INTRODUCTION

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I-1. Soil Around Us

Soils were found from the time that the land was first colonized by living organisms where the multicelluler lands appeared in the Ordovician period about 450 million years ago, and trees have been developed by middle Devonian period about 370 million years ago. The soils similar to those of the present day have been found in sedimentary rocks from the Devonian and later geological periods.

Soils have so closed relationship of humankind, where people are dependent on soils and, conversely, good soils dependent on people and the use they make of the land. So the greatest civilizations have depended on good soils. The ancient dynasties of the Nile were made possible by the food- producing capacity of the fertile soils of the river valley and its irrigation systems. Soils are the natural bodies in which plants grow, they provide the starting points for successful agriculture, and the farmer earns living from the soil, and therefore this must be forced the humans to pay more attention to soils characteristics. To the farmer, soil is more than useful- it is indispensable.

Generally good soils helped to build flourishing civilization, also soil destruction was contributing factor in their downfall.

Today, many do not fully recognize the long term significance of soil. They are ignorant of what soils are, what they have meant to past generations, and what they mean today and to the future generations.

Soils are deposited materials consisting of organic matter in stages of decomposition, particulate in mineral matter and inorganic materials of biogenic origin. They have been proven an efficient tool to identify environmental impacts. Due to the exposure time to industrial effluents, they are valid for long-term studies. Soils constitute a pollutant trap and are an important factor to establish the assimilative capacity of the environment. Soils may contain a high level of pollutants ready to pass on to the food chain or be mobilized by anthropogenic or natural means. Therefore, soil

can act as indicators for the relationship between natural and anthropogenic variables.

I-2. The Soil

I-2-1. Definitions

Much of the problem in defining soil arises from the diversity of land surfaces. Some surfaces grow higher plants in great abundance, whereas others support no higher plants, only microorganisms. Also diverse are the people who work with soil, some of whom might describe it as a naturally occurring geologic medium or the Earth's ecosystem. According to the U.S Department of Agriculture (**USDA**), soil is "a natural medium for the growth of land plants", or more formally, soil is " a natural body comprised of solids, liquid, and gases that occurs on the land surface occupies space, and is characterized by one or both of the following:

i) Horizons or layers that are distinguishable from the initial material as a result of additions, losses, transfers and
ii) Transformations of energy and matter, or the ability to support rooted plants in a natural environment. The upper limit of soil is air, shallow water, or plants, the lower limit of biological activity, or a depth of 2m whichever comes first.

Using the formal (**USDA**) definition, soils do not cover all of the earth's land, Nonsoil land surface (i.e., surface that do not have horizons and will not grow plants) include the moving dunes. In contrast, an engineer might simply consider soil be material that can be excavated with a shovel. A more formal engineering definition of soil is "rock particles and minerals derived from preexisting rocks".

I-2-2. Components of soil

Mineral soils are composed of four major components: inorganic or mineral materials, organic matter, air and water, where air and water occupy pores between soil solids. The solid mineral particles comprise about 45% of the soil volume, organic matter 5%, about 25% of the volume being water space and 25% air. Soils whose properties are dominated by organic materials are termed

organic soils, they commonly contain more than 50% organic matter by volume.

The proportions of water and air are subjected to rapid and great fluctuation. The amount of air in soil pores varies inversely with the amount of water. In a wet soil the pores may be mostly water filled, but the water is replaced by air as the soil dries. The air in soil is typically lower in O_2 and higher in CO_2 than surface air because of the respiration of plant roots and millions of soil microorganisms. Water in soil is called the soil solution and contains dissolved ions and other substances, many of which are plant nutrients, whereas the solids in soils are mineral and organic substances. Usually minerals such as sand and clay dominate, with lesser amounts of organic particles called humus.

I-2-3. The Soil profile

A soil profile can be defined as "The vertical face of the soil that can be exposed". Soil solids are typically arranged in horizontal layers called horizons which are forming the soil profile. Because this pattern of horizontal soil layers was observed to be universal, the layers were named A, B and C.

- The A horizon is called surface soil. These few upper inches (several centimeters) of soil are usually enriched in organic matter because of the growing on the surface. How far this reason the A horizon is an eluvial horizon (eluvail = washed out an emigrant leaves a country). Because it is enriched in humus and low in soluble salts, the A horizon is the most favorable environment for plants. It is also the part of the soil susceptible to erosion loss.
- The B horizon lies below the A horizon. It may be lower in organic matter than the A horizon, but it is higher in the soluble or suspendible materials such as salts and clays that migrated downward out of the A horizon. The B horizon is an illuvial horizon (illuvial = washed in an immigrant enters a country).
- The C horizon lies below the B horizon. It is deep enough in the ground to be relatively unaffected by the migration of materials, because it is the materials in which the A and B

horizons developed, the mineral material in which soils from originated from the Earth's bedrock. Through various processes this solid rock became unconsolidated mineral particles. The upper part of this unconsolidated material becomes the A and B horizons. The lower part remains nearly unchanged.

Often the transition from one horizon to another is so gradual that establishing boundaries is difficult. The properties of soil horizons greatly influence the use that can and should be made of soils.

I-2-4. Mineral composition of soils

The rocks and minerals of the earth's crust provide the mineral constituents of soils. Minerals are inorganic (nonliving) substances that are homogeneous, have a definite composition and have characteristic physical properties such as shape, color, melting temperature, and hardness. Minerals may be either primary (formed by the cooling of molten rock) or secondary (precipitated or recrystallized from solutions that contained elements from dissolution of other minerals).

I-2-5. Topsoil and subsoil

When a soil is plowed and cultivated, the natural state of the upper 12-18 centimeters (5-7inches) is modified. This part is referred as the surface soil or the topsoil.

Topsoil or surface soil is the major zone of root development for crop plants. It contains many of the nutrients available to plants and supplies much of the water necessary for their growth. Through proper cultivation and the incorporation of organic residues, the topsoil can be kept loose and open to assure balanced air and water supplies for plant roots. It can be treated easily with commercial fertilizers and limestone permitting the soil's fertility, and to a lesser degree its productivity, to be raised or stabilized at levels consistent with economic crop production.

The subsoil is comprise of those soil layers underneath the topsoil. It is not seen from the surface and is not commonly

disturbed by soil tillage, but there are few land uses that are not influenced by subsoil characteristics. Certainly crop production is affected by root penetration into the subsoil and the reservoir of moisture and nutrients it present.

I-2-6. Soil classification

The soils are classified into 9 larger groups, based on the major factor that conditioned their formation:

1- Organic soils: *Histesols,* which are derived from incompletely decomposed plant remains, most of them formed in boreal regions.
2- Mineral soils: in which soil formation is conditioned by human influences: *Anthrosols,* which are derived from parent materials, modified by man through addition of materials from elsewhere.
3- Mineral soils: in which soil formation is conditioned by parent material: *Andosols - Arensols - Vertisols,* they occur in volcanic regions.
4- Mineral soils: in which soil formation is conditioned by topography / physiography: *Fluvisols - Gleysols – leptosols - Regosls,* They occur in alluvial deposits with shallow groundwater.
5- Mineral soils: in which soil formation is conditioned by limited age: *Cambisols,* They are characterized by the absence of appreciable amounts of organic matter, aluminum and / or iron.
6- Mineral soils: in which soil formation is conditioned by climate and vegetation: *Ferralsols – Nitisols - Acrisols – Alsols – Lixisols,* They are strongly acid soils with low base saturation.
7- Mineral soils: in which soil formation is conditioned by climate and vegetation of arid and semiarid regions: *Solonchaks – Solonetz - Gypsiols – Calcisols,* They are saline soils with high sodium saturation.
8- Mineral soils: in which soil formation is conditioned by climate and vegetation of steppes and steppic regions: *Kastanozems – chernozems – phaeozems – Greyzems,* They are dark brown soils high in organic matter derived from predominantly basic material.

9- Mineral soils: in which soil formation is conditioned by Climate and vegetation of subhumid forest and grassland regions: *luvisols – podzoluvisols – Planosols – prozols,* they are soils in which clay is washed down from the surface soil to an accumulation horizon at some depth.

I-2-7. Soil studies

There are two concepts of soil has evolved through two centuries of scientific study. One treats soils as a natural entity, a biochemically weathered and synthesized product of nature. The other treats soils as a natural habitat for plants and justifies soil studies primarily on that basis. These conceptions illusrate the two approaches that can be used in studying soils–that of the pedologist and that of the edaphologist.

The origin of the soil, its classification, and its description are examined in *pedology*. *pedology* (from the Greek word pedon, which means soil or earth) is the study of soil as natural body and does not focus primarily on the soil particle use. Pedologist studies, examines, and classifies soils as their natural environment. *Edaphology* (from the Greek word edaphos, which also means soil or ground) is the study of soil from the standpoint of higher plants. An edaphologists consider the various properties of soils in relation to plant production, and determine the reasons for the productively of soil.

I-3. Physical Properties of Soil

The physical properties of a soil are those characteristics which can be seen with the eye or felt between the thumb and fingers. They are the result of soil parent materials being acted upon by climatic factors (such as rainfall and temperature), and affected by topography (slope and direction, or aspect) and life forms (kind and amount, such as forest, grass, or soil animals) over a period of time. A change in any one of these influences usually results in a difference in the type of soil formed. The physical properties of soil are extremely important in determining how soils can and should be used. They concern not only soil solids but soil water and soil air. The physical properties ranged from the

properties that determine soil suitability for building, foundation, roadbed to its suitability for a production of different crop plants.

Economically we can rarely afford to make great changes in soil physical properties, but understanding the properties can improve our ability to mange soils. Physical properties concern not only soil solids, but also the soil air and water, where the most important physical properties of soil are density, texture, structure, soil air and color.

I-3-1. Density

Density can be defined as the mass of an object per unit volume and it is considered as specified characterize property. The soil density is an important physical property that affects both agricultural and engineering operations, the denser the soil, the less permeable the soil.

