erosion on topsoil.

**H<sub>0,1</sub>:** There is no correlation between wind direction and the concentration of heavy metals in the soils in which the presence of metals does not increase along wind direction due to the wind erosion on topsoil.

**Hypothesis rejection criteria 1:**

If there is either a direct or indirect prevalence between the concentration of heavy metals and wind direction, the null hypothesis will be rejected. On the other side, when there is no correlation between heavy metals content and the main wind direction, the first hypothesis will be disapproved.

**H<sub>2</sub>:** There is a mining impact on the increase in arsenic concentration.

**H<sub>0,2</sub>:** There is no impact on arsenic concentration due to mining activities.

**Hypothesis rejection criteria 2:**

When there is an increase in the concentration of arsenic in the soils in and around the mining area, the second hypothesis will be approved, otherwise, the null hypothesis will be confirmed.

**H<sub>3</sub>:** There is a significant relation on As concentration between the current study and the previous study conducted by Walk J, 2016.

**H<sub>0,3</sub>:** There is a change of As concentration between the current study and the previous study conducted by Walk J, 2016.

**Hypothesis rejection criteria 3:**

If the p – value is less than the alpha (5% = 0.05) means, there is a significant positive relationship between these studies. Otherwise, there is no significant relationship and there is a change on Arsenic concentration by any reason.

## 3. State of the Art

### 3.1 Heavy metals in the soils of mining regions

Heavy metals constitute more than 35 % of the chemical elements in the periodic table with a density of higher than  $5 \text{ g/m}^3$  (6) such as arsenic, cadmium, chromium, cobalt, copper, lead, manganese, mercury, nickel, uranium and vanadium. Some of them including zinc (Zn), iron (Fe), copper (Cu), manganese (Mn), and molybdenum (Mo) are essential nutrients for plant and animal in a very low concentration (6).

Occurrence of heavy metals in the soils can be the result of pedogenesis and weathering processes of the natural rocks or could be present as a part of pollution loads generated by human activities such as application of pesticide, smelting, mining, and agricultural activities, industrialization and disposal with metal content from military activities (6 & 7). Since the concentration of metals is highly accumulated in the soils than water and air, soil plays an important role for nutrient cycles whereas it can be a reservoir for many harmful substances depending on their forms, quantity, and phases (8).

The mining operation is always associated with environmental impacts (9) like pollution of heavy metals (10 & 11) which are accumulated either direct or indirect way. In general, heavy metals in coal gangue are transported by the processes of eluviation, erosion, weathering, and wind driven-particle and soil retention as well (11).

Typically, the heavy metals, around a coal mining area get into the soils in two main paths, including:

- i. coal dust is eroded by the wind in which heavy metals are suspended and dispersed in the atmosphere and sediments in and around mining areas, and
- ii. the pollutants can be formed by the eluviation process in which dissolved or suspended metals inside the soils are transported by a run-off or surface water due to rainfall (11).

Any contaminated site causes a problem for a municipal government and it must be remediated with respect to its sustainability for different land uses. In the lack of control and restoration measures for heavy metals, polluted soils and sediments from mining

are always dispersed by wind and water erosion after their exposure on the earth surface (12).

In arid or semi-arid climate areas like Nalaikh, due to the low amount of precipitation and high rates of evaporation, a mining extraction causes greater impacts in the dispersion of heavy metals since the soils in a dry climate are generally sparsely vegetated (12). The tailings from coal mining usually contain a large number of heavy metals and have low fertility (13).

The total concentration of heavy metals can be applied as a useful indicator for assessing contamination of sediments (14). Although it cannot be appropriate for determining the environmental impacts of contaminated sediments or geochemically enriched soils because depending on their chemical forms, each of them has different remobilization potential and affects its respective toxicity and bioavailability (7). Moreover, the solubility of the organic matter in sediment always determines the mobility of heavy metals in which insoluble organic compounds can strongly reduce the mobility (7). Mobility and bioavailability of the metals are dependent on each other, when the concentrations of mobile toxic metals (As, Pb, Cd, and Cu) are high in the soils, it results in an increase of potential for plant uptake and more probability to the consumption of animal and human (8). The presence of heavy metals in the soils is very dangerous to human, animals, and environment when it is accumulated in a long period (15).

A coal mining operation generates both environmental and social problems among pollution of heavy metals exposure in the soils due to processes of weathering, leaching and decomposing (11).

When heavy metals enter to the soils, they interact with the active phase like clay minerals, oxides, and hydroxides of iron and manganese, and organic substances and then the minerals initial activity is changed either increasing or decreasing its toxicity (16). For example, lead (Pb) becomes less hazardous than metal ions in soil by forming very stable complexes with organic substances (16).

Particularly, emissions and tailings from coal mining or coal-related activities are one of the main sources of arsenic exposure in the topsoil (11 & 17). Therefore, the presence

of arsenic in coal mining area is studied more in detail. However, arsenic is a metalloid, it is considered as one of the most toxic and carcinogenic heavy metals.

In Mongolia, the concentrations of heavy metals are guided by the (MNS 5850:2008) standard for soil quality, soil pollutants elements and substances which define the permissible maximum level for heavy metals concentration depending on the texture of the soils, in which when the soil has more metals than the permissible values as shown in (Table 1), the soil is considered harmful for water bodies, plants, animals and human health. Therefore, protection and prevention measures for remediating, reducing the emissions and more monitoring must be taken.

*Table 1. Permissible max level of heavy metals for soil MNS 5850:2008 guideline in (mg/kg). (Translated from Mongolian) (18).*

Heavy metals	Soil texture			Maximum permissible level
	Clay	Silt	Sand	
Lead (Pb)	100	70	50	100
Cadmium (Cd)	3	1.5	1	3
Mercury (Hg)	2	1	0.5	2
Arsenic (As)	6	4	2	6
Chromium (Cr)	150	100	60	150
Tin (Sn)	50	40	30	50
Strontium (Sr)	800	700	600	800
Vanadium (V)	150	130	100	150
Copper (Cu)	100	80	60	100
Nickel (Ni)	150	100	60	150
Cobalt (Co)	50	40	30	50
Zinc (Zn)	300	150	100	300
Molybdenum (Mo)	5	3	2	5
Selenium (Se)	10	8	6	10
Boron (B)	25	20	15	25
Fluorine (F)	200	150	100	200
Cyanide (CN)	25	15	10	25

In Germany, heavy metals for soils are regulated by the Federal Soil Protection Act and classified for different specific utilization of land. In our study, data were collected from various types of the area which is used for diverse purpose. Therefore, we can apply the heavy metals guideline for any purpose of land use as shown in (Table 2), which indicates preventive values for the soils depending on its characteristic of texture (19).

*Table 2. Preventive action values for heavy metals in the soils by German Federal regulation on soil protection, differentiated by soil texture in (mg/kg) (19).*

Heavy metals	Clay	Silt/ Loam	Sand
Cadmium (Cd)	1.5	1	0.4
Lead (Pb)	100	70	40
Mercury (Hg)	1	0.5	0.5
Chromium (Cr)	100	60	30
Copper (Cu)	60	40	20
Nickel (Ni)	70	50	15
Zinc (Zn)	200	150	60

The EU Community regulates that the presence of arsenic in the agricultural soils should not exceed the content of 20 mg/kg, whereas in the UK, the maximum permissible level for As is 50 mg/kg and the maximum allowable limit in paddy soils is recommended as 15 mg/kg (20).

## 3.2 Arsenic

### 3.2.1 Background of Arsenic

Arsenic is one of the trace elements of Group 15 of Mendeleev's periodic table which is discovered by the famous Alchemist Albertus Magnus (21). It is a metalloid with an atomic number of 33 and has a molecular weight of 74.92 with a chemical formula of As.

Arsenic is the 20<sup>th</sup> most abundant element in the Earth's crust (22) and the average concentration of arsenic is estimated as 1.8 mg/kg and primarily occurs in argillaceous sediments up to 13 mg/kg (20).

The element exists in the anionic state as a part of salt with covalent bonds (21). It occurs in organic and inorganic forms as constituents of various minerals with oxidation states of -3 ( as arsenide), 0, +3 ( arsenite compounds) and +5 ( arsenate compounds), of which more than half are arsenates with a valance of (V) (20) and is less harmful for human and environment than inorganic arsenic (arsenite) due to its solubility (22).

The mobility and toxicity of As (III) in the soil is much greater than As(V) under aerobic conditions (23). Inorganic arsenic is the compounds which exist naturally both in the soil and groundwater in formations of oxide, sulfide, chloride, and sulfate (21). It is a grayish metallic solid which turns black when released into the atmosphere.

### 3.2.2 Chemistry of Arsenic

Toxicity and mobility of elements chemical species are highly dependent on the oxidation states and structures (21).

As(III) is stable at intermediate to low redox potentials, whereas As(V) is the dominant components under oxidized conditions (24). The form of arsenic with an oxidation state of -3 is extremely hazardous and can be found under very high reducing conditions but the presence is very rare in nature (21).

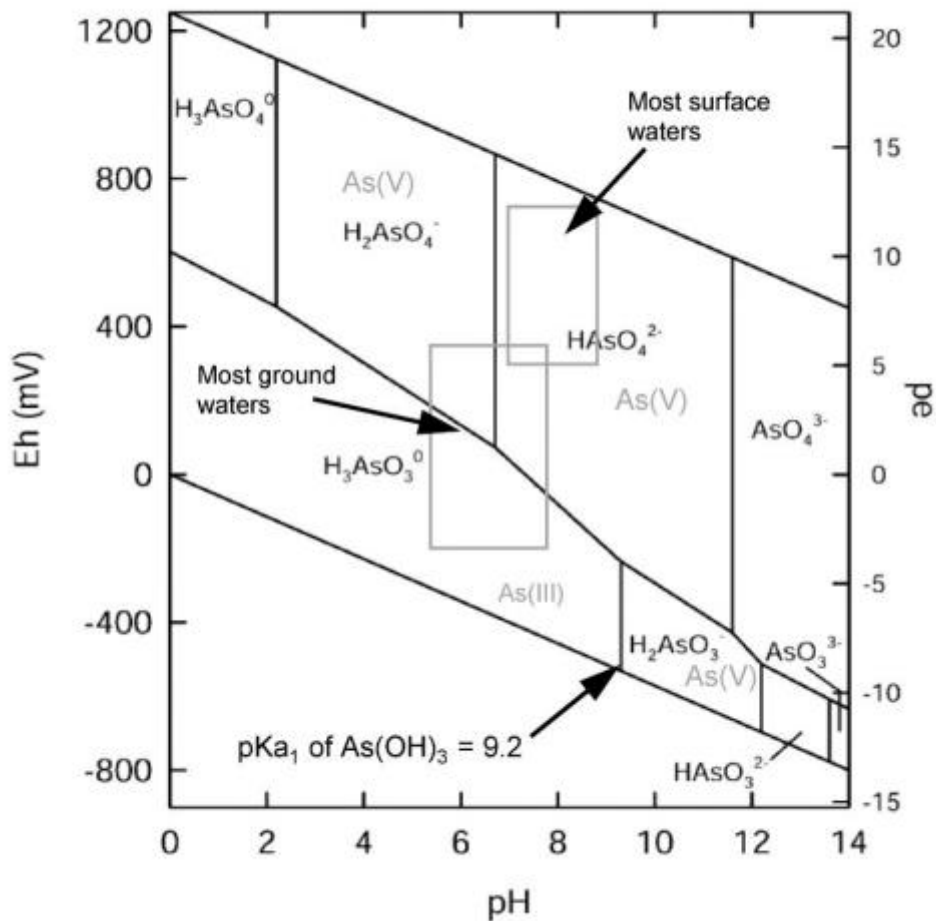


Figure 2 Eh-pH diagram of aqueous arsenic species in the water at 25°C and 1 bar total pressure. Boundaries indicate equal activities of both species (1).

The Figure 2, shows the formation of arsenic under different condition of pH value and redox potential. Arsenate and arsenite are the most common inorganic form in groundwater. It also occurs in both oxic and anoxic waters and sediments as well (21).

In aerobic waters, arsenic acid predominates only at extremely low pH value of less than 2 with a high Eh value. When the pH value is more than 12, the occurrence of As (V) appears as a constituent of  $HAsO_3^{2-}$ . Under moderately reduced conditions, arsenious acid forms at low pH value.

