# MINISTRY OF EDUCATION AND TRAINING HA NOI UNIVERSITY OF MINING AND GEOLOGY

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### "THE SOIL GEOCHEMICAL CHARACTERISTICS IN THE LEFT BAND OF THE RED RIVER IN HANOI TERRITORY

Specialization: Mineralogy and Geochemistry. Code. 9440205

## PhD. DISSERTATION SUMMARY

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The thesis is executed at: **Department of Mineralogy**, **Petrology and Geochemistry**, **Faculty of Geology**, **Ha Noi University of Mining and Geology** 

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#### FOREWORDS

#### 1. Urgent requirement

Soil is a natural formation located at the top of the Earth's crust, that are the products of the complete weathering of the host rocks or sedimentary products of these formations. Soil is the place where all activities of living, habilitation, mobilising, agricultural - industrial production, human's exploiting resources. With such characteristics, the soil is the object to pollution, accumulating pollutants from various sources.

The left band of the Red River in Hanoi Territory is an important economic area of the Capital. In addition to the role of the northern shield of Hanoi city, this is also a dynamic development area with industrial parks, residential clusters that are forming and developing very fast, the left bank of the Red River Left bank. It is also a food source for the inner city. Especially in the area, a green belt of vegetables, fruit trees, flowers and ornamental plants has been established for the city such as Dai Thinh, Hat Mon communes of Me Linh district; Van Noi and Tien Duong communes of Dong Anh district; Dong Du and Giang Bien communes of Gia Lam district. The study of soil geochemistry is an urgent issue, besides providing a scientific basis for land use planning, it also contributes to ensure the safety and sustainability of the Northern green vegetable belt of Hanoi.

To clarify soil geochemical characteristics to provide a scientific basis for the sectors of agriculture, environment and sustainable development, it is necessary to define the material composition and environmental characteristics of the soil, focusing on three main issues: (1) Particle composition and mineralogical composition of soil groups in the study area; (2) Soil geochemical characteristics and (3) Soil environment parameters: pH, Eh, Ec, cation exchange capacity (CEC) as well as adsorption of heavy metals in soil groups distributing in the study area and initially proposing measures to protect the soil environment to serving the environmental and resources management and sustainable development of the Capital.

The thesis: "The soil geochemical characteristics in the left band of the *Red River in Hanoi Territory*" is designed to solve the urgent requirements mentioned above.

#### 2. The aims of the thesis

Clarify the geochemical characteristics of the left bank area of the Red River in Hanoi Capital to provide a scientific basis for assessing the soil environmental status, serving the planning of appropriate land use and sustainable socio-economic development in the area.

#### 3. Object and scope of the thesis

- Objects: Planted soil (with a depth of 1m upwards) in the left band of the Red River in Hanoi, focusing on grain composition, mineral composition and chemical composition of major soil groups in the study area.

- Scope of the study: The area on the left band of the Red River belongs to Me Linh district, most of Dong Anh district (south of Ca Lo river), Gia Lam district and Long Bien districts, Hanoi Territory.

#### 4. Research Methodology

- Methods of synthesizing, analyzing and inheriting previous research results.

- Methods of field survey, sampling.

- Methods of analysis: Particle analysis (dry sieve / wet sieve); measuring geochemical indicators (pH, Eh, Ec); Methods of determining mineral and chemical composition of soil (heavy minerals, electron microscopy, differential thermal analysis (DTA) and X-ray Diffraction (XRD), Scanning electron microscopy (SEM), ICP - MS method; X-ray fluorescence method (XRF); Mass spectrometry method and Fluorescent flame spectroscopy (ICP - MS / ICP-AES / OES); Methods of determining organic carbon content in soil; Determination for Cation exchange capacity (CEC); Modeling method, processed by software such as MINPET, Excel ...

#### 5. Scientific and practical significances of the thesis

#### 5.1. Scientific significances

- The thesis's data is very important to clarify the grain composition, mineral composition and soil geochemical characteristics, especially the distribution of heavy metals in the main soil groups in the study area. (Me Linh district, Dong Anh district, Gia Lam district and Long Bien district, Hanoi).

- Provide scientific basis to explain the grain composition as well as the existence regulation of heavy metals: As, Cr, Pb, Zn, Cu ... and clarify the correlation of the grain composition and mineral composition with geochemical parameters in the soil environment of the study area.

- The dissertation's research results contribute to supplementing the scientific database on material composition and soil geochemical characteristics of Hanoi in general and Me Linh, Dong Anh, Gia Lam and Long Bien districts in particular.

#### 5.2. Practical significance

- The research results of the thesis provide a solid scientific basis for the rational exploitation and use of land resources in the region. These are reliable data to help authority's agencies and departments in the sectors of natural resources and environment, agriculture and industry to formulate regional planning works to effectively develop land budget, plant growth, suitable for livestock types and also a reliable document for accessment and monitoring soil pollution, thereby establishing regulations on land

management and use to limiting and minimizing the causes of pollution. contributing to the sustainable development of the Capital in general and the left band of the Red River in particular.

#### 6. Argument Points to defend

**Argument Point 1**. In the study area, there are 3 main soil groups: (1) alluvial soil, derived mainly from sediments of the Thai Binh Formation, (2) soil with patchy clay horizone and (3) grayish soil, originating from sediments of the Vinh Phuc Formation. There is a quite clear difference in mineral composition between the soil groups, in addition to the common minerals such as quartz, illite, kaolinite, the alluvial soil rich in hematite, magnetite, rutile; there are vermiculite, talc, jarosite in the soil with patchy clay horizone; In grayish soil, there are gibsite, calcite and dolomite.

Argument Point 2. Most of the soil in the study area is slightly acidic, having a weak to medium oxidation environment, and is poor nutrient soil, with a very high silicon content. The concentration of aluminum and iron varies quite widely between the soil groups, in which the alluvial soils have higher Fe oxide content compared to the grayish soil and the soil with patchy clay horizone; alkaline and earth alkaline oxides (K<sub>2</sub>O, Na<sub>2</sub>O, CaO, MgO) in the alluvial soil group are also higher than those of the other two groups. Trace elements with very high variation content do not have clear distribution rules in the soil groups of the study area.

Argument Point 3. In the Southeast of the study area, there are quite high anomalies of the elements: Pb, Zn, Cr, Cu and As ... Comparing with the national standards of soil environment, there was been a pollution of heavy metals in the alluvial soil; especially As and Cu content in some samples exceeded the permissible limit by dozens of times. Other heavy metals have lower levels of pollution.

#### 7. New issues in the thesis

The research results of the thesis have determined systematically and detaily material composition and geochemical characteristics of the soil in the study area (Me Linh district, Dong Anh district, Gia Lam district and Long Bien district, Ha Noi), specifically:

- Clarify the grain composition and mineral composition as well as their correlation with soil geochemical characteristics (distribution of main elements, trace elements, especially heavy metals in soil).

- Initial determination of soil environment characteristics in the study area (pH of soil and water, Eh, Ec, Cation exchange capacity ...)

- Access the characteristics of distribution of trace elements (heavy metals: As, Cr, Pb, Cu, Zn, ...) and identify anomalies of heavy metals that may cause pollution in the area.

- In the thesis, a number of modern methods has been applied to assess the potential risks to the ecosystem and to assess the level of risks of the carcinogenic elements in the soil, thereby providing a scientific basis for guidance to planning works, sustainable development and rational use of land resources.

#### 8. The volume and structure of the thesis

The thesis content is presented in 146 pages of A4 paper, including 27 tables and 64 figures, consisting of introduction, 4 chapters, conclusions, recommendations and reference list.

#### 9. The documentation basis for the thesis

The thesis was completed based on the research results of the PhD student with analytical data of 324 samples on geochemical indices (pH, Eh and Ec); 146 samples of particles composition, 48 samples of X-ray diffraction analysis (XRD), 46 samples of differential thermal analysis (DTA), 42 samples of scanning electron microscopy (SEM); 42 samples for determining major oxides concentration: SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO, MnO, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>; By X-ray fluorescence spectroscopy (XRF): analysis of 40 soil samples; 168 samples of ICP - MS including elements: As, Ba, Be, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, Sn, Ti, Zn, Hg, Mn ...; 30 samples for CEC and organic carbon... Inheriting the Hanoi Land Planning Map of the Institute of Planning and Agricultural Soil Fertility, Geological Map of Hanoi sheet at 1: 50,000 scale and the results of the University-Level project managed by the author.

#### CHAPTER 1. NATURAL - SOCIAL CHARACTERISTICS OF THE RESEARCH AREA

#### **1.1.** The natural characteristics of the study area

#### 1.1.1. Geographic location and population of the study area

The study area is located in the north (left band) of the Red River, in the territories of Me Linh, Dong Anh, Gia Lam and Long Bien districts, Hanoi Capital with an area of 504.61 km<sup>2</sup>. The total population of the study area is 1,091,860 habitants.

