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College of Natural and Computational Science

Department of Chemistry

M.Sc. Thesis on:

Physico-Chemical Analysis of Peat Land Soil Found in Guna Mountain (Mehil Chemaw) and Semen Mountain National Park (Debela) Amhara Region, Ethiopia

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Thesis submitted to the school of graduate studies University of Gondar Colleges of Natural and Computational Science Department of Chemistry in Partial Fulfillment of the Requirement for the Degree of Master of Science in Chemistry (inorganic)

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Thesis approval sheet

This is to certify that the thesis entitled **"Physico-Chemical Analysis of Peat Land Soil Found in Guna Mountain (Mehil Chemaw) and Semen Mountain National Park (Debela) Amhara Region, Ethiopia"** has been submitted for examination with my approval as university advisor and submitted and approved for the degree of Masters of Science in chemistry (Inorganic) with specialization in Inorganic Chemistry complies with the regulation and meets the accepted standards with respect to originality and quality.

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DECLARATION

I, the undersigned, declare that this M.Sc. thesis is my original work and has not been presented for my degree in this and other university and that all sources of materials used for this thesis have been duly acknowledged.

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Acknowledgment

List of Abbreviations

AAS   Atomic Absorption Spectrometer

AEC   anion exchange capacity

CEC   cation exchange capacity

DI   De-ionized

DTPA   diethylenetriaminepenta acetic acid

EC   Electrical conductivity

EPA   Environmental Protection Agency

FA   fulivic acid

GDC   Gondar control

GPS   Global Positioning System

HMA   hymatomelanic acid

HS   humic substance

OM   organic matter

PH   power of hydrogen ion

ppm   parts per million

SNP   Semen national park

SOC   soil organic matter

TN   total nitrogen

TOC   Total organic carbon

ds/m   decisiemns per meter

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Abstract

Peatland is available in considerable quantities in Ethiopia. The current investigation was aimed on analysis of physicochemical properties, heavy metal concentration and micronutrient availability of Peat land soil found at GUNA Mountain (Mehil Chemaw), Siemen Mountain National Park (Debela) and one control sample at Gondar zuria woreda Amhara region, Ethiopia. Soil samples were randomly collected to a depth of 20cm using auger. Samples were air-dried, sieved by <2 mm mesh and analyzed using standard procedures. The following physicochemical properties such as color, texture, pH, EC, CEC, OC, OM, TN of the soil and some selected metal concentrations (Cr, Mn, Fe, Cu, Zn, Cd, and Mg) were analyzed. The result shows that the color of soil at GUNA, SNP and GDC is dark black, dark brown and light black, respectively. The soil textural class of GUNA and SNP is clay, while GDC is sandy clay. pH and EC determined in soil/water (1:2.5, v/v) the soil pH of GUNA (4.83) and SNP (5.1) are strong acid and GDC (6.63) slightly acid. The EC of GUNA and SNP is 0.136 and 0.121 ds/m, respectively but GDC soil 0.062 ds/m. The CEC in GUNA (51.2cmol (+)/kg) and SNP (48.8 cmol (+)/kg) have very high and GDC (32.2cmol (+)/kg) high. The organic matter content of GUNA and SNP is 8.74% and 9.41%, respectively, which was rated as very high, while GDC have 2.02% rated as medium OM. In GUNA (0.25%) and SNP (0.22%) the TN value has a similar value but in GDC is 0.06%. Among the studied available micronutrients Mn and Cu in GDC and Fe in GUNA, SNP and GDC are optimum the rest of micronutrients and heavy metals are below the optimum point. Generally, the color, organic matter, CEC, TN, and pH of the properties of the soils of GUNA and SNP are indicators of peat soils characteristics as observed from the value. Micronutrient availability and heavy metals of the soil except Fe and Cu in all soil samples and Mn in GDC soil are minimum (below the permissible limit) this might be the extraction method difference or leaching of metals due to its geographical positioning or the sampling season or time factors.

Key words: peat soil, soil physicochemical analysis, micronutrients, heavy metals

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1. Introduction

1.1 Background

Soil consists of inorganic minerals, organic matter, water and air. The organic matter of the soil also comprised of carbon, oxygen, hydrogen, nitrogen and smaller quantities of sulphur and other inorganic mineral aggregates. The composition and proportions of these components greatly influence soil physico-chemical properties [1].

Peat land is the type of landscape where in wet and oxygen deficiency conditions part of organic matter will not degrade and accumulates as peat [2]. Peat is a mixture of fragmented organic materials formed in wetlands under appropriate climatic and topographic conditions and it is derived from vegetation that has been chemically changed and fossilized [3].Peat covers approximately 0.5 billion hectares, 3.5–4.0 % of the land area of the world. Peat soils are found in most countries and regions except for desert and polar zones [4]. It contains high organic content and its formation take place in conditions where the rate of accumulation is more than the rate of microbial degradation. The content of peat differs from location to location due to the factors such as the origin of fiber, temperature, climate and humidity in the environment [1, 3].

Applications as adsorption using low cost adsorbents such as agricultural wastes (orange skins, banana peels etc.), saw dust, peat clay and zeolites are effective alternatives to precipitation, membrane technology and floatation for metal removal from wastewater. Peat soils are promising adsorbents for heavy metal removal easily harvested and are economical. Peat characterization has remained a difficult task since peat soils may form under a variety of conditions of vegetation and environment [5].

Peat and various peat preparations have been successfully used in the balneological practice of clinical medicine. Balneological peat as ecologically clean and natural substance is more human friendly than synthetic substances. There are many indications that a peat chemical component may contribute to the clinical success of cutaneous peat treatment because several pharmacological effects have been detected, which cannot be ascribed to the well-established physico-thermal effects. The physical effect influences through temperature and biochemical effect through bioactive substances. The biochemical effect of peat is related to the content of humic substances which participate in the peat healing effect. Humic substances are natural

products that develop during decomposition of organic matter in humus and constitute the most stable fraction of organic substances in soils [2].

Soil organic matter is derived from organic materials that are added to the soil and the majority of soil organic matter derives from the breakdown of residues remaining after plants and animals have died. Soil organic matter is not a single uniform material but is very diverse in its chemical and physical properties which will influence its capacity to do certain functions. The humic and fulvic acids seem to have the highest chemical activity, but the particulate organic carbon has the highest capacity to maintain the stability of larger soil aggregates. The need for soil organic matter to provide cation exchange capacity (CEC) is most important in sandy soils and a food and energy source for the microbial population in all soils [6].

The elemental properties of peat are generally between that of wood and coal. The elemental proportion of lowly decomposed peat approximates to that of wood, while highly decomposed peat resembles to that of lignite [7].

Soils are the major sinks for heavy metals released into the environment due to the disturbance and acceleration of nature's slowly occurring geochemical cycle of metals. Heavy metal contamination of soil may pose risks and hazards to humans and the ecosystem.

Heavy metals may chemically or physically interact with the natural compounds, which change their forms of existence in the environment. In general, they may react with particular species, change oxidation states and precipitate.

Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs.

Heavy metals may be distributed in soil components as exchangeable, adsorbed on soil organic matter, precipitated or complexes. In terms of bioavailability, various species of metals (e.g. Cu, Co, Ni and Zn) are more biologically available than others [8].

Trace quantities of certain heavy metals are essential to animals and plant growth, they are of considerable environmental concern due to their toxicity and cumulative behavior. These metals which are not biodegradable are accumulated in living organisms when released into the environment. Most of these heavy metals are essential for growth of organisms but are only required in low concentrations. Metal transport is not only dependent on the physiochemical properties of the metals but mostly on the physical and chemical properties of the soil, like for

example: soil organic matter content, clay fraction content, mineralogical composition, pH, and more, all of which collectively determine the binding ability of soil [9].

This study will principally focus on the analysis of Peat land soil's physico-chemical properties, heavy metal analysis by using standard analytical techniques and high tech instrument in which atomic absorption spectroscopy(AAS) is used for metal analysis in the soil. This investigation were carried out in three areas at GUNA Mountain (at mehil chemaw) Southern Gondar, Semen Mountain National Park (Debela) , Northern Gondar Ethiopia, and one control sample Gondar zuria woreda.

1.2 Statement of the Problem

The study areas have a potential fossil fuel resource, based on the primary information obtained from the residential areas. The people, currently, are using it as a potential energy source for traditional cooking by igniting the peat land soil aggregates directly. In addition, there is also a decrease in crop productivity of the soils in the peat land and even it does not support plant growth as we have acquired the information and seen.

However, there are no reported studies on analysis of physico-chemical properties, some micronutrient and heavy metal contents of the Peat land soils of these specified study areas. Therefore, this study was intended on investigations of physico-chemical properties, some selected metal contents of soil found at GUNA mountain and semen mountain national park.

1.3   Significance of the study

By volume, about 8 trillion m³ of peat are in the world, covering a total of around 3.5- 4% of the global land area (about 50 million km²), containing about 16 billion terajoules of energy. Upon drying, peat can be used as fuel. It has industrial importance as a fuel in some countries, such as Ireland, Russia, Scotland, England and Finland, where it is harvested on an industrial scale. In developed countries, large-scale domestic and industrial peat usage is widespread and have a state-owned company which is responsible for peat production management. These companies produce milled peat, to produce naphtha, which is used in power stations. However, in Ethiopia, in spite of the abundance of peat and manpower, the use of peat covers insignificant percentage due to lack of information about the properties and the use of peat for fuel, application in agriculture, water filtration (for the treatment of septic tank effluents) and balneotherapy (the use of bathing to treat disease).

The main significance of this study is to give informative data about the physicochemical, micronutrient availability heavy metal concentration of the soil which is a base line for the different uses (applications) of peat soil i.e. beneficiary for researchers.

1.4 Objectives of the study
1.4.1 General objective

The overall objective of this research is to evaluate soil physical and chemical properties of the selected sites in the proposed peat deposit areas at GUNA Mountain at (mehil chemaw) and Semen Mountain National Park (Debela) in Amhara region, Ethiopia.

1.4.2 Specific objectives

The objective of this study was
  - To assess the physicochemical properties, and some selected metal contents of peat soil samples found at GUNA Mountain (mehil chemaw) and Semen Mountain National Park (Debela);
  - To collect and compare the physic-chemical properties, heavy metal contents of peat soil samples with other type of soil;
  - To determine concentration of trace, heavy metals (Cr, Mn, Fe, Cu, Cd, Zn) and Mg contents of the collected soil samples.

2. Literature review

The following is a brief review of scholarly work of different researchers in the field of soil and peat land soil classification, physicochemical properties, heavy metal enrichment and use studies.

2.1. Soil

Soil is mixture mainly composed of minerals, organic matter having different texture, structure, consistency, color, chemical, biological and other features. Soil as a general term usually denotes the unconsolidated thin, variable layer of mineral and organic material usually biologically active that covers rest of the earth land surface [10].

Soil consisting of solid, liquid and gaseous a three-phase components system. The solid phase, which comprises about 50 % of the total soil volume, includes inorganic and organic compounds. Mineral matter usually accounts for more than 95 % of the solid phase, except in the peat and muck soils, which are composed predominantly of organic matter.

Soil acts as an important part of all terrestrial systems, providing habitat for micro-organisms, plants, and animals and also act as a storage system for several natural resources. Soil supports life through main five processes, biomass productivity, detoxification of pollutants, cycling of C, N, P, S, and H_2O; and also acts as carbon sink [11].

2.2. Formation of Soil

Soil is complex mixture being made up of some six constituents' namely inorganic matter, organic matter, soil organisms, soil moisture, and soil solution and soil air. Roughly, the soil contains 50-60 % mineral matter, 25-35 % water, 15-25 % air and little percentage of organic matter [12].