### 3.2.3 Arsenic in Soil

The presence of the arsenic in soils is due to biogeochemical distribution from its both natural and anthropogenic sources. The natural phenomena for increasing the content of arsenic in soil is usually volcanic eruption (21), erosion and weathering processes whereas the agricultural and mining activities, burning fossil fuels, smelting operations, cement manufacturing and a production of waste from different industries are the main contributors for accumulation of arsenic in soils by human activities (23). The several numbers of products can pollute the soils, which have been used in pesticides, animal feed additives, wood preservatives and treatment processes (15).

Anthropogenic elements are all those deposited into soils as direct or indirect results of man's activities. There have been many studies that the behaviour of trace elements in soils and in consequence of their bioavailability differs as to their origin (24).

The study (15) has noted that the presence of arsenic in the soils damages the ecological functions and it has a decrease in biodiversity and activities of soil microorganisms. Arsenate in the soils is less mobile because typically it is insoluble and strongly sorbed in the soils (15). Hazard assessment associated with arsenic enrichment in soils highly depends on the determination of the mobility of minerals (24).

Arsenic exists in nature mostly as a combination with pyrite and sulfide minerals and mostly found with gold in ore deposits or in hard coal and lignite as described in (15 & 24).

## 3.3 Arsenic toxicity in plants

Arsenic does not carry biological functions, but a very low concentration of arsenic can induce growth of the plants depending on several factors, including inadequate phosphate nutrition and displacement of phosphate by arsenate (21). The toxicity of arsenic for plants relies on its chemical properties and availability in the soils. Plants can uptake both arsenite and arsenate (15) in which arsenite causes the main detrimental effects on plants cell whereas arsenate is quickly reduced in the plant cell. The most common symptoms of arsenic in plants are weak root development, loss of plant weight, degradation, poor seed germination and loss of water (21). Disorders of the nutrients especially phosphorous and iron are largely affected by arsenic with a result of too high

levels of micronutrients and excess of toxicity level (21). Additionally, reactive oxygen species might be produced due to the conversion of arsenate to arsenite, using oxygen as a final acceptor of electrons (21).

### 3.4 Effects of Arsenic on Health

Arsenic has carcinogenic and toxic effects on human, animals and nature and the level of toxicity are depending on its oxidation state (25).

The chronic exposure of arsenic even at very low concentration increases harmful effects on inner organs of the human body, especially liver, kidney, and lungs (15 & 21) and can lead to many kinds of cancer, cardiovascular diseases, skin diseases and diabetes (21).

The inorganic form of the As is highly toxic and it usually found in water whereas organic As compounds in seafood are less harmful to human health (24).

According to the guidelines for drinking water arsenic content recommended by the World Health Organization (WHO) is 10 micrograms per liter (10ppb) and used as a maximum level of contamination in European Union and the USA.

According to the classification by the International Agency for Research on Cancer (IARC), arsenic and arsenic compounds are carcinogenic to humans (26). Many studies have found that arsenic exposure has negative impacts on cognitive development, memory, and intelligence (26).

### 3.5 Arsenic studies in Nalaikh

In the study of soil quality overview in Ulaanbaatar, heavy metals in the soils from 93 different sampling points within all 9 districts including Nalaikh, Baganuur, Khan-Uul, Songinokhairkhan, Chingeltei, Sukhbaatar, Bagakhangai, Bayanzurkh, and Bayangol were investigated by XRF spectrometry in 2017 (27).

As a result, the average concentration of heavy metals in Nalaikh area were below the Mongolian guideline for heavy metals content in the soils MNS 5850:2008 in which concentration of Cd (0.1 mg/kg), Pb (24.8 mg/kg), Hg (0.2 mg/kg), Br (0.2 mg/kg), Cr (2.5 mg/kg), Sr (735 mg/kg), Rb (194.7 mg/kg) and Zr (453.1) were estimated (27).

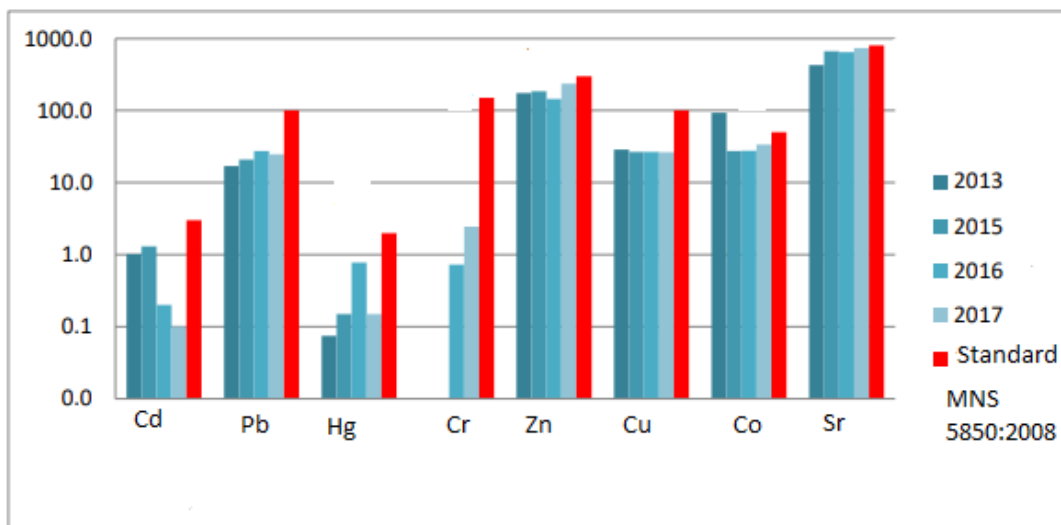


Figure 3 The average amount of heavy metals in the soils compared to the guideline values, Nalaikh between 2013 and 2017 (27).

As shown in Figure 3, the presence of heavy metals such as cadmium, lead, mercury, chromium, zinc, copper, and strontium in Nalaikh soils was below the MNS5850:2008 guideline except for the sampling area around the “Soyoliin Tuv” was polluted by the metal cobalt in 2013.

In 2016 a research (1) has done within the project “Rehabilitation concept for Nalaikh Mining Licence Area (N-MLA)” funded by GIZ. In this study pollution of water and sediments in Nalaikh basin were examined by X-ray fluorescence spectrometry (XRF) and the research has found the average amount of arsenic in topsoil with the value between 12 to 13 mg/kg and the geo-accumulation index values were tended to zero. Moreover, the natural geogenic concentration of arsenic is considered as 8.6 mg/ kg in the soils. The study (1) has analysed the spatial patterns of arsenic contents, which indicates the distribution of As in and around Nalaikh small-scale mining area as shown in Figure 4.

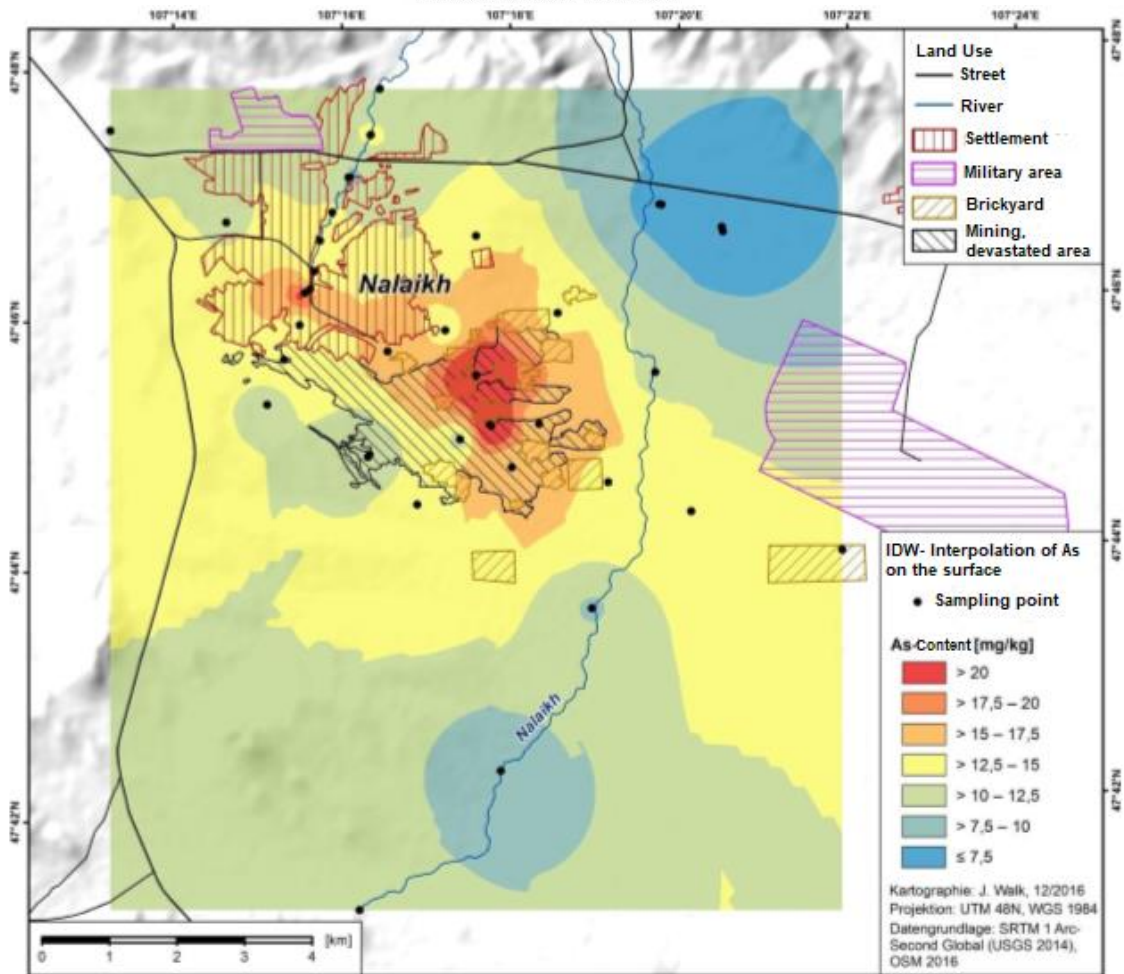


Figure 4 Content of arsenic near the surface in Naliakh basin was interpolated in the study (Translated from German)(1).

From the result of this interpolation, in most topsoil, the content of As were estimated between 10 and 15 mg/kg (in Figure 4) and the maximum amount of arsenic concentration has found in the ash basin from the coal-fired power plant and in the mining area while the measured values of arsenic concentration in the ash basin were range between 108 mg/kg to 121 mg/kg (1). Therefore, the study (1) has concluded that the combustion of As-rich coal and ash which produced in power plants and ger settlements areas is considered as a primary source of pollution in the soils.

### 3.6 Arsenic Remediation Technologies

Arsenic is one of the nonessential trace elements and its presence in the soil is difficult to be degraded and remediated. It can enter both directly or indirectly into the food chain through crops and water bodies.

The principal mechanism for immobilizing arsenic in the soils is sorption to solid phase and the significant As adsorbents which associated with soils are hydroxides of iron, manganese, and aluminium, clay and sulphide minerals and natural organic matters (28).

By adding biochar to the soil, of which heavy metals can be immobilized through the reduction process and bioavailability will be reduced significantly (29). However, the remediation of arsenic by biochar is not appropriate because it will reduce As (V) to As (III) in which more toxic arsenic is formed and mobility will be increased (29).

According to the earlier study (29), they have found that the use of iron oxide magnetizes biochar and reduces the mobility of arsenic by anion exchange. Moreover, an application of biochar can reduce the absorption of heavy metals by plants (21).

Many arsenic polluted sites use the same remediation technology as lead, even there are some differences since they have different behaviours and chemical characteristics (15). Phosphorous amendments can be used for reducing lead bioavailability, but they have reverse effects on arsenic (15). Therefore, it is not proper for arsenic remediation. On the other hand, the application of organic amendments can reduce the bioavailability of arsenic by forming a complex of organo-As with a dilution of arsenic in the soils (15). However, organic amendments can also increase the bioavailability due to its poor choice of amendments which introduces a significant amount of phosphorous with a result of increasing arsenic availability. Moreover, iron mineral amendments can reduce the bioavailability of arsenic by producing complexes of As-Fe (15).