A dense, compacted soil inhibits plant growth, yet it provides the engineer and the architect with a strong support for building foundations. Soil mass exerts pressures on dams and tunnels and contributes to landslides.

The density of soil refers to the mass of soil per unit volume of soil **(Brady, 1990)**. It is a means of expressing the amount of soil, and its value depends partly on the minerals, organic matter content and on the amount of pore space or soil porosity. The mass of a given volume of soil can be expressed in terms of bulk and particle density.

I-3-1-1. Bulk density

Bulk density can be defined as the weight of soil per unit volume of undisturbed soil and the volume includes any airspace and organic materials and soil volume.

The bulk density volume is assumed not to have changed by drying only the water has been removed leaving empty pores. Bulk density is calculated for a dried soil, so water isn't included in the soil weight. The formula for determining the bulk density is as follows:

$$\text{Bulk density} = \frac{\text{Soil volume}}{\text{Dry soil weight}}$$

The unit of measurement of soil weight is gram and unit of volume is cubic centimeter, Hence the unit of bulk density is g / cc.

Range and significance of bulk density

Soils of low bulk density values (1-1.5 g/cc) generally indicate favorable physical condition for soils plant growth. This soil has a good structure and many pore spaces for optimum balance of air and water content in natural conditions. Low bulk density values are detected in surface soils which are high in organic matter content. While high bulk density values (1.8-2 g/cc) indicted a poor physical conditions of soils for plant growth. These soils are usually compacted and contain relatively few pore spaces. In general conditions high bulk density values are found in subsoil.

A soil in excellent conditions for plant growth should has a bulk density that is not low for adequate support, and also not to high for proper porosity and aeration. Unfortunately, because of the wide variety of soil textures and humus content, bulk density alone isn't an indication of soil suitability for plant growth, soil of different bulk density, because of different textures, may be equally good for pant growth. But generally, coarse textured soil exhibit higher bulk density values than do finer textures soils. Sands and sandy loam soils may vary in bulk density from 1.2 to 1.8 g/cc, whereas siltloam, clayloam and claysoils may have bulk density is ranging from (1.0 – 1.6 g/cc).

Bulk density values have various uses for examples, firstly density values are needed to calculate total water storage capacity per soil volume, secondly soil layers can be evaluated to determine if they are too compacted to allow root penetration or to provide adequate aeration.

I-3-2. Texture

Physically called soil separates, they are sands (the largest), silts and clays (the smallest). "The relative proportions of soil separates in a particular soil determine its soil texture".

Texture is an important soil characteristic because it greatly affects water intake rates (infiltration), water storage in the soil, the ease of tilling the soil, the amount of aeration (vital) to root growth and soil fertility. For instance a coarse sandy soil is easy to till, has plenty of aeration for good root growth, and is easily wetted – but it also dries rapidly and easily loses plant nutrients, which are drained away in percolating water. High – clay soils (more than 30 percent clay) have very small particles that fit closely together. Clays have few large pores which mean there are only tiny opening for water to flow into the soil. Small pores make high-clay soils difficult to wet, difficult to drain, and difficult to till.

I-3-2-1. Size of soil separates

The U.S. Department of Agriculture (**USDA**) has established size limits for the soil separates and has assigned a name to each size class as shown in Table 1.

Table 1: Size limits for the soil separates.

Soil separate name	Diameter range (mm)	Familiar size comparison
Very coarse sand	2.0 – 1.0	Thickness of coin.
Coarse sand	1.0 – 0.5	
Medium sand	0.5 – 0.25	Sugar or salt crystal.
Fine sand	0.25 – 0.10	
Very fine sand	0.10 – 0.05	Thickness of a book page.
Silt	0.05 – 0.002	
Clay	< 0.002	Smaller than bacteria.

I-3-2-2. Soil texture classes

Texture names are given to soils based on the relative proportions of each of the three soil separates: *sand, silt,* and *clay.* Soils that are predominantly clay are called *clay* (texture class), and those with high silt content are called *silt* (textural class), and those with a high sand percentage are called *sand* (textural class). A soil that does not exhibit the dominant physical properties of any of these three groups (such as a soil with 40 percent sand, 40 percent silt and 20 percent clay) is called *loam.* Note that loam does not

contain equal percentages of sand, silt, and clay, It does, however, exhibit properties of sand, silt, and clay.

The textural triangle Fig.1 is used to determine the soil textural name after the percentages of sand, silt, and clay are determined from a laboratory analysis.

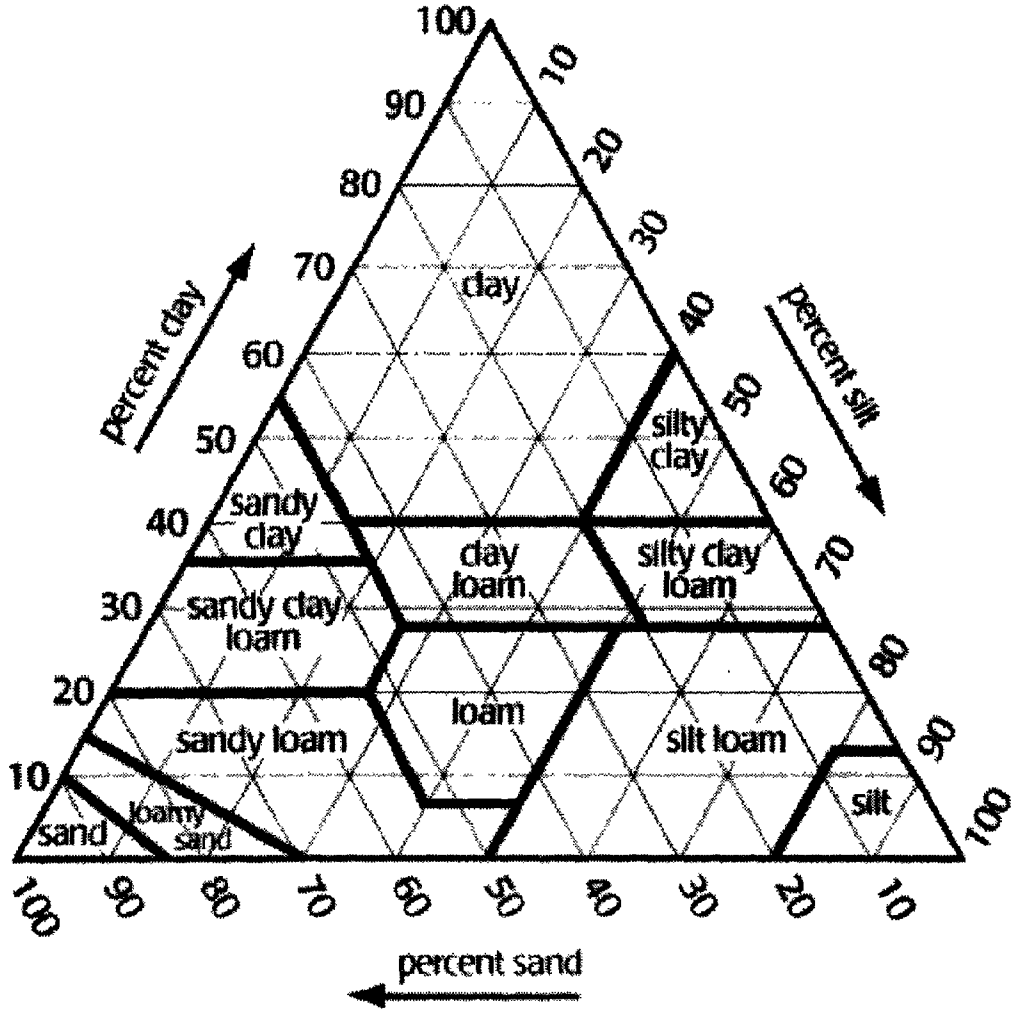


Fig. 1: The composition of textural classes of soil used by the United States Soil Survey.

Because the soil's textural classification includes only mineral particles and those of less than 2 mm diameter, the sum of percentages of sand, silt and clay equals 100 percent. Note that organic matter is not included in this percentage. Knowing the amount of any two percentages automatically fixes the percentage of the third. In reading the textural triangle, any two particle

fractions will locate the textural class at the point where those two and the third fraction intersect.

I-3-2-3. Particle–size (mechanical) Analysis

The procedure used to separate a soil into various size groups from the coarser sand, through silt, to the finest clay is *particle size analysis*, also called *mechanical analysis* for mechanical analysis the mineral matter less than 2 mm (0.08 inch) in diameter is considered separately from the larger particles. All rocks pebbles root and other rubble are removed (and measured) by screening the finer soil parts through a 2 mm sieve before analysis humus are removed from the soil sample by destroying it with an oxidizing chemical (such as hydrogen peroxide) before particle size separation is done. Routine (approximate) textural values are usually obtained without removal of organic matter.

I-3-3. Structure

Structure is "the arrangement of soil particles into aggregates". Aggregates are secondary units or granules composed of many soil particles held together by organic substances, iron oxides, carbonates, clays and/or silica. Natural aggregates are called ***peds*** and it varies in their water stability. A soil profile may be dominated by a single type of structure, however several types could be encountering different horizons.

I-3-3-1. Soil structural classes

Soil structural units (peds) are described by three characteristics: ***class*** (size), and ***grade*** (strength of cohesion), ***shape*** (type).

A - Structure classes: are the ped sizes such as very fine, fine, medium, coarse (or thick) and very coarse (or very thick).

B - structure grades: are evaluated by the distinctness, stability, and strength of the peds, and divided into:

1-structured: The following structural grades are used to describe it:

Weak: Peds are barely distinguishable in part of the moist soil, only a few distinct peds can be separated.
Moderate: Peds are visible in place, many can be handled without breaking.
Strong: Most of the soil mass is visible as peds, most of which can be handled with ease without breaking.
2-Structureless: The soils which have no noticeable peds, It might be an unconsolidated mass such as noncoherent sand called *single grain* or it might be a cohesive mass, such as could occur in some loams or clayey soils, called *massive*.