Soil formation is a function of five soil forming factors, namely climate, biological influence, topography, parent materials and time. Some of natural environmental factors that cause variability of soil physico-chemical properties in the space along different slope position include parent materials, topography, land use types, climatic factors and graze intensity and various range land management [13].

Soil formation process is both a constructive as well as destructive. Destructive process predominates the physical and chemical breaking down of materials, plants and animal structures, which result in the partial loss of more soluble and volatile products. Constructive

forces develop new chemical compounds, both mineral and organic and provide new distribution or association characteristics, structural properties as well as chemical compositions [14].

The formation of a particular soil is due to the combined action of a number of different physical and chemical processes, which are collectively referred to as weathering, and biological activity, which is carried out by soil organisms, such as soil micro-organisms and burrowing animals (e g worms). Soil formation is a dynamic and slow process and it involves several stages of development, which are usually occurring concurrently. It is the dominance of one or more of the weathering/biological processes which results in the formation of a particular soil type.

Table 1. The Weathering and Biological Processes Occurring in Soil

Process	Mechanism of action
Physical	Abrasive processes leading to the break-up of bed rock by the action of water, wind, glacial movement and the freeze-thaw cycle
Chemical	Transformation of primary minerals to secondary minerals by hydration, hydrolysis, oxidation, reduction, complexation, dissolution
Biological	Action is principally on organic matter by decomposition, transformation

2.3. Physical properties of peat soil

Properties of soil, such as soil texture, color, structure, bulk density, and soil porosity, determine nutrient, gas exchange, and carbon budget in the soil are all intimately connected with physical characteristics of soil. The physical properties of soil such as soil color, texture, bulk density, particle density, total porosity and water content are the dominant factors affecting the use of a soil [13].

2.3.1. Soil texture

The relative size distribution of the primary particles in a soil refers to soil texture. Particle size, using USDA classification scheme is divided into three measurements are made of the solution

density at a major size classifications: sand (2.0–0.05 mm), silt (0.05– 0.002 mm), and clay (> 0.002 mm). Soil textural composition (% sand, silt, and clay) affects soil-water retention characteristics, leaching and erosion potential, plant nutrient storage, organic-matter dynamics, and carbon-sequestration capability. Soil textural analysis is a key component of any minimum data set to be used for assessing of agricultural management practices [15].

2.3.2. Soil Color

Soil Color is probably of the simplest and most easily determined which can easily be identified in the field using Munsell color chart. It indicates several important soil characteristics including geologic origin and degree of weathering of the soil material, degree of oxidation and reduction, content of organic material, and leaching or accumulation of such chemical compounds as iron, which may greatly influence soil quality. Some broad generalizations showed that it is also possible, for instance, black soil usually indicate the presence of organic matter; red colors indicate the presence of free iron oxides in well oxidized soil, while gray or bluish gray usually occur under reducing conditions of free iron [13].

Soil color indicates the composition of the soil and give clues to the conditions that the soil is subjected but does not affect the behavior and use of soil. Soil can exhibit a various range of color gray, black, white, reds, browns, yellows and under the right conditions green. Color and distribution pattern of soil results from both chemical and biological processes, especially redox reactions. As the combination of minerals and organic compounds lead the soil contains various new and colorful compounds. Yellow or red soil indicates the presence of iron oxides. Dark brown or black color in soil indicates that the soil has high organic matter content. Due to presence of water wet soil appears darker than dry soil. Soil color is get affected by oxidation rate which is dependent upon water content. High water content means less air in the soil, specifically less oxygen. In well drained (oxygen rich soils) red and brown colors caused by oxidation are more common, as opposed to in wet (low oxygen) soils where the soil usually appears grey. Soil color affected by the presence of specific minerals. Manganese oxide causes a black color, glauconite makes the soil green and calcite can make soil appearance white [16].

2.4. Chemical properties of soil

Soil chemical properties that studied include the soil reaction (pH), cation exchange capacity (CEC), soil organic matter (OM), total nitrogen (TN) etc. [13, 17].

2.4.1. Soil carbon content

Carbon in soils may be present in three basic forms. They are: (i) elemental C, (ii) inorganic C, and (iii) organic C.

i. Elemental carbon forms

Elemental carbon forms include charcoal, soot, graphite, and coal. The primary sources for elemental carbon in soils are as incomplete combustion products of organic matter (i.e., charcoal, graphite, and soot), during mining processing, or combustion of these materials.

ii. Inorganic carbon forms

Inorganic carbon forms are derived from geologic or soil parent material sources and present in soils typically as carbonates. The two most common carbonate minerals found in soils and sediments are calcite ($CaCO_3$) and dolomite [$CaMg(CO_3)_2$] although other forms may be present (e.g., siderite, $FeCO_3$) depending on where the soils were formed or where the source was located.

iii. Organic carbon forms

Naturally-occurring organic carbon forms are derived from the decomposition of plants and animals. In soils a wide variety of organic carbon forms are present and range from freshly deposited litter (e.g., leaves, twigs, branches) to highly decomposed forms such as humus. In addition to the naturally occurring organic carbon sources, the can also be are sources derived as a result of contamination through anthropogenic activities. The spills or releases of contaminants into the environment increase the total carbon content present in the soil or sediment [18].

2.4.2. Organic matter of soil

Soil organic matter includes all living soil organisms together with the remains of dead organisms in their various degrees of decomposition. The organic carbon content of a soil is

made up of heterogeneous mixtures of both simple and complex substances containing carbon. The sources for organic matter are crop residues, animal and green manures, compost and other organic materials [19].

The organic matter inside peat soil will have some differences in its physical properties during peat transformation process, the degree of decomposition, peat's specific gravity and compaction are increased while the peat's moisture content is decreased. In addition, the color of peat will change into dark brown and black color due to calorific value. The behavior and types of organic matter of peat soil will be affected by the environmental condition such as the types of forest, vegetative, temperature and weather as well as bog hydrological conditions [20].

Rating of organic matter

Table 2. Rating of organic matter [63]

Rating	Percent organic matter
Very High	>6 %
High	4.3-6 %
Medium	2.1-4.2 %
Low	1-2 %
Very low	<1 %

The organic carbon content of soil can be determined by one of several methods, namely, dry combustion (loss on ignition (LOI)), Walkley and Black procedure (1934) or CN auto-analyzer [21]. SOM stabilize soil pH, which plays an important role in controlling the supply of nutrients and their availability for plant intake [22].

2.4.3. Soil pH

Many important property and processes that occur in soils influenced by Soil pH. These include soil development processes, such as mineral weathering, ion-exchange and specific adsorption as well as carbon turnover and biological processes, all of which significantly affect soil development, growth of crops in agricultural systems and habitat development in semi-natural systems. The measured pH values found show a broad correlation with the carbon contents and clearly delineate the highly organic soils of the Highlands and Uplands from the mineral soils of

the lowland areas. In the organic soils the values of pH are almost all below 5 with many falling below 4 [23].

Soil pH is a measure of the soil solution's acidity and alkalinity. Because pH is a logarithmic function pH = -log [H^+], each unit on the pH scale is ten times less acidic (more alkaline) than the unit below it. Soil pH is influenced by both acid and base-forming ions in the soil. Common acid-forming cation are hydrogen (H^+), aluminum (Al^{3+}), and iron (Fe^{2+} or Fe^{3+}), whereas common base-forming cation include calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+) and sodium (Na^+). Most agricultural soils have basic conditions with average pH values ranging from 7 to 8. In contrast, acid conditions occur in soil having parent material high in elements such as silica (rhyolite and granite), high levels of sand with low buffering capacities (ability to resist pH change), and in regions with high amounts of precipitation. An increase in precipitation causes increased leaching of base cation and the soil pH is lowered. Most soils have a net negative charge, the soil's cation exchange capacity (CEC) is higher than the anion exchange capacity (AEC). Soils with high CECs are able to bind more cation such as Ca^{2+} or K^+ to the exchange sites (locations at which ions bind) of clay and organic matter particle surfaces. A high CEC soil will also have a greater buffering capacity, increasing the soil's ability to resist changes in pH. Soils with high amounts of clay and/or organic matter will typically have higher CEC and buffering capacities than more silt or sandy soils. Since H^+ is a cation, it will compete with other cation for exchange sites. When the soil pH is high (i.e., more basic, low concentration of H^+), more base cation will be on the particle exchange sites and thus be less susceptible to leaching. However, when the soil pH is lower (i.e., less basic, higher concentration of H^+), more H^+ ions are available to "exchange" base cation, thereby removing them from exchange sites and releasing them to the soil solution (soil water). As a result, exchanged nutrients are either taken up by the plant or lost through leaching or erosion [24].

2.4.4. Cation exchange capacity

The exchange of ions between soil particles and plant roots via the soil solution next to photosynthesis and respiration is more vital to plant and animal life. The cation exchange capacity (CEC) is the sum of the exchangeable cation that a soil or other material can absorb at a specific pH and CEC is commonly expressed as cent mole of positive charge per kilogram (cmol (+) kg-1). As soil pH is increased, the surface negative charge on clay colloids increases and

repulsive forces between particles dominate. Thus, soil CEC is dependent on pH, and is positively correlated with, soil pH. CEC of variable-charge soils is often expressed as a function of pH and electrolyte Concentration. Soil components known to contribute to soil CEC are clay and organic matter, and to a lesser extent, silt [13].

The cation exchange capacity of a soil measures the surface electric charge of soil components [25].

2.5. Types of peat land

Peat land classification are difficult because of their floristic diversity and their stratigraphic, hydrological and geomorphological variety. They have been classified on the basis of origin, but the most widely used classifications are based either on vegetation or on water source. The current classification identifies a series of mire types on the basis of ecological gradients in attributes such as wetness, nutrient status and the distinction between the mire margin and the mire center, e.g. forested types *vs*. treeless types. Based on mire vegetation and nutrient status classified as,minerotrophic and oligotrophic. Three peat land types, namely raised bogs, transition mires and fens, are distinguished on the basis of the source of water. Raised bogs depend solely on precipitation (i.e. they are ombrogenous) and, like mountain mires with nutrient-poor water supplies, are classed as oligotrophic peat lands. Transition mire is an intermediate type where neither precipitation nor surface/groundwater dominates the water balance. The mineral components of peat are derived from inorganic matter contained in sediments and by adsorption from groundwater, so that the source of water significantly influences peat geochemistry. On the other hand, relatively few papers deal with the basic geochemical properties of peat that has similar botanical composition but was formed under different conditions .The chemical properties of peat formed in mires that differ in their geological origin, geomorphology, hydrology and botanical composition [17].

2.5.1. Formation of Peat

The process of peat formation and the chemical and physical properties of the peat are closely related to the topography, geology, hydrology, and climate of a site [26].

The formation of peat is basically due to the fact that the rate of accumulation of plant material in the bog is faster than its rate of decomposition. As a result, there is a gradual build-up of semi-

decayed vegetative matter at various stages of decomposition, this material is referred to as peat. For a well-established bog, the rate of peat deposition is usually about 3 cm per 100 years. This rate does vary depending on several factors such as, seasonal conditions, the location of the bog, the plant species present, etc. The slow rate of decomposition is a result of the water logged environment of the bog which severely inhibits the process of decay as carried out by soil microorganisms. The more readily degradable materials are the first to be removed from newly dead vegetative matter. These consist of the water soluble components of the plant cell, such as the simple sugars, nucleic acids and proteins. The materials which make up the cell wall of the plant, such as cellulose, pectins, hemicellulose, ligmn, etc. are more resistant to decay. They are attacked by the soil micro-organisms at a much slower rate compared to the plant cellular components. The first cell wall constituents to be removed include cellulose and pectin's, due to their simple structures which make them accessible to microbial attack Ligmn is more resistant to decay than the other cell wall components and as a consequence its rate of removal is much slower than the other materials [27].