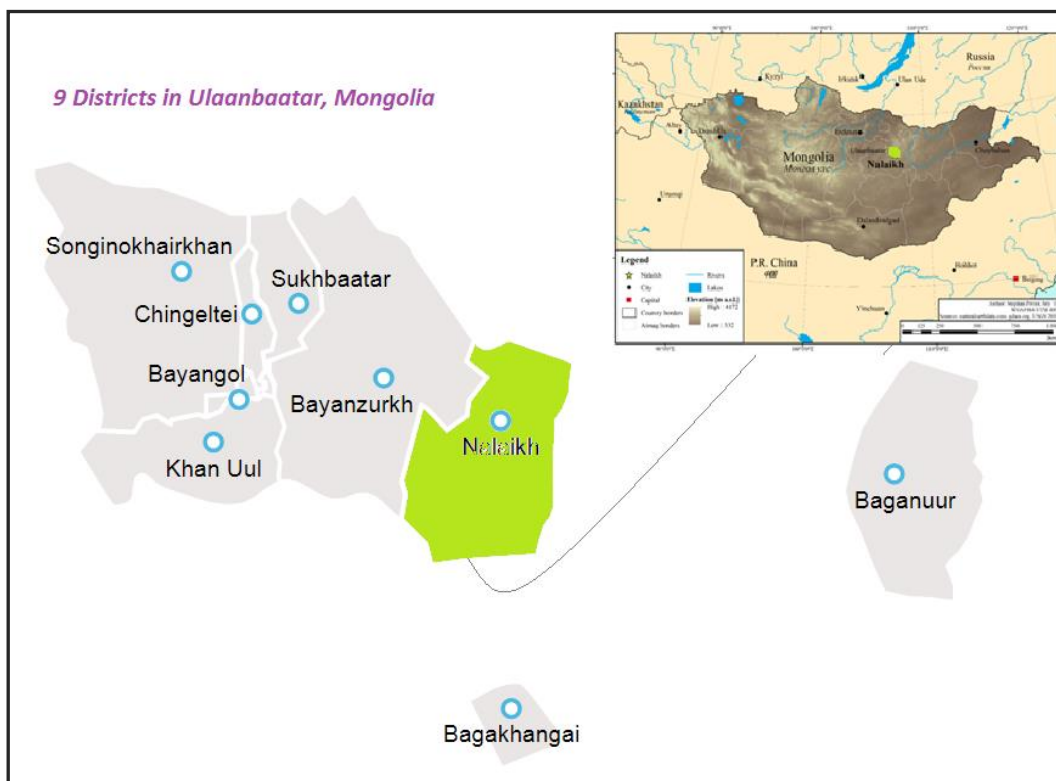
## 4. Study area

### 4.1 Introduction to the study area

In 1954-1958, Nalaikh was built based on the large mining operation (30) and became one of the districts in Ulaanbaatar, bordering with Bayanzurkh district as shown in *Figure 5*.

Nalaikh district is located around 36km southeast of the capital of Mongolia, Ulaanbaatar (UB) city and covers a total area of 68.7 thousand square hectares (31) with a population of 36,425 (1). Nalaikh has 7 administrative khoroos and more than half of its population live in ger settlement areas (31).

The land surface of the Nalaikh basin is a hilly prairie land at 1,410 - 1,500 meters above the sea level (32). The topography of the Nalaikh is mostly dominated by its depression which is described by its flat appearance (33). Nalaikh basin is surrounded by ranges of the Khentii mountains.



*Figure 5 Location of the Nalaikh district, Mongolia*

In the study region, the enrichment of heavy metals in the soil could be linked to mining activity and coal combustion in the thermal power plant.

## 4.2 Climate

Climatology is one of the most important soil forming factors. In this study, a climate condition of the Nalaikh valley is considered the same as the city UB which is as shown in Figure 6 (1).

Duration of the sunshine in Nalaikh is around 2804 hours per year and the daily average sunshine duration is 7.7 hours (30). Based on the average amount of precipitation between 1986 and 2016 is 258.5mm of which 90% is precipitated from April to September (30). January is the coldest month in Nalaikh with an average temperature of  $-24.1^{\circ}\text{C}$ , whereas the warmest month is July with an average temperature of  $14.7^{\circ}\text{C}$  (30).

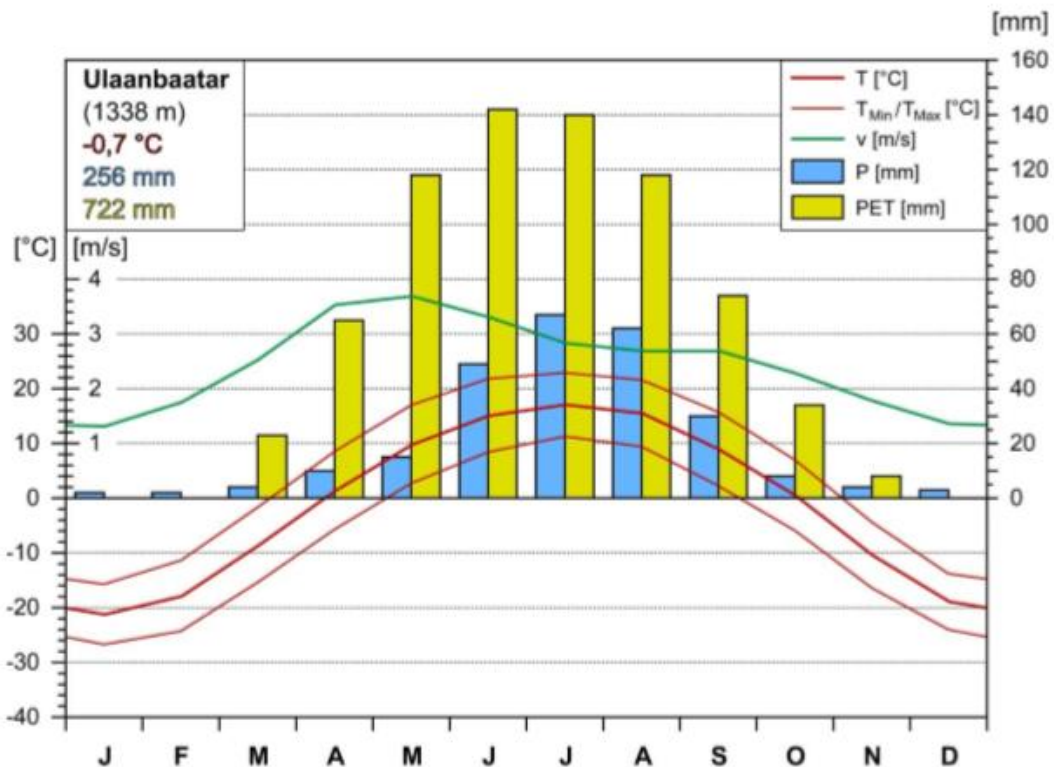


Figure 6 Climate diagram of Ulaanbaatar showing the average temperature ( $T$ ), wind speed ( $v$ ), precipitation ( $P$ ), and potential evapotranspiration ( $PET$ ) with respects to the average value of every month (1).

As shown the Figure 6, our study area has a cold, arid and semi-arid condition because the temperature line is below the precipitation bar and the annual precipitation is 256 mm with an average temperature of  $-0.7$  degree Celsius. During the months from November to March, the amount of average precipitation is lower than 10mm with a very cold weather condition. The maximum speed of the wind is around 3.5 m/s in spring (Fig.6) with the dominant wind direction line from west to the northwest all year round (1).

The wind direction in Nalaikh is mainly oriented from northwest to southeast but varied by its seasonal changes (33).

### 4.3 Geology

Nalaikh basin is located in the Khentii mountains which have been built from Proterozoic age to early Mesozoic age as a part of the Altai-Central Asian belt due to subduction and accretion of various small terranes (1). The Devonian layer reaches the depth of 2500m to 3000meters and the Carboniferous sediments in northwest basin reach vertically from 1500 to 2500 meters in Nalikh (1 & 32). During the age of Mesozoic magmatic activity is increased in which the Ulaanbaatar terrain was affected through powerful granite plutons in the Triassic and Jurassic periods (1). Moreover, the intramontane basin filled with the lower Cretaceous sediments was created due to an extensive area of tension in which magmatism was accompanied by a result of coal lithological basin (1 & 5). The Cretaceous sedimentary filling can be classified as an upper and lower group of which lower section is between 300 to 350 meters of mainly siltstone and shale with the first layer of coal whereas the upper section has 280 to 300 meters thick layer with rich content of coal (1). The coal deposit has a total of 12 coal seams with a depth up to 15 meters which stretch over 10km in the east to west (E-W) direction around 3.5 km long distance which referred to Choir-Nairga basin (1 & 16). In general, coal is formed by a mixture of 18% ash, 47.3% volatile substance and 0.75% sulfur with a 9.3% moisture content and calorific value of 6536 kcal/kg and 27347 KJ / kg respectively (1). The geological overview of the Nalaikh basin is characterized by a large number of disturbances of various generations (1 & 5).

### 4.4 Land use

A purpose of land use in Nalaikh is various in which one-third of the area is used as pasture land, 17% of the land is characterized by urban and semi-urban settlements including concrete apartments and ger area. A very small part of the total area around 2% is used in infrastructures such as paved streets and asphalt roads (30 & 33).

The most important utilization of the land in Nalaikh is coal mining activities. The deposit of the coal is present within the Middle-East Megablock and situated in Tov Province (32).

Nalaikh coal mine was established in 1922 and the operations were stopped in the 1990s. While the operation of mine was going deeper, the emission of methane gas was

increased by up to 15 m<sup>3</sup> per ton of coal extraction. Due to the mine closure, many people were unemployed and since then illegal mining activities were started. There is a governmental decision to stop mine, there is still small scale, artisanal mining activities going on until today by “ninja” miners. In the mining region, there are more than 200 active mine shafts, in which 26 are authorized (31). During the peak season, up to 2000 “ninja” (illegal) miners work in Nalaikh license mining area with the extraction of around one million tonnes of hard coal, of which 70% are transported into UB and burned during the winter time in Ger districts for the heating (31). Although, working conditions cannot fulfill the standard of occupational health and safety environment and the occurrence of fatal accidents in mine site and health problems of miners are increasing year by year and even some of them lost their life.

## 5. Materials, and Methodology

This thesis is based on the collected data of heavy metals in the soils by XRF, also physical and chemical properties were analysed in field methods for investigating pollution load index, potential ecological risks, and geo-accumulation index in the soils. The soil samples were collected and measured along the main wind direction which is oriented from northwest to southeast (NW-SE) in Nalaikh basin. An estimation of the arsenic content was used to make an interpolation of special distribution in Nalaikh basin, in which 19 sampling points on topsoil were investigated and based on that and the results were compared with the previous study (1).

Moreover, by the request from Nalaikh government, 7 soil samples from 5 gardens in Nalaikh ger settlement area were examined and heavy metals content were measured by X-ray fluorescence spectrometry in the field. To differentiate the results of heavy metals from different locations, the reference soil (*Figure 8*) which has a type of Kastanozem soil was investigated in Nalaikh depression.

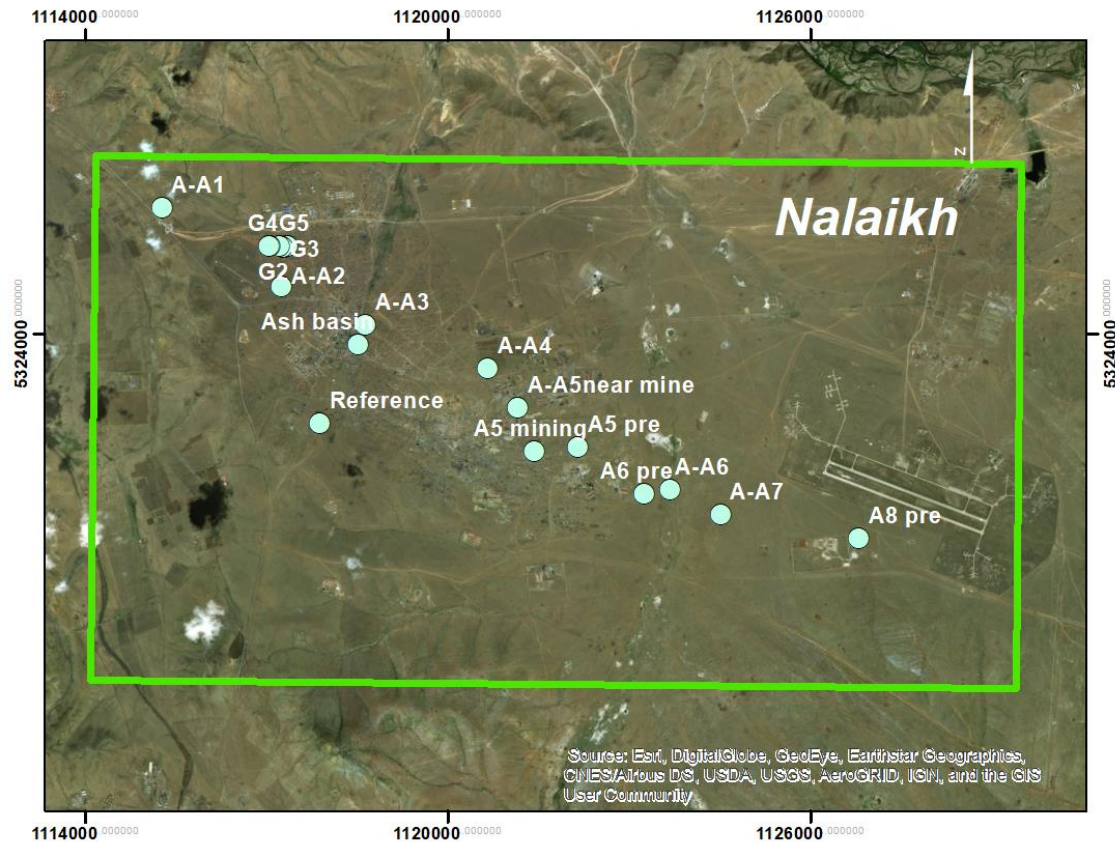


Figure 7 Locations of soil sampling points along the main wind direction from NW-SE.