C-structure shape: There are four major types of shape:
1-Spheroid (granular and crumb subtypes): Rounded peds or aggregates are placed in this category. They usually lie loosely and are separated from each other. Relatively nonporous aggregates.
2-Plate – like (platy): In this structural type the aggregates (peds) are arranged in relatively thin horizontal plates leaflets or lenses, platy structure is found in the surface layers of some Virgin soils but may characterize the lower horizons as well.
3-Prism – like (columnar and prismatic subtypes): These subtypes are characterized by vertically oriented aggregates or pillars that vary in height with different soils and may reach a diameter of 15 cm or more. Prism- like structures usually occur in subsurface horizons in arid and semiarid regions.
4-Block – like (blocky and sub angular blocky subtypes): In this case the aggregates have been reduced to blocks, irregularly six – faced, with their three dimensions more or less equal. These fragments range from about 1 to 10 cm in thickness. In general, the design is so individualistic that identification is easy. The block – like is usually confined to subsoil.

Soil structure may exist as a compound structure in which large peds such as prisms or blocks may further fall apart into smaller blocks or smaller peds. Soil structure influences many

important properties of the soil, such as the rate of infiltration of water and air. Both spheroidal and structureless soils have rapid infiltration, while blocky and prismatic soils have moderate rates, in the case of platy and massive soils have slow infiltration rates.

I-3-4. Soil air

To survive, all living organisms require gaseous exchange, usually free oxygen (O_2). In soil, plant roots require (O_2) for respiration and microorganisms need it for organic matter decomposition. The desired condition for growth of most plants is well – aerated soil, a condition in which oxygen exchange between soil air and atmospheric air is rapid. Factors that influence the rate of gaseous exchange include soil pore sizes and continuity, temperature, depth in the soil, wetting and drying of soil, and coverings (mulches) on the soil surface.

I-3-4-1. Composition of soil air

The atmospheric air has approximately the following composition of the gases that are also important in soils:

Nitrogen (N_2) = 79 %.
Oxygen (O_2) = 20.9 %.
Carbon dioxide (CO_2) = 0.035 %.
Water vapor (expressed as relative humidity) = 20 – 90 %.

Because O_2 required in respiration and for organic material decomposition, soil air is different from atmospheric air. Some O_2 is used and considerable CO_2 is produced. The differences are as follows:

Soil air	*Surface soil%*	*Subsoil %*
Higher in carbon dioxide	0.5 – 6	3-10
Lower in oxygen	14 – 20.6	7- 18
Higher in relative humidity	95 – 100	98- 100

I-3-4-2. Rates of oxygen exchanged

The oxygen diffusion rate (***ODR***) is "The rate at which the oxygen in the soil is exchanging with oxygen in the atmosphere". Many large soil pores allow rapid air exchange (diffusion), small pores or pores with bottleneck portions filled with water decrease

exchange rates. Diffusion of CO_2 gas through water is about 10,000 times slower than through air–filled pores. At a depth of 1 m (39 inch) in the soil, the exchange rate may be only one – half to one – fourth as fast as in the top few centimeters.

Therefore, it is easy to visualize reduced root growth occurring in deep clayey subsoil when they are wet because the water–filled portions of pores would block oxygen diffusion further. The small pores of clays usually have a slow **(ODR)**.

I-3-5. Soil color

When soil is examined, color is one of the first things noticed. It indicates extremely important soil conditions. In general, color is determined by: (1) organic matter content, (2) drainage conditions, and (3) degree of oxidation (extent of weathering).

Surface soil colors vary from almost white, through shades of brown and gray, to black. Light colors indicate a low organic matter content and dark colors can indicate a high content. Light or pale colors in the surface soil are frequently associated with relatively coarse texture, highly leached conditions, and high annual temperatures. Dark colors may result from high water table conditions (poor drainage), low annual temperatures, or other conditions that induce high organic matter content and, at the same time, slow the oxidation of organic materials. However, soil coloration may be due to the colors imparted by the parent material. Shades of red or yellow, particularly where associated with relatively fine textures, usually indicate that subsoil material has been incorporated in the surface layer.

Subsoil colors, in general, are indications of air, water, and soil relationships and the degree of oxidation of certain minerals in the soil. Red and brown subsoil colors indicate relatively free movement of air and water allowed by the soil. If these or other bright colors persist throughout the subsoil, aeration is favorable. Some subsoils that are mottled (have mixed colors), especially in shades of red and brown, are also well-aerated.

Yellow-colored subsoils usually indicate some drainage impediment. Most mottled subsoils, especially those where gray

predominates, have too much water and too little air (oxygen) much of the time. The red-to-brown color of subsoils comes from iron coatings under well-aerated conditions. In wet soils with low oxygen levels, the iron coatings are chemically and biologically removed, and the gray color of background soil minerals shows.

I-4. Chemical Properties of Soil

I-4-1. Total elements

A logical starting point for examining chemical properties of soils is to look at a total analysis of the elements. The major and some minor elements ranges and their values present in the mineral portion of soils are listed in Table 2.

Table 2: The ranges of values for major and minor element composition of the mineral component of soils.

Major elements, %		Minor elements, ppm	
Si	30-45	Zn	10-250
Al	2.4-7.4	Cu	5-15
Fe	1.2 –4.3	Ni	20-30
Ti	0.3-0.7	Mn	400
Ca	0.01-3.9	Co	1-20
Mg	0.01-1.6	Cr	10-50
K	0.2-2.5	Pb	1-50
Na	trace – 1.5	As	1-20

The Chemical composition is determined by the nature of the starting materials from which the soil was formed and by the processes that it has undergone over time. The compositional data are not particularly useful because they don't indicate whether the element are found as a component of the mineral lattice or are associated with surface adsorption phenomena.

I-4-2. Soil pH

Soil pH means the pH of water in equilibrium with soil and it measures the degree of acidity or alkalinity in soils. Also pH known as soil reaction, and is determined by the hydrogen ion (H^+)

concentration in the soil solution. An acid soil has more (H^+) than (OH^-) ions, whereas a basic or alkaline soil contains more (OH^-) more than (H^+) ions. To characterize these conditions, the term soil pH was introduced by Sőrensen in 1909 **(Tan, 1982)** and is calculated by the following equation:

$$pH = - \log (H^+)$$

In this equation, p refers to the negative logarithm and (H^+) to the free (H^+)ion concentration. The unit of (H^+) is measured in activity or in moles/L activity, also known as the effective concentration, is that the part of the actual (H^+) ion concentration which participates in chemical reactions.

The mass action law states that the product of the concentration of (H^+) and (OH^-) ions is always constant. This law may be written as an equation:

$$(H^+)\,(OH^-) = 10^{-14}$$

By taking the negative logarithms on both sides, the equation becomes:

$$pH + pOH = 14$$

Since the sum of pH and pOH is constant, the concentration of (H^+) and (OH^-) ions are interrelated, and vary inversely. Thus only one ion, needs to be determined, the (H^+) ion, in order to know the other (OH^-).

I-4-2-1. Soil pH potential and total acidity

The (H^+) ions may be present in soils as adsorbed (H^+) ions on the surface of the colloidal complex, or as free (H^+) ions in the soil solution. The adsorbed (H^+) ions create the reserve acidity, also called the potential or exchange acidity of soils. The free (H^+) ions are the reason for the so–called active acidity. Taken together, the active plus potential acidities are called the total acidity.

I-4-2-2. The pH scale

From pH 7 to 0 the soil is increasingly more acidic and from pH 7 to 14 the soil is increasingly more alkaline or basic. Descriptive terms commonly associated with certain ranges in soil pH are shown in Table 3.

Table 3: Descriptive terms commonly associated with certain ranges in soil pH and familiar products.

Descriptive term	pH range	Familiar products
Extremely acid	< than 4.50	stomach acid=2.0 ; soda=2-4 and lemon=2.5.
Very strongly acid	4.50–5.09	tomatoes=4.5 and beer=4.5–5.0.
Strongly acid	5.10–5.59	carrots=5.0 ; cabbage=5 ; boric acid=5.2 and asparagus=5.5.
Moderately acid	5.60–6.09	potatoes=5.6
Slightly acid	6.10–6.59	salmon=6.2 and cow's milk=6.5
Neutral	6.60–7.39	Saliva=6.6–7.3; shrimp=7.0 and blood=7.3.
Slightly alkaline	7.40–7.89	eggs=7.6–7.8
Moderately alkaline	7.90–8.49	sea water=8.2 and sodium bicarbonate=8.4
Strongly alkaline	8.50–9.09	borax=9.0
Very strongly alkaline	> than 9.10	milk of magnesia=10.5 ; ammonia=11.1 and lime=1

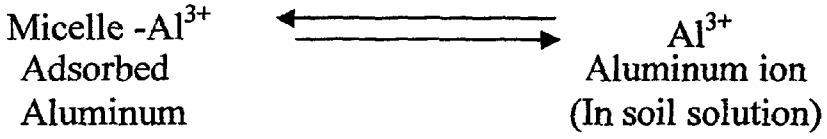
The measurement scale is not a linear scale but a logarithmic scale. That is, a soil with a pH of 8.5 is ten times more alkaline than a soil with a pH of 7.5 and a soil with a pH of 6.5 is a hundred times more acid than a soil with a pH of 8.5. The pH condition of soil is one of a number of environmental conditions that affect the quality of plant growth. A near-neutral or slightly acidic soil is generally considered ideal for most plants. Some types of plant growth can occur anywhere in a 3.5 to 10.0 range. With some notable exceptions, a soil pH of 6.0 to 7.0 requires no special cultural practices to improve plant growth.

I-4-2-3. Soil acidity

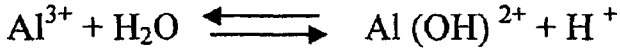
Two adsorbed cations (hydrogen and aluminum) are largely responsible for soil acidity. The properties of aluminum are central to an understanding of soil acidity, gibbsite and Kaolinite are the source of aluminum in mineral soils. The mechanisms by which these two cations exert their influence depends on the degree of soil acidity and on the source and nature of the soil colloids.