2.5.2. The Classification of Peat

There are several different systems for the classification of peat currently in use. These systems are based on such characteristics as the geology of the peat deposit, its botanical content, or its physiochemical properties. The characteristic of greatest importance in a peat deposit from a geological perspective is its relationship to the water table of the surrounding mineral soil .This relationship results in the division of bogs into three broad categories, namely low-moor, transitional-moor, and high-moor peats .In the low-moor and transitional-moor deposits, the water level in the bog is continuous with the water table of the adjacent mineral soil, the low-moor is being somewhat wetter than the transitional-moor. The high-moor peats arc raised significantly higher than the surrounding water table and they tend to be the driest of the three types of moor. The botanical classification system of peat soils is based on the identification of the major plant species present in the peat. The botanical classification system has been developed in greatest detail in Russia, and a total of 38 different classes are recognized. The system is based on the three main groups namely the low-moor, transitional-moor, and high-moor peats, and is further divided into six subgroups woody, woody-grassy, woody-mossy, grassy, grassy-mossy, and mossy. Within each subgroup the peat is classified by the nature of the

dominant plant species present. Botanical classification is relatively straight forward for the undecomposed peats, but identification of plant residues becomes progressively more difficult with increasing degree of decomposition or depth of the sample .In addition, there can be significant changes in the plant species present in the peat deposit with increasing depth in the bog. The botanical classification is applied mainly to the peats of the northern-temperate regions, and is not applicable to the peats found in tropical and semi-tropical areas, which contain different types of vegetation, such as mangroves and cypresses. For the high-moor peat the principal species which may be present include the mosses (Sphagnum), which are the most common, and cotton grass (Eriophorum). The low-moor peat contain plants such as the fondiferous mosses (Hypnum), reeds (Phragmites) and sedges (Carex). Also, present are woody plants, such as alder (Alnus) willow (Sahx) birch (Betula), and conifers. The transitional-moors have variable mixtures of the above species. Neither the geological nor are the botanical classification systems completely satisfactory for the characterization of peat soils. These systems do not consider the nature of the peat material itself, and in particular ignore the state of humification of the peat which does significantly influence the nature and properties of the organic soil. The most useful classification systems are based on the physiochemical properties of the peat, one of the most important physiochemical characteristics being the degree of decomposition of the soil sample. A widely employed classification system in Europe is the von Post scale of humification, a modified version of which defines 10 degrees of humification from H 1 for the slightly decomposed peats which contain recognizable plant residues to H 10 for the highly decomposed varieties which are usually referred to as mucks [27].

2.5.3. Distribution of peat lands

Peat lands are composed by soils which contain at least 30 % by weight of organic matter, in the top of 40 cm and cover at least 80% of the area. Approximately 29 million ha is tropical peat lands worldwide [28].

Globally, peat lands occupy approximately 3 % of global land area, but they store roughly 30 % of the world's soil carbon (C). In the boreal and temperate regions, peat lands store an estimated 200–400 Giga tone C. However, these estimates of peat C stocks are global estimates with large uncertainties as many nations have incomplete or non-existent peat C inventories [29].

2.5.4. Difference between peat and mineral soils

Peat soils differ from mineral soils in structure, Carbon organic content, bulk density, distribution of carbon in the soil profile and the ease of burning and oxidation. Therefore, the tools used for soil sampling and the soil depths that are sampled are also different between the two soil types [21].

Table 3.Some differences in the characteristics of peat and upland soils [21].

Characteristics	Peat soil	Mineral soil
1.C organic content	Range 18-60 %	Ranges 0.5-6 % on most upland soils;around 10% on recent volcanic Andisols; and 8-20 % on submerged wetland soils
2.structure	Structure less and does not form clods	Depending on texture and degree of compaction ,ranges from loose aggregated to massive
3.Bulk density (BD)	Ranges 0.03-0.3 g/cm^3 and under extreme condition can be between <0.01 and >0.4 g/cm^3	Ranges 0.6-1.6 g/cm^3 with values below1g/cm^3 for undisturbed forest soils
4.Carbon distribution in the profile	High carbon content ,homogeneously distributed from soil surface to soil to the mineral soil interface at peat bottom	Mostly concentrated in the 0-30cm layer
5.Ease of burning	Easily burn when dry; can be used as fuel	Not easily burned
6.Types of soil analysis for determining carbon stock	Carbon content and BD by layer from the soil surface to the bottom of the peat	Carbon content and BD by layers to a depth of 30-100 cm
7.Divice used for sampling bulk density	Peat auger, for BD, the unsaturated surface peat layer can be retrieved using sample rings. Soil block can be used to assess bias in the use of augers for bulk density estimates	Sample rings or small soil blocks

2.6. Use of peat land soil

2.6.1. Balneotherapy

Balneological peat as ecologically clean and natural substance is more human friendly than synthetic substances. Peat and various peat preparations have been successfully used in the balneological practice of clinical medicine. The quality, type and amount of the biologically active substances in peat make certain peat more medically useful. Several European countries (Germany, Austria, Czech Republic, and Hungary) have long traditions of using balneological peat. In recent decades, it has also been studied and used in Finland. However, it is well known that the composition of peat in general is very complex and varies according to the source of peat. In addition, the quality and composition of peat depend on many different factors such as the place of origin, the primary types of the plants of origin and a whole spectrum of environmental factors. The most common types of peat application in balneotherapy are peat muds, poultices, and suspension baths [30].

Balneology is largely used for the treatment of rheumatic diseases that are also common in Estonia. Humic substances of peat have anti-inflammatory and pro-inflammatory, antiallergic, and antibacterial, antifungal, immunomodulatory and photoprotective effects. They sorb many biological molecules like peptides, sugars, nucleic acid residues and fats. Biochemically active humic, fulvic and hymatomelanic acids are successfully used against musculoskeletal, gynaecological and skin diseases. Fulvic, ulmic and humic acids, all of which have been isolated from peat, have been found to be of particular importance in the biological effects of peat. According to experience of other countries, the peat suitable for balneology has to be well humified (40- 50 %). Its natural moisture content has to be at least 85% and the peat layer has to be under the peat water level. The content of humic substances should exceed 20 % of dry weight. Balneological peat should not contain harmful bacteria and heavy metals. Moreover, it should contain humic acid, hymatomelanic acid and fulvic acid, the ash content should be less than 12 % and the thickness of the proper peat layer at least 0.7 m [31].

2.6.2. Fuel

Another promising area of energy development is the use of biomass as a fuel feedstock. Biomass includes wastes, wood, peat etc. The advantage of using biomass over traditional types

of fuels is that the common environmental situation in surrounding plant areas is much better and it is much cheaper than using inexhaustible sources of energy [32].

Researches show that efficiency of using biomass as feedstock can be increased significantly by implementation of deep processing technologies a number of by-products: synthetic gas, synthetic oil, high-carbon materials and others. The peat soils are potential fuel for continuous fires in drought. Its vulnerability to fire depends on its ground water level [33].

Upon drying, peat can be used as fuel. It has industrial importance as a fuel in some countries, such as Ireland and Finland, where it is harvested on an industrial scale. In many countries, including Ireland and Scotland, where trees are often scarce, peat is traditionally used for cooking and domestic heating. Stacks of drying peat dug from the bogs can still be seen in some rural areas. The world leader in production energy from peat is Finland, where over 60 % of country's energy balance consists of peat. This abundant resource (often mixed with wood at an average of 2.6 %) is burned to produce heat and electricity. Peat provides around 6.2 % of Finland's annual energy production, second only to Ireland. In Ireland, large-scale domestic and industrial peat usage is widespread. It produces milled peat which is used in power stations. It sells processed peat fuel in the form of peat briquettes which are used for domestic heating in rural areas.

Use of energy production from peat was famous during the Soviet Union, with the peak occurring in 1965 and declining from that point. In 1929, over 40 % of the Soviet Union's electric energy came from peat, which dropped to 1 % by 1980 [34].

2.6.3. Agriculture

Peat can store nutrients although it is not fertile itself – it is a polyelectrolytic with a high ion exchange capacity due to its oxidized lignin. The most important property of peat is retaining moisture in container soil when it is dry and yet preventing the excess of water from killing roots when it is wet. Peat remains an important raw material in horticulture in Canada, as well as parts of the United States [34].

2.6.4. Freshwater aquaria

Peat is most commonly in soft water by acting as an ion exchanger sometimes used in freshwater aquaria. In addition to being soft in texture and therefore suitable for bottom-dwelling species such as Corydoras catfish, peat is reported to have a number of other beneficial functions in freshwater aquaria. It also contains substances that are beneficial for plants, and for the reproductive health of fishes. It can even prevent algae growth and kill microorganisms. Peat often stains the water yellow or brown due to the leaching of tannins [20].

2.6.5. Water filtration

Peat is used in water filtration, such as for the treatment of septic tank effluent, as well as for urban runoff. Due to its purifying properties, peat also serves as a filter for septic tanks and may be used as a water purifier [30].

The main functional groups present in humic and fulvic acids are carboxylic and phenolic groups in which alkaline and alkaline earth cation may be substituted for H^+ ions and which are able to interact with metal ions from solution. The presence of these acidic groups, as well as its high specific surface area, suggest the potential ability of peat to be used as a low- cost and low efficient natural adsorbent of metals from point and non-point environmental pollution sources such as industrial effluent or solid waste dumps [30].

2.7. Importance of soil which have high organic carbon content

organic fraction of the soil serves as a reservoir for the plant essential nutrients, nitrogen, phosphorus, and sulphur, increases soil water holding and cation exchange capacities, and enhances soil aggregation and structure [35].

Organic matter in the soil is often found to be intimately associated with the soil mineral components due to the active binding sites in both classes of compounds. Mineral and organic matter can interact directly through charge sites or H-bonding sites or may interact via a cation bridge.

Important characteristics of the organic matter include their ability to form water-soluble and water insoluble complexes with metal ions and hydrous oxides; interact with clay minerals and bind particles together; sorb and desorb both naturally occurring and anthropogenically

introduced organic compounds; absorb and release plant nutrients; and hold water in the soil environment. As a result of these characteristics, the organic carbon used as:

Nutritional

  ➢ Increases the nutrient holding capacity of soil.

  ➢ Creates a pool of nutrients for plants.

  ➢ Food for soil organisms, from bacteria to worms.

Water Dynamics

  ➢ Improves water infiltration.

  ➢ Decreases evaporation.

  ➢ Increases water holding capacity, especially in sandy soils.

Soil Structure

  ➢ Encourages root development.

  ➢ Improves aggregation, preventing erosion.

  ➢ Prevents compaction [19, 36]

2.8. Metals in the soil

Soils are the major sinks for heavy metals released into the environment due to the disturbance and acceleration of nature's slowly occurring geochemical cycle of metals, most soils of rural and urban environments may accumulate one or more of the heavy metals above defined background values high enough to cause risks to human health, plants, animals, ecosystems, or other media. Heavy metal contamination of soil may pose risks and hazards to humans and the ecosystem through: direct ingestion or contact with contaminated soil, the food chain, drinking of contaminated ground water, and reduction in food quality [36].

Heavy metals may chemically or physically interact with the natural compounds, which change their forms of existence in the environment. In general, they may react with particular species, change oxidation states and precipitate [37] .