## 5.1 Sampling

The total concentration of heavy metals can be determined by two types of chemical methods and by one instrumental method using X-ray fluorescence spectrometry (XRF) (14). In the first chemical method shows true total concentration by dissolving all soil constituents into the concentrated nitric acid (HNO<sub>3</sub>) and hydrofluoric acid (HF) whereas the other method dissolves all soil components except that strongly bound in silicate minerals by involving digestion in hot concentrated nitric acid (HNO<sub>3</sub>) and hydrochloric acid (HCl) (14).

In this study, the heavy metals were measured by XRF portable device on topsoil from different sampling areas along the main direction of the wind in Nalaikh basin from 27<sup>th</sup> of March to 10<sup>th</sup> of April, 2019. The results of heavy metals concentration were expressed as milligram per kilogram (mg/kg). In totally 19 different sampling points from both natural

soils and soils with anthropogenic effects were examined, in which seven samples from gardens around ger settlements area were collected and analysed by field methods.

The soil samples were passed through a 2mm size of sieve before analyses.

Background levels of the heavy metals in soils were evaluated by measuring reference soil as shown in the (Figure 8) at coordinates of 47.75868° N and 107.2474° E for taking into account the natural presence of metals in soils.



Figure 8 Reference soil - Kastanozem

The reference soil has four main horizons including A, A<sub>h</sub>, C<sub>1</sub> and C<sub>2</sub> which differs from each other by their chemical and physical properties.

Typically, a very young soil consists of a thin layer of mineral particles with organic matter atop parent material which labelled by A and C (34).

The layers indicate the type of soil, texture, OM or minerals content and origin of the soils as well. From the Figure 8, a black color defines the content of organic matter in the A horizon, whereas the white color shows the carbon-rich minerals in C horizon where usually parent rock of the soil is presented, and the presence of bubbles was observed when the hydrochloric acid (HCl) was added. Even the geogenic background value of arsenic concentration in the soils was 8.6 mg/kg which is higher than the Mongolian standard for soil quality and heavy metal

concentration in the soils MNS 5850:2008.

Table 3. Coordinates of the measured soils

ID	Depth [cm]	N [°]	E [°]
----	------------	-------	-------

Reference	0-5	47.75868	107.2474
A-A1	0-5	47.79284	107.21799
A-A2	0-5	47.77934	107.24223
A-A3	0-5	47.7724	107.2597
Ash basin	0-5	47.76961	107.25773
A-A4	0-5	47.76404	107.28539
A5 mining	0-5	47.75119	107.29358
A-A5near mine	0-5	47.75784	107.29115
A5 pre	0-5	47.751107	107.303326
A6 pre	0-5	47.743083	107.316607
A-A6	0-5	47.74323	107.32238
A-A7	0-5	47.73885	107.33283
A8 pre	0-5	47.733175	107.362464
G1 Mix	0-5	47.78525	107.24442
G1-Natural	0-10	47.78518	107.24401
G1-5 years used	0-10	47.78525	107.24453
G2	0-10	47.78521	107.24339
G3	0-10	47.78536	107.24272
G4	0-10	47.7855	107.24074
G5	0-10	47.78558	107.24053

## 5.2 Data processing and Evaluation

Soil tests for heavy metal content, including antimony (Sb), arsenic (As), barium (Ba), cadmium (Cd), cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), lead (Pb), nickel (Ni), manganese (Mn), mercury (Hg), strontium (Sr), tin (Sn), rubidium (Rb), and zinc (Zn) were carried out and of those, a few metals which have a content of below the detection limit has not been taken into account for further analyses.

The guideline and approaches for heavy metals in the soils is defined separately associated with different concentrations in almost every country. In this study various types of permissible levels for metal guidelines which determined in Mongolian Standard for soil quality *MNS 5850:2008* (18), EU standard, (35), WHO standard (36) and limits

that differentiated by soil texture and regulated by German Federal (*Table 2*) (19) were used and compared as shown in *Table 4*. If the concentration is exceeded than those permissible limits, it is considered that the area has a contamination level which could cause ecological or health risks. The different guideline values are set depending on the purpose of land use. By the way, those aforementioned limits are applied for the general soils that can be used for any kind of intention in which there are no specific object for land use. The unit of measurement was milligram per kilogram (mg/kg) for each metal. In the *Table 4*, the mean value which is the arithmetic average, and the median were calculated and analysed using Microsoft Excel based on measured concentrations of metals. Moreover, the significance of As content in the previous study (1) and this study were estimated for getting the standard error by using the statistical tests of significance ANOVA ( $p < 0.05$ ) whereas the alpha is usually equal to 5% probability of errors, thus if the p value is less than the alpha means it is statistically significant.

Table 4. The measured value of heavy metals (mg/kg) by portable XRF in Nalaikh area along main wind direction NW-SE.

ID	Mn (mg/kg)	Fe	Co	Cu	Zn	As	Rb	Sr	Zr	Cd	Ba	Pb
Reference	544.1	20675.7	123.1	13.6	60.8	8.6	70.1	325.6	296.7	11.31	617.1	19.9
A-A1	680.1	23411.7	132.4	22.1	72.1	13.3	73.4	298.1	223.0		460.1	22.6
A-A2	377.4	13947.2	96.5	26.3	117.4	7.1	81.2	294.8	207.2	5.24	524.9	37.4
A-A3	467.0	19155.7	126.6	26.9	95.6	13.1	66.7	328.8	203.8		253.3	26.7
Ash basin	399.4	22012.0	162.5	15.7	53.3	24.0	66.0	467.8	138.2		154.3	14.6
A-A4	808.7	24713.9	305.6	27.2	84.8	18.4	78.7	221.1	254.1	16.45	743.5	20.2
A5 mining	1148.0	30705.3	244.8	24.9	105.1	31.1	79.8	280.0	202.4		414.6	26.8
A-A5near mine	1056.0	24449.3	179.0	29.3	97.5	30.9	67.0	183.8	173.2		230.6	18.8
A-A6	537.4	14984.2	< LOD	22.1	65.0	11.9	57.4	249.1	172.4		361.7	12.3
A-A7	530.0	14618.8	189.6	16.2	53.1	12.0	68.6	241.2	279.7	16.62	629.4	17.1
G1 Mix	426.4	16209.8	88.5	13.9	49.4	8.5	58.5	232.2	130.9		95.4	13.3
G-Natural	502.0	20856.0	68.6	18.9	54.6	14.6	77.2	317.7	225.6	3.97	611.8	15.5
G-5 years used	496.6	21346.7	69.3	17.0	51.7	11.9	70.6	284.1	215.4		313.4	16.8
G2	638.3	26424.7	97.8	6.3	79.5	11.8	82.5	318.1	216.4		389.2	16.3
G3	614.3	24902.1	77.9	16.2	63.6	12.3	69.7	281.3	222.7		264.2	13.0
G4	645.3	26186.6	<LOD	8.0	72.7	14.0	77.1	364.8	243.6		492.3	15.6
G5	634.4	24256.6	108.3	11.1	53.1	18.2	71.5	341.1	259.3	15.3	670.1	10.9
Mean	618.0	21697.4	138.0	18.6	72.3	15.4	71.5	295.8	215.6	11.5	425.1	18.7
Median	544.1	22012.0	123.1	17.0	65.0	13.1	70.6	294.8	216.4	13.3	414.6	16.8
MNS 5850:2008 (mg/kg)			50.0	100.0	300.0	6.0		800.0		3.0		100.0
EU Standard (mg/kg)				140.0						3.0		300.0
WHO (1996)				36.0	50.0					0.8		85.0
Common ranges in soils (*)		7,000-550,000		2-100	10-300	1.0-50				0.01-0.07	100-3000	2-200

(\*) – Heavy metals range that naturally occurring in the soils. Limits taken from Lindsay, 1979 and revised by Everett Wilson and Carl Solomon (35).

As shown in the Table 4, the concentration of heavy metals including, copper (Cu), zinc (Zn), strontium (Sr) and lead (Pb) were far below the Mongolian guideline for soil quality and heavy metals MNS 5850:2008, whereas the concentration of cobalt (Co), arsenic (As), and cadmium (Cd) were exceeded the all those aforementioned different guidelines.

### 5.3 Calculation

To evaluate the degree of heavy metal contamination and magnitude, the pollution index ( $PI$ ), pollution load index ( $PLI$ ), geo-accumulation index ( $I_{geo}$ ) and potential ecological risk ( $E_r$ ) were calculated as following.

- a) Geo-accumulation Index ( $I_{geo}$ ):

$$I_{geo} = \ln(C), \quad [1]$$

where  $C$  is defined by measured value divided by the background value and multiplication of 1.5 which is applied to take into account for lithological variations of the respective geogenic background (Chakravarty and Patgiri, 2009). The  $I_{geo}$  is classified as not contaminated ( $I_{geo} < 0$ ), not to moderate contaminated ( $0 < I_{geo} < 1$ ), moderate contaminated ( $1 < I_{geo} < 2$ ), and moderate to heavily contaminated ( $I_{geo} > 2$ ). In this study, the geo-accumulation index is calculated for the only specific metals as introduced by Muller, (1981) and in our case arsenic is studied in detail.

b) Pollution Load Index (PLI)

$$PLI = \sqrt[n]{CF1 * CF2 * CF3 * CFn}, \quad [2]$$

Where:  $n$  is a number of heavy metals,

$CF$  is a contamination factor and determined by metal concentration in samples divided by the background value of the certain metal. According to Chakravarty and Patgiri, the result of PLI is classified as, polluted when ( $PLI > 1$ ) whereas it is not polluted if ( $PLI < 1$ ) (37).

c) Pollution index (PI) for each metal is determined by the following formula and is defined the same as  $C$  value as shown in equation [1] & [2].

$$PI = \frac{C_i}{S_i}, \quad [3]$$

where

$C_i$  is the measured concentration of each metal,

$S_i$  is the background value from reference soil (11).

$PI$  for each metal is classified as non-pollution ( $PI < 1$ ), low level of pollution ( $1 < PI < 2$ ), moderate level of pollution ( $2 \leq PI \leq 3$ ), high level of pollution ( $3 < PI < 5$ ), and very high level of pollution ( $PI = 5$ ) (11).

d) Potential Ecological Risk ( $E_r$ ):

The proposed method for investigating the Potential Ecological Risk has advanced by Hakanson in 1980 (11) and evaluated based on the relation between the degree of contamination and toxic-response factor.

$$E_r = T_r * C_f \quad [4]$$

$$C_f = \frac{C_s}{C_n} \quad [5]$$

where

$C_f$  (is nondimensional) - contamination coefficient of a given heavy metal,

$C_s$  (mg/kg) - measured concentration of a given heavy metal in the topsoil of the sample,

$C_n$  (mg/kg) - background value of heavy metal.

$T_r$  (is nondimensional) - toxic response factor of heavy metal, which has been determined by Hakanson in 1980 (26) and is certain for specific metals (Zn = 1, Cr = 2, Cu = Pb = 5, Cd = 30, As = 10, Hg = 40).