#### 1.1.2. Topographic and geomorphologic features

The study area is located on the northern edge of the Red River Delta with the area elevation is mainly from 3 -10 m in height. The land surface is relatively flat and tends to gradually lower from northwest to southeast.

#### 1.1.3. Geological characteristics

The geological formations in the study area are mainly modern sedimentary formations, without magmatic rocks.

#### <u>Stratigraphy</u>

According to the results of geological studies, the exposed rocks in the area is mainly Quaternary sediments of the Vinh Phuc and Thai Binh formations.

#### Vinh Phuc Formation $(a, lbQ_1^{3}vp)$

The Vinh Phuc Formation is derived from rivers, lakes – swamps sediments, upper Pleistocene age. The upper part has been weathered and changed in their compositions (washed with fine clay particles and added with organic matter). On the delta margin, they have been weak lateritization, creating clay, sandy clay with yellow color - red - brown red - yellowish brown patchy (patchy clay).

#### Thai Binh Formation $(Q_2^{2-3}tb)$

Modern sediments of Thai Binh formation are mainly of river origin, distributed along the banks of large rivers covered with a thin layer of alluvium: sand, silt, clay.

#### 1.2. Hydrological characteristics of the study area

#### 1.2.1. Surface water characteristics

The study area has the Red River and a large distributary, the Duong River. The Red River has a total length of 1,149 km, originates from Yun Nan (China), flowing through the study area to Tonkin Bay.

#### 1.2.2. Groundwater characteristics

Most of the area, including the left band of the Red River, has the characteristics of low-lying areas influenced by sea-progressive processes, continental erosion creating unconsolidated sediments including many thin covered layers with different cohesive level of the rocks.

The aquifers include: - Cavity aquifers (Aquifer of Holocene sediments (qh); Pleistocene sediments (qp).

The aquifer qp has a hydraulic relationship with surface water sources and hydrological geological windows. The water-poor formations and the water-proof formations are the Pleistocene sediments of the Vinh Phuc Formation  $(Q_2^2 vp)$ .

#### **1.3.** Socio-economic characteristics of the study area

The area of cereals planting is 31,018 ha. The output of food crops is 154,504 tons, an average of 493 kg per person. There are 11,958 enterprises and cooperatives. The number of individual non-agricultural, forestry and fishery individual economic establishments was 53,477. The aquaculture area is 2.223 ha. The number of businesses doing trade works and services is 43,936 units.

## **1.4.** Overview of the status of production activities and the environment of the studied area

#### 1.4.1. Current situation of production activities and environment in Me Linh district

The 1st and 2rd Quang Minh Industrial Parks occupy 847ha, with main production sectors: Manufacture of mechanical parts, electronics, refrigeration, interior equipment, food and foodstuff production and processing, etc. The Parks have the wastewater treatment system with a handling capacity of 3.000m<sup>3</sup> / day.

# 1.4.2. Current situation of production activities and environment of Dong Anh district

Thang Long, Ngu Huyen Khe Industrial Parks with total area of 295 ha, including: Clean industry, electronic components assembly, motorbikes, packaging production... with central wastewater treatment system with a processing capacity of  $5.000m^3 / day$ .

#### 1.4.3. Current situation of production activities and environment in Gia Lam district

In the area, there are 05 industrial clusters and handicraft villages including textile, dyeing, cardtoon board, plywood, food, wine, mechanical manufacturing, materials, ceramics manufacturing.

#### 1.4.4. Current situation of production and environment in Long Bien District

Two industrial parks Sai Dong B and Dai Tu cover an area of 137.11 ha, major productions: mechanics, electronics, precision mechanics, light industry, informatics, electronic and mechanical assembly, food processing, consumable goods, jewelry, motorbike components, cars, ... They all built centralized wastewater treatment system and discharged into Cau Bay river ..

## CHAPTER 2. THEORICAL BASE AND RESEARCH METHODOLOGY 2.1. Theorical base

#### 2.1.1. Soil concept and soil classification

#### 2.1.1.1. Concept of land

- From the soil component (Soil) point of view of the Geotechnical Geology, the soil is a loose object located on top of the hard rock; their features depending on the degree of cohesion and the mechanical properties, so the zonality of the soil section is similar to the zonation in weathered crust.

- According to the concept of Argiculter Sector: Soil is an independent natural formation formed on the Earth's surface under the influence of inorganic and organic substances (parent rocks, climate, topography, time, organisms, their activities) and have fertility. The soil is composed of three phases: Solid phase (primary, secondary, organic materials, colloidal substances); liquid phase (soil solution containing inorganic compounds, organic, ...); gas phase (gases in the soil porous space, gases absorb by colloidal particles such as O<sub>2</sub>, CO<sub>2</sub>, NH<sub>3</sub> ...). 2.1.1.2. Landform process

According to Nguyen Van Pho (2002) soil is one of the most important stages of the geochemistry cycle. Soil is formed by weathering of the original rocks as a result of the complex interaction between different geochemical processes. Soil has a large porosity and is divided into layers with different composition and properties as a result of water filtration and biological processes including growth and decomposition of organisms. The soil formation process is affected by 5 main factors, including: Materials from parent (host) rock (PM), climate (C), biosphere (O), topography (R) and time (T).

The soil is derived mainly from weathered products come from upstream cachment of the Red River system, which are brought by river water to deposite on the Northern margine of the Red river Delta. The soil undergone weathering (dissolution, deposition, washing, redistribution of material) at different levels depending on the topography (location) of formation and duration, resulting in into different types of soil profiles.

2.1.1.3. Select the basis of land classification

The choice of soil classification method has a great influence on the representativeness and objectivity of soil research in the study area. The major source of sedimentary materials in the study area is weathering products transported by the Red River system along with two major tributaries, the Da and Lo Rivers. Soil (from 1m deep upwards) is a later product, when the loose sediments have been exposed on the surface and subjected to not long-lasting processes of washing, re-accumulation and redistribution of materials with the sediments of the Vinh Phuc Formation, but it is still sufficient to overprint the original features of the previous geological formations. And for the sediments of the Thai Binh Formation, the time is too short for those processes to have a noticeable impact.

Choosing the method of classifying soil according to the origin of soil formation (which geological formations it originates) will require further detail studies on the source of materials, transporting catching and deposition basin, weathering of parent rock, and the depth of soil layer out of development of plant roots ... All are beyond the scope of the thesis research. Therefore, the author uses the classification of soil which is popular in agriculture, in which depending on the characteristics of the composition of particles, minerals, soil profiles are divided into different layers or zones (Horizon). The name of a soil type is called based on the presence of a typical soil layer (diagnostic layer) in that soil profile.

2.1.1.4. Types of soil classification are in common use in the world and in Vietnam

## a. Some typical classification systems are in use in the world in the recent time

The developed countries such as the United States, China, Australia, Canada, ... have their own soil classification. In the world, there are two common classification systems: the United States (Soil Taxonomy) and the United Nations (FAO-UNESCO) classification.

#### b. Types of soil classification, used in Vietnam

Based on the above classifications, the popular soil classification used in

Vietnam has complied with Vietnam standart: 9487 - 2012 issued by the Ministry of Science and Technology in 2012.

Published research results show that in the reasech area, there are 3 main soil groups: alluvial soil, gray soil and patchy clay soil. Each soil group has their own typical mineral composition, specific geochemical characteristics.

#### 2.1.2. Mineral and chemical composition of the soil

2.1.2.1. *Mineral composition of the soil:* Mineral composition is one of the important factors affecting soil properties, expessing on the solid phase of the soil and its minerals. The mineral composition determines the chemical composition of the soil, its ability to bind and adsorb matter (including toxic compounds) ....

2.1.2.2. Chemical composition of soil

*a- Major compounds*:Generally, the richest major compounds in soil are Si and Al oxides; other måo compounds in less popular extends are Fe, Ca, Na, and K oxides but they are important in the growth cycle of plants, especially higher caterogy plants.

b-*Trace elements in soil*: Geological characteristics and physico-chemical conditions play an important role in trace content in soil. Some trace elements contribute important role in organisms and are called micro nutrition elements.

c- *Organic matter in soil*: (Organic Matter - OM) is a product of decomposition from plants and animals. This is an important source of nutrients for plants and an important indicator for assessing soil fertility.

#### 2.1.3. The process of soil formation and variation

In the study area, the soil with a depth of up to one meter is the top layer of two sediment formation: The Thai Binh  $(Q_2^{2^3}tb)$  and the Vinh Phuc (a,lbQ<sub>1</sub><sup>3</sup>vp) sediments.

Sources of these sediments are mainly from weathering products in the upper catchments transported by the river systems and eroded products from surrounding hills and mountains to form mixed products in the study area.