Excess heavy metal accumulation in soils is toxic to humans and other animals. Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy,

and multiple sclerosis. Allergies are not uncommon and repeated long-term contact with some metals or their compounds may even cause cancer [38].

Heavy metals may be distributed in soil components as exchangeable, adsorbed on soil organic matter, precipitated or complexes. In terms of bioavailability, various species of metals (e.g., Cu, Co, Ni and Zn) are more biologically available than others. If bioavailability is related to the mobility of heavy metals, then higher concentrations of mobile toxic metals in the soil column increases the potential for plant uptake as well as leaching into environmental soil and water bodies, and their eventual presence in man [8].

Trace quantities of certain heavy metals are essential to animals and plant growth, they are of considerable environmental concern due to their toxicity and cumulative behavior .These metals which are not biodegradable are accumulated in living organisms when released into the environment. Most of these heavy metals are essential for growth of organisms but are only required in low concentrations. They exert toxic effects when their concentrations are increased, and at this stage, they could be referred to, as toxic metals [39].

In general many soils contain a wide range of heavy metals with varying concentration ranges depending on the surrounding geological environment and anthropogenic and natural activities occurring or once occurred. These metals can be Fe, Cr, Mn, Ni, Zn, Cu, Pb, Cd, Hg, etc. Metal transport is not only dependent on the physiochemical properties of the metals but mostly on the physical and chemical properties of the soil, like for example: soil organic matter content, clay fraction content, mineralogical composition, pH, and more, all of which collectively determine the binding ability of soil [40].

The solid state of soils composes an average of 45 % of soil bulk. It consists of mineral particles, organic matter and organic-mineral particles. They all play a very important role in giving the soil the ability to adsorb, exchange, oxidase, reduce, catalyze and precipitate chemicals and metal ions in particular. The inorganic colloidal fraction of soil is the most responsible for sorption by its mineral particles [9].

3. Materials and Methods

3.1. General Description of the Study Areas

This study was conducted at mount Guna (mehilchemaw) located near the city of Nifas Mewcha and Debretabor in the Northern Amhara Region of Ethiopia. It is the highest mount in the southern zone with an elevation of 4,120 meters above sea level and it is 42 Km away from Debretabor town, and the other study area is Semen Mountain National Park in North Gondar of Amhara regional state (figure 1). Simien Mountains National Park is located in the North Gondar Zone of the Amhara National Regional State and it is 146 km away from Gondar town by road. The park lies within five woredas (district): Debark, AddiArkay, Beyeda, Jan Amora and Tselemt, bordering 38 kebeles (farmers' associations) of these woredas. To investigate the physico chemical properties of peat soil in the selected area two peat land soil and one control soil in Gondar Zuria Woreda in Amhara Region of Ethiopia was selected for comparison. The criteria for consideration of sampling sites in each soil are based on topographical, accessibility of the sampling site, and purpose of the study.
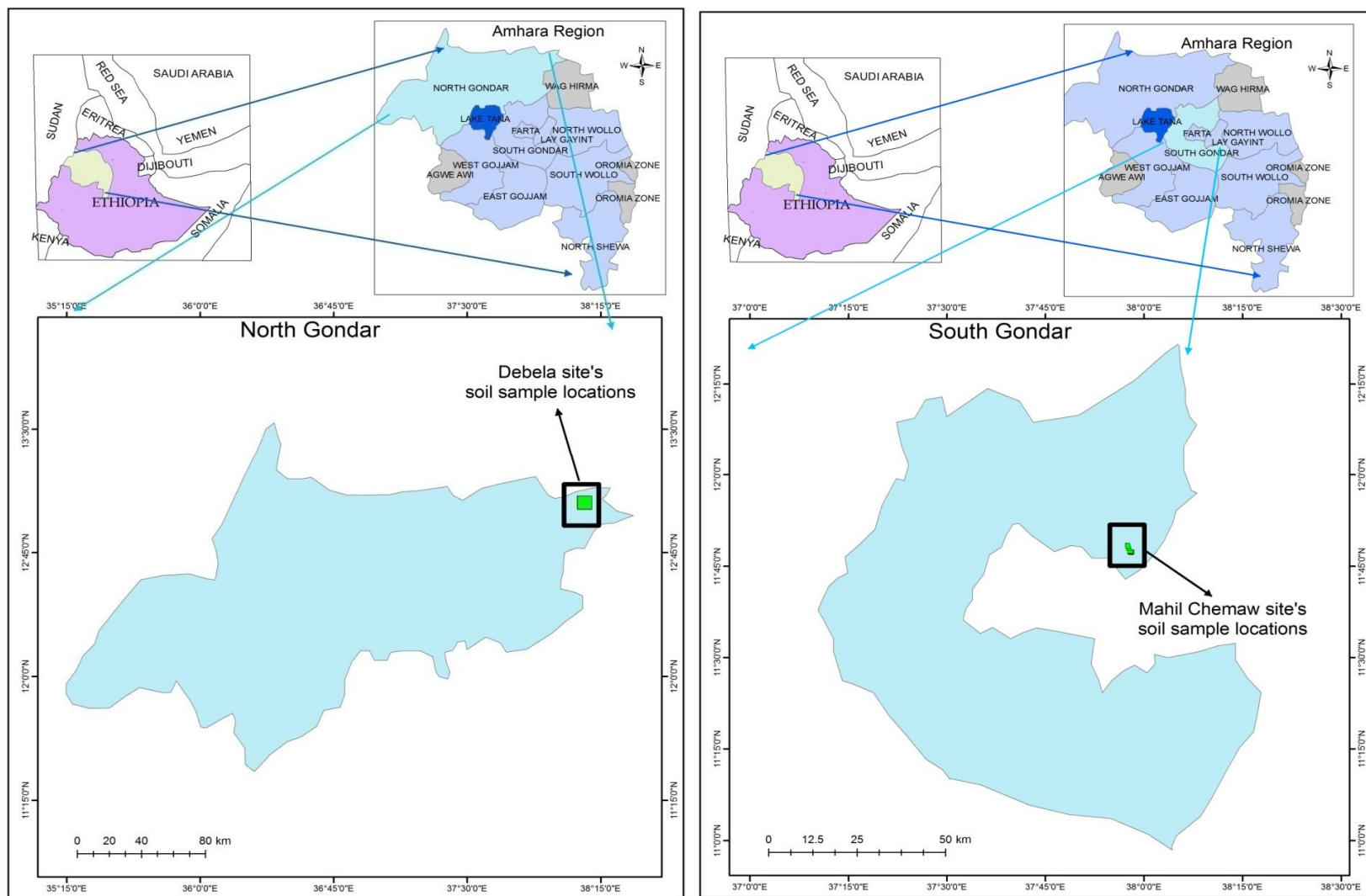
Figure 1. Map of sampling sites, North Gondar (Debela) and South Gondar (MehalChemaw)

3.2. Cleaning Procedures of Sampling Equipment

Soil samples being tested for inorganic metals constituents and other parameters should be collected in contaminant-free plastic. All plastic bags, augers, soil core/core sampler/ were thoroughly washed with detergent, rinsed with water and then with distilled water before soaking in 10 % HNO_3 for about 24 hours. Containers were finally rinsed with deionized water before being used for sampling.

3.3. Collection of Soil Samples and Transportation

Two Peat containing and one control containing soil samples were collected though systematic random method. The sampling was in GUNAMountain at (mehil chemaw), and SNP (Debela) in North Gondar of Amhara regional state Ethiopia peat soil samples and one control group at Gondar Zuria woreda in North Gondar, Amhara regional state of Ethiopia were collected by the aid of a soil Auger at a depth of 20 cm referred to topsoil. The soil sampling spots were cleared of debris before sampling. From each sampling points, 16 soil sub-samples were gathered and mixed thoroughly to obtain a representative composite sample. Sampled soils were placed in white polyethylene plastic bags properly tagged with marker containing sample information so as not to mix up the samples. Each composite soil samples were placed in plastic bags labeled then taken to the laboratory for pre-treatment and analysis by drying the soil for two week after dried then grinded and sieved by >2mm mesh stainless steel sieve [41].

3.4. Chemicals and Standard Solutions

All chemicals were used as received without further purification and most of them were of analytical grade. The major reagents were used are; Deionized water, pH 7.0 and 4.0 buffer solution, $K_2Cr_2O_7$, CH_3COOH, H_2SO_4 (98 %), Concentrated H_3PO_4, $(NH_4)SO_4FeSO_4.6H_2O$] Ferrous ammonium sulphate, Diethylenetriaminepentaacetic acid (DTPA), Phenolphthalein indicator, Diphenylamine indicator (($C_6H_5)_2NH$), KCl, $FeSO_4.7H_2O$, 70 % HNO_3 (Spectra , BDH, England), 37 % HCl (Riedel-deHaën), 30 % H_2O_2, amyl alcohol, 5 % calgon, $CaCl_2$, Triethanolamine, KCl, NaOH 40 %, Salicilic acid, 10 % NaCl Scientific pure graphics calibration standards (Norwalk, USA) for Cr, Mn, Fe, Cu, Zn, Cd and Mg were used as received.

3.5. Instrumentation and determination of physicochemical Properties

Soil Particle size analysis was done using the hydrometer method [42]. The pH and EC of the soil samples were determined in soil/water (1:2.5, v/v) suspension by a pH meter and a conductivity meter. Total organic carbon (TOC) concentration were determined with the titration method of Walkey and Black [43]. Total organic matter (TOM) concentration will be quantified by multiplying TOC with 1.724 (Osuji and Nwoye 2007) [44]. Soil cation exchange capacity (CEC) was measured after leaching the ammonium acetate extracted (ammonium ion standard) soil samples with 10% sodium chloride solution. Total nitrogen will be measured by Kjeldahl digestion and steam distillation method [45]. Micronutrient (Fe, Cu, Zn and Mn) were extracted by DTPA method and analysed using novAA4DDP and heavy metals (Cr, Mn, Fe, Cu, Zn Cd) and Mg extracted by acid and analyzed by Buck SCIENTIFIC FAAS 210VGP.

3.6. Quality assurance mechanisms

Quality assurance (QA)/control (QC) protocol prescribed by the U. S Environmental Protection Agency (EPA) were used for organic compounds as well as other chemical analysis. So as to control the analytical procedure, precision of the analytical results were carried out by replicate analysis. In addition, all laboratory equipment to be used for analysis are from Pyrex glass, washed with acids 0.1 N HNO3, rinsed twice with deionized water and were placed in a clean environment until dry. All reagents to be used are of analytical grade. Not only had this but also, in this study, certified standard reference materials were used to assure the quality control.

3.7. Optimization of digestion procedure and soil digestion

In this study digestion time, reagent volume ratio and temperature were optimized by varying one parameter at a time and making the others constant for the soil samples. According to the determination of the total concentration of Cr, Mn, Fe, Cu, Zn, Cd and Mg were done by keeping all optimized parameters.

3.8. Digestion of Soils Samples

For the analysis of soil samples different digestion methods were tested and the optimum procedures that produce pure colorless residue, consumed minimal reagent volumes ratio, and required shorter digestion time was selected from the different alternatives with a slight modification by used aqua-regain digestion method. The procedures tasted are given in Table 7.