Strong acid soils

Under very acid conditions (pH less than 5.0) much aluminum ions becomes soluble and is either tightly bound by organic matter or is present in the form of aluminum or aluminum hydroxy cations. These exchangeable ions are adsorbed in preference to other cations by the negative charges of soil colloids which at low pH values are dominantly permanent charges. The adsorbed aluminum is in equilibrium with aluminum ions in the soil solution, and aluminum ions contribute to soil acidity through their tendency to hydrolyze. Two simplified reactions illustrate how adsorbed aluminum can increase acidity in the soil solution.



The aluminum[3] ions in the soil solution are then hydrolyzed.



The (H^+) ions thus released lower the pH of the soil solution and are the major source of hydrogen in most very acid soils.

Adsorbed hydrogen ions are a second source of acid acidity but much more limited source of (H^+) in very acid soils. As a soil becomes more acidic (pH becomes lower), more soluble aluminum is available for absorption by plants. The more aluminum that is absorbed, the greater is its toxic effect and greater will be the reduction in root growth of many plants. Thus, it can be seen that both adsorbed hydrogen and aluminum ions are responsible for increasing the (H^+) ion concentration in the soil solution.

Iron is also solubilized under acid conditions and forms hydroxy cations just as does aluminum. However, since the acidity generated by iron much less than that generated by aluminum, only the aluminum involvement will be considered.

Factors affecting the soil acidity

There are many factors affecting the soil acidity, the most important factors are:

1) Rainwater leaching away basic ions (calcium, magnesium, potassium and sodium).
2) Carbon dioxide from decomposing organic matter and root respiration dissolving in soil water to form a weak organic acid.
3) Formation of strong organic and inorganic acids, such as nitric and sulfuric acid, from decaying organic matter and oxidation of ammonium and sulfur fertilizers. Strongly acid soils are usually the result of the action of these strong organic and inorganic acids.

Lime is usually added to acid soils to increase soil pH. The addition of lime not only replaces hydrogen ions and raises soil pH, thereby eliminating most major problems associated with acid soils but it also provides two nutrients, calcium and magnesium to the soil. Lime also makes phosphorus that is added to the soil more available for plant growth and increases the availability of nitrogen by hastening the decomposition of organic matter. Liming materials are relatively inexpensive, comparatively mild to handle and leave no objectionable residues in the soil. Calcic limestone which is ground limestone, dolomitic limestone from ground limestone high in magnesium, and miscellaneous sources such as wood ashes are considered some of the liming materials.

The amount of lime applied to correct a soil acidity problem is affected by a number of factors, including soil pH, texture (amount of sand, silt and clay), structure, and amount of organic matter. In addition to soil variables, the crops or plants to be grown influence the amount of lime needed.

Neutral to alkaline soils

Soils that are neutral to alkaline are not dominated by either hydrogen or aluminum ions. The permanent charge exchange sites are now occupied mostly by exchangeable Ca^{2+}, Mg^{2+} and other base – forming cations, both the hydrogen and aluminum hydroxy ions have been largely replaced. Most of the aluminum hydroxy ions have been converted to gibbsite by reactions such as:

$$Al(OH)_2^+ + OH^- \rightleftharpoons Al(OH)_3$$

Gibbsite (insoluble)

More of the pH dependent charges have become available for cation exchange, and the (H^+) ions released therefore move into the soil solution and react with (OH^-) ions to form water. The place of hydrogen on the exchange complex is taken by Ca^{2+}, Mg^{2+} and other base – forming cations.

Soil basicity, which is more difficult to alter than soil acidity, may be just as undesirable for plants. None leached soils or those high in calcium, (low rainfall areas) may have pH values near 8.5, with increased exchangeable sodium, and soils may reach values of over pH 10. Plants on soils of pH greater than about 9 usually have reduced growth or even die. However some plants (halophytes) are tolerant of high pH and / or salt.

For a soil to have a pH above 7, it must either be calcareous contain calcite ($CaCO_3$), dolomitic contain dolomite, ($CaCO3.MgCO3$) or sodic (Na_2CO_3). The soil becomes more alkaline (pH 7-8.5), the concentration of (OH^-) increases with associated increases in the bicarbonate which become the dominate anion.

In calcareous soils, calcite has a low solubility, but its reaction with water control the soil pH as given below;

$$CaCO_{3(S)} \rightleftharpoons Ca^{2+}_{(aqu)} + CO_3^{2-}_{(aqu)}$$

$$H_2O + CO_3^{2-}_{(aqu)} \rightleftharpoons HCO_3^-_{(aqu)} + OH^-_{(aqu)}$$

(s) means solid, (aqu) means aqueous

In sodic soils, Na_2CO_3 react with water and rise the pH to give a value up to 10.5. The major effect of a basic pH is to reduce the solubility of iron, zinc, copper, and manganese. Also, phosphate

is often not readily available to some plants because of its precipitation in the soil solution by calcium or precipitation on solid calcium carbonates. Solutions of high pH have low solubilities of iron, zinc, manganese, and copper.

Importance of soil pH

Soil pH is easily determined and provides various clues about other soil properties. It greatly affects the solubility of minerals. Strongly acidic soils (pH 4 to 5) usually dissolve high, even toxic concentrations of soluble aluminum and manganese. The effect of soil pH is great on the solubility of minerals or nutrients. Fourteen of the seventeen essential plant nutrients are obtained from the soil. Before a nutrient can be used by plants it must be dissolved in the soil solution. Most minerals and nutrients are more soluble or available in acid soils than in neutral or slightly alkaline soils.

Phosphorus is never readily soluble in the soil but is most available in soil with a pH range centered around 6.50. Extremely and strongly acid soils (pH 4.0-5.0) can have high concentrations of soluble aluminum, iron and manganese which may be toxic to the growth of some plants. A pH range of approximately 6.0 to 7.0 promotes the most ready availability of plant nutrients.

Soil pH influences plant growth by its effect on activity of beneicial microorganisms. Most nitrogen–fixing legume bacteria are not very active in strongly acidic soils. Bacteria that decompose soil organic matter, releasing nitrogen and other nutrients for plant use, are hindered by strong acidity. Fungi usually tolerate strong acidity better than do other microbes. Because of the above, **(Jackson, 1973)** the soil pH may be the most important soil chemical property.

I-4-3. Cation exchange

Soils contain clay minerals and organic matter, and because of their structure and chemical composition, the clay minerals and humus usually bear a negative charge. The humus (organic matter) is a temporary intermediate product left after considerable decomposition of plant and animal remains- temporary because the organic substances continue to decompose slowly-humus is an

organic colloid. It consists of various chains and rings of linked carbon atoms. Humus has a negative charge, and it comes from the ionization of hydrogen from R-OH groups. Acids and other functional groups on these large organic molecules release (H^+) ions, leaving a negative charge site where the (H^+) had been. While the negative charge on clay minerals due to isomorphous substitution and at the broken surface and edges of clay minerals.

The soil colloids usually have a negative charge, this negative charge will attract and hold positive charge ions (cations) to their surface. Other cations in the soil solution that approach and held cation might be able to replace it, then exchanging it. This replacement of one adsorbed cation by another cation in soil solution called *cation exchange.* In saline soils, the amounts of sodium exchanged are increasing. The cations commonly held in this way are calcium, magnesium, potassium and ammonium.

The adsorbed cations resist removal by leaching water but can be replaced (exchanged)by other cations in solution. However for every cation that adsorbs, the cation originally on that site moves out into the solution as it is replaced.

I-4-3-1. Factors increasing the adsorption strength

1- The valence of the cation increases.
2- The cations hydrated size is smaller.
3- The strength of the sites negative charges increases.

Thus the adsorptions strength of cations increases in approximately the following order:

$$Na^+ < K^+ = NH_4^+ < Mg^{2+} = Ca^{2+} < Al(OH)_2^+ < H^+$$

Whereas the cation exchange reaction characterized by that it is rapid, it is reversible and exchange of equal cations (mole/valency). The most numerous cations on exchange sites in soils are calcium, magnesium, hydrogen, sodium, potassium and aluminum. The proportions of these cations on the colloid surface are constantly changing as ions are added from dissolving minerals or by adding of lime or fertilizer. Thus when potassium fertilizer with its cation K^+ is added to the soil many of numerous potassium ions replace other cations already adsorbed to exchange sites.

Liming the soil to correct the acidity is a cation exchange reaction. When the lime is added to neutralize acidic soils, most of exchangeable (H^+) and $Al(OH)_2^+$ are neutralized to alter the soil pH. The amount of lime required for neutralization is determined directly or indirectly by the amount of exchangeable (H^+) and $Al(OH)_2^+$ that must be replaced by calcium or other cations.

I-4-3-2. Importance of cation exchange

Cation exchange is very important in soil because of the following:

1-The exchangeable K, Mg and Ca are a major source of plant K, Mg and Ca.

2-The amount of lime required to raise the pH of an acidic soil increases as the cation exchange capacity (**CEC**) increases.

3-Cation exchange sites hold Ca^{2+}, Mg^{2+}, Na^{2+}, and NH_4^+ ions and slow their losses by leaching.

4-Cation exchange sites hold fertilizer K^+ and NH_4^+ and greatly reduce their mobility in soils.

I-4-4. Cation exchange capacity

Cation exchange capacity *(CEC)* is defined as the quantity of exchangeable cation sites per unit weight of dry soil sample. It is measured in centimoles of cations per kilogram of dry soil (cmol/kg) or milliequvalent per 100 gram of soil (mEq / 100 g).

$$CEC=\sum \text{exchangeable cations (mEq)/100g soil}$$

The CEC is a quantitative measure of all cations adsorbed on the surface of the soil colloids. And it is a function in the surface area and the negative charge on the surface.

Types of CEC

Because of the difference in the presence of permanent and variable charges contributing to cation exchange reaction, several types of CEC have been identified:

1-**CEC**: where the CEC is obtained by the NH_4OAC method

2-**(ECE_C)** Effective CEC: which is equals to the exchangeable bases
3-**CEC_p**: which is the permanent CEC produced by negative charge of clay minerals.
4-**CEC_t**: which is the total CEC caused by both permanent and variable charges of soil colloids.