$E_r$  indicates the value of potential ecological risk (PER), and classified as ( $E_r < 30$ ) low ecological risk, ( $30 < E_r < 60$ ) moderate, ( $60 < E_r < 120$ ) considerable, ( $120 < E_r < 240$ ) high, and ( $E_r > 240$ ) very high ecological risk as defined by Hakanson, 1980 (11).

The calculated results are summarised in *Chapter 6*.

## 5.4 Soil Texture

The texture is an important physical soil property which describes the proportion of different grain sizes including sand, silt, and clay. By determining the texture, we can get an idea of water holding capacity, aeration and the rate at which water can enter and move through the soil. In most soils, all three types are found.

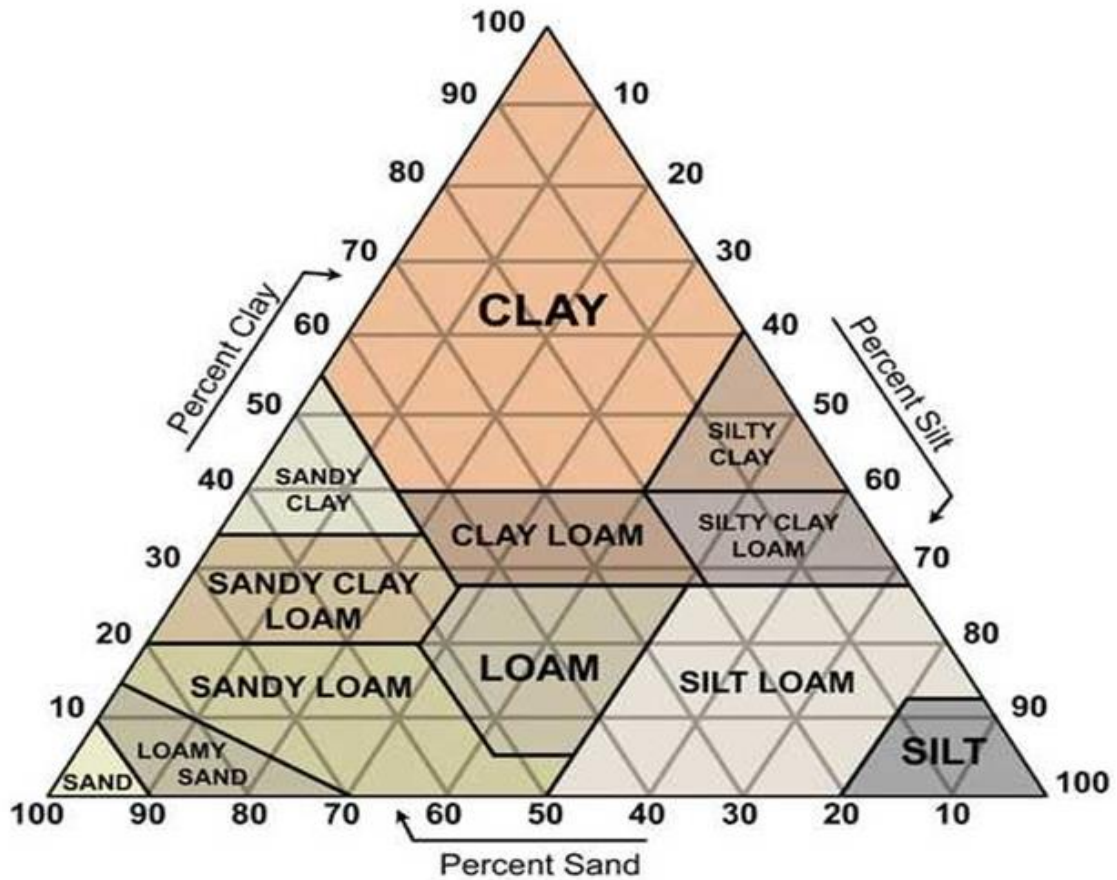


Figure 9 Soil textural triangle. The numbers on each side of the triangle represent the percentage of soil particles type.

As shown in Figure 9, textural class of loam is a mixture of all three types of soil, in which equal contribution of sand, silt, and clay affect the soil properties. Soils with the smallest particle size are called clay and when it becomes larger and has the coarsest particle, it is called sand.

In this study, the soil texture is determined by using the textural triangle as referred to Figure 9, and used the USDA textural classification approach which applied only if the particle fractions smaller than 2mm.

Thus, the soil samples collected from gardens were sieved with the 2mm size of the sieve and the texture is determined by hand texture method which is a qualitative but is not easy to discern a perfect and exact textural class.

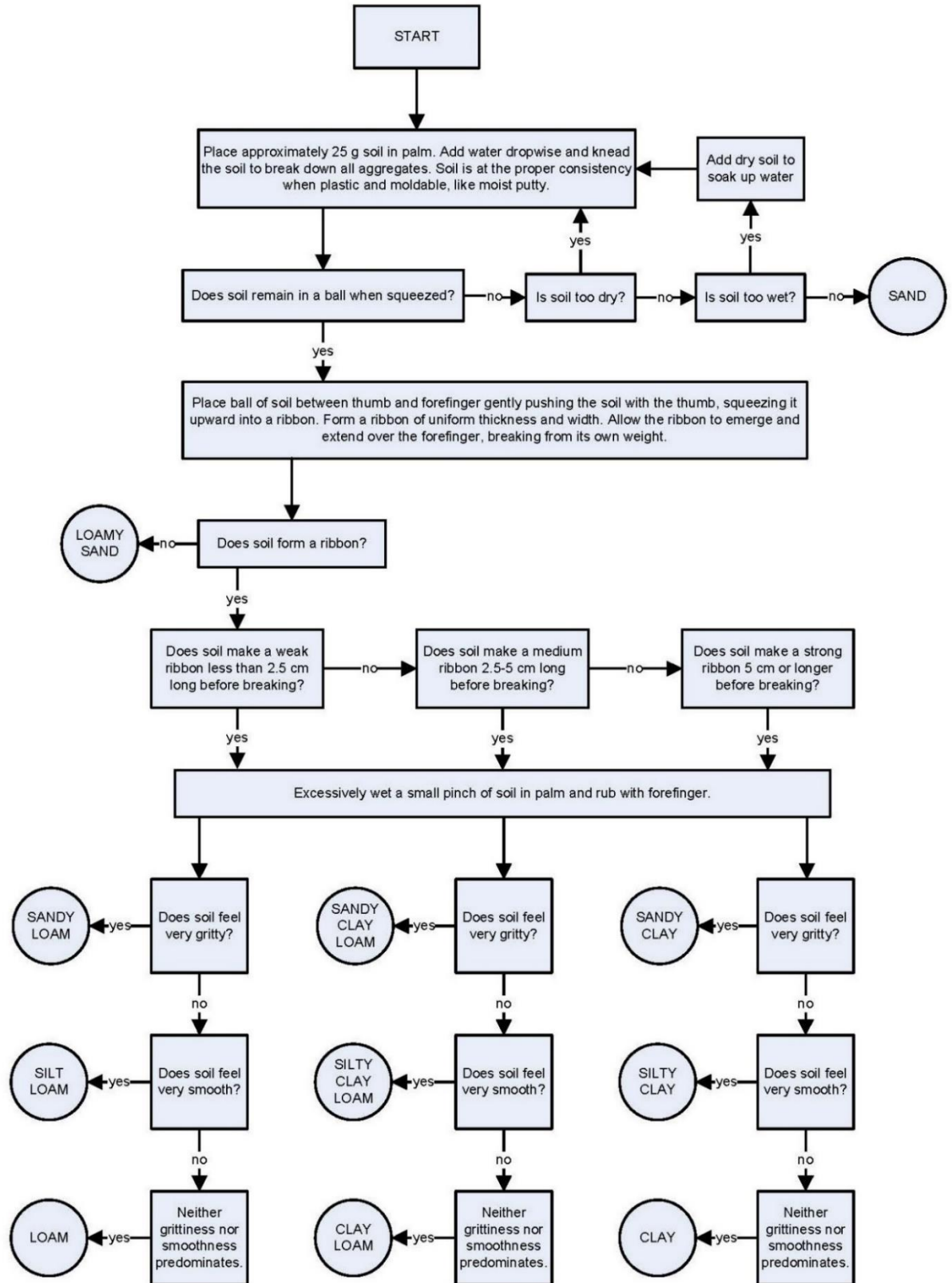


Figure 10 A flow diagram for teaching texture by feeling analysis from S.J. Thien, 1979 modified by USDA (38).

## 5.5 Organic matter (OM)

Organic matter in the soils is determined by the presence of organic constituents such as animals and plants leftover at various stage of decay and components synthesised by soil organisms (34). OM has important benefits for soil quality and functions including nutrient supply, water holding capacity, soils structure aggregation, and erosion prevention.

The organic matter of the samples from the garden are calculated based on the color and texture of the soil. The content of the organic matter in garden samples was relatively higher than the natural soils due to the additional constituent of animal manure and composts which are added by farmers for improving the soil quality and getting more harvest.

## 5.6 Cation Exchange Capacity (CEC)

Cation exchange capacity (CEC) is determined by the number of cations which can be retained on a soil colloids surface and it plays an important role in the soils for holding and storing the plant nutrients (34). When the soil has a value of CEC between 11 and 50cmol/ kg, it usually has more clay mineral whereas it is sandier, if the value is below 11 units and CEC is highly dependent on physical parameters like texture and consistency (34). Cation exchange capacity can be measured in either laboratory or field. In our study, CEC is calculated by field method based on the determination of pH value, texture and content of organic matter (OM). The field method is easy to find CEC and is time efficient as well. However, the result is highly dependent on how the soil texture and organic matter content was measured.

Available nutrients, S-value:

- rough estimation of available nutrients = S-value

- S-value derives from CEC, due to its relation to soil texture, organic matter content

texture	X/G	gS	S	1S,uS	tS	U	sU,1U	sL,uL	tL	T	
	1	2	3	5	6	8	11	20	25		mval/100 g
OM	%	1-2	2-4	4-8	8-15	15-30	> 30	(s. Kap. 5.2)			
		h 2	h 3	h 4	h 5	h 6	H	Of	Oh		
mval/100 g		3	6	12	25	25-50	50-200	50	150		

S-value (mval/100 g) by multiplication with a factor, derived from pH (by saturation of H- and Al-ions)

pH	< 3	4	5	6	7	>
S-SL		0.2	0.4	0.7	0.9	1
sL-T		0.2	0.6	0.8	0.9	1
Ah(5-15%)	0.1	0.2	0.5	0.8	0.9	1
o u. U	0.1	0.2	0.5	0.8	0.9	1

Figure 11 Field method for determining CEC

As shown in Figure 11, the cation exchange capacity is calculated for the samples from the garden.

The larger CEC value, the more cations including  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , the soil can absorb and make it available for plants.

## 5.7 Soil Acidity (pH value)

Soil reaction strongly affects the growth of the plant and is measured by the pH scale in which alkalinity or acidity of a soil is determined (34). When a solution has more hydrogen ion ( $\text{H}^+$ ) means the solution is acidic whereas it is base if there is more hydroxyl anion ( $\text{OH}^-$ ) (34). Usually, soils do not reach the extreme pH limits in which most acidic soil has around a pH value of 3.5 and the most basic soil has a pH of 10.5. In general, most soils are found within the pH ranges of 5 to 8 depending on the interactions between soil minerals, ions in solution and cation exchanges (34). The acidity of the soils can vary due to the climate when the annual precipitation is less than the annual evapotranspiration then soils tend to be alkaline (34).

The samples from the garden were taken in sampling packages and the pH value is determined in a laboratory by pH meter. Multimeter which used to measure pH value had pH probe which has a thin glass bulb at the tip and inside the bulb, there are two different

electrodes, one contains liquid with known pH value and another responds to pH of the solution. Electrometric pH measurement is an accurate method because it is free from interferences and is calibrated before measurement for avoiding errors and getting exact values.

Firstly, 10g of dry samples were weighted and filled into a 100ml beaker. Then 25ml of deionized water was added into the samples and stirred in every 15 minutes. After 1 hour stand the pH values were measured and recorded.