#### 2.1.3.1 Process of soil formation

Depending on the depositon time, the recent formations in study area are divided into 5 units (from early to late time): Sediments of the Ha Noi Formation, Vinh Phuc Formation, Hai Hung Formation and Thai Binh Formation. In which only sediments of Vinh Phuc and Thai Binh formations are exposed on the surface of the study area.

Clay - silt sediments of the Vinh Phuc Formation are formed in the lake, marsh (swamp) and river environment plus erosion products such as sand, silt, clay from the oder rocks formations in the North. The thickness varies to tens of meters and covered by Thai Binh formation sediments. The surface layers of Vinh Phuc sediments is often lateritized to create patchy yellow-reddish-brown clay-sand clay.

The sediments of the Thai Binh Formation occupies a major area in the study area.

2.1.3.2. The process of forming soil profile and material distribution in the soil Soil in the study area, after being formed and exposed on the surface, will be affected by physicochemical processes (weathering), living activities of organisms (including human activities) leading to changes.

a) The humus process of the top layer of soil: after the soil is formed and exposed on the ground, due to the activities of microorganisms and organisms (animals and plants), the soil becomes humus. Decomposition products of plants and animals are organic acids that reduce the pH of the soil.

b) The processes of hydrolysis, hydration, oxidation (chemical weathering) change mineral composition. These processes take place with weak intensity because the environment of the soil itself so not much different in compared to intial time of soil formed (oxidized environment and rich in water). Main soil minerals such as quartz and kaolinite, illite are very stable in the surface conditions.

c) Disolution, washing, transportation and re-deposition of soil components: these are most important processes leading to the redistribution of material composition (mineral as well as chemical composition) in the soil profile of the research area. In the E-horizon, it is rich in wathering resistent minerals (mainly quartz). This zone is often found in soils formed over a relatively long period.

#### 2.1.4. Concepts related to geochemical soil environment

2.1.4.1 Soil environment parameters

a) Soil acidity (pH - acidity and basic of soil)

b) Redox potential (Eh)

2.1.4.2. Existence form and mobility of trace elements in soil environment

Most of the elements exist in different environments. The value of Eh (Redox potential) and pH (acidity - base value of the environment) greatly affect the existing form, the ability to move them in nature.

2.1.4.3. Cation adsorption and exchange in soil (CEC)

*a) The adsorption capacity of soil components:* Because the soil contains colloids that bearing different electric charged, so the colloids have the high ability to adsorb opposite ions.

*b) Cation exchange capacity (CEC)*: is the sum of the positively charged electrodes on the surface of absorbable soil constituents under certain pH conditions and strongly dependent on mineral composition as well as, colloids component.

2.1.4.4. Pollution of heavy metals in soil

This is the case heavy metals accumulate in soil with the content exceeding the allowable limit. Pollution of heavy metals in soil lead to a very strong toxicity to biota.

**2.1.5.** Status of soil geochemical research in the world and in Vietnam 2.1.5.1. Status of soil geochemical research in the world

Soil geochemistry has been strongly developed in countries with strong scientific and technical potentials such as the United States, Canada, United Kingdom, France, Germany, Japan and more recently Korea, China and Thailand. Some countries such as United Kingdom and Scotland, the United States have established soil geochemical Atlas on whole territory.

2.1.5.2. Status of soil geochemical research in Vietnam

In Vietnam, the study of soil geochemistry has been interested just only in recent years. Research works on soil chemical, classification, making planning maps have been done in Dong Nai province, Ho Chi Minh City. and other municipalities. Initial research results show that soil in many areas has been seriously polluted.

#### 2.2. Các khối lượng thực hiện và cơ sở phân tích

#### 2.2. The field work volume and analytical works

The author excavated 318 pits for soil profile study and took 788 samples of all kinds, conducted analyses myself and sent them to reliable analysis laboratories such as in the the Geological Institute; Institute of Chemistry - Vietnam Academy of Science and Technology; Center for Geological Experiment and Analysis, Ministry of Natural Resources and Environment; Wuhan University, China, Hanoi University of Natural Resources and Environment. The results of the analysis are the basis for the interpretation of the research contents.

#### CHAPTER 3. CHARACTERISTICS OF MATERIAL COMPONENTS AND RESEARCH AREA

#### 3.1. Distribution characteristics of soil groups in the study area

Based on the soil classification according to TCVN 9487: 2012, in the area there are 3 main soil groups: alluvial soil (PS); soils with patchy clay layer (LL); gray soil (XA).

The alluvial soil (PS) group is widely distributed in Gia Lam district with an area of 6,097 ha, Me Linh with an area of 5,689 ha, Dong Anh with an area of 3,599 ha and the district with the least area is Long Bien 1,486 ha. The soil originates from the sediments of Thái Bình Formation.

The patchy clay soil has an area of 1,477 ha, concentrated in Dong Anh and Me Linh, belonging to the Vinh Phuc Formation.

Gray soil has an area of 5,950 ha, distributed in Dong Anh and Me Linh, derived from sediments of Vinh Phuc formation.

#### 3.2. Grain composition characteristics of soil groups in the study area

The alluvial soil group has clay batch of 21.93%; Silt batch of 45.71%; Coarse (Sand-gravel) batch of 35.15%. The group of soil with patchy clay layer has clay batch of 4.66%; Silt batch 27.9%; coarse-grained batch (sand)

67.48%. The gray soil group has fine batch (clay) of 13.4%; Silt batch 49.1%; Coarse grain batch (sand) 35.9%.

## **3.3.** Mineral composition characteristics of soil groups in the region *3.3.1. Mineral composition characteristics of alluvial soil*

+ The main mineral composition of this soil includes: Quartz 58.14%, hydromica (Illit) 14.28%, kaolinite 6.43%, feldspar 5.43%, geothite 4.3%. The mixed mineral group of chlorite - montmorilonite and montmorilonite 4.43%. There are also other minerals: lepidocrokite, magnetite, gibsite, amphibol, hematite and mixed clay. The presence of goethite and montmorilonite enhances cation exchange capacity as well as adsorption of the soil.

#### 3.3.2. Characteristics of mineral composition of soil group with patchy clay layer

Main minerals include: Quartz 80.3%, hydromica (mostly illit) 4.43%, kaolinite 4.14%, feldspar 2.72%, geothite 2.3%. Chlorite and montmorilonite range from 3% to 7%. There are also other minerals: Talc, vermiculite, rutile, jarosite. In this soil, the presence of vermiculite and the montmorilonite group reflects the ability of increasing soil flexibility as well as the soil ability to exchange cations and adsorb.

#### 3.3.3. Mineral composition characteristics of gray soil group

Main minerals: Quartz 69.4%, illit (hydromica) 10.6%, kaolinite 4.2%, feldspar 4.2%, geothite 2.6%, chlorite and montmorilonite minerals range from 6% to 9%. These three soil groups all share the same geological origin and supplying source from weathering products brought by the same river system (only different in time) and are products developed on modern sediments of Vinh Phuc formation and Thai Binh formation.

# **3.4. Characteristics of the chemical composition of water in the study area** Studying the geochemical characteristics of water contributes to definding the origin, mechanism of movement and accumulation of sensitive elements in the soil, assessing the causes of soil pollution, forecasting the development trend of the soil environment and propose solutions to minimize and prevent pollution.

#### 3.4.1. Distribution characteristics of heavy metals of surface water

In surface water in the study area, the Cd content exceeds 4.6 times (3.57% samples with the exceeded content) comparring to those of coresponding Vietnam Standard (QCVN 08-2015); Pb content exceeded from 1 to 4.28 times (41.2% samples with the exceeded content); the content of Cr exceeds from 1.12 to 1.45 times (25% samples with the exceeded content); Fe content exceeds from 1.23 to 5.6 times (15% samples with the exceeded content) of QCVN08-2015.

#### 3.4.2. Characteristics of the chemical composition of ground water

The results showed that comparing to the coresponding Vietnam Standard

(TCVN09-2015), Cd content exceeded 1.4 to 9.2 times (28.67% with exceeding concentration); Pb exceeded from 8.6 to 17.2 times (13.64% with exceeding concentration); Cr content exceeded from 1.04 to 1.14 times (18.18% with exceeding concentration); Fe content exceeds from 1.64 to 4.14 times (accounting for 17.64%); Mn content exceeds from 1.48 to 1.56 times (14.28% with exceeding concentration). In the area, there are localized geochemical anomalies for the elements Cd, Pb, Cr, Fe, Mn with 13-15% samples having heavy content exceeded the reference standards. This result shows that the ground water has begun to be polluted in some heavy metals such as Mn, Fe, Cd, Pb, Cr, but the pollution level is lower than that of surface water. However, the important fact that pollution of heavy metals in groundwater will badly affect the soil environment of the study area.