The CEC of a soil changes with a change in the soil pH (acidity or basicity). In acidic solutions {high (H^+) concentration}, fewer (H^+) ions ionize off the R-OH, While in the basic solution fewer (H^+) are in solution, and more (R-OH) sites are ionize to ($R\text{-}O^-$), which becomes a cation exchange site. Thus the CEC is measured at a standard pH usually at 7.

I-4-5. Soil organic matter

Soil organic matter is by definition the organic fraction derived from living organisms. It includes the living organisms, partly decomposed and decomposed plant and animal residue. The decomposed organic fraction is usually called "Humus". It is composed of nonhmic substances, and humic substances. The nonhumic substances include carbohydrates, amino acids, lipids, lignins, all of which are the metabolic products of organisms. On the other hand, humic substances, such as fluvic acids, humic acids, and humin, which are brown to black in color, they are high molecular weight compounds that are synthesized by soil microorganisms. These substances can differentiate by difference in solubility as shown in Table 4.

Table 4: Major types of humic substances differentiated by differences in solubility.

Type of humic matter	In Alkali	In acid	In water
Fluvic acid	Soluble	Soluble	Soluble
Humic acid	Soluble	Insoluble	Insoluble
Humin	Insoluble	Insoluble	Insoluble

Approximately 50 % to 85 % of the total organic composed of humic matter while the remaining 50 to 15 % consists of nonhumic matter **(Davis, 1984)**.

This organic fraction of the soil is constantly undergoing physical and chemical changes as a result of decompositions and mineralization processes. The end result of these processes is the production of CO_2, H_2O nutrients, and inorganic and organic acids.

On weight basis, the dry matter is mostly carbon and oxygen, with less than 10 % each of hydrogen and inorganic elements (ash), while, on an elemental basis (number of atoms of the elements) hydrogen is predominates. In representative plant residues there are 8 hydrogen atoms for every 3.7 carbon atoms and 2.5 oxygen atoms. These three elements dominate the bulk of organic tissue in the soil. The other elements are present only in small quantities, and they are playing a vital role in plant nutrition and in meeting microorganism body requirements. These elements include nitrogen, phosphorus, potassium, calcium and magnesium.

I-4-5-1. General composition of organic compounds

The dry matter consists of carbohydrates, fats and oils, lignins, and proteins. The carbohydrates, which range in complexity from simple sugars and starches to cellulose, are usually the most prominent of the organic compounds found in plants, lignins, which are complex compounds with "ring" type structures, are found in older plant tissue and especially woody tissues, and they are very resistant to decomposition. Fats and oils, which are somewhat more complex than carbohydrates and less, so than lignins, are found primarily in seeds.

Proteins contain – in addition to carbon, oxygen, and hydrogen–nitrogen and smaller amounts of other essential elements such as sulfur, manganese, copper and iron. Proteins are primary sources of these essential elements. The simple proteins are decomposed easily while the more complex crude proteins are resistant to break down.

I-4-5-2. Decomposition of organic compounds

Decomposition is an oxidation process. In a well–aerated soil, all of the organic compounds found in plant residues are subject to oxidation. Since the oxidizable fraction of plant materials

is composed largely of carbon and hydrogen, the oxidation of the organic compounds in soil may be represented as follows:

$$\underset{\text{Carbon and hydrogen containing compounds}}{(C, 4H)} + 2O_2 \xrightarrow[\text{Oxidation}]{\text{Enzymatic}} CO_2 + 2H_2O + \text{Energy}$$

Many intermediate steps are involved in this overall reaction, and it is accompanied by important side reactions that involve elements other than carbon and hydrogen. Even so, this reaction accounts for most of the decomposition of organic matter in the soil as well as the oxygen consumption and release of carbon dioxide.

I-4-5-3. Rate of decomposition

Organic compounds vary greatly in their rate of decomposition. They may be listed in terms of ease of decomposition as follows:

1- Sugars and starches ⟶ Rapid decomposition
2- Crude proteins
3- Cellulose
4- Fats waxes
5- Lignins ⟶ Very slow decomposition

All organic compounds usually begin to decompose simultaneously when fresh plant tissue is added to a soil. The sugars and simple proteins decompose most readily, at the other extreme, lignins are the most resistant to breakdown.

When organic tissue is added to soil, three general reactions take place, The first is that the bulk of the material undergoes enzymatic oxidation with carbon dioxide, water, energy, and heat as the major products. The second is that the essential elements such as nitrogen, phosphorus, and sulfur are released and / or immobilized by a series of specific reaction relatively unique for each element, while the third is for the compounds of high resistant to microbial action which are formed either through modification

of compounds in the original plant tissue or by microbial synthesis **(Tan, 2003)**.

I-4-5-4. Significance of soil organic matter

Notwithstanding its low content, organic matter is a very important soil constituent. It affects the physical, chemical and biological properties of soil. From the standing point of the physical properties, organic matter increase the water holding capacity of soils and promotes the development of stable soil structures by increasing granulation. Chemically it is a source of nutrients for plants, especially of N and S, in soils. The total N content is found to be a function of soil organic matter content. Biologically organic matter is the source of food and energy for microorganisms. These organisms are vital to the many biochemical reactions in soils m such as ammonification, nitrification, N- fixation, and nutrient cycling. Upon decomposition of organic matter, inorganic nutrientsin the plant issue, N, P, K, Mg, Cu and Mn, etc, are released into the soil. At the same time humus is formed, which increase the cation exchange capacity of soil.

I-5. Oil Pollution in Soil

Three major types of hydrocarbons are generally found in the environment (1) Petrogenic i.e. crude oil and its refined products, (2) Biogenic i.e. hydrocarbons generated by biological processes or in the early stages of diagnoses in soils and (3) Pyrogenic i.e. compounds generated in combustion processes. Of all pollutants, petroleum hydrocarbons have received the greatest attention internationally, politically and scientifically due to the negative impact of such materials on human health and the environment.

Oil pollution problems occurs everyday worldwide causing a severe global environmental problems. Egypt is suffering from oil pollution owing to the increasing petroleum activities in the last decades. Environmental protection is currently an important subject of increasing public and research concern, and as a result, special efforts have already been done so as to develop oil spill detection and fingerprinting. Prior to the 1960s, most work conducted in

organic geochemistry and petroleum chemistry focused on the exploration for fossil fuels. Petroleum chemistry and hydrocarbon fingerprinting developed further in the 1970s with the passage of certain environmental regulations in the US (e.g. the Clean Water Act). The US Coast Guard used some of the earliest techniques to fingerprint oil slicks following methods that had been used earlier to examine the alkane distribution of fresh oils through gas chromatographic analyses.

The need to analyze for petroleum hydrocarbons in contaminated soils may arise for different reasons, (a) Because of the desire to establish the nature and the level of oil polluting the studied area, (b) To assess the effect of the different petroleum activities on the surrounding soil environment, (c) To know how wide spread is the oil and to what extent it has affected soil properties. (d) It can provide the result of atmospheric fallout over time.

Despite the recent rapid advances in analytical technology and in understanding of the environmental fields, oil spill identification still needs more efforts **(Wang and Fingas, 2003).** No single technique can sufficiently quantify all the crude oil and its products components polluting the environment since they are extremely complex and variable mixture of chemical compounds, mostly organic **(Kathryn, 1993).** The choice of specific technique from among the multiplicity of analytical procedures depends on many factors such as sampling methods, personal analytical performance, the aim of analysis and perhaps most important, the availability of instrumentation. Developments of chemical fingerprinting strategies are useful for future spills and release.

Oil spills cause extensive damage to terrestrial life, marine life, human health and natural resources. Characterization of spilled oils and to linking them to known sources is extremely important for environmental damage assessment, understanding the fate and behavior and predicting the potential long–term impact of the spilled oils on the environment, selecting appropriate spill response and taking effective clean-up measures. The chemical fingerprinting of petroleum is made possible by the multitude of individual present hydrocarbon compounds that are present and by the great variability in the relative abundance of these compounds

among different crude oils or between crude oils and their refined products. This variability, which is the basis for chemical fingerprinting, is due to the variability in the organisms contributing to the organic matter, the environment in which this organic material was deposited, the thermal maturation history of the soils, and post-generation modifications.

Successful forensic investigation and analysis of oil and refined product hydrocarbons in contaminated sites and receptors yield a wealth of chemical fingerprinting data. These data, in combination with historic, geological, environmental, and any other related information on the contaminated site can, in many cases, help to settle legal liability and support litigation against the spillers.

Advances in both interpretive and analytical methods over the past 10 years indicated that there was a need for further improvements to the existing methodologies. It was anticipated that various technical refinements would lead to a more quantifiable, objective and defensible means to differentiate among qualitatively similar oils from a spill and any available candidate sources.

Soils are often the best available medium for long term monitoring of many contaminants. The needs to measure the petroleum hydrocarbons in soils are of great importance for soils **(Lee et al., 1988).** Petroleum substances or their metabolities are persistent, bioaccumulable, toxic and some are carcinogenic. Therefore, characterization of soil contamination is environmentally significant in terms of assessing oil pollution status.

The fate and behavior of spilled oils in the environment depends on a number of physicochemical and biological factors including evaporation, dissolution, photo-oxidation, microbial degradation and interaction between oil and soils. Petroleum hydrocarbons entering the environment have different ultimate fates, biochemical or chemical alteration to non hydrocarbon molecules, and / or deposition to surface soils (where further biochemical or chemical alteration takes place). Hydrocarbons are more likely to accumulate in soils causing a massive kill to benthic organisms or bottom community in the soil system. Knowledge of

the hydrocarbon types and concentrations in soil samples can be used to detect possible effects in the soil environment.