During the optimization of the procedure a part of the powdered sieved grain size fraction of 0.3 g soil was weighted directly in to 250 mL Pyrex beaker and various acid mixtures of 15mL were (3mL H_2O_2, 3mL HNO_3 and 9 mL HCl) added, and then evaporated to semi-dryness on hot plate by covering watch glass at 300 ^{o}C temperature until 5mL left then adding 5mL of 5 % HNO_3 the solution become clear and colorless and then the mixture again evaporated to semi-dryness. After cooling the mixture the samples were filtered, using Whatman type # 42 filter paper to remove residue, washed with de-ionized (double-distilled) water, then transferred quantitatively to a 50 mL volumetric flask. The digested sample solutions were kept in cooled place until analysis and then the metals(Cr, Mn, Fe, Cu, Zn, Cd and Mg) sample solutions were determined by flame atomic absorption spectroscopy (FAAS) and the filtrate was used for the analysis of triplicates were performed for each soil samples by FAAS. Blank samples were prepared side by side with the samples [46].

Fig.2. Digestion of soil using hotplate and standard preparation for AAS

The measurements of the concentration of (Cr, Mn, Fe, Cu, Zn, Cd and Mg) were carried out using flame atomic absorption spectrophotometer. Cathode lamps of Cr, Mn, Fe, Cu, Zn, Cd and Mg were used as radiation source. Air acetylene gas was used as source of flame maximum absorption was obtained by adjusting the cathode lamps at specific slit, current, energy and wavelengths as indicated in (Table 4).

Table 4. Instrumental operating conditions for determination of heavy metal

Element	Wavelength (nm)	Slit width (nm)	Lamp current (mA)	Energy (J)	Flame type
Cr	357.9	0.70	5A	3.75	Air-C_2H_2
Mn	279.5	0.70	3A	3.885	Air- C_2H_2
Fe	248.3	0.2	7A	3.844	Air- C_2H_2
Cu	324.7	0.70	1.7A	3.180	Air- C_2H_2
Zn	213.9	0.70	2A	3.044	Air- C_2H_2
Cd	228.9	0.70	2A	3.126	Air- C_2H_2
Mg	285.2	0.70	1A	4.501	Air- C_2H_2

The instrumental and sample blanks were also prepared in similar manner with standards and samples, respectively and intensity of each analyze in the blank samples was subtracted from that of the sample. Three replicates of each sample were measured and the average mean concentration were calculated using Microsoft Excel (Microsoft Excel 2013) work sheet.

Calibration standard preparation

Standard aqueous solutions of different elements were used to calibrate the atomic spectrophotometer. Each solutions of standard was prepared by de-ionized water. For each of the metals seven standards; Cr, Mn, Fe, Cu, Zn, Cd and Mg were used for the calibration of the flame atomic spectrophotometer. The calibration curves were plotted by using linear regression analysis of the concentrations of the standard solutions versus absorbance value.

4. Results and discussion

4.1. Physico-Chemical Analysis

In the present study, all parameters were selected and analyzed by standard method and the obtained results are discussed below.

4.1.1. Analysis of Physical Properties of the soil

Color of the soil

The color of the soil as it was observed using Munsell color chart the GUNA soil was very black whereas, the SNP was dark brown color and the GDC soil was found to be light black color (Table 5). Dark brown or black color in soil indicates that the soil has high organic matter content. This is due to the organic matter inside peat soil will have some differences in its physical properties during peat transformation process, the degree of decomposition, peat's specific gravity and compaction are increased while the peat's moisture content is decreased. In addition, the color of peat will change into dark brown and black color due to calorific value [20].

Texture

The texture of the soils at GUNA and SNP were clay and the GDC soil were sandy clay. The particle distribution analysis seen that clay is the dominant fraction in all of the soil studied (Table 5). The textural class of the surface (0-20 cm) Soil textural composition (% sand, silt, and clay) affects soil-water retention characteristics, leaching and erosion potential, plant nutrient storage, organic-matter dynamics, and carbon-sequestration capability. Soil textural analysis is a key component of any minimum data set to be used for assessing of agricultural management practices [15]. SOM has a correlation with soil texture. Soil texture influence the rate of SOM decomposition. Soils with a high clay content may have higher SOM content, due to slower decomposition of organic matter [22]. The GUNA and SNP have high clay content this may be the slow decomposition of organic matter because of cool and highland areas.
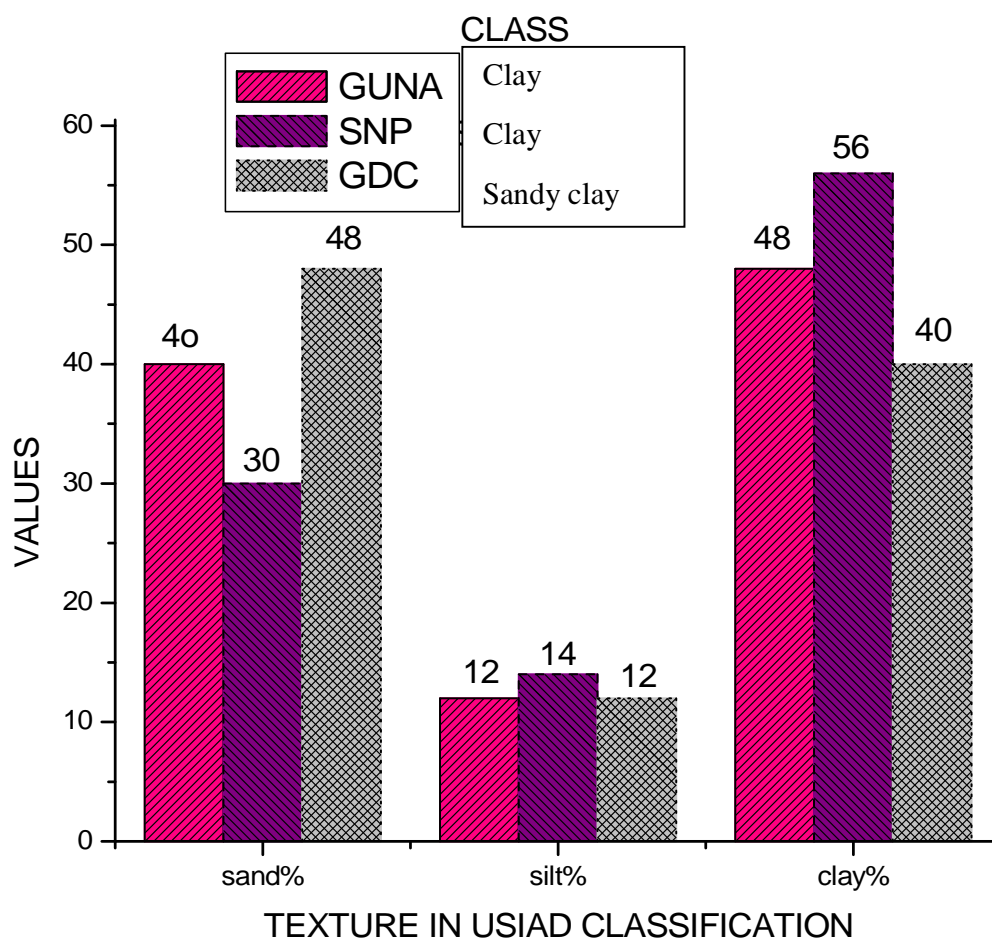
Figure 3. Textural value of the soil samples.

4.1.2. Analysis of chemical properties of soil

pH analysis

pH is a measure of their acidity or alkalinity and is one of the stable measurements. As it is depicted in (Table 5) The GUNA Mountain and SNP pH of soils were strongly acid whereas, GDC soils were found to be slightly acidic. From (Table 5), the highest (6.63) and the lowest (4.83) soil pH-H_2O values were recorded under the GDC and the GUNA lands, respectively. The lowest value of pH under the GUNA land may be due to its highest microbial oxidation that

produces organic acids, which provide H$^+$ ions to the soil solution and thereby lowers soil pH. Generally, the pH values observed in the study area are within the ranges of strongly acid to slightly acidic soil reactions [47].

Soil pH can affect CEC and AEC by altering the surface charge of colloids. A higher concentration of H$^+$ (lower pH) will neutralize the negative charge on colloids, thereby decreasing CEC and increasing AEC. The opposite occurs when pH increases. It affects mineral nutrient soil quality and much microorganism activity [10]. In the organic soils the values of pH are almost all below 5 with many falling below 4 [23]. Based on the acidity the GUNA and SNP soil is moderate acidic [3]

Electrical Conductivity

The EC of soil were measured with conductivity meter the values obtained for GUNA Mountain were 0.136 ds/m, for SNP 0.121 ds/m and for GDC 0.062 ds/m. EC is positively and significantly correlated with PH. Soils having lower PH value have high EC value (Table 6).

The measurement of conductivity is to measure the current that gives a clear idea of soluble salt present in the soil. Conductivity depends upon the dilution of soil suspension. The conductivity values ranges from 0.062 ds/m to 0.136 ds/m. Conductivity of GDC samples was less as compared to samples at SNP and GUNA.

The value of conductivity is the measure of ions present in the sample. The conductivity values can vary with the chemical properties of soil, if the soil is contaminated by chemicals or if it is saline, the depth of soil sample. The chemical effects on soil compaction characterizations through electrical conductivity. If the soil is more acidic it shows electric conductivity value very high [12]. As the value correlates with the standards the soil is low to very low nutrient status [48].Based on EC the soil salinity value is low and its salinity class is none saline [49].
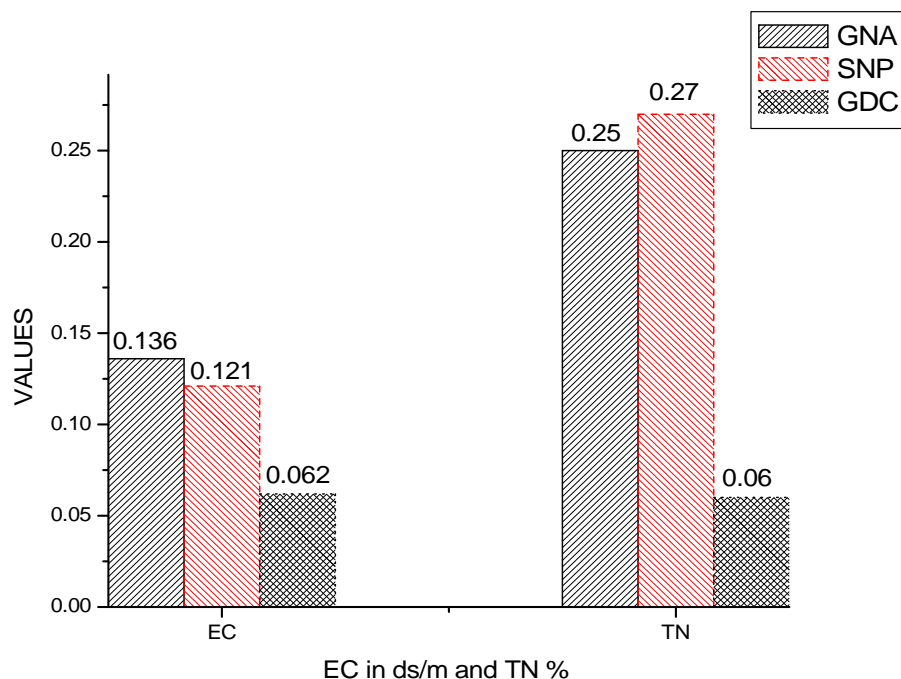
Figure 4. EC and TN values of GUNA, SNP and GDC soil.