#### **CHAPTER 4: GEOCHEMICAL CHARACTERISTICS OF RESEARCH AREA 4.1. Characteristics and distribution rules of important components in** soil groups in the study area

## **4.1.1.** Distribution characteristics of the elements in soil of the study area 4.1.1.1. Distribution characteristics of the major oxides in the soil

The analysis of the oxides of Si, Al and Fe elements shows that these are the predominant oxides with a large content in the soil, especially the  $SiO_2$  oxide.

- The content of SiO<sub>2</sub> averaging 71.66% is the oxide that accounts for the highest proportion in the soil;  $Al_2O_3$ : 12.4% showed as a second one after silicon oxide;  $Fe_2O_3$  oxide: 4.95%. These oxides have small levels of content variation compared to those of Al and Fe oxides and are less dependent on soil groups. In addition to the predominant (major) oxides, there are also less common oxides with smaller contents such as K<sub>2</sub>O, MgO, TiO<sub>2</sub>, CaO, Na<sub>2</sub>O, (see Figure 1).



Figure 1. The concentration variation of major oxides in the 3 soil groups in study area

#### a. Distribution of oxides in alluvial soil

The content of oxides:  $SiO_2$ ,  $Al_2O_3$  and  $Fe_2O_3r$ : 63.6%, 15.76%, 6.64% espectively. This is a rich group riched in aluminum and iron oxides than other oxides. Less common oxide content with no variation rules, such as:  $K_2O - 2.33\%$ , MgO-1.67%, TiO<sub>2</sub>-0.85%, CaO-0.62%, Na<sub>2</sub>O-0.26%. The irregular variation is due to local differences in sediment source and sediment environment in the study area.

b. Distribution of oxides in soil group with patchy clay layer

Content of oxides: SiO<sub>2</sub>:76,42%; Al<sub>2</sub>O<sub>3</sub>:10,97%; Fe<sub>2</sub>O<sub>3</sub>:3,56%. The content of less common oxides is:  $K_2O - 0.69\%$ , MgO- 0.97%, TiO<sub>2</sub> - 0.07%, CaO - 0.28%, Na<sub>2</sub>O - 0.19%. This group is rich in Si and poor Al, especially the Fe

content is much lower than alluvial soils. Similarly, the content of CaO, MgO,  $K_2O$  and  $Na_2O$  oxides are also poor, due to the washing process from the O layer of fine-grained components. (clay rich in aluminum) and alkaline oxides for a long time of this soil group (belonging to Vinh Phuc layer); alluvial soil is distributed within youngest Thai Binh formation, so it is less likely to be washed or with washed in only short time.

c-Distribution of the main components in the gray soil group

The predominant oxide as SiO<sub>2</sub>: 77,7%; Al<sub>2</sub>O<sub>3</sub>: 9,3%; Fe<sub>2</sub>O<sub>3</sub>:3,63%. Less common oxides: K<sub>2</sub>O, MgO, TiO<sub>2</sub>, CaO, Na<sub>2</sub>O respectively: 2.81%; 0.68%; 0.98%; 0.25%; 0.24%. SiO<sub>2</sub> content is much higher than those in the other two soil groups while aluminum oxide content is quite lower. Especially, the potassium content is much higher than the content of other oxides in comparison with the alluvial soil and pathchy clay soil. The cause of the difference is due to local differences, conditions of formation, or human action? (farming activities - potassium fertilizing human?).

4.1.1.2. Distribution of trace elements (dispersion) in soil

a. Trace element content

The trace element content varies in a very large range, from a few dozen times (Cr, Mo) to hundreds of times (Ni, Zn, Cu, Mn ...), even up to thousands of times (Cd, Sb). ). Especially, the anomalies of toxic heavy metals appear in some places such as in Dai Thinh, Me Linh, Kim Hoa communes, Me Linh district, especially with a relatively high Cd content; Besides, it is also anomalies in Gia Lam district such as in the Dong Du guava planting area.

b. Correlation between heavy metals in soil

The correlation between As and Zn pairs has a clear positive relation: Cr and Zn have r = 0.62; Ni and Cu pairs há a quite clear relation (r = 0.53); Similarly to the Cd and Pb Pairs (r = 0.56); Cd and Sn have a positive relationship (r = 0.6); Zn with As and Sn (r = 0.63) ... Especially As and Sn pairs (r = 0.85). This may be related to human activities in the area, (see Figure 2).



According to the above correlation, it is clear that they have a common origin. The linear relationships are either positive or negative to show the variation in the content of these elements. Especially the group elements As and Sn (r = 0.85). That may be due to the production activities of the local people.

4.1.1.3. Variations of trace element content along the section depth in the study area The author has established cross-section profile (Horizonal sections) with the common structure of the region (perpendicular to the sedimentary bands) distributed along the flow direction of the Red River system, starting from the more ancient sediments of the Vinh Phuc Formation next to the Triassic rocks in the hills from the North (see cross sections ...), extending close to the band of the Red and Duong Rivers. Besides, there are the section lines along the longitudinal direction (extending in the center of the research area, alonging the flow direction of the Red River).



Figure 3. Average variation of heavy metals content in the study area from North to South (section lines AB, CD, EF, GH in order from West to East - from Me Linh to Gia Lam districts)

a) Lateral (Horizontal) variation of trace element content (in the North - South direction of the study area)

Looking at the figure 3, it is clear difference in the cross-section direction (from North to South). There is a certain similarity between the AB (cut through Dai Thinh common) and CD (cutting through Van Noi common) and the GH (cutting from Dong Anh town to Giang Biên).

The Figures 3a, b, c, d, show the heavy metals content tends to increase on the northern edge, the center and the southern edge. The increase is probably related to human activities (distribution of residential areas and production activities). The concentration of Zn, Cr, Pb has a rather large variation, and the level of variation of Cu, Cd and As is smaller. It may be due to the human life activities or caused by the industrial production facilities that release these elements. Particularly, the section 3c crossing Dong Anh town, through Mai Lam, Cau Duong to Long Bien area has a completely different form: Pb and Cd content is low at both ends of the section (Soc Son and Red River sides), but in the middle. quite high content. It may be related to the operation of production facilities in Dong Anh, Co Loa, Cau Duong areas .

b) Variation in content of major oxides and trace elements along longitudinal direction (along the Red river's flow direction).

The variations in content of major oxides and trace elements along longitudinal direction illustriated in figure 4.



Figure 4. Graph of variation in average concentration of heavy metals in soil in the study area along Red river flow direction (IK section)

The figure 4 shows that the content of heavy metals along the longitudinal direction (after Red River Flow direction) varies without rules. It proves that the origin and location of the formation as well as the age of the host rock materials of the soil groups play little role in the variation of the distribution of these metals. The distribution characteristics along cross-section and Red river flow direction reinforce the anthrological cause of the abnormalities of the heavy metals in the study area.

4.1.1.4. Variations in content of major oxides and trace elements according to depth

The variation of the content of major oxides after the soil depth illustriated in Figure 5.



Figure 5. Variation of the content of major oxides after the soil depth in the area The concentration of major oxides is stable along the soil depth, except for some oxides such as SiO<sub>2</sub> from the soil developed on sediments of the Vinh Phuc formation (soil with patchy clay and gray soil),  $K_2O$  in gray soil;  $K_2O$ and MgO in alluvial soil. In addition to the chemical properties of the elements (solubility, mobility), the environmental indics (pH, Eh, etc.) are considered as well as the soil development history in those areas.

\* Trace element content variation (Heavy Metals) according to depth The variation of the content of the heavy metals according to the depth of selected typical profiles of each soil type from different areas to evaluate, the results are shown in Figures 6, 7 and 8 (a, b, c).



Figure 6. Variable content of heavy metals in the soil with patchy clay along to the soil depth

The figures 6a, b, c show that the level of variation in the contents of the heavy metals in the different profiles is not similar, and there is no clear variation rule according to the depth in the layer of the soil with patchy clay layer.

The content of heavy metals varies in a quite large range. In Lo Khe commune (Dong Anh dist), the content of heavy metals decreases significantly from the surface (O horizone /Layer O /  $1^{st}$  layer) to the deeper layer (Horizone A / Layer 2); In Van Noi, there is a reverse trend: Heavy metals concentration (except for Cu) tends to increase significantly from the O to A horizones.



Figure 7. The change of heavy metal content in gray soil group Along to section depth In Tien Duong area, the heavy metal content in patchy clay soil also tends to decrease in depth but not much. Except the content of Cu decreases rapidly from layer O to layer A, while the content of Cr changes in the opposite direction.

Looking at the Figure 7, it is clear that the Cr content increases remarkably from the O/1 layer to the A/2 layer in the gray soil sections of Dai Thinh commune (Me Linh Dist) and Van Noi commune (Dong Anh Dist). The Cu content also increased dramatically from the O / 1st layer to the A / 2rd layer in gray soil in Tien Duong commune (Dong Anh). The cause of the variability is not cleare and requires further, more detailed studies of the origin and behavior of the soil elements.