I-5-1. Hydrocarbons in soil

Hydrocarbons are common contaminants found in soil and groundwater as a result of past and current industrial activity. The greatest concern regarding the contamination by hydrocarbons lies in the mutagenic, carcinogenic and toxic characteristics of such contaminants. The extent of environmental contamination depends on the chemical composition and concentration of the contaminant and the properties of the soil. In general, the presence of high molecular weight compounds characterized by very low solubility in water hinders the natural biodegradation for soils contaminated by hydrocarbons **(Caravaca and Roldán, 2003).**

For soils from semiarid Mediterranean regions, their low organic matter contents can directly affect sorption of hydrocarbons by the soil and indirectly affect biodegradation of hydrocarbons. The contamination of soils by hydrocarbons may induce changes in the physical condition and biological activity of the soil, and prior knowledge of these processes is considered necessary in order to choose and develop the most suitable methodology for remediation of contaminated soils. Thus, for example, measurements of soil porosity and texture are a prerequisite for applying methods of bioremediation **(Morgan and Watkinson, 1989).** However, few studies have examined the effect of contamination by hydrocarbons on soil structure in semiarid environments. The quantification of soil porosity and pore size distribution is essential for characterization of soil structure. These parameters are closely related to storage and movement of water and gases, and to the ease of root penetration. The micromorphometric method, based on image analysis of soil thin-sections, supplies useful information about the complexity of pore patterns in soil, the pore shape and the relative positions of the aggregates and pores **(Sartori et al., 1985).**

Biological and biochemical properties, including soil respiration measured by the rate of CO_2 released or O_2 consumption, microbial biomass and the activities of soil enzymes, are considered to be sensitive indicators of contamination because

of their importance in cycling of organic matter and regulating active nutrient pools in soils. Contaminated soils are a system of great complexity and the behavior of many enzymatic activities in such soils may be very variable, which has thrown doubts on the possibility of their use as reliable indicators of soil contamination. Hence, the quantification of soil contamination may require the combined determination of several biochemical soil properties. This information would help to predict the rate and extent of intrinsic bioremediation of the contaminated soil **(Morgan and Watkinson, 1989).** It was found that the contamination by hydrocarbons increased biochemical and microbial activities and improved soil structure. However, the rate of mineralization of the pollutant was low which possibly due to the high chemical complexity of hydrocarbons that would require long periods of time to degrade.

I-6. Fingerprinting Techniques of Hydrocarbons Pollutants

Chemical fingerprinting is the application of analytical chemistry to identify the sources of complex environmental pollutants, including petroleum **(Boehm et al., 1997).** Petroleum is a complex mixture of gaseous, liquid and solid organic compounds. It contains thousands of different organic compounds. For environmental scientists, chemical fingerprinting is an important component of oil spill investigations and site assessments and often supports in determining responsibility of pollution **(Boehm et al., 1997).** As enforcement of oil spill and other pollution laws increases, so has the need to determine the fair share of responsible parties for clean up and remediation. Part of these needs stems from the fact that hydrocarbons are ubiquitous in the natural environment from petrogenic, biogenic and anthropogenic combustion. For the petroleum geochemist, the comparable application of chemical fingerprinting to organic geochemistry is an exploration and assessment tool that provides information on hydrocarbon source facies, depositional environments, thermal maturation history, water washing, biodegradation, and oil-oil and oil-source rock correlations. Successful oil fingerprinting involves appropriate sampling. A wide variety of instrumental and non-instrumental techniques are currently used in the analysis of oil

hydrocarbons, which include gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS), high performance liquid chromatography (HPLC), infrared spectroscopy (IR), thin layer chromatography (TLC), ultraviolet (UV) and fluorescence spectroscopy, isotope ratio mass spectrometry, and gravimetric methods. The accuracy and precision of analytical data have been improved and optimized by a series of quality assurance / quality control measurement. The laboratory data handling capability has been greatly increased through advances in computer technology **(Wang and Fingas, 2003).**

I-6-1. Trace metals fingerprinting

It is considered to be one of the earliest techniques used for hydrocarbon fingerprinting. Determination of trace metals can assist in the characterization of crude oil spillages. Vanadium and nickel are recommended among the most abundant metallic constituents of crude petroleum. Both are slightly affected by weathering, and the exposure has an identical effect on both of them. So, the vanadium over nickel ratio is used as a fingerprint to identify the source of crude oil polluting the environment. Their identification by means of atomic absorption (A.A) and inductively coupled plasma (ICP) techniques have been reported **(Molinero and Castillo, 1998).** Recently, this last new approach (ICP) has advantages over using A.A with graphite among these are, low detection limit, relatively high precision and long term stability. A method was developed for the determination of trace elements in crude oil by inductively coupled plasma mass spectrometry. It offers better sensitivity than both AA and ICP.

I-6-2. Gas chromatographic fingerprinting

The most widely used methods for hydrocarbon detection are based on gas chromatography. It has a number of advantages over other separation techniques. It is fast and extremely sensitive due to the variety of detectors, which are still generally unavailable to other forms of chromatography. Both packed and capillary columns have been used in an effort to attain high resolution of the n-alkane fingerprinting components. The advantages in capillary columns over packed columns are in obtaining practically improved separations in order to give fine structured

chromatographic fingerprints useful for source recognition. GC enables one to determine specific characteristic patterns for the contamination and its source **(Trabelsi and Driss, 2005).** The chemical nature of hydrocarbon pollutants is influenced by the type of crude oil spilled and the environmental conditions affecting the nature and degree of weathering. Real spill samples may have their fingerprint patterns distorted by the so-called weathering effects. It can drastically alter the profiles of the chromatogram obtained.

Gas chromatographic profile is of prime importance to detect the origin of pollutant hydrocarbon (petrogenic or biogenic). It is possible to identify petrogenic contamination by looking at n-alkane profiles. The gas chromatograms of petrogenic origin are characterized by broad spectrum of regularly spaced aliphatic hydrocarbon peaks, protruding over an unresolved envelop (hump) known as unresolved complex mixture (UCM). The hump comprising the complex mixture of unseparated naphthenic and aromatic hydrocarbons. However, biogenic n-alkanes are dominated by odd numbered carbon atoms, shorter chain $\leq$nC25 reflecting a phytoplankton input and a larger chain $\geq$nC25 a terrestrial or vascular plant input. The absence of homologus series of n-alkanes may indicate that the sample is either very highly weathered crude oil or is not contaminated by crude petroleum. Terrestrial plant waxes, aquatic phytoplankton, biomass combustion and natural oil seeps contribute natural inputs of hydrocarbons including aliphatic and aromatic hydrocarbons **(Masters and Root, 1987)**

I-6-2-1. Distinguishing biogenic from petrogenic hydrocarbons

Characterization and differentiation of hydrocarbons from different sources is an essential part of any contamination. After contamination, oil hydrocarbons often mix with other background hydrocarbon sources in the impacted area. One of the potential sources of hydrocarbons contributing to the background is biogenic hydrocarbons. The backbone detection of the origin of hydrocarbon pollutants mainly depends on the gas chromatographic profile.

Due to the specificity of biosynthetic pathways, the number of individual hydrocarbons synthesized by organisms is very much smaller than that found in crude oils or oil products. Among aliphatic hydrocarbons synthesized by organisms, those containing an odd number of carbon atoms predominate, although the biogenic production of even numbered carbon chain has been observed, whereas aromatic hydrocarbons are scarce. The main producers of biogenic hydrocarbons are phytoplankton, zooplankton land plants, phytoplankton, animals, and bacteria, macroalgae and benthic algae.

It has been recognized that the biogenic hydrocarbons have the following chemical composition characteristics:

- N-alkanes show a distribution pattern of odd carbon-numbered alkanes being much abundant than even carbon-numbered alkanes resulting in unusually high CPI values.
- Notable absence of the "unresolved complex mixture" hump in the GC chromatogram.

GC can bused for determining the degree of weathering, although the particular composition of a crude oil in its natural reservoir may be stable over geological time spans, its composition changes once it is exposed to water, sunlight, microorganisms and other factors. The product of all physical, chemical and biological processes known as weathering changes occur rapidly in the initial stages, but with diminishing speed as thermodynamic equilibrium with conditions in the environment is approached. The gas chromatographic patterns are thus distorted and the fingerprints may be substantially altered, or extensive weathering may drastically change it. By weathering, there is a reduction in the n-paraffin peak areas (height) and increase in the UCM hump. Accordingly, crude oils can be classified into:

i) Fresh crude oil (waxy crude oil), high n-paraffin peaks with relatively small envelope (UCM) Fig. 2.

ii) Weathered crude oil pattern, show comparatively less abundant n- paraffin peaks Fig. 2.

III) Very highly weathered crude oil, minor or reduced peaks with an increase in the UCM hump Fig. 2.

Hydrocarbon fingerprinting has allowed for the detailed qualitative and quantitative examination of oil pollution. Weathering means that the crude has been exposed to a number of physical, chemical and biochemical processes.

Among these processes are, natural dispersion, spreading and movement, solution and dissolution, vaporization, emulsification, photooxidation and microbial degradation. The sum of all these processes is collectively called "weathering of oil". So, weathering cause differences in components distribution between the crude oils and their spilt or pollutant samples. The gas chromatographic patterns are thus distorted and the fingerprints may be substantially altered, or it may be drastically changed. There is a change in the GC profiles such as a reduction in areas or disappearance of a number of n-paraffin peaks. Also, the fractions of petroleum with boiling points up to n-C_{14} alkanes will rapidly dissolve, vaporize, disperse or degrade. So, weathering affects the n-paraffin peak heights, especially in the low range $\leq$ n-C_{15}. By extensive weathering the characteristic gas chromatogram patterns are changed, where the unresolved complex mixture (UCM) are shown as a very large hump in the chromatogram. Modeling seeks to describe and predict process rates. Knowledge of the relationship between oil properties and oil weathering is the focus of interest.