## 5.8 Soil Color

In this study, a soil color is determined by the Munsell color chart which can arrange 450 different standard color chips and is easy to identify the colors in the way the human eye sees (39). The principle of Munsell color chart is based on three color attributes which include hue, value, and chroma. Hue defines the color behaviour of the soil and indicates its relation to colors red, yellow, green, blue, and purple whereas value determines how soil dark or bright is and chroma shows soils color saturation or brilliance as shown in the following the figure.

Hue is preceded by numbers between 0 and 10 in which it becomes more yellow and less red as a number increases and symbolized by letter abbreviation like R for red, Y for yellow and YR for yellow to red (39). When the value is 0, it indicates black and the value of 10 for white color.

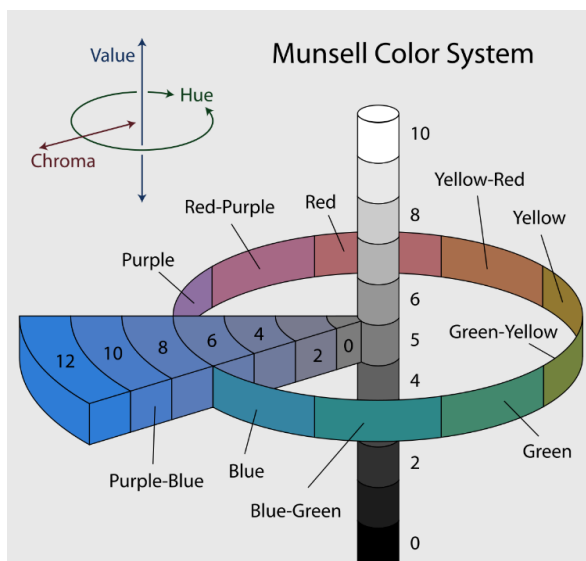


Figure 12 Munsell Color System (39)

The color is determined by holding the soil sample directly beside the closest matching color chips. The color test has done after drying the soil in the oven at 105<sup>0</sup> C for 1 hour and the color is defined during the daytime in normal sunlight because the determination of color is inaccurate early in the morning and late in the evening (39).

## 6. Results and Discussion

In this section, the results of *Chapter 5.3* were described in detail, in which the pollution load index, pollution index for specific metal, potential ecological risks and geo-accumulation index in the soil samples along the main wind direction and gardens were calculated based on the aforementioned formulas. Moreover, heavy metals in the garden soils were investigated and both chemical and physical properties of the samples were determined and analysed.

As discussed in *Chapter 5.2*, in the most cases, the content of elements did not exceed the maximum permissible values. However, the concentrations of arsenic (As), cobalt (Co) and cadmium (Cd) were above the Mongolian guidelines as well as EU and WHO permissible levels for heavy metals in the soils in which the mean value of As 15.4 mg/kg, Co 138 mg/kg and Cd 11.5 mg/ kg were measured. The contents of cadmium were presented only in a few soils and the rest of them were below the detection limit. Even the natural presence of these three metals in the reference soil were above the permissible level, which suggested that those metals concentration may come entirely from natural processes. Additionally, the presence of arsenic was much higher in and around mining area and in the ash basin than the settlement area and other sampling regions which is far from mine.

*Table 5. Calculation of Pollution Load Index, Environmental risks for arsenic and Geo-accumulation Index in the soils along the main wind direction.*

Index	PI for As	PLI	ER for As	I(geo) for As
A-A1	1.553	1.097	15.530	0.035
A-A2	0.828	1.026	8.277	-0.595
A-A3	1.519	1.031	15.192	0.013
Ash basin	2.793	0.906	27.928	0.622
A-A4	2.140	1.319	21.397	0.355
A5 mining	3.624	1.408	36.240	0.882
A-A5near mine	3.600	1.149	35.995	0.875
A-A6	1.388	0.862	13.877	-0.078

A-A7	1.402	0.993	14.016	-0.068
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According to the Table 5, the pollution index for arsenic is calculated as equation [3] and the highest As pollution ( $PI = 3.624$ , classified as the high level of pollution) is at the sampling point A5 which is just next to the Nalaikh mine. Although, there is no significant indication for the relation between wind direction and the arsenic concentration due to the source of As emission. The area around the power plant (A-A3, A-A4 and the ash basin) has a moderate level of pollution ( $2 \leq PI \leq 3$ ), and as it goes far from the mine it is classified as non-pollution to low level of pollution. Therefore, the accumulation of arsenic is dependent on the mining and its related activities.

The pollution load index which is calculated based on all measured heavy metals and indicates whether the area is polluted or not. If we classify the result of PLI as polluted when it is more than 1, and consider as a not polluted while PLI is less than 1 according to Chakravarty and Patgiri, our study area is defined as both polluted and not polluted as shown in Table 4. The maximum potential ecological risks for arsenic was 36.240 at the sampling point A5 and near to the mine site and is classified as a moderate ecological risk level, whereas the other area has low ecological risks. The geo-accumulation index is an indicator that used to assess the occurrence of the metal and intensity of the anthropogenic contaminant deposition on topsoil. Arsenic exhibited in two different classes in which the  $I_{geo}$  value is less than 0, indicates not polluted, while 0 to 1 means, not to moderate polluted soil quality.

#### ***In the garden soils:***

Heavy metals in garden soils can be accumulated from several sources, including polluted water, air and other emissions into the environment and soils. The bioaccumulation and the uptake by plants are dependent on climate, the concentration of heavy metals in the soils, the natural presence of metals, and atmospheric deposition (40). In the ger settlements area, the potential anthropogenic source of arsenic pollution in the soils could be presented as a result of ash emissions due to the combustion of As-rich coal from Nalaikh which has an As content of 121ppm (1) and Baganuur coal up to 183ppm (1).

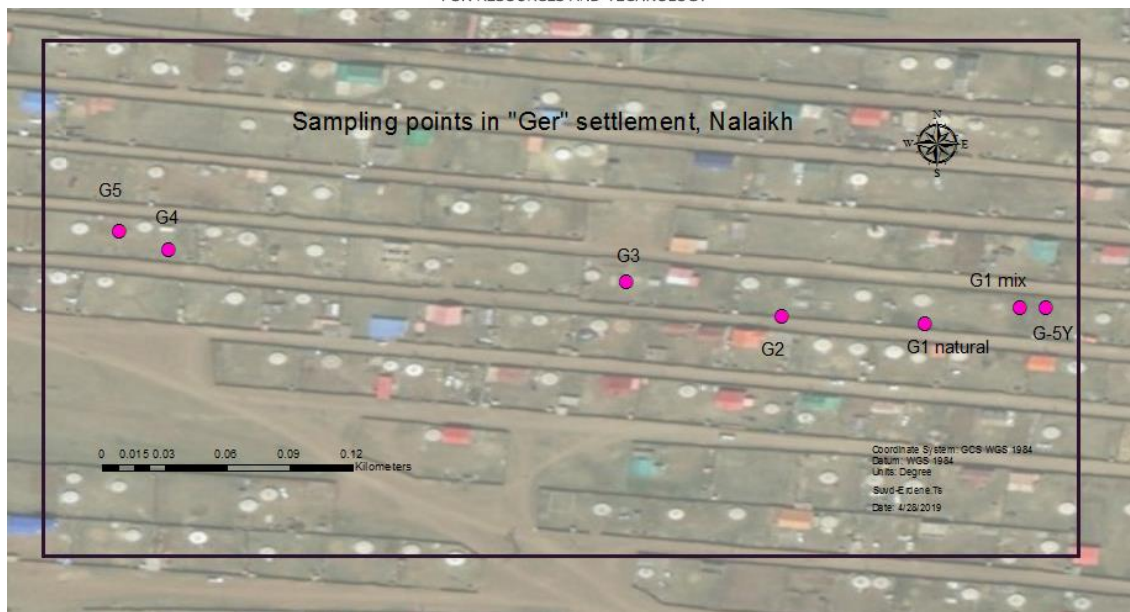


Figure 13 Sampling points of garden soils in the ger settlement area, Nalaikh.

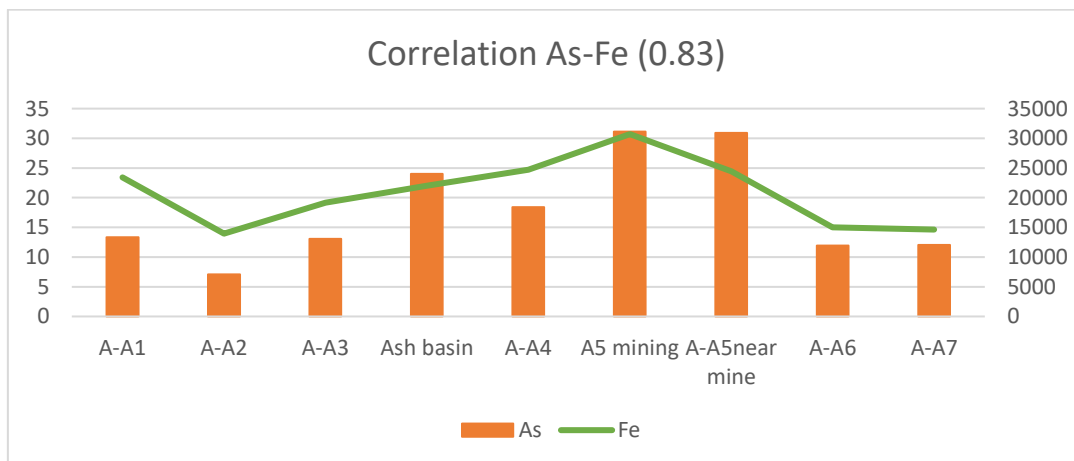
The most of the heavy metals in a garden soils did not exceed the guideline of EU (1994) and MNS 5850:2008 except As, Co, and Cd. The presences of cadmium were in the samples from G1-natural soils and G5, whereas the measured values of Cd from other gardens were below the detection limit, as shown in Table 4. The maximum level of the arsenic in the garden soils was 18.2 mg/kg in the fifth garden soils. Accumulation of arsenic in the garden soils could be the result from utilization of contaminated water bodies or distributed by erosion and weathering processes due to the transportation of ash from As-rich coal combustion in ger settlement areas.

Table 6. Calculation of Pollution Load Index, Environmental risks for arsenic, Geo-accumulation index and mobility for selected metals in garden soils

Samples(garden)	PI	PLI	ER for As	I(geo) for As
G1 Mix	1.201	0.641	12.011	-0.222
G-Natural	2.046	0.942	20.464	0.311
G-5 years used	1.679	0.848	16.793	0.113
G2	1.657	0.902	16.568	0.099
G3	1.730	0.867	17.300	0.143
G4	1.966	0.956	19.662	0.271

G5	2.564	0.975	25.640	0.536
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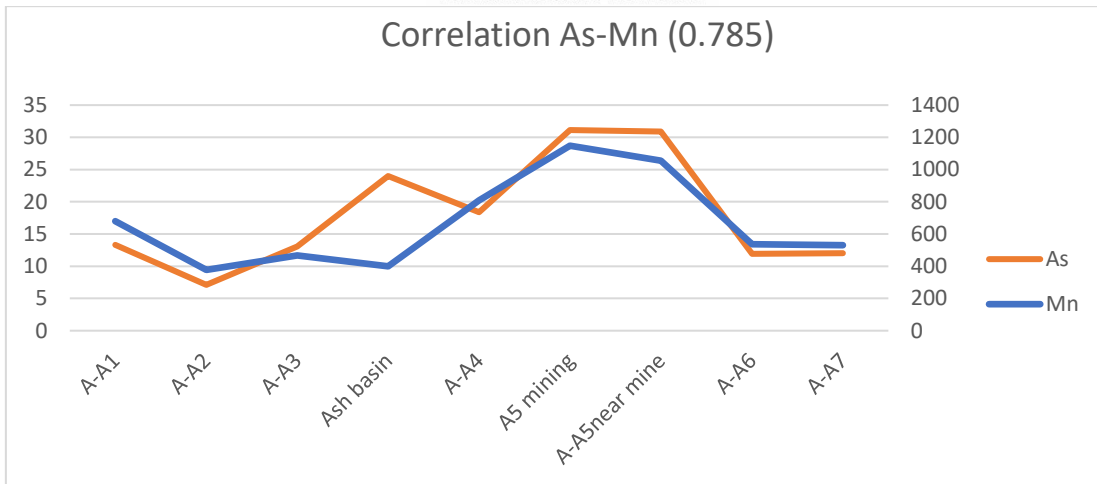
The pollution index for arsenic in the garden soils were between 1 and 2, which indicates the soil with a low level of pollution, based on the *Equation 3*. By the way the results of the pollution load index for all garden samples were below 1, ( $PLI < 1$ ) means the soil is not polluted as defined by Chakravarty and Patgiri. Moreover, the potential ecological risks for As in the garden were below  $ER < 30$ , which classified as low ecological risk. According to the calculated geo-accumulation index for arsenic, all samples except the first garden soil, have the contamination level of not to moderate whereas the last soil sample in the garden area (G5) had the highest level of contamination.