Total nitrogen

The total nitrogen content of the soil at GUNA and SNP were 0.25 % and 0.27 % which have nearly identical TN % while, GDC soil were 0.06 % which is relatively small TN value. Except GDC soil GUNA and SNP have above the critical values of Nigerian soil test [50]. Generally, as organic matter increases the organic carbon and total nitrogen also increases as seen from the (fig.7 and 6)

Cation Exchange Capacity (CEC)

Cation Exchange Capacity (CEC) is pH dependent the standard value of CEC for peat soil was in range of 40-135 meq 100 g^{-1}. As the pH increases, the CEC also increases and vice versa [51]. The cation exchange capacity of soil at GUNA and GDC were 51.2 cmol (+)/kg & 48.8 cmol (+)/kg which was very high and SNP 33.2 cmol (+)/kg were high cation exchange capacity (Table 5). The CEC decreased as pH decreased because of low base saturation of organic soils in

SNP which highly saturated with hydrogen ions. The cation exchange capacity of a soil measures the surface electric charge of soil components [52]

Generally CEC is mainly dependent upon the type and quantity of colloids in peat. Cation exchange capacity is a means of estimating soil fertility. Soils with high CEC values are considered fertile and vice versa. In general, CEC ranges from a minimum of 2 cmol (+) kg^{-1} soil in sands and up to a maximum of 60 cmol (+) kg^{-1} in clay soils. This trend is consistent with rising pH above 5.5, CEC generally increases and also found that CEC of some clay soils was constant between pH 2.5 and 5.0 but increased between pH 5.0 and 7.0 [53].

There is a strong correlation between CEC values and the amount of clay and organic matter present in the soil, because organic matter and clay are a major source of negative electrostatic sites. The CEC helps characterize the soil type under consideration [54]. As it is shown in the (fig.7.) The higher values of organic matter and clay fractions have higher values of CEC values in this study.

Table 5. Physical and chemical properties of the value of SNP, GUNA, and GDC soil.

Soil physico-chemical parameters		Sample site		
		GUNA	SNP	GDC
Color		Black	Dark Brown	Light black
Texture (%)	Sand	40	30	48
	Silt	12	14	12
	Clay	48	56	40
Textural Class		Clay	Clay	Sandy clay
PH		4.83	5.1	6.63
EC (ds/m)		0.136	0.121	0.062
CEC (cmol(+)/kg)		51.2	33.2	48.8
OM (%)		8.74	9.41	2.02
OC (%)		5.07	5.46	1.17
TN (%)		0.25	0.27	0.06

Organic Matter (OM)

Since organic matter is the product of organic carbon and 1.724. As it is shown in (Table 5), the organic matter content of GUNA and SNP were 8.83 % and 9.51 %, respectively and for GDC it was found to be 2.03 %. Both SNP and GUNA have very high % of organic matter but GDC were rated as medium organic matter [51]. Organic matter content is one factor which indicates vast arrays of carbon-containing compounds in the soil. This is typically created by the decay of plants, microbes and other organisms, such as decomposed wood, dead animals and organic wastes, which play vital roles in nutrient water and biological cycles. This also increases the water holding capacity of soil [8].

Altitude also influences SOM/TOC by controlling soil water balance, soil erosion and geologic deposition processes and have positive correlations [22].

In this study, GUNA and SNP are at high altitude they have both high SOM and TOC. Many studies indicated that soil texture affects aggregation and thus increasing clay content combines with increasing aggregation or aggregate stability. It was found that, on the condition that soil aggregation increased, soil clay content indirectly affected carbon storage and thus protected soil carbon against oxidation and organisms [55]. In this study the clay content of GUNA and SNP is higher than that of GDC as clearly seen from the (fig.7) high content of clay particles have very high organic matter and organic carbon shows strong relationship between SOC and clay + silt.

Organic Carbon (OC)

The OC of the GUNA and SNP were 5.07 % and 5.46 % respectively which is high organic while GDC soil was 1.17 which was low organic carbon (Table 5). Higher organic carbon could be evidence of weakly advanced processes of mineralization [56].

Soils with high clay content tend to have higher soil organic carbon than soils with low clay content under similar land use and climatic conditions. Generally wetland soils have more organic carbon content than terrestrial soil [57].

Soil of GUNA and SNP are fertile soils. Soil organic carbon (OC) and organic matter (OM) have long been identified as factors that are important for soil fertility in natural ecosystems [58].The amount of SOM/TOC in soil depends also on vegetative growth or soil cover which included agricultural activities [22]. In the two studying areas there is an indication of undecomposed OM due to the geographical nature land and much cooled weathering which makes inhibit the

microorganisms decomposing organic matter due to this the two parks having very high organic carbon and organic matter content.
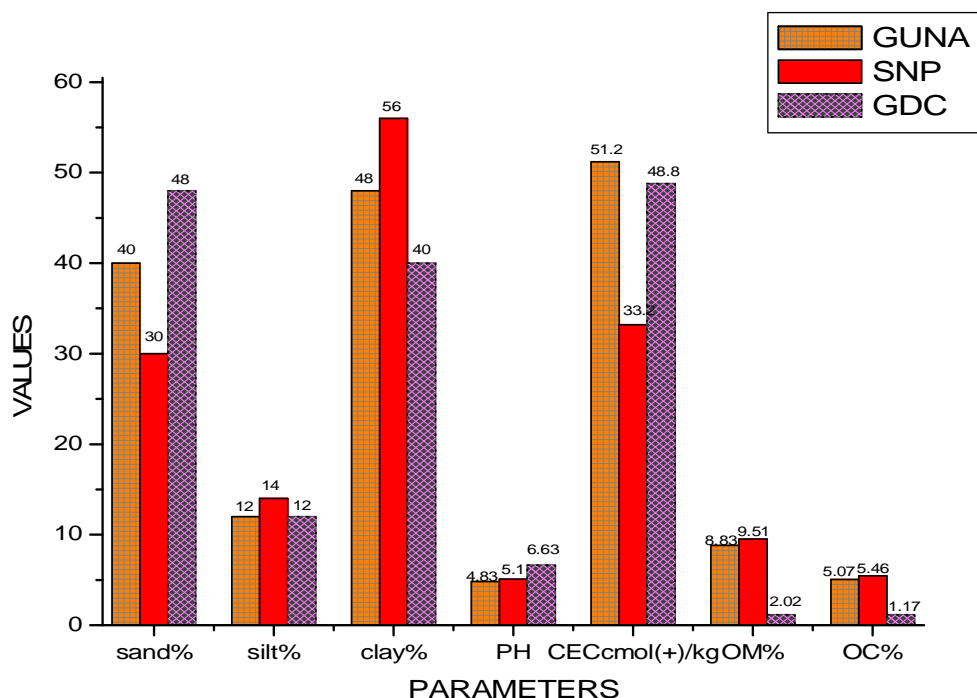
Figure 5. Physicochemical properties of soils

4.2. Micronutrients and heavy metals of the soil

4.2.1. Micronutrient of the soil extraction using DTPA method

The availability of trace elements for plants is influenced by many soil and environmental factors [59]. The concentration of Cu is adequate (high) in GDC whereas in SNP and GUNA very low. The total Cu contents in the soil generally fall in the range 2-100 ppm. The strong interaction which is generally held to occur between Cu and soil organic matter does not affect Cu availability to plants, although it does influence the concentration of Cu in soil solutions [48]. From the results (Table 6), the value of Cu level is low in SNP and GUNA soils as compared to the critical value given. Cereal plants such as wheat and maize are particularly sensitive to Cu deficiency. The low Cu content (<2ppm) in the soils may account for the poor yield in crops experienced in the SNP and GUNA farmland [49]. Available Fe content of SNP 29.6μg g^{-1} and

GUNA 29.1µg g^{-1} in the soil samples is considered as sufficient(high) but GDC 12.1µg g^{-1} is medium [48, 59-60].

A wide range of crops are respond to Mn deficiency, which is common in calcareous soils and soils of high pH. In soil, Mn originates primarily from the decomposition of ferromagnetism rocks and its content varies from 20 to 10,000 ppm with an approximate mean of 1,000 ppm (54). On the other hand the concentration of Mn in soil is sufficient between 1-5ppm [61]. Since the concentration of Mn is in the given range it is sufficient. The deficiency in Mn observed in SNP soil samples may be attributed to the mildly acidic soil pH and the potential adsorption of Mn on Fe or aluminum oxide present in the soils and the adequate concentration of Mn in GUNA and GDC is due to high cation exchange capacity. Generally, the concentration of Mn in GUNA and SNP is medium and the GDC is very high.

Plants vary in their zinc need as well as their ability to extract zinc from soil. The usual range of Zn in soil (1-900 ppm) with an approximate mean of 90 ppm .On the other hand, total zinc content in soil generally falls within the range of 10 to 300 ppm [62]. From (Table 6), a very low level of Zn is obtained for all the soil samples. Zn availability is mainly related to pH and complexions, and as pH increases organically-bound Zn decreases, which could be responsible for the apparent Zn deficiency in the soil samples [14]. A zinc soil test above 1.5 ppm using the DTPA extraction method is sufficient for most crops [61]. Zn in all site soils are sufficient in .Generally, Cu and Mn in GDC and Fe in GUNA and SNP are optimum the rest of micronutrients are below the optimum point as described by [48]. The availability of most micronutrients decreases as pH increases. Micronutrient deficiencies rarely occur when the soil pH is below 6.5. [61]
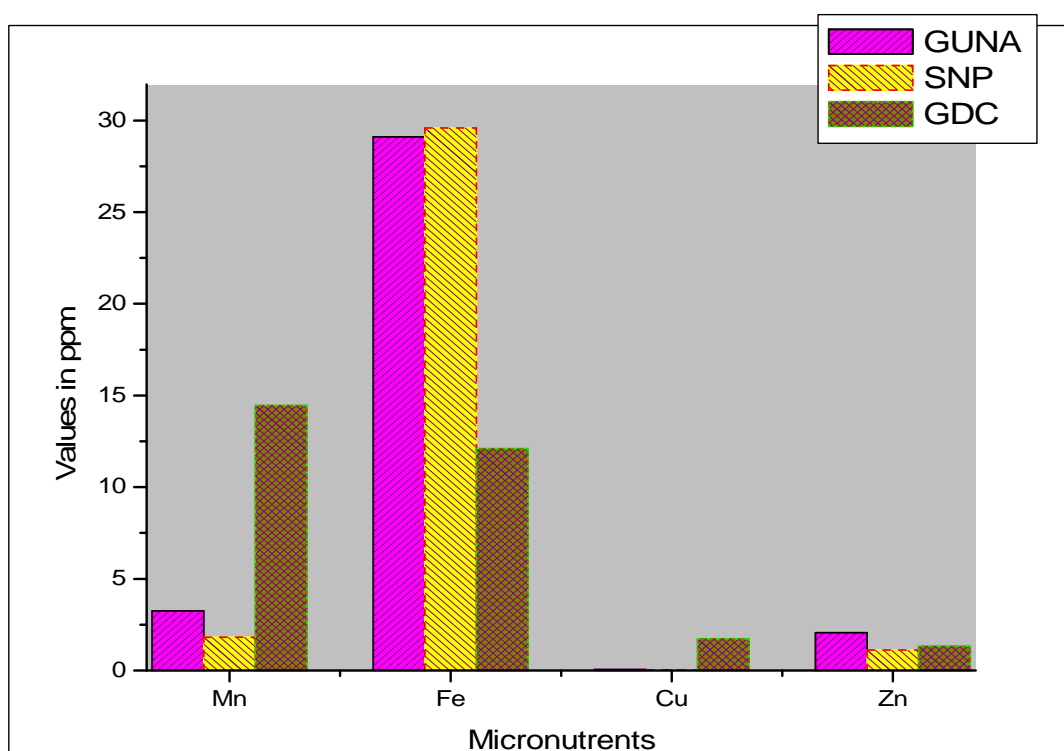
Figure 6. DTPA extraction of micronutrients

Table 6. Micronutrients value of soil extracted by DTPA method

Sr.No	Site	Micronutrients ($\mu g/g$ = ppm)			
		Mn	Fe	Cu	Zn
1	GUNA	3.25	29.1	0.05	2.06
2	SNP	1.816	29.6	0.04	1.12
3	GDC	14.46	12.1	1.73	1.32

4.2.2. Determination of heavy metals in soil using aqua-regain digestion method by

Optimization of the method

Mixtures of acids were used for soil samples to decompose along with heating of the samples in a beaker. For the analysis of soil samples different digestion methods were tasted and the optimum procedures that produce pure colorless residue, consumed minimal reagent volumes ratio, and required shorter digestion time was selected from the different alternatives with a slight modification by used aqua-regain digestion method in a hotplate.