The variation of trace elements (heavy metals) content in the alluvial soil group is as follows:

The results as illustriated in Figure 8 (a, b, c) show a difference in the distribution of the heavy metals in the old alluvial soil group (DT12 and VN05) with modern alluvial soil (DT20). In old alluvial soils, the content of the heavy metals tends to increase from the O / 1st layer to A/2nd layer) whereas the opposite trend occurs in the young alluvial soil.



Figure 8. Variations in the content of the heavy metals in the alluvial soil group along to the section depth

#### 4.1.2. Distribution of organic matter content in soil

To clarify the distribution characteristics of organic components in soil, the author analyzed 30 soil samples belonging to 3 groups. The indices OM, OC are important parameters to evaluate the quality of the soil and the fertility (nutrition) of the soil. It also clarifies the adsorption capacity of organic matter in soil.

The average organic carbon content in the soil is 0.81%, compared with the Walkley - Black standards which show that all three soil groups are poor and very poor in organic carbon (see Figure 9).



Figure 9. The variation of Organic Matter (OM) and Organic Carbon (OC) in the three soil groups in study area

The figure 9 shows that the soil group with the patchy clay soil is richest in organic matter, gray soil is poor in organic matter (called imfertile soil). This difference is determined by the conditions of formation and the impact of human cultivation.

## 4.1.3. Cation exchange capacity (ability) (CEC) of soil groups

The CEC of alluvial soil is highest. Due to its rich clay content and significant organic matter content or high cation exchange capacity due to its rich clay composition or minerals with good cation adsorption and exchange capacity. The soil riched in nutrient and having a potential fertility higher than other soil groups.

# **4.2.** Environment geochemical characteristics of soil in the study area *4.2.1.* Soil environment geochemical indices

The author analyzed 324 soil samples belonging to the groups: alluvial soil, soil with patchy clay and gray soil to determine geochemical indicators of soil environment (pH, Eh, Ec), (see table 1).

		pН			Eh			Ec				
	Common pH Value	pH in Alluvium soil	pH in Soil with Patchy Clayish layer	pH of Grey soil	Common pH Value	pH in Alluvium soil	pH in Soil with Patchy Clayish layer	pH of Grey soil	Common pH Value	pH in Alluvium soil	pH in Soil with Patchy Clayish layer	pH of Grey soil
Max	8.34	8.34	8.11	7.92	569	569	521.8	960	1321	1321	791	437.7
Min	3.67	3.87	3.67	4.54	60	66	60	58.7	45.7	57.4	45.7	108
Average	6.67	6.93	6.48	6.43	269.4	277	269	261	248.72	236	252	263
Number of Samples	324	126	114	84	324	126	114	84	324	126	114	84

Table 1. Statistic data of geochemical indicators in 3 soil groups in the study area

4.2.1.1. pH value

The soil pH value varies in a fairly large range, averaging 6.67 (slightly acidic soils); 35.19% of analysed samples in acidic to weak acidic environment (pH <6.5), (see figure 10).



The alluvial soil, with average pH 6.87, having 30.16% of sample in acidic - weak acidic environment; soil with patchy clay layer has the average pH 6.98 and 65.78% samples in neutral-alkaline environment; gray soil group, pH 6.43, having 49.81% samples in acidic-weak acid environment (pH < 6.5).

4.2.1.2. Soil Eh value (Redox Potential)

In general, the redox potential of the 3 soil groups is in the oxidizing environment at different levels (from weak to medium and strong), but most are at medium oxidation. Gray soil group is more oxidized because this group is usually distributed in high fields and has coarse grained composition so the air circulation level in soil is better, leading to increased oxidation capacity. The soil group with patchy clay layer comparing with the alluvial group, the oxidation level is weaker due to the distribution in the lower area and the presence of a larger content of fine particles (silty clay), leading to the prevention of air circulation in the soil, affecting to the activity of aerobic microorganisms and the roots of plants.

4.2.1.3. Conductivity of soil (Ec): The average Ec value of soil groups is not much different. However, the Ec value of many soil samples is slightly higher than normal soil, which affects the activity of soil microorganisms.

## 4.2.2. The distribution characteristics of the heavy metals and other toxic substances in the soil

The samples were selected to represent 3 alluvial soils, soils with patchy clay layer and gray soil. Samples analysed for trace element composition, such as (Hevy metals): As, Cd, Cr, Pb, Zn, Cu, Se, Hg, Mn. The analytical number of alluvial soil in the soil group is 44 samples; soil has a patchy clay layer is 64 samples and gray soil is 51 samples. The statistic data results shown in the table 2.

							~ .		<u> </u>	
Elements	As	Cd	Со	Cr	Cu	Mo	Ni	Pb	Be	Zn
Max	693	1.5	123.3	660.7	1894.8	8.1	374.4	333.3	5.8	1173.3
Min	1.1	0.008	1.6	9.9	2.2	0.1	0.9	2.6	0.4	14.2
Average	22.1	0.4	16.2	60.0	50.6	0.8	25.1	38.9	2.5	66.0
Number of Samples	141.0	148.0	157.0	157.0	125.0	125.0	157.0	157.0	119.0	157.0
Elements	Se	Sb	Sn	Zn	Tl	Hg	Mn	Bi	Ba	Ce
Max	4.9	44.5	122.3	1173.3	9.7	0.1	5933.3	10.5	872.8	115.0

Table 2. Variable content of trace elements in soil group (mg / kg)

Min	0.01	0.0	0.4	14.2	0.01	0.001	20.8	0	.2 1.1	40.0
Average	1.8	5.3	11.5	66.0	1.84	0.009	413.3	3 2	.3 169.7	82.6
Number of Samples	113.0	146.0	121.0	157.0	119.0	101.0	56.0	2	1.0 129.0	12.0
Elements	Pr	Nd	Sm	Gd	Tb	Dy	Но	Er	Tm	Yb
Max	11.7	43.5	8.1	6.7	1.1	6.5	1.3	3.6	0.5	3.4
Min	4.4	16.2	3.0	2.9	0.5	3.5	0.7	2.3	0.3	2.3
Average	6.8	27.0	4.8	4.3	0.7	4.6	1.0	2.8	0.4	2.8
Number of Samples	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0

The results in the Table 2 show that the content of trace elements vary in a fairly large range, from several dozen times to thousands of times. Table 3. Variations in the concentration of heavy metals of the three main soil groups in the study area.