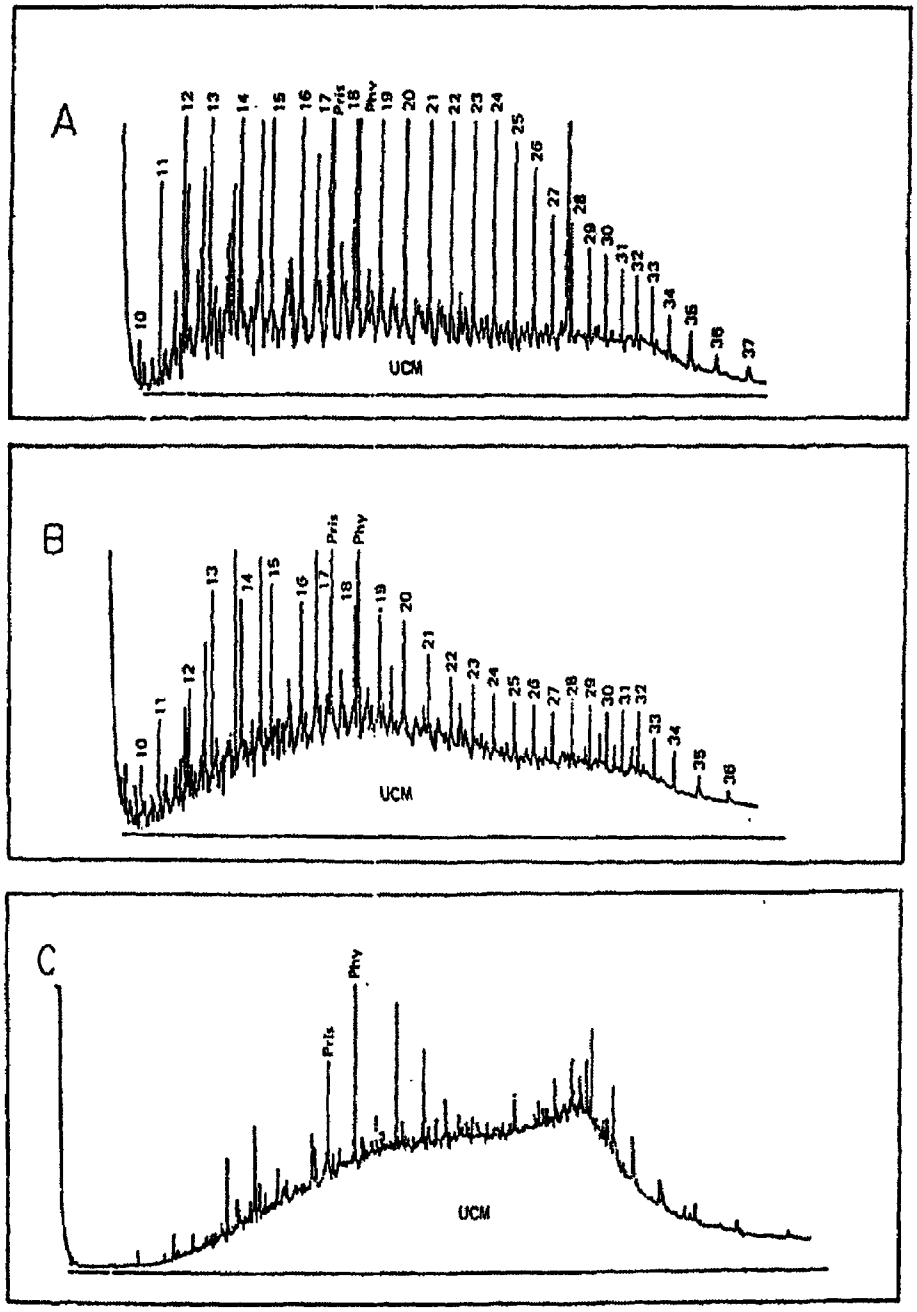


Fig. 2: Gas chromatograms for (A) Waxy crude oil, (B) Weathered and (C) Very highly weathered crude oil.

The gas chromatograms of petrogenic origin are characterized by broad spectrum of regularly spaced aliphatic hydrocarbon peaks, protruding over an unresolved envelope (hump) known as unresolved complex mixture (UCM). The hump comprising the complex mixture of unseparated alicyclic,

hydrocarbons show comparatively few irregular spaced peaks usually spread over a smaller molecular weight range. The gas chromatographic profile can also be used to detect the type of pollutants and give an idea about the degree of weathering as follows:

1) Used lubricating oil can be detected by an unresolved hump in the higher boiling region with small peaks of n-paraffins, chromatogram of Fig. 3.

2) Light petroleum fractions, show n-paraffin peaks in the range of low molecular weight compounds, light fuel oil is easily detected in GC screening because of its limited boiling range: compounds end at about nC25.chromatogram of Fig. 4.

3) Chromatogram of biogenic pollutant Fig. 5.

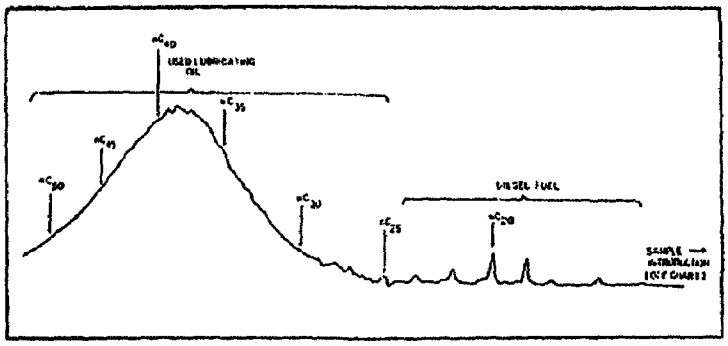


Fig. 3: Gas chromatogram for used lubricating oil.

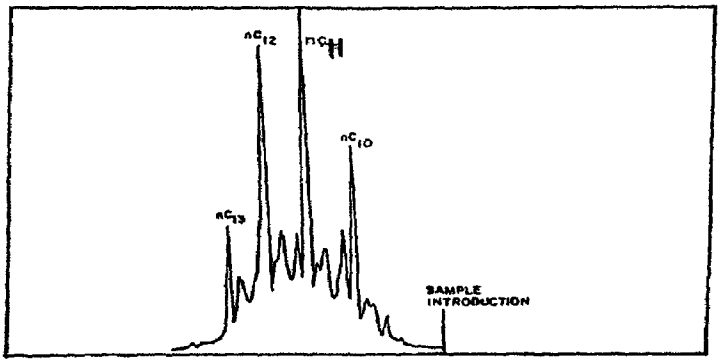


Fig. 4: Gas chromatogram for light petroleum fraction.

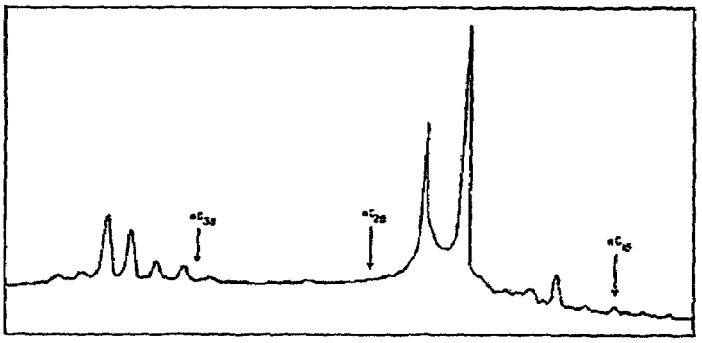


Fig. 5: Gas chromatogram of biogenic pollutant.

I-6-2-2. Gas chromatographic parameters

Several investigators **(Burns and Kanp, 1989 and Tolosa et al., 2004)** used numbers of parameters, depending on gas chromatographic analysis, which can be used for the identification of oil pollution especially concerning their origin, type and weathering degree. Among these are the following:

Pristane / phytane ratio

The two isoprenoids pristane (Pr) and phytane (Ph) are commonly found in petroleum and its derivatives. They are derived from the phytol side chain of chlorophyll, either under reducing conditions (Ph) or oxidizing conditions (Pr). While, pristane is synthesized by zooplankton fish and is often a major component in the hydrocarbon matrix of marine samples **(Gassmann, 1981).** Phytane characterizes crude oil and is not synthesized by most biota. Thus, the presence of phytane is used as a marker compound for petroleum. Pr/Ph value greater than unity identifies the biogenic origin of pollutants. Also both Pr and Ph became dominant saturated hydrocarbon components of highly weathered crude oils until they are degraded.

Carbon preference index (CPI)

This index is expressed numerically as the ratio obtained by dividing the sum of the odd carbon-numbered alkanes to the sum of the even carbon-numbered alkanes. It is a measure of the abundance of odd-to- even numbered n-alkanes in a given sample.

Petroleum origin contaminants characteristically have CPI values close to one **(Tolosa et al., 2004).**

Normal alkane / isoprenoid alkane ratio

The early effect of microbial degradation is monitored by the ratios of biodegradable to the less degradable compounds. Isoprenoid hydrocarbons are generally more resistant to biodegradation than n-alkanes. Thus, the ratio n-C_{17}/Pr and n-C_{18}/Ph are provided as rough indications to the relative state of weathering (mainly biodegradation) processes **(Wang et al., 1995).**

Unresolved complex mixture (UCM)

It is a common feature of the gas chromatograms of crude oils and certain refined products such as lubricating oils, and it is pronounced for weathered and biodegraded oils. It is perhaps surprising that virtually little is known about UCM compositions and molecular structures, even though the concentrations of these compounds in oils are significant. Works by several authors **(Gough and Rowland, 1990)** have shown that the oxidative degradation of UCM yields some gas chromatographically resolved products. It has been suggested that these products, which were identified to be acids, lactones and ketones may be useful for fingerprint UCM. There is much to be learned about UCM and the subject should provide a fruitful area for further research.