Graph 1. Correlation between As and Fe in the soils along the main wind direction.

Arsenic ions could be rather fixed in the soils by the hydroxides of iron (Fe) and clay fraction (20). There is a significant positive relationship between the presence of arsenic (As) and iron (Fe) with the correlation value of  $r = 0.829$ ,  $p = 0.0057 (< 0.05)$ .

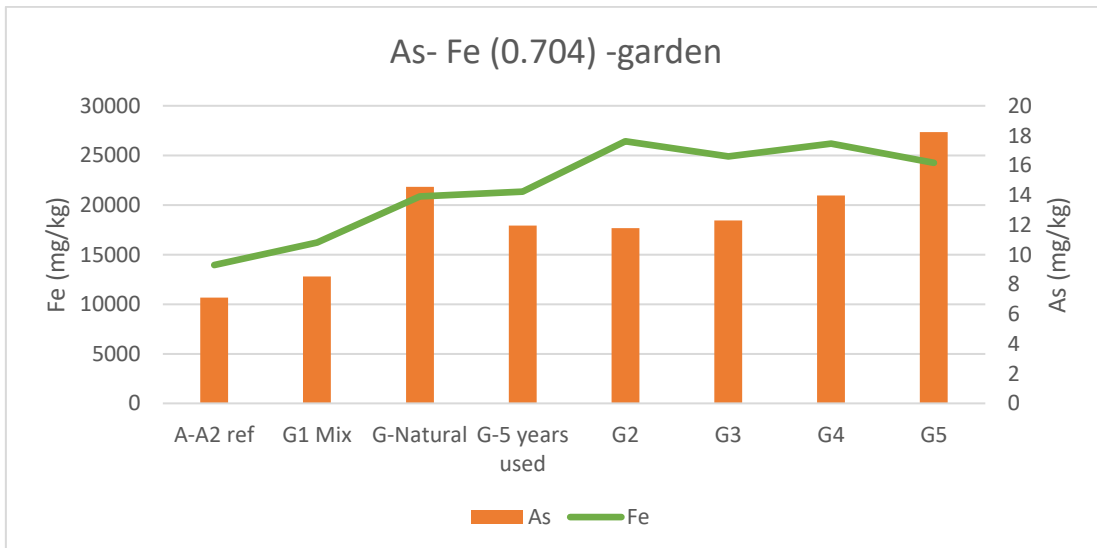
Arsenic and its components are rather soluble, and that arsenopyrite can be oxidized easily by oxygen and  $Fe^{3+}$ , and the positive correlation between arsenic and iron (III) oxides, the main components of amorphous soil, which indicates its close relationship with  $FeO_x$  (20).



Graph 2. Correlation between As and Mn in the soils along the main wind direction.

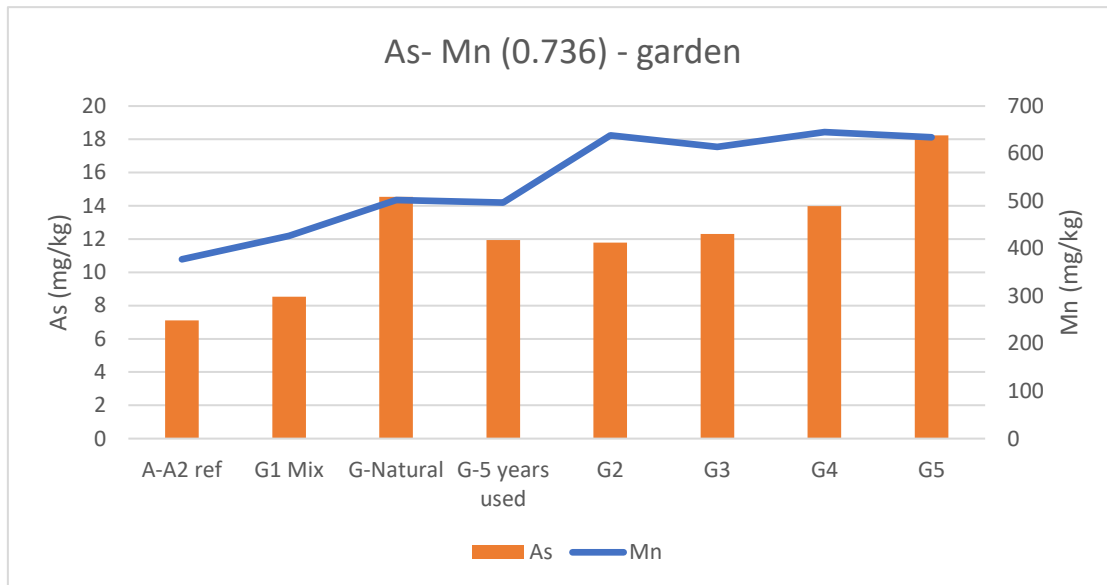
There is a significant positive relationship between the presence of arsenic (As) and manganese (Mn) with the correlation value of  $r = 0.785$ ,  $p = 0.012$  which is much less than alpha 0.05.

According to the study conducted by Deschamps (2003), the function of metals, including manganese (Mn) and iron (Fe) in arsenic sorption have increased in ferricrete sediments (20). A combination of arsenic components with Fe and Mn have a significant impact on its behaviour in the soils (20).



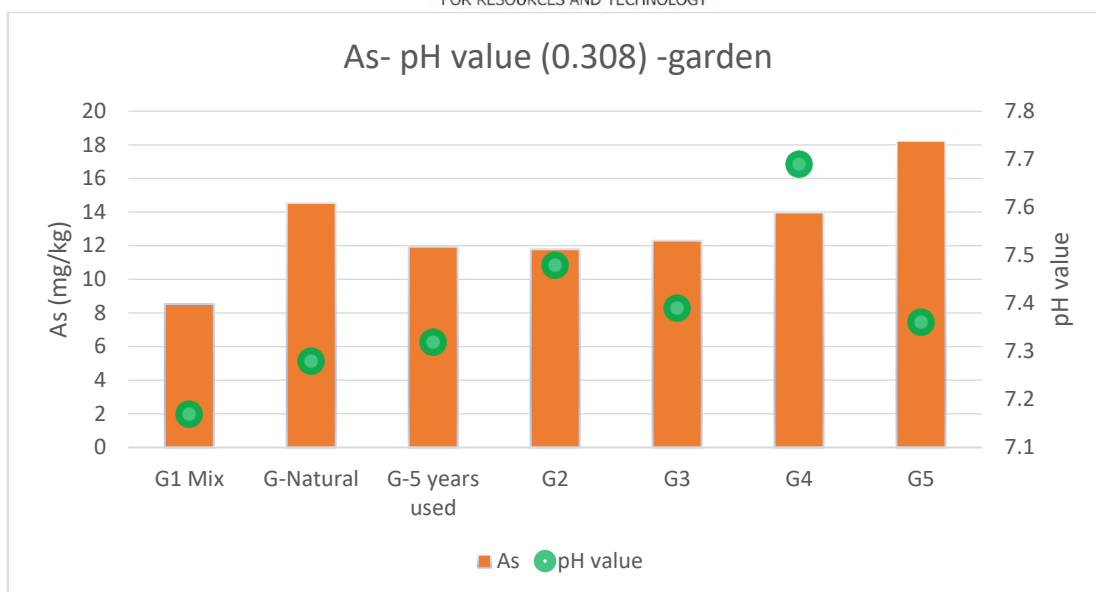
Graph 3. Correlation between As and Fe in the garden soils

There is almost no or weak relationship between the amount of arsenic (As) and iron (Fe) with the correlation value of  $r = 0.7$ ,  $p = 0.0512$  ( $>0.05$ ). The positive correlation of As with Fe, indicates its close association with oxides, especially high affinity to  $FeO_x$  (20).



Graph 4. Correlation between As and Mn in the garden soils

The relationship between the concentration of arsenic (As) and the content of manganese (Mn) is a significantly positive because the correlation value is equal to 0.736 and the  $p$  – value is 0.00375 which is less than the alpha (0.05).



Graph 5. Correlation between As and pH value in the garden soils

The behaviour of As and its species are predominant in low pH value and low Eh environments (20). As shown in Graph 5 there is no relationship between the presence of arsenic (As) and pH value in the garden soils and those variables are independent on each other because the correlation value is  $r = 0.3$ ,  $p = 0.5$  which is much more than 0.05.

Table 7. Determined properties of garden soils and calculated mobility for selected heavy metals.

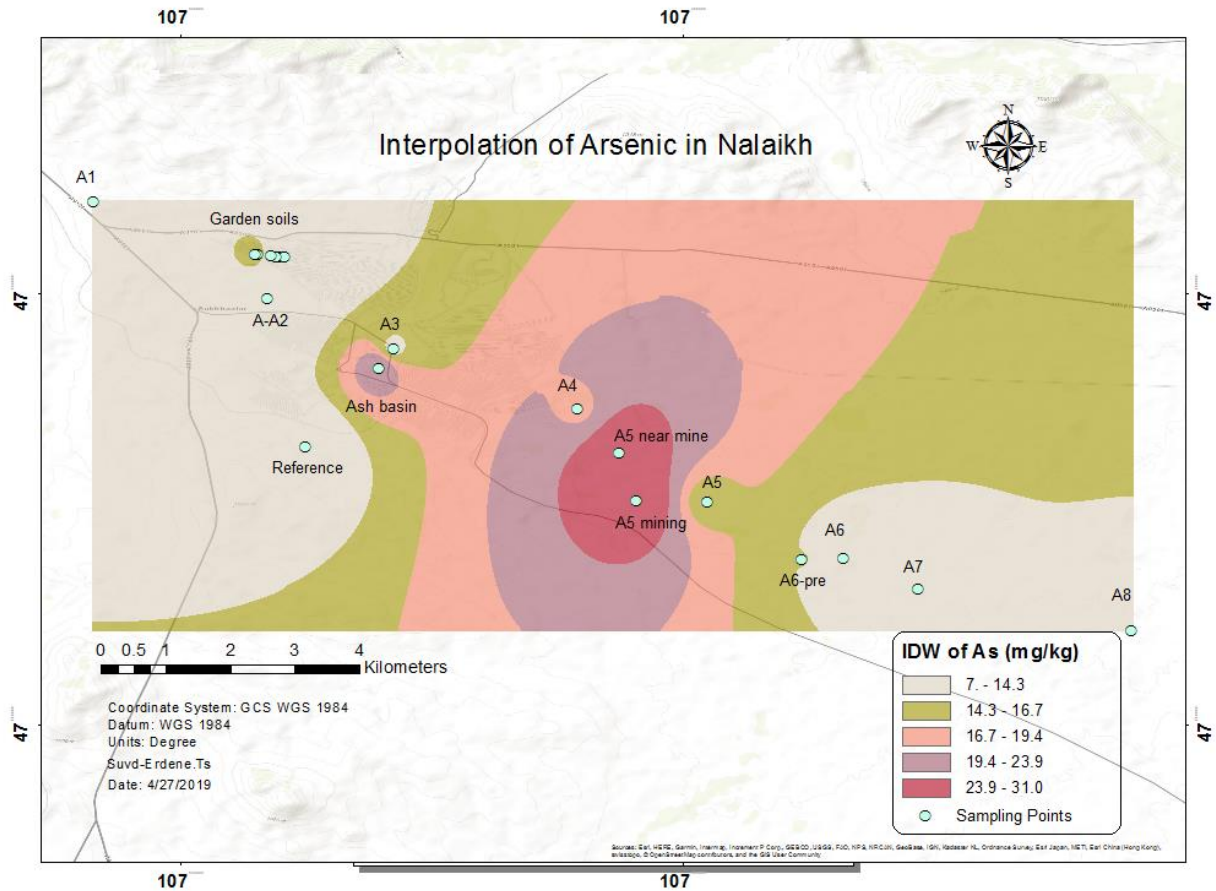
Samples	Munsell 10YR	Texture	pH value	OM (percent)	CEC (cmol/kg)	Mobility in Garden soils ( $\mu\text{g/kg}$ )				As mobile part in %	Co mobile part in %
						Mn	Co	Cu	As		
G1 Mix	3/3.	silty loam	7.17	16	28	7.79E-13	530.47	1.01E-06	25.27	0.296	0.5996
G-Natural	4/3.	sandy silt	7.28	9	15	2.60E-13	452.47	8.53E-07	49.14	0.338	0.6592
G-5 years	3.5/4.	clayey loam	7.32	14	24	1.62E-13	473.47	6.46E-07	42.40	0.355	0.6834
G2	4/2.	sandy silt	7.48	9	16	3.19E-14	778.93	1.18E-07	51.76	0.439	0.7966
G3	3/3.	sandy loam	7.39	14	23	8.87E-14	568.02	4.52E-07	47.83	0.389	0.7295
G4	4/3.	sandy silt	7.69	9	18	2.57E-15		6.13E-08	83.60	0.598	
G5	4/3.	sandy loam	7.36	10	19	1.30E-13	767.75	3.54E-07	68.16	0.374	0.7092

The content of organic matter and CEC were relatively high in the garden soils with the amount of 9 to 16% of OM and CEC of 15 to 28cmol/kg. The main reason for that is people add the animal manure and silty soils into the initial natural soils before they plant vegetables. The organic matter plays an important role in arsenic sorption under reduces conditions (20).