					,				U	1		
Element		As	-		Cd			Со			Cr	
		Soil with			Soil with			Soil with			Soil with	
Soil	Alluvium	Patchy	Gray	Alluvium	Patchy	Gray	Alluvium	Patchy	Gray	Alluvium	Patchy	Gray
group	soil	Clavish	soil	soil	Clavish	soil	soil	Clavish	soil	soil	Clavish	soil
8 F		laver			laver			laver			laver	
Max	693	32.2	29.3	1.4	1.5	1.1	93.9	123.3	32.6	147.1	130.1	128
Min	4.01	11	24	0.01	0.001	0.01	2 33	21	16	9.87	99	10.5
Average	37.17	11.5	14 74	0.01	0.001	0.01	18.67	19.4	12.06	62.16	50.1	55.14
Number of	40	44	CA	20	44	6110	40	51	12:00	42	51	60.11
Samples	40	44	04	39	44	04	42	51	04	43	51	04
Element		Cu			Мо			Ni			Pb	
		Soil with			Soil with			Soil with			Soil with	
Soil	Alluvium	Patchy	Gray	Alluvium	Patchy	Gray	Alluvium	Patchy	Gray	Alluvium	Patchy	Gray
group	soil	Clavish	soil	soil	Clavish	soil	soil	Clavish	soil	soil	Clavish	soil
0 1		layer			layer			layer			layer	
Max	1894.8	575.7	52.3	6.2	8.1	2.6	374.4	232	57.9	106.1	83.2	97.5
Min	10.63	8.2	2.2	0.05	0.1	0.06	3.4	3.7	4	4.46	2.6	3.5
Average	131.25	40.8	17.11	0.83	1.1	16.03	40.63	23	16.03	35.19	31.4	41.49
Number of Samples	26	43	60	42	51	64	43	51	64	43	51	64
Sumptes												
Element		Sb			Sn			Zn			Se	
Element		Sb Soil with			Sn Soil with			<b>Zn</b> Soil with			Se Soil with	1
Element	Alluvium	Sb Soil with Patchy	Gray	Alluvium	Sn Soil with Patchy	Gray	Alluvium	Zn Soil with Patchy	Gray	Alluvium	Se Soil with Patchy	Gray
Element Soil group	Alluvium	Sb Soil with Patchy Clavish	Gray	Alluvium	Sn Soil with Patchy Clavish	Gray	Alluvium	Zn Soil with Patchy Clavish	Gray	Alluvium	Se Soil with Patchy Clavish	Gray
Element Soil group	Alluvium soil	Sb Soil with Patchy Clayish layer	Gray soil	Alluvium soil	Sn Soil with Patchy Clayish layer	Gray soil	Alluvium soil	Zn Soil with Patchy Clayish laver	Gray soil	Alluvium soil	Se Soil with Patchy Clayish layer	Gray soil
Element Soil group Max	Alluvium soil 44.5	Sb Soil with Patchy Clayish layer 28.8	Gray soil	Alluvium soil 401	Sn Soil with Patchy Clayish layer 64.8	Gray soil	Alluvium soil 401	Zn Soil with Patchy Clayish layer 184.1	Gray soil	Alluvium soil	Se Soil with Patchy Clayish layer 4.9	Gray soil
Element Soil group Max Min	Alluvium soil 44.5 0.03	Sb Soil with Patchy Clayish layer 28.8 0.02	Gray soil 18.8 0.01	Alluvium soil 401 0.36	Sn Soil with Patchy Clayish layer 64.8 0.6	Gray soil 122.3 0.5	Alluvium soil 401 16.7	Zn Soil with Patchy Clayish layer 184.1 16.3	Gray soil 136 14.2	Alluvium soil 4.6 0.02	Se Soil with Patchy Clayish layer 4.9 0.01	Gray soil 4.7 0.01
Element Soil group Max Min Average	Alluvium soil 44.5 0.03 4.1	Sb Soil with Patchy Clayish layer 28.8 0.02 6.1	Gray soil 18.8 0.01 5.32	Alluvium soil 401 0.36 35.01	Sn Soil with Patchy Clayish layer 64.8 0.6 8.6	Gray soil 122.3 0.5 11.11	Alluvium soil 401 16.7 82.9	Zn Soil with Patchy Clayish layer 184.1 16.3 48.3	Gray soil 136 14.2 49.4	Alluvium soil 4.6 0.02 1.2	Se Soil with Patchy Clayish layer 4.9 0.01 3.4	Gray soil 4.7 0.01 1.48
Element Soil group Max Min Average Number of Samples	Alluvium soil 44.5 0.03 4.1 38	SbSoil with Patchy Clayish layer28.80.026.144	Gray soil 18.8 0.01 5.32 64	Alluvium soil 401 0.36 35.01 26	Sn           Soil with Patchy Clayish layer           64.8           0.6           8.6           43	Gray soil 122.3 0.5 11.11 60	Alluvium soil 401 16.7 82.9 43	<b>Zn</b> Soil with Patchy Clayish layer 184.1 16.3 48.3 51	Gray soil 136 14.2 49.4 64	Alluvium soil 4.6 0.02 1.2 22	Se Soil with Patchy Clayish layer 4.9 0.01 3.4 26	Gray soil 4.7 0.01 1.48 60
Element Soil group Max Min Average Number of Samples Element	Alluvium soil 44.5 0.03 4.1 38	Sb Soil with Patchy Clayish layer 28.8 0.02 6.1 44 Hg	Gray soil 18.8 0.01 5.32 64	Alluvium soil 401 0.36 35.01 26	Sn           Soil with Patchy Clayish layer           64.8           0.6           8.6           43           Mn	Gray soil 122.3 0.5 11.11 60	Alluvium soil 401 16.7 82.9 43	Zn Soil with Patchy Clayish layer 184.1 16.3 48.3 51 Bi	Gray soil 136 14.2 49.4 64	Alluvium soil 4.6 0.02 1.2 22	Se Soil with Patchy Clayish layer 4.9 0.01 3.4 26 Fe	Gray soil 4.7 0.01 1.48 60
Element Soil group Max Min Average Number of Samples Element	Alluvium soil 44.5 0.03 4.1 38	Sb Soil with Patchy Clayish layer 28.8 0.02 6.1 44 Hg Soil with	Gray soil 18.8 0.01 5.32 64	Alluvium soil 401 0.36 35.01 26	Sn Soil with Patchy Clayish layer 64.8 0.6 8.6 43 43 Mn Soil with	Gray soil 122.3 0.5 11.11 60	Alluvium soil 401 16.7 82.9 43	Zn Soil with Patchy Clayish layer 184.1 16.3 48.3 51 Soil with	Gray soil 136 14.2 49.4 64	Alluvium soil 4.6 0.02 1.2 22	Se Soil with Patchy Clayish layer 4.9 0.01 3.4 26 Fe Soil with	Gray soil 4.7 0.01 1.48 60
Element Soil group Max Min Average Number of Samples Element Soil	Alluvium soil 44.5 0.03 4.1 38 Alluvium	Sb Soil with Patchy Clayish layer 28.8 0.02 6.1 44 Hg Soil with Patchy	Gray soil 18.8 0.01 5.32 64 Gray	Alluvium soil 401 0.36 35.01 26 Alluvium	Sn Soil with Patchy Clayish layer 64.8 0.6 8.6 43 Mn Soil with Patchy	Gray soil 122.3 0.5 11.11 60	Alluvium soil 401 16.7 82.9 43 Alluvium	Zn Soil with Patchy Clayish layer 184.1 16.3 48.3 51 Soil with Patchy	Gray soil 136 14.2 49.4 64 Gray	Alluvium soil 4.6 0.02 1.2 22 Alluvium	Se Soil with Patchy Clayish layer 4.9 0.01 3.4 26 Fe Soil with Patchy	Gray soil 4.7 0.01 1.48 60 Gray
Maple           Element           Soil           group           Max           Min           Average           Number of Samples           Element           Soil           group	Alluvium soil 44.5 0.03 4.1 38 Alluvium soil	Sb Soil with Patchy Clayish layer 28.8 0.02 6.1 44 Hg Soil with Patchy Clayish	Gray soil 18.8 0.01 5.32 64 Gray soil	Alluvium soil 401 0.36 35.01 26 Alluvium soil	Sn Soil with Patchy Clayish layer 64.8 0.6 8.6 43 43 Mn Soil with Patchy Clayish	Gray soil 122.3 0.5 11.11 60 Gray soil	Alluvium soil 401 16.7 82.9 43 Alluvium soil	Zn Soil with Patchy Clayish layer 184.1 16.3 48.3 51 Bi Soil with Patchy Clayish	Gray soil 136 14.2 49.4 64 Gray soil	Alluvium soil 4.6 0.02 1.2 22 Alluvium soil	Se Soil with Patchy Clayish layer 4.9 0.01 3.4 26 Fe Soil with Patchy Clayish	Gray soil 4.7 0.01 1.48 60 Gray soil
Element Soil group Max Min Average Number of Samples Element Soil group	Alluvium soil 44.5 0.03 4.1 38 Alluvium soil	Sb Soil with Patchy Clayish layer 28.8 0.02 6.1 44 Hg Soil with Patchy Clayish layer	Gray soil 18.8 0.01 5.32 64 Gray soil	Alluvium soil 401 0.36 35.01 26 Alluvium soil	Sn Soil with Patchy Clayish layer 64.8 0.6 8.6 43 Mn Soil with Patchy Clayish layer	Gray soil 122.3 0.5 11.11 60 Gray soil	Alluvium soil 401 16.7 82.9 43 Alluvium soil	Zn Soil with Patchy Clayish layer 184.1 16.3 48.3 51 Bi Soil with Patchy Clayish layer	Gray soil 136 14.2 49.4 64 Gray soil	Alluvium soil 4.6 0.02 1.2 22 Alluvium soil	Se Soil with Patchy Clayish layer 4.9 0.01 3.4 26 Fe Soil with Patchy Clayish layer	Gray soil 4.7 0.01 1.48 60 Gray soil
Element Soil group Max Min Average Number of Samples Element Soil group	Alluvium soil 44.5 0.03 4.1 38 Alluvium soil 0.1	Sb Soil with Patchy Clayish layer 28.8 0.02 6.1 44 Hg Soil with Patchy Clayish layer 0.02	Gray soil 18.8 0.01 5.32 64 Gray soil 0.04	Alluvium soil 401 0.36 35.01 26 Alluvium soil 2724 8	Sn Soil with Patchy Clayish layer 64.8 0.6 8.6 43 Mn Soil with Patchy Clayish layer 1351 3	Gray soil 122.3 0.5 11.11 60 Gray soil 504	Alluvium soil 401 16.7 82.9 43 Alluvium soil 8.9	Zn Soil with Patchy Clayish 184.1 16.3 48.3 51 Bi Soil with Patchy Clayish layer 10 5	Gray soil 136 14.2 49.4 64 Gray soil 3	Alluvium soil 4.6 0.02 1.2 22 22 Alluvium soil 67352 7	Se Soil with Patchy Clayish layer 4.9 0.01 3.4 26 Fe Soil with Patchy Clayish layer 27992 3	Gray soil 4.7 0.01 1.48 60 Gray soil 46742.8
Element Soil group Max Min Average Number of Samples Element Soil group Max Min	Alluvium soil 44.5 0.03 4.1 38 Alluvium soil 0.1 0.001	Sb Soil with Patchy Clayish layer 28.8 0.02 6.1 44 Hg Soil with Patchy Clayish layer 0.02 0.001	Gray soil 18.8 0.01 5.32 64 Gray soil 0.04 0.003	Alluvium soil 401 0.36 35.01 26 Alluvium soil 2724.8 20.81	Sn Soil with Patchy Clayish layer 64.8 0.6 8.6 43 Mn Soil with Patchy Clayish layer 1351.3 34.2	Gray soil 122.3 0.5 11.11 60 Gray soil 504 31.5	Alluvium soil 401 16.7 82.9 43 Alluvium soil 8.9 0.51	Zn Soil with Patchy Clayish layer 184.1 16.3 48.3 51 Bi Soil with Patchy Clayish layer 10.5 0.3	Gray soil 136 14.2 49.4 64 Gray soil 3 0.2	Alluvium soil 4.6 0.02 1.2 22 Alluvium soil 67352.7 19822.94	Se Soil with Patchy Clayish layer 4.9 0.01 3.4 26 Fe Soil with Patchy Clayish layer 27992.3 10835.7	Gray soil 4.7 0.01 1.48 60 Gray soil 46742.8 3628.5
Element Soil group Max Min Average Number of Samples Element Soil group Max Min Average	Alluvium soil 44.5 0.03 4.1 38 Alluvium soil 0.1 0.001 0.013	Sb Soil with Patchy Clayish layer 28.8 0.02 6.1 44 Hg Soil with Patchy Clayish layer 0.02 0.001 0.001	Gray soil 18.8 0.01 5.32 64 Gray soil 0.04 0.003 0.007	Alluvium soil 401 0.36 35.01 26 Alluvium soil 2724.8 20.81 418.1	Sn Soil with Patchy Clayish layer 64.8 0.6 8.6 43 Mn Soil with Patchy Clayish layer 1351.3 34.2 251.2	Gray soil 122.3 0.5 11.11 60 Gray soil 504 31.5 166,52	Alluvium soil 401 16.7 82.9 43 Alluvium soil 8.9 0.51 2.15	Zn Soil with Patchy Clayish layer 184.1 16.3 48.3 51 Bi Soil with Patchy Clayish layer 10.5 0.3 3.1	Gray soil 136 14.2 49.4 64 Gray soil 3 0.2 1.31	Alluvium soil 4.6 0.02 1.2 22 Alluvium soil 67352.7 19822.94 290356.3	Se Soil with Patchy Clayish layer 4.9 0.01 3.4 26 Fe Soil with Patchy Clayish layer 27992.3 10835.7 19679.1	Gray soil 4.7 0.01 1.48 60 Gray soil 46742.8 3628.5 30865.7
Element Soil group Max Min Average Number of Samples Element Soil group Max Min Average Number of Soil group	Alluvium soil 44.5 0.03 4.1 38 Alluvium soil 0.1 0.001 0.001 24	Sb Soil with Patchy Clayish layer 28.8 0.02 6.1 44 Hg Soil with Patchy Clayish layer 0.02 0.001 0.001 0.001	Gray soil 18.8 0.01 5.32 64 Gray soil 0.04 0.003 0.007 40	Alluvium soil 401 0.36 35.01 26 Alluvium soil 2724.8 20.81 418.1 26	Sn           Soil with           Patchy           Clayish           layer           64.8           0.6           8.6           43           Mn           Soil with           Patchy           Clayish           layer           1351.3           34.2           251.2	Gray soil 122.3 0.5 11.11 60 Gray soil 504 31.5 166.52	Alluvium soil 401 16.7 82.9 43 Alluvium soil 8.9 0.51 2.15 0	Zn           Soil with           Patchy           Clayish           layer           184.1           16.3           48.3           51           Bi           Soil with           Patchy           Clayish           layer           10.5           0.3           3.1	Gray soil 136 14.2 49.4 64 64 Gray soil 3 0.2 1.31	Alluvium soil 4.6 0.02 1.2 22 Alluvium soil 67352.7 19822.94 290356.3 9	Se           Soil with Patchy Clayish layer           4.9           0.01           3.4           26           Fe           Soil with Patchy Clayish layer           27992.3           10835.7           19679.1	Gray soil 4.7 0.01 1.48 60 Gray soil 46742.8 3628.5 30865.7