Table 7. Optimization parameters for wet digestion of soil samples for heavy metals.

Condition	Reagent volume ratio (mL)			Temp.	Time	Result
	HNO3	HCl	H2O2	(oC)	(Hrs.)	
1	15	-	-	300	2:30	Black and cloudy
2	12	3	-	300	2:30	Dark white
3	9*	3*	3*	300	2:30	Clear and colorless
1	9	3	3	200	2:30	Cloudy
2	9	3	3	250	2:30	White but not clear
3	9	3	3	300*	2:30	Clear and colorless
1	9	3	3	300	1:30	Dark
2	9	3	3	300	2:00	Gray
3	9	3	3	300	2:30*	Clear and colorless

* = optimized condition

Calibration curve

Calibration curves were prepared for each metal to determine their concentration in the soil sample solutions. A series of seven working standards were prepared from the stock standard solutions by diluting with de-ionized water for each metal as given in the calibration curves of the elements are listed in the appendix A.

Table 8. Intermediate standards, working standards and correlation coefficients of the calibration curve for the determination of metals in soil sample using FAAS.

Metal	Concentration of stock standards solution(mg/L)	Concentration of intermediate solution(mg/L)	Concentration of working standards(mg/L)	Correlation coefficient of calibration curve
Cr	1003	25	0.25,0.75,1.25,1.75,2.00	0.9986
Mn	100	25	0.5,1.5,2.5,3.5,4.5	0.9902
Fe	1000	25	1,3,5,7,9	1
Cu	1000	25	0.25,1.25,2.25,3.25,4.25	0.9943
Zn	997	25	1,2,3,4,5	0.9978
Cd	1002	25	0.15,0.4,0.65,0.9,1.15	1
Mg	1000	25	1,3,5,7,9	0.992

Determined selected heavy metals in selected soil samples by agua-regian digestion. The concentration of metals are also determined by aqua-regain extraction method and the results are interpreted as follows. Essential micronutrients as well as heavy metals from the soil assimilated by plants for healthy growth, flowering, fruiting etc. The very low concentration as well as very high concentration shows deficiency and toxicity to the plants. Copper content was found from 13.5±2.1 ppm to 8.5±0.5 ppm.The higher concentration of Cu is observed in all the three soil samples this may be the extraction method of cu in aqua- regain (Table 9) is favorable than DTPA method (Table 6).

The iron content was found from 54.0±0.6 ppm to 52.0±0.9 ppm which was in medium range. Available Fe content (54.0±0.6 to 52.0±0.9 ppm) in all the soil samples is considered sufficient. Manganese content was in the range of 11.3±0.3to 3.8±0.63.5 ppm indicating low range of manganese. Zinc content varied from 5.7±0.3 to 1.6±0.2ppm for samples, respectively. Zn availability is mainly related to pH and complexion, and as pH increases organically-bound Zn decreases, which could be responsible for the apparent Zn deficiency in the soil samples[59].And the way of extraction for Zn in agua-regian is favorable than DTPA method. Chromium content was in the range1.5±0.1-0.6±0.1ppm and cadmium content was 0.7±0.0-0.4±0.1ppm in

samples respectively. Magnesium available to plants as the ions Mg^{2+} [14]. The concentration of magnesium's in the range 32.6 ± 0.9 to 21.0 ± 0.3 in the three soil samples.

The concentration of the heavy metals in the studied soils samples are below the maximum allowable limit of heavy metals concentrations in soil (mg /kg) for different countries [63].

As the result shows, it is true even if the acid digestion value is better than DTPA extraction method, although the type of acid also governs the product concentration. Since I were not use HF used for extraction of heavy metals in soil because it bonds with silicate to form SiF_4 enabling total digestion that gives best result [64].

Generally micronutrients availability of Mn, Cu, and Zn in DTPA extraction Mn in GDC, Fe and Zn in all sites have high levels of concentration but Cu in SNP and GUNA have low and Mn in SNP and GUNA have medium level of concentration.

Except Mn in GUNA and SNP all the rest heavy metals in aqua-regian extraction have high level of concentration but above the maximum allowable limits value of the different countries.

Table 9. The metals concentration mean vales and standard deviation of different soils using aqua-regain extraction.

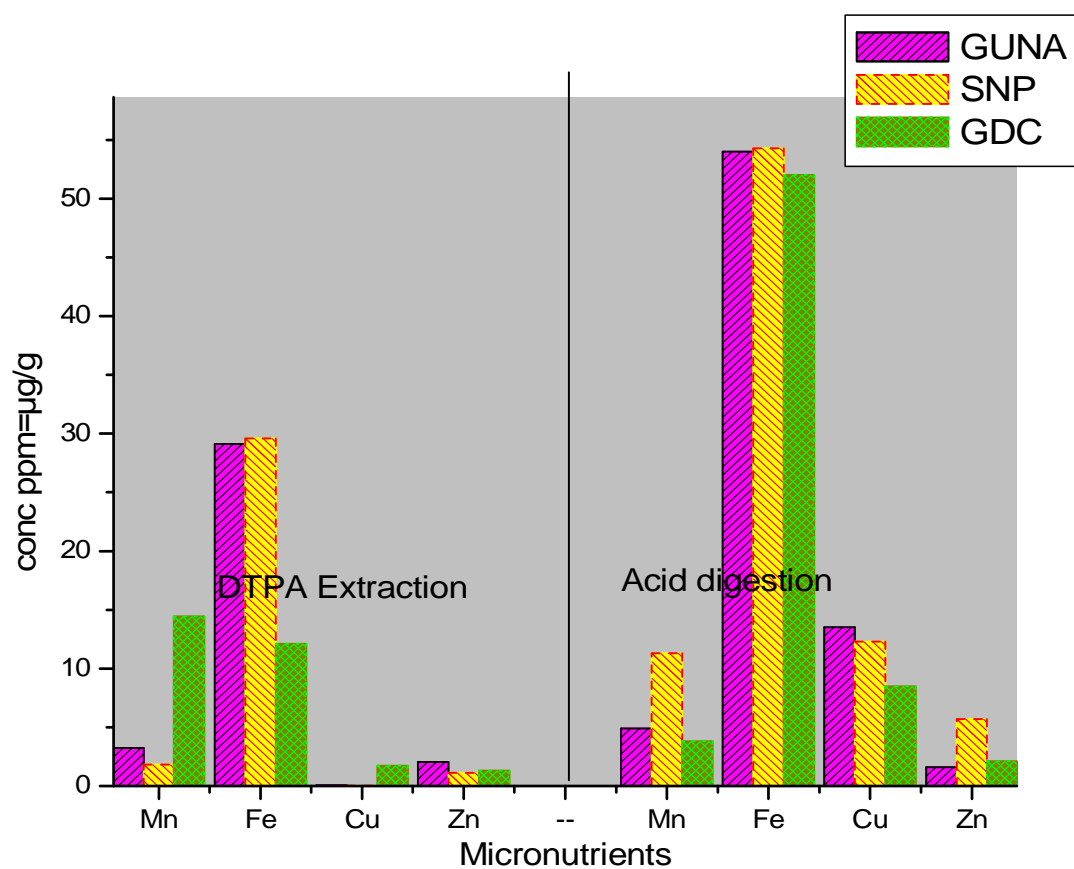| NO	SITE	Concentration of metals mg/kg=ppm						
		Cr	Mn	Fe	Cu	Zn	Cd	Mg
1	GUNA	1.0 ± 0.1	11.3 ± 0.3	54.3 ± 0.3	12.3 ± 1.6	5.7 ± 0.3	0.7 ± 0.0	21.0 ± 0.3
2	SNP	0.6 ± 0.1	3.8 ± 0.6	52.0 ± 0.9	8.5 ± 0.5	2.1 ± 0.2	0.4 ± 0.2	22.7 ± 1.5
3	GDC	1.5 ± 0.1	4.8 ± 0.1	54.0 ± 0.6	13.5 ± 2.1	1.6 ± 0.2	0.4 ± 0.1	32.6 ± 0.9

Figure 7. Comparisons of DTPA extraction with aqua-regain extraction method.

5. Conclusion and Recommendation

5.1. Conclusion

The current investigation was aimed on analysis of physicochemical properties, heavy metal concentration and micronutrient availability of selected sites of Peat land soil by using standard methods. The color of GUNA soil is black and SNP is dark brown this shows the properties of peats soil color having high organic matter but GDC soil is light black. The texture of GUNA and SNP soil have high clay content this indicates that the two site soils having high organic matter but the GDC have sand and relatively low organic matter. The result of organic matter content of GUNA and SNP was very high which also confirmed that peat land soils are richer in organic matter.

The pH of GUNA and SNP is highly acidic but GDC soil is slightly acidic this may be due the oxidation of organic matter producing H^+ in SNP and GUNA but not in GDC. The EC of soil of GUNA and SNP are approximately equal i.e. 0.136 and 0.121 but EC of GDC (0.062 ds/m) soil is less than GUNA and SNP. The CEC of GUNA and GDC is higher than SNP. The total nitrogen value of the soil of GUNA and SNP are almost equal and greater than GDC. SNP and GUNA have very high organic matter. Generally, the color, organic matter, CEC, TN, and pH of the properties of the soils of GUNA and SNP are indicators of peat soils characteristics as observed from the value.

Micronutrient availability and heavy metals of the soil except Fe and Cu in all soil samples and Mn in GDC soil are minimum (below the permissible limit) this might be the extraction method difference or leaching of metals.

5.2. Recommendations

The primary focuses of this study was to assess the physico-chemical characteristics of soil samples. I strongly recommended that the peat soil have a potential application for adsorbents, biomass fuel, agricultural and medicines that requires further study. Thus, the following points are forwards as recommendations:

➢ To evaluate the micronutrient availability and metal concentration of the soil agua-regain open digestion is preferable than the ammonium acetate method of extraction.

➢ The soil have very high organic matter due to this it can be used for absorption purpose, medication, and agricultural application, so further investigation should be performed.

➢ More comprehensive studies are also required to fully characterize like its humification TPH to evaluate its fuel content and the types of organic matter present to use for different application.

➢ Characterizing the soil also have its own significance to validate the park biodiversity of life so it needs further study the other properties of the soil.