Only a limited fraction of the total amount of arsenic in the soil is easily mobile and over 80% is strongly related with Fe and Al oxides and those are not available for plants (20).

The mobile fraction of arsenic (As) in this study was very low with maximum 0.598 % in case of the fourth garden soil, as shown in Table 7. According to the classification of mobile trace elements in soils by Prüss, A. 1994, the precautionary value for arsenic (As) within the pH range of 7 to 7.5 is defined as equal to 45 µg/kg, while the mobile part of the cobalt (Co) is 20 µg/kg (41) and that the precautionary values are differentiated by the soil types exist for the metals such as chromium, nickel, cadmium, lead, mercury and organic substances and is dependent on ecotoxicological effect thresholds and compared with rural background concentrations. Precautionary values contain a safety margin in regard to the hazard-based trigger values (42). If the precautionary values are exceeded the acceptable amount, the addition of pollutants via all pathways must be limited to a maximum permissible load due to the possible occurrence of adverse effect (42). These values can also be used as targets for the treatment of contaminated soil (42). In the soils from garden, the maximum number of mobility of the As is 83.6 µg/kg at G4, whereas it is 767.8 µg/kg for Co with 0.797 % of the mobile part at G2 and those values were much higher than the precautionary value (41), as shown in Table7.

Heavy metals in the soils are associated with different chemical forms and states which defines the mobility, and bioavailability depending on their solubility. When heavy metals have high solubility, it is easy to uptake by plants (40).



The spatial distribution of arsenic contents in and around Nalaikh mining area were estimated by means of inverse distance weighting (IDW) areal interpolation, in which heavy metals were measured on topsoil.

The highest presence of As has found in the surrounding area of mine site with a concentration of 31.1 mg/kg arsenic whereas the amount of arsenic in ash basin from As-rich coal fired power plant was 24 mg/kg. The minimum value of arsenic has found in the sampling point A-A2 which has the location coordinates of 47.77934° N and 107.24223° E, with 7.1 mg/kg and which is used as a background soils for garden samples because it is the nearest natural soil to the garden and away from human impacts.

**Comparison to the previous study (1):**

- a) Significance:

The significance of As content in the previous study (1) and the current study were estimated for getting the standard error by using the statistical tests of significance ANOVA ( $p < 0.05$ ) based on the data collected from almost the same areas.

SUMMARY OUTPUT								
<i>Regression Statistics</i>								
Multiple R	0.525947761							
R Square	0.276621047							
Adjusted R Square	0.186198678							
Standard Error	7.910904351							
Observations	10							
<i>ANOVA</i>								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	1	191.4527488	191.4527488	3.059210343	0.118402007	p > 0.05 INSIGNIFICANT		
Residual	8	500.6592612	62.58240766					
Total	9	692.11201						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept (As)-Current	2.0750419	8.918065809	0.232678469	0.821853466	-18.49005473	22.64013853	-18.49005473	22.64013853
As previous study (1)	1.084138892	0.619840936	1.749059845	0.118402007	-0.34521687	2.513494654	-0.34521687	2.513494654

As shown in table, the p – value is equal to 0.118 and more than 0.05, and means there is no positive significance between these 2 studies. Thus, there is a change (elevation) on arsenic concentration especially near to the mining areas and it could be a result from anthropogenic activities.

b) In general:

In both studies, the one (1) which is conducted by Walk J, in 2016 and the current study, a high presence of the arsenic concentration has found in the ash basin from coal-fired power plant in Nalaikh district. However, there are no significant change on arsenic concentration along the main wind direction due to the location of source emission of the pollution is located in the middle of our study area and could affect the results and the hypothesis one cannot be approved. In general, the accumulation of arsenic was high near to the mining area than the other areas which has less As when it goes far from the mine and the distribution of arsenic is entering into the settlement area from the mining region and near the power plant area. Thus, the second hypothesis of the study is approved.

## 7. Conclusion and Recommendation

This study is conducted as a monitoring part of “Rehabilitation Concept Pyramid” (2) regarding the increase on heavy metals concentration due to the Nalaikh coal mining and a regular monitoring is an essential part of its rehabilitation concept and is important for determining the negative tendency of environmental parameters and helps to establish appropriate countermeasures.

This thesis presents a study on the heavy metal pollution assessment, especially focused on the arsenic content, the pollution load index, potential ecological risks, and the geo-accumulation index were determined in the garden soils as well as in and around the Nalaikh small-scale mining area. This study was conducted via investigation, field methods and statistical analyses.

As a conclusion, the results of pollution index for arsenic indicated that the soil around mining area was highly polluted whereas the other regions around ger settlement and areas that far from mine sites were not to moderate contaminated by arsenic.

The results of significance analyses suggested that there were significant correlations between Fe – As and Mn- As, while there was no relation between pH value and As content in the top soils. Furthermore, we can assume that the source of As in the soils mainly originated from Nalaikh coal mine. The rehabilitation pyramid (2) has already showed its transferability to coal which is also proved in this study and other products besides coal, the different metals like arsenic and cobalt.

The results of potential ecological risk assessment shows that the soils in our study area has a low to moderate level of ecological risks with the maximum value of 36.24.

The range of geo-accumulation index was -0.595 to 0.882, indicating that some soils were not polluted and others not to moderate contaminated by arsenic. Currently, the area does not require any urgent protection and prevention actions for remediating and reducing the emissions in this area but more or constant monitoring measures must be taken in the future.

The measured values for arsenic mobility in the garden soils were above the precautionary values except for the samples from G1-Mix which has the addition of silty soil and animal manure, and from G-5years which has been used for 5years. Whereas the mobile parts of cobalt were much higher than the precautionary value (20 µg/kg) with

the ranges of 452,47 to 778,93  $\mu\text{g}/\text{kg}$ . Therefore, soils where precautionary values are exceeded, the additional input of pollutants via all pathways must be limited and the constant monitoring and further research on cobalt are necessary.

The results of this thesis may offer a contribution for developing the precautionary strategy in the Nalaikh basin, and will be crucial for rehabilitation concept in order to monitor and assess the pollution of heavy metals, especially arsenic in and around Nalaikh small-scale mining area.

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# Acknowledgements

First of all, I would like to express my deepest gratitude towards my supervisors, Dr. Martin Knippertz, and Dr. Daniel Karthe for their huge supports and valuable advices and recommendations during my bachelor thesis study.

My sincere thanks also go to Mrs. Enkhjargal and Mr. Tsogtgerel for taking the samples from garden soils and to Mr. Ganbaatar for his enormous services of transportation for taking the samples.

Moreover, much appreciation goes to Mr.Walk.J, and Mrs. Gunsmaa for supporting me with the huge source of data and their research literatures.

Finally, I would like to thank my family and my friends for motivating and inspiring me all the time.

## Appendices

*Annex 1. Calculated statistics, relation between the contents of Mn and As in the soils along the main wind direction*

SUMMARY OUTPUT								
<i>Regression Statistics</i>								
Multiple R	0.785444101							
R Square	0.616922435							
Adjusted R Square	0.562197069							
Standard Error	186.2615508							
Observations	9							
ANOVA								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	1	391100.45	391100.45	11.27306177	0.012125073	SIGNIFICANT		
Residual	7	242853.5572	34693.36531					
Total	8	633954.0072						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Mn	212.6697332	148.91408	1.428137173	0.196310939	-139.4561118	564.7955781	-139.4561118	564.7955781
As	25.26619966	7.525216179	3.357538051	0.012125073	7.471890989	43.06050834	7.471890989	43.06050834

*Annex 2. Calculated statistics, relation between the contents of Fe and As in the soils along the main wind direction*

SUMMARY OUTPUT								
<i>Regression Statistics</i>								
Multiple R	0.829065971							
R Square	0.687350384							
Adjusted R Square	0.642686153							
Standard Error	3385.822845							
Observations	9							
ANOVA								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	1	176419579.4	176419579.4	15.38928067	0.005727532	SIGNIFICANT		
Residual	7	80246574.35	11463796.34					
Total	8	256666153.7						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Fe	11236.61488	2706.928465	4.151057194	0.004289422	4835.746183	17637.48358	4835.746183	17637.48358
As	536.6228446	136.7917788	3.922917367	0.005727532	213.1616871	860.084002	213.1616871	860.084002

**Annex 3. Calculated statistics, relation between the contents of Fe and As in the garden soils**

SUMMARY OUTPUT								
<b>Regression Statistics</b>								
Multiple R	0.704005932							
R Square	0.495624352							
Adjusted R Square	0.411561744							
Standard Error	3554.428928							
Observations	8							
<b>ANOVA</b>								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	1	74488537.4	74488537.4	5.895895498	0.051291553	weak significant		
Residual	6	75803790.03	12633965					
Total	7	150292327.4						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Fe-garden	10215.89144	4920.041468	2.076383198	0.083149809	-1823.016338	22254.79921	-1823.016338	22254.79921
As	938.7636747	386.6173927	2.428146515	0.051291553	-7.255005318	1884.782355	-7.255005318	1884.782355

**Annex 4. Calculated statistics, relation between the contents of Mn and As in the garden soils**

SUMMARY OUTPUT								
<b>Regression Statistics</b>								
Multiple R	0.735598567							
R Square	0.541105251							
Adjusted R Square	0.464622793							
Standard Error	77.13901717							
Observations	8							
<b>ANOVA</b>								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	1	42098.64457	42098.64457	7.074893567	0.037530683			
Residual	6	35702.56782	5950.42797					
Total	7	77801.21239						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Mn-garden	267.2347676	106.7758481	2.502764177	0.046354577	5.963679504	528.5058557	5.963679504	528.5058557
As	22.3175034	8.390457735	2.659867209	0.037530683	1.786792926	42.84821386	1.786792926	42.84821386

*Annex 5. Calculated statistics, relation between the contents of pH value and As in the garden soils*

SUMMARY OUTPUT								
<i>Regression Statistics</i>								
Multiple R	0.30785413							
R Square	0.094774165							
Adjusted R Square	-0.086271002							
Standard Error	0.172401983							
Observations	7							
<i>ANOVA</i>								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	1	0.01555921	0.01555921	0.523483542	0.501780319	INSIGNIFICANT		
Residual	5	0.148612218	0.029722444					
Total	6	0.164171429						
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept pH	7.162212777	0.313774063	22.82601919	3.00098E-06	6.355630871	7.968794683	6.355630871	7.968794683
As	0.017022674	0.023527526	0.723521625	0.501780319	-0.043456757	0.077502104	-0.043456757	0.077502104

# Statutory Declaration

Tsend-Ayush, Suvd-Erdene

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Last Name, First Name

Student ID Number

I hereby affirm in lieu of an oath that I provided the submitted bachelor thesis

Rehabilitation concept for Nalaikh Mining Licence Area (N-MLA):  
Monitoring of heavy metals in the soils in and around N-MLA.

independently and without undue external help. I did not use any sources other than those stated. In case that the work is additionally submitted on a data medium, I declare that the written and the electronic form are completely identical. The work was not submitted in the same or similar form to any examination authority.

Nalaikh, Mongolia 07, May 19

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Place, Date

Signature