Concentrations of typical heavy metals: As, Cd, Cr, Hg, Pb, Cu, Zn in some soil samples (especially As, Cu, Cr, Zn) have exceeded reference standard (QCVN03) from several times to dozens of times (see Table 3). Strong anomalies of some heavy metals such as As, Cr, Cu ... distributed mainly in

the southwest of the study area, in Long Bien and Gia Lam districts, where the urbanization rate is very high and distribution of a number of specialized Industrial Parks and handicraft production workshops.

4.2.2.1. Arsenic distribution characteristics in soil groups in the study area The average As concentration is 22.1mg/kg. There is 37.74% of the samples with the content exceeding 1.1 to 46.2 times. Soil polluted especially with As anomalies concentrated in the Southeast of Long Bien and Gia Lam districts (sample GL21/2: 693mg/kg). The origin of the anomaly is still unknown, but it is likely related to human industrial production (printing industry facilities) or the strong exploitation of underground water, leading to lower water levels and changing environment parameters and releasing As, especially in the area riched in organic sediments (see Figure 11).

The As concentration in alluvial soil exceeding reference standard (QCVN 03), most in layer O and layer A and tends to decrease to the depths. Increased Increasing As content may be originated from factories and Industrial Parks with the mechanical and printing worrks or as a result of groundwater extraction lowers the water level, leading to oxidation and the release of As stored inside organic rich sediments.



4.2.2.2. Cadmium distribution characteristics in the soil groups The Cd content of 100% samples is smaller than the QCVN 03 standards 4.2.2.3. Chromium distribution of soil groups in the study area The Cr content in the alluvial soil group exceeds 4.4 times comparing to those of QCVN03, typically in Gia Lam (see Figure 12), the distribution area of Cr is quite similar to the distribution of As anomalies, while these two elements have different behaviors and origins in the surface geological processes, so this is possibly related to industrial production activities in the area.



4.2.2.5. Lead distribution in soil groups in the study area

The Pb content was 41.13mg / kg, 19.6% of the samples exceeded 1.02 to 4.76 times, especially Pb in alluvial soil exceeded 4.76 times, concentrated

in Me Linh district and in Van Noi commune, Dong Anh district and scattered in some other areas. The difference is that Pb anomalies occur quite a lot in Long Bien - Gia Lam but mainly in alluvial soils, see Figure 14.

4.2.2.6. Zinc distribution among soil groups in the study area

The Zn content is 65.47mg / kg. A 1.27% of the sample with the Zn content exceeding 2.0 to 5.86 times of QCVN03 standards and concentrated in the inmsdustral areas in Gia Lam and Long Bien dítricts. The Zn content in alluvial soil exceeds 5.9 times QCVN, concentrated in the Southwest of Long Bien, Gia Lam (see Figure 15). That coincides with other high anoanomalies of As, Cu, Cr ... in this area.

#### 4.2.3. Distribution characteristics of soil nutrients in the study area

The analytical results of content of the main nutrient components in the soil shows that: The average  $K_2O$  content of gray soil is 1.98%; alluvial soil 2.2%; soil with loam clay is 1.8%. In which, effective (easily digestible)  $K_2O$  content of alluvial soil is 16,34 mg / 100g soil; gray soil is 6.5 mg / 100 grams of soil.

The average content of  $P_2O_5$  is 0.095%, about 72.72% of the samples have  $P_2O_5$  content smaller than 0.1%. Meanwhile, the effective  $P_2O_5$  content of alluvial soil is 20.3 mg / 100g soil; gray soil is 5.6 mg / 100g of soil,

## **4.3.** Assess the current status of soil environment in the study area *4.3.1. Overview*

The status of soil environment is assessed by a number of important indicators such as pH, Eh, Heavy Metals content ..., which are database to evaluate the load capacity of pollutants and the heavy metals of the soil through baseline values. and comparative values from which to estimate the environmental tolerance, combining interpeneting data on background values and minimum anomalous threshold of the elements for a comprehensive assessment.

## **4.3.2.** Assess the current status of soil environment in the study area 4.3.2.1. Assess the level of pollution in the soil

Some soil samples have concentrations of As and Cu exceeding those in QCVN03 from several times to dozens of times. The highest is nearly 50 times (for As) and more than 20 times (for Cu), (Figure 16). The content of Pb and Zn in some samples is higher than those of Vietnamese standards.