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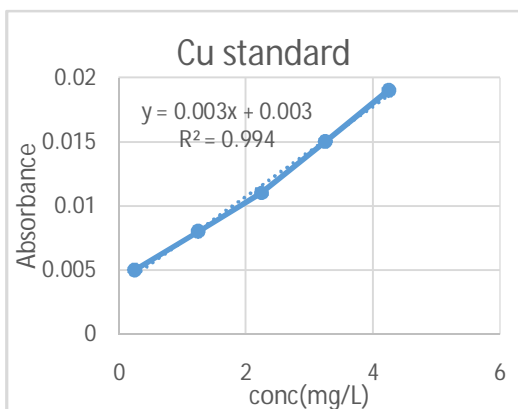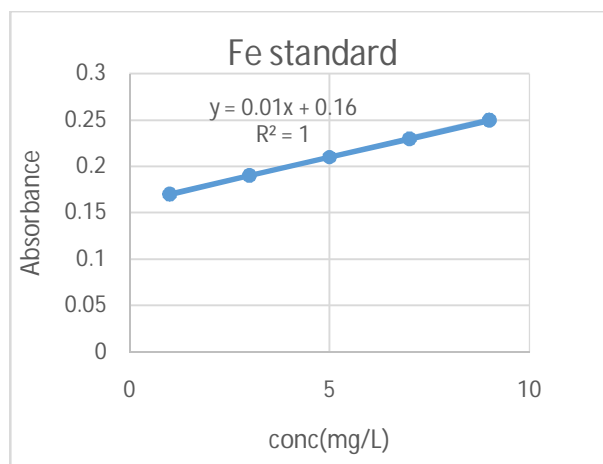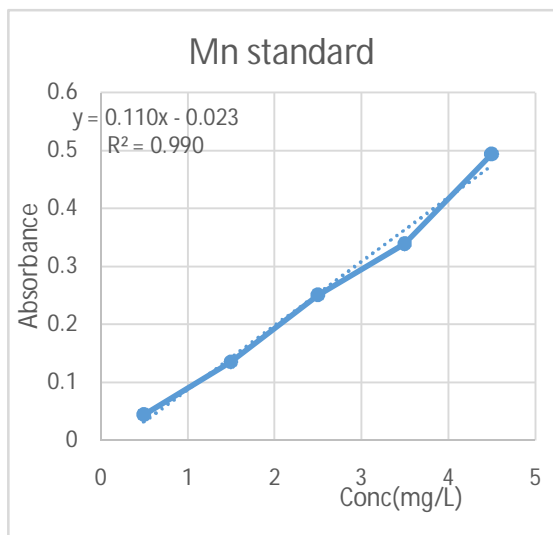[38] Anoliefo, G. O, B. Ikhajiagbe, Okonokhua and B. O, J. Appl. Sci. Environ **2007**, 11, 147-152.

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7. Appendix

Appendix A

Mn standard

y = 0.110x - 0.023
R² = 0.990

Fe standard

y = 0.01x + 0.16
R² = 1

Cu standard

y = 0.003x + 0.003
R² = 0.994

Zn standard

y = 0.035x - 0.032
R² = 0.997

Mg standard

y = 0.005x + 0.133
R² = 0.992

Cd standard

y = 0.008x - 0.000
R² = 1
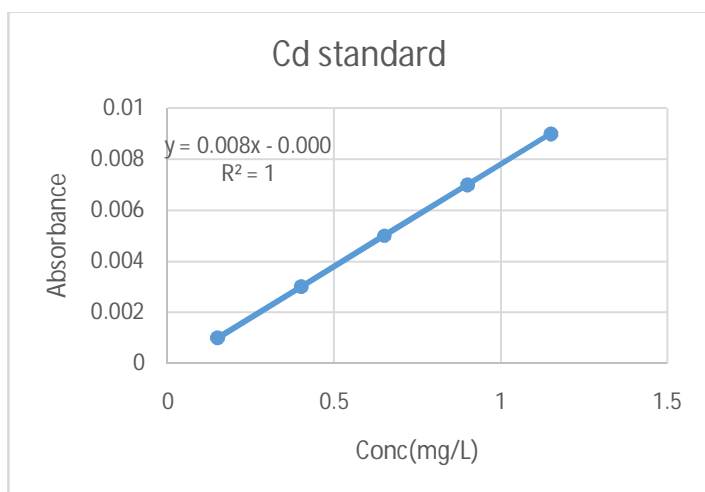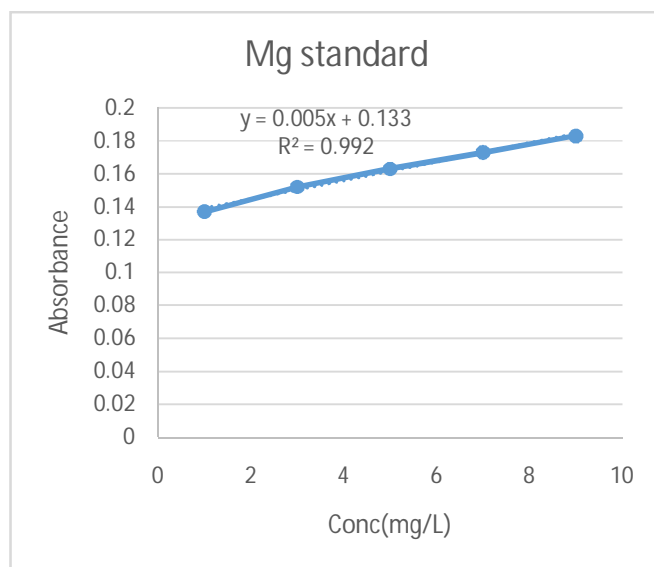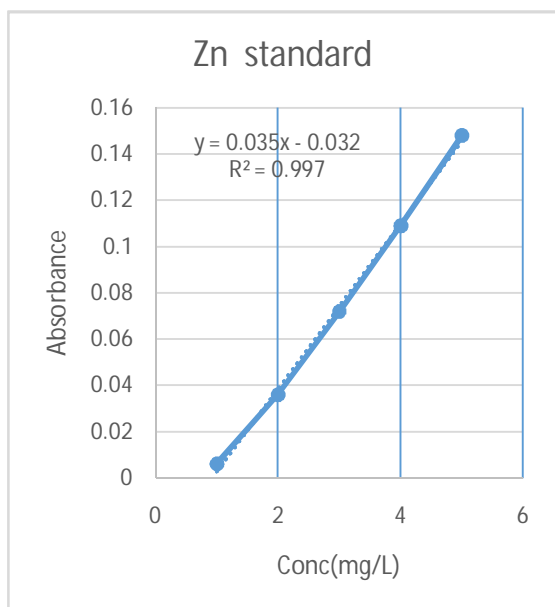
Appendix B

No	Metal	Data's of digestion absorbance of standards analyte (sample)										
		Absorbance of standards					Absorbance of sample			WAVE LENGTH		
							SNP				CURENT	ENERGY
		std 1	std 2	std 3	std 4	std 5	1	2	3			
1	Cr	0.003	0.008	0.013	0.017	0.022	0.008	0.007	0.007	357.9	5A	3.75
2	Mn	0.044	0.135	0.251	0.339	0.494	0.369	0.403	0.493	279.5	3A	3.885
3	Fe	0.17	0.19	0.21	0.23	0.25	0.598	0.607	0.616			
4	Cu	0.005	0.008	0.011	0.015	0.019	0.031	0.034	0.034	324.7	1.77A	3.18
5	Zn	0.006	0.036	0.072	0.109	0.148	0.353	0.331	0.313	213.9	2A	3.044
6	Cd	0.001	0.003	0.005	0.007	0.009	0.004	0.003	0.006	228.9	2A	3.126
7	Mg	0.137	0.152	0.163	0.173	0.183	0.269	0.285	0.281			

No	Metal	Absorbance of standards					Absorbance of sample			WAVE LENGTH		
							GUNA				CURENT	ENERGY
		std 1	std 2	std 3	std 4	std 5	1	2	3			
1	Cr	0.003	0.008	0.013	0.017	0.022	0.01	0.012	0.01	357.9	5A	3.75

No	Metal	Absorbance of standards					Absorbance of sample			WAVE LENGTH	CURENT	ENERGY
		std 1	std 2	std 3	std 4	std 5	1	2	3			
2	Mn	0.044	0.135	0.251	0.339	0.494	1.289	1.227	1.254	279.5	3A	3.885
3	Fe	0.17	0.19	0.21	0.23	0.25	0.631	0.627	0.632			
4	Cu	0.005	0.008	0.011	0.015	0.019	0.043	0.043	0.053	324.7	1.77A	3.18
5	Zn	0.006	0.036	0.072	0.109	0.148	0.691	0.743	0.743	213.9	2A	3.044
6	Cd	0.001	0.003	0.005	0.007	0.009	0.008	0.007	0.008	228.9	2A	3.126
7	Mg	0.137	0.152	0.163	0.173	0.183	0.27	0.267	0.27			

No	Metal	Absorbance of standards					Absorbance of sample CONTROL(GDC)			WAVE LENGTH		
											CURENT	ENERGY
		std 1	std 2	std 3	std 4	std 5	1	2	3			
1	Cr	0.003	0.008	0.013	0.017	0.022	0.015	0.016	0.016	357.9	5A	3.75
2	Mn	0.044	0.135	0.251	0.339	0.494	0.57	0.588	0.464	279.5	3A	3.885
3	Fe	0.17	0.19	0.21	0.23	0.25	0.63	0.631	0.621			
4	Cu	0.005	0.008	0.011	0.015	0.019	0.059	0.045	0.048	324.7	1.77A	3.18
5	Zn	0.006	0.036	0.072	0.109	0.148	0.269	0.296	0.259	213.9	2A	3.044
6	Cd	0.001	0.003	0.005	0.007	0.009	0.005	0.006	0.004	228.9	2A	3.126
7	Mg	0.137	0.152	0.163	0.173	0.183	0.339	0.332	0.329			

No	Metal	Absorbance of standards				Absorbance of sample	WAVE LENGTH				CURENT	ENERGY
							BLANK					
		std1	std2	std3	std4	std5	1	2	3			
1	Cr	0.003	0.008	0.013	0.017	0.022	0.002	0.001	0.002	357.9	5A	3.75
2	Mn	0.044	0.135	0.251	0.339	0.494	0.005	0.007	0.002	279.5	3A	3.885
3	Fe	0.17	0.19	0.21	0.23	0.25	0.06	0.109	0.092			
4	Cu	0.005	0.008	0.011	0.015	0.019	0.005	0.001	0.004	324.7	1.77A	3.18
5	Zn	0.006	0.036	0.072	0.109	0.148	0.085	0.109	0.092	213.9	2A	3.044
6	Cd	0.001	0.003	0.005	0.007	0.009	0.002	0.001	0.001	228.9	2A	3.126
7	Mg	0.137	0.152	0.163	0.173	0.183	0.156	0.152	0.145			

Amhara Design & Supervision Works Enterprise
Soil Chemistry and water quality section

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Soil Analyses of Laboratory Report
Client:- Shiferaw Desie (Gonder University)

Sr. No.	Lab. No.	Cleint Code	pH (H₂O) 1:2.5	EC dS/m	Texture			Class	CEC cmol(+)/kg	OC	TN	Fe	Zn	Cu	Mn
					%sand	% clay	% silt			%			ppm		
1	0230/17	Guna	4.83	0.136	40	12	48	Loam	51.2	5.07	0.25	29.1	2.06	0.05	3.25
2	0231/17	SNP	5.1	0.121	30	14	56	Silt Loam	33.2	5.46	0.27	29.6	1.12	0.04	1.816
3	0232/17	GDC	6.63	0.062	48	12	40	Loam	48.8	1.17	0.06	12.1	1.32	1.73	14.46

Name of Technician _Getaneh D._
Date _17/08/09_
Sign _____

Checked by _Hailu Cefalu_
date _17/08/2009_
sign _____

Approved by _Hailu Cefalu_
Date _17/08/2009_
sign _____