In the study area, it was initially contaminated by some heavy metals, especially As, Cu; and to some extent: Pb and Zn. As a basis for alerting the attention of the authorities for environmental management, development of local land use and management planning works.

4.3.2.2. Assess the rick to environmental health from the data of heavy metals in soil in the study area

The potential ecological risk index is a common method for assessing the overall ecological risk of soil pollution, based on the sum of separate ecological risk factors calculated for each metal (Er), calculated by the ratio of metal concentration in soil (Ci) and in the substrate (C0) multiplied by the toxic reaction coefficient (Tr). Different levels of risk are divided on the basis of Er (low, moderate, high, serious) and ERI (low, moderate, high, severe) values with respective thresholds of 0, 40, 80, 160, 320 and 0, 150, 300, 600.

Ecological risk indices were calculated for As, Cd, Cr, Cu, Ni, Pb, Sb and Zn according to Hakanson's method, with recently established toxic reaction factors for Sb. The distribution of ecological risk indicators in the established area (Figure 17) and the frequency chart of ecological risk factors (Figure 18) show that the majority of sampling locations have moderate environmental risks and about 50% of the 157 sample locations had a high to serious risk due to Cd, As and Sb. High to serious risk associated with pollution point sources: the sampling points in Long Bien and Gia Lam, most likely related to groundwater use leading to accumulation of these elements in soil in Me Linh and Dong Anh. The ecological risk is more serious if heavy metals can be found in biological fractions. The two locations have ERI higher than 600 (serious risk, near Long Bien and Gia Lam Industrial Parks).



Figure 18. The distribution area of the overall cancer risk (a) and the carcinogenic risk of the elements Cr (b), As (c) and Cd (d); are calculated based on samples of the top soil layer

+ Non-carcinogenic risks: Based on high concentrations of metals / metals and high potential ecological risks mentioned in the previous section, noncarcinogenic risks (potential risk index) and carcinogenic risk (CR and TCR) are assessed to determine the level of risk to human health. Since the concentration of heavy metals in surface water and vegetables, according to the published results, is lower than the corresponding Vietnam standards, dietary participation will have a negligible impact to the rick index. In addition, contact processes of heavy metals are more likely to be related to the top soil layer compared to the deep soil layer. The deep soil layers were excluded in this calculation using only the heavy metal content of the top soil layer (the O layer).

As a result, the risk of not causing cancer for most factors is less than 1, there is the minimum risk for the popular population. However, in the Southeast of Gia Lam and Long Bien districts, there are anomalies of very high levels of As, Cr, Ni, Sb, Zn (Figure 18) and potential health risks related to high As concentration. This site has the highest ecological risk and the cause, has been shown to be related to the source of local pollution sites (wastewater discharged from chemical, fertilizer and Industrial Parks).

+ Carcinogenic risks (related to As, Cd, Cr): The toxicity of As, Cd and Cr differs from other metals because they have the potential to cause cancer. Although the high ecological risks are associated with As, Cd and Sb and the non-carcinogenic risks associated with As, Cd. The carcinogenic threats of Cd are insignificant, but attention should be paid to As and Cr (Figure 18). In fact, there is no evidence of a link between Cr and As carcinogenic risk and documented cancer cases, the author's study points out the need for an integrated risk assessment program and call on socio-economic development policy makers and planners to build the planning overcome land pollution and health risks of residents.

## 4.3.3. Origin, mechanism of accumulation and dispersion of sensitive components in soil

The heavy metals are characterized by easy released ability from the original materials, they participate in chemical reactions to create new compounds, the heavy metals causes environmental pollution when their content exceeds the permissible limit. The origin and distribution of soil types, as well as the characteristics of population distribution, factories, related Industrial Parks can allow forecast the cause and the law of accumulation and dispersion pattern of the heavy metals in the land as follows: :

- Due to the use of chemicals such as inorganic fertilizers, pesticides, herbicides, including persistent organic components or polychlorinated biphenyls (PCBs) and heavy metals.

- By moving the heavy metals out of the original distribution position to concentrate in favorable places with increased levels (creating anomalies and pollution).

+ Increasing urbanization, industrialization, due to industrial activities, infrastructure construction, handicraft villages, use of pesticides also contribute to contaminated soil, emission sources due to accumulation of heavy metals; substances emissions from internal combustion engines are the source of pollution, accumulating directly and indirectly the heavy metals to the soil and surface water.

The high concentrations of As, Pb and Zn masses in soil are a real threat to the environment, especially in the rainy season, when they can easily be spread by

surface water and groundwater to low areas. moreover, polluting the whole area. Measures are needed to improve and restore the soil and prevent pollution.

**4.4. Some suggestions on soil environment protection in the study area** Acidic soil, especially in low-lying areas, through pH indexes, it is necessary to take acid remedy by the traditional liming method.

- Need to grow plants with high capacity of absorbing heavy metals such as Arsenic that are popular, easy to grow, and quick growing, for example: ferns.

- Improve soil mechanical composition - increase clay content in soil, increase use of composted organic fertilizer.

- Using environmentally friendly biological products, using soil improvement microorganisms. For areas contaminated As, Pb, Cu, Cr need complete mitigation measures including biological, chemical and physical methods, such as ion exchange method, adsorption method and membrane method for the area. polluted areas ...

\* Strengthening the administration measures and promoting propaganda to raise the awareness of the residence in the study area, namely:

+ Directing environmental management agencies to strengthen, inspect and supervise polluted areas and take strict measures to control pollution from chemicals and herbisides.

+ Mobilizing people voluntarily in waste collection, building hygienic water drainage systems.

#### CONCLUSIONS AND RECOMMENDATIONS

The PhD student completed the thesis with the objectives of clarifying the geochemical characteristics and material composition of the soil in the study area, providing a scientific basis for the planning of socio-economic development; rational use of land resources in the study area. Through the obtained results, the author would like to draw some conclusions as follows:

+ The study area has 3 soil groups: alluvial soil, soil with patchy clay layer and gray soil, of which the alluvial soil group occupies the main area.

+ Soil groups have a remarkable difference in the composition of soil particles among soil groups, in which the soil with patchy clay layer tends to have coarse grain batch, accounting for a higher proportion than the two alluvial and gray soil groups.

+ The mineral composition among soil groups in the area varies quite clearly. In addition to the main minerals including quartz (50% on average), Ilit (hydromica) 14.2%, kaolinite 4.14%, there is also montmorilonite and goethite (content varies in a few%). The alluvial soil group has minerals like hematite, magnetite and rutile; the soils with patchy clay layer have vermiculite, talc, jarosite and gray soil with gibsite, calcite, dolomite. + The chemical composition of oxides such as aluminum oxide and iron oxide in the soil in the study area varies in a fairly large range, such as the alluvial group has higher Fe oxide content than those in the two gray soil groups and the patchy clay layer soil group. Alkaline and earth alkaline oxides (K<sub>2</sub>O, Na<sub>2</sub>O, CaO, MgO) in the alluvial soil group are also higher than those in the other two groups. Specifically, the content of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> oxides of alluvial soil group is 63.6%; 15.76%; 6.64%; in the group of soil with patchy clay layer: 79.42%; 8.33%; 3.96%; in gray soil: 78.3%; 9.44%; 3.14%.

+ Trace elements (heavy metals) along to section depth have variable content in a wide range; there is no clear rule according to the horizontal (crossing line) and the longtitudinal directions of study area. The vertical variation rule is also not very clear, depending heavily on the origin of soil, development history and environment in the study area.

+ The soil has light acidic feature (acidic soil) with pH value of soil samples averaging 6.67. Alluvial soil and gray soil are more acidic. The soils are oxidized in the weak to medium range (Eh from 60 to 569 mV). Cation exchange capacity (CEC) is not high (average 18,8405 meq / 100g).

+ The geochemical characteristics of water and soil environment also indicate that the soil has initially been contaminated with heavy metals: As, Pb, Zn, Cd, Cr, Cu, ... especially As, Pb, Cr and Cu Pollution has a level at dozens of times higher than those in QCVN03. Some heavy metals have the potential to cause cancer and long-term damage to health such as As, Pb are in quite high concentration ...

#### The thesis has not completely solved the following issues:

- Comprehensive assessment of the risk of soil pollution in the area (for example, bio issue) has not been made.

- Existence form of sensitive components (heavy metals) in soil in the study area.

- Exactly assessing the causes of pollution of some heavy metals in the study area and other isues (pesticides, herbicides isuem, for example).

#### Recommendation

Aparting from the above limitations, it is suggested that the University and the authority management agencies allow to conduct more researches to provide addition data to thoroughly solve the following issues:

- Existence type, mechanism of movement, accumulation and dispersion of sensitive components (heavy metals) in the area.

- Load capacity for toxic elements in soil in the study area.

- Widely publicizing research results to serve as a basis for the rational planning, management and use of land resources, ensuring sustainable so-cio-economic development in the study area.

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