Weathering index

It is defined as the ratio of unresolved (UCM) to resolved (R) compounds. This index is used to estimate the extent of degradation of hydrocarbons. Low values <4 are indicative of relatively less weathered or recent input **(Tolosa et al., 2004).**

I-6-3. GC-MS fingerprinting

Gas chromatographic techniques have now been augmented by more sophisticated analytical techniques, such as gas chromatography- mass spectrometry (GC-MS) which is a true combination of its separate parts. Mass fragmentography provides a satisfactory tool for obtaining specific fingerprints for classes and homologous series of compounds, resolved by gas

chromatography. Detection of polycyclic aromatic hydrocarbons (PAHs) is another application of this technique. Fortunately a subset of these compounds proved less affected by weathering than the alkanes, and there were sufficient differences in the make up of various petroleum and refined products that they could serve as a fingerprinting tool. Mass fragmentography provides a satisfactory tool for obtaining specific fingerprints for classes and homologous series of compounds, resolved by gas chromatography.

GC-MS technique has been developed for the differentiation and identification of crude source, weathered and biodegraded oils using the relative abundances of three isomeric methyldibenzothiophene compounds **(Wang and Fingas, 1995).** Data base of the ratios of the C_1-DBT isomers for several hundred crude, weathered and biodegraded oils and petroleum products have been established for future fingerprinting.

A rapid and simple fractionation procedure using solid-phase extraction (SPE) cartridges was developed for an accurate determination of aliphatic and polycyclic aromatic hydrocarbons in petroleum residues and further application in chemical fingerprinting by GC-MS. The SPE fractionation procedure when compared with the conventional silica-alumina adsorption chromatography show similar results but practically advantages in terms of reproducibility, analysis time, solvent reduction and cost. Moreover, it is particularly suitable for routine analysis with a high sample throughput. The developed methodology was tested in characterization of contaminated oil samples collected along Spanish north-west coast, after the Prestige oil spill accident.

Biomarkers fingerprinting using GC-MS have historically been used by petroleum geochemists in characterization of marine oils in terms of source rock, genetic family, migration and maturation properties and in identification of petroleum deposits. Chemical analysis of source-characteristic and environmentally persistent biomarkers generates information of great importance in determining the source of spilled oil, differentiating oils, monitoring the degradation process and weathering state of oils under a wide variety of conditions. Biomarker terpane and steranes are common constituents of crude oils, however, a few specific biomarker compounds including several geologically rare acyclic

alkanes are found to exist only in certain oils and, therefore, can be used as unique markers to provide an interpretational advantage in fingerprinting sources of spilled oils and to provide additional diagnostic information on the types of organic matter that give rise to crude oil. These compounds are very resistant to biodegradation and extensive weathering of other more labile compounds left the biomarkers as the primary analytical chemistry alternative for use in fingerprinting of oils **(Wang and Fingas, 2003).**

In the past decade, use of biomarker fingerprinting techniques to study spilled oils has greatly increased, and biomarker parameters have been playing a prominent role in almost all spill work. Some of the biomarker approaches to petroleum geochemistry also carried over to oil spill fingerprinting, where extensive weathering of other more labile compounds left the biomarkers as the primary analytical chemistry alternative for use in fingerprinting of oils. Much of the knowledge of biomarkers and their diagnostic ratios comes from the oil geochemistry **(Peters and Moldowan, 1993).** A wide variety of biomarkers have been identified as being of use in characterization of crude oils and oil fractions, including tricyclic, tetracyclic and pentacyclictetrpenes, methylhopanes and steranes, methylsteranes and diasteranes. The distribution patterns are in general, different from oil to oil. As for refined products, no biomarker compounds are detected in jet fuel and only trace C_{20}-C_{24} terpanes were present in the diesel, while most lube oils and hydraulic fluids contain very high quantity of biomarkers. Obviously, refining processes have removed or concentrated most high molecular mass biomarkers from the corresponding crude oil feed stocks.

The presence of petroleum biomarkers not only serves as a clear indicator of oil contamination, but the distribution of compounds present can actually reveal the primary sources contributing to a system, as different sources may contribute distinct fingerprints.

The ratio of the abundance of cyclic terpenoids to the size of the UCM further reflects the degree of weathering or degradation that petroleum residues have undergone (increase with increasing degradation or weathering). Because of the different resistance of biomarkers to biodegradation, comparisons of their

relative ratios can be used to rank oils as the extent of biodegradation **(Chosson et al., 1991).** However, it should be noted that in severely weathered or long term weathered oil, degradation of some biomarkers was observed.

Although more study is required to better understanding the effect of weathering in altering the distribution of biomarkers of petroleum contamination, more comprehensive and detailed analysis of the biomarker fingerprints of the oil enhance the utility of these compounds in tracing and determining the sources of petroleum contamination in the environment.

I-6-4. High performance liquid chromatography fingerprinting

It is a very useful technique in the field of analysis of polynuclear aromatic hydrocarbons (PAHs), which has been identified as the most suitable class of compounds for oil fingerprinting.

Crude oils from different sources can have very different polycyclic aromatic hydrocarbons (PAHs) distribution. PAHs are widespread environmental contaminants, derived from anthropogenic or natural sources **(Trabelsi and Driss, 2005).** They has toxic, mutagenic and /or carcinogenic properties. They are also highly lipid-soluble and thus readily absorbed from the gastrointestinal tract of mammals **(Samanta et al., 2002 and King et al., 2004).** They are more resistant to weathering than their saturated hydrocarbon counterparts (n-alkanes and isoprenoids) and volatile alkylbenzene compounds, thus making PAHs one of the most valuable fingerprinting classes of hydrocarbons for oil identification.

I-6-4-1. PAHs distribution

Polycyclic aromatic hydrocarbons (PAHs) are chemicals containing two or more fused benzene rings in a linear, angular or cluster arrangement. PAHs contain only carbon and hydrogen. The PAHs contamination may result from either pyrogenic sources (incomplete combustion of organic matter, emission sources and exhausts) or from the release of petroleum into the environment

(Doong and lin, 2004). After entering the environment, PAHs are widely dispersed by atmospheric transport or through stream pathways, and eventually accumulate in soil and aquatic sediments. They possess physical properties, such as low aqueous solubility and high solid-water distribution ratios, which stand against their ready microbial utilization and promote their accumulation in the solid phases of the terrestrial environment. The microorganisms (naturally occurring or genetically engineered) can mineralize toxic PAHs into CO_2 and H_2O **(Samanta et al., 2002 and Guo et al., 2005).**

The adverse effects of these compounds on human health including genotoxicity, carcinogenicity and physiological disorders have been well documented. Sixteen PAHs have been identified as priority pollutants by both China and the United States Environmental Protection Agency **(U.S.EPA)** and seven of them are considered as probably carcinogenic. PAHs widely distribute at various levels in soils, water, sediments, aerosols, sewage sludges and plant.

According to the distribution of individual PAHs of the reference 16 PAHs listed by the United States Environmental Protection Agency **(U.S.EPA)** using HPLC. They can be divided corresponding to the number of rings into low and high molecular weights PAHs. The low molecular weights consist of two and three aromatic rings which are 6 LPAHs. While the high molecular weight consists of tetra, penta- and hexa-aromatic rings, they are 10 HPAHs **(Viguri et al., 2002 and Salvo et al., 2005).** Four to seven-ring PAHs is highly mutagenic and carcinogenic. Two- or three-ring PAHs are less mutagenic but can be highly toxic **(Shi et al., 2005).**

Low molecular weight PAHs cause acute toxicity, whereas some of the higher molecular weight PAHs is carcinogenic. The toxicity occurs when UV excites the electrons in PAHs, resulting in the formation of toxic singlet oxygen as a by-product, which can damage biological membranes **(Hatch and Burton, 1999).**

Even differences between the same types of products are discernible through examination of their distribution from the crude oils and from each other. Jet B fuel has extremely high content of

the naphthalenes series (99%) with the other four alkylated PAHs series being only 15 in total. In addition, no 4- to 6- ring PAHs were detected. Diesel No. 2 has high naphthalene content (86%), low phenanthrene content (5%), and no chrysenes. In the Bunker C/Diesel mixture, the unusually high contents of the alkyl phenanthrene and chrysenes were pronounced accounting for approximately 35% and 18% respectively **(Wang et al., 1995).**

It is often difficult to identify which PAHs have been introduced from petrogenic or pyrogenic sources. This is because there are many ways in which PAHs are introduced into the environment that the PAHs signature from one source could be obscured by PAHs from another sources. In addition, under the comparable combustion conditions, the same amounts of organic materials can yield largely different amount of PAHs at different temperatures. Therefore, in addition to qualitative criteria, quantitative criteria should be defined to recognize sources of PAHs **(Zhang et al., 2004).** The sources of PAHs contamination (pyrogenic and petrogenic) were achieved using both PAHs distribution and molecular indices based on ratios of selected PAHs concentrations. Numerous quantitative diagnostic ratios have been defined to differenciate pyrogenic and petrogenic PAHs **(Zhang et al., 2004).**

A number of diagnostic ratios of target alkylated PAHs species have been successfully used as indicators for oil spill identification. It have defined the C_3D/C_3P and C_3D/C_3C as source ratios (the ratios that be almost constant because the compounds degraded at the same rate) and weathering ratios (the ratios that change substantially with weathering and biodegradation), respectively. A method using the double ratio plots of alkylated PAHs homologues, in particular the alkylated dibenzothiophenes and phenanthrene (C_2D/C_2P versus C_3D/C_3P), for identification and differentiation petroleum product sources has been developed and extensively used in the studies of the Gulf war oil spill.

The polycyclic aromatic hydrocarbon (PAHs) contaminations in 138 soil samples collected throughout Hong Kong have been studied by **Chung et al, (2007)** since the hydrocarbons of the most notorious and ubiquitous pollutants are polycyclic aromatic hydrocarbons (PAHs). It is also one of the

Persistent Toxic Substances (PTS). PTS typically share the major characteristics of 12 Persistent Organic Pollutants (POPs) in the Stockholm Convention. They maked a detail descriptive statistics of individual PAHs in each land use. The results provided valuable information for regulatory purpose concerning PAHs pollutions in soils. And also, was found that the pollution of $\sum 16$ soil PAHs was generally low at around 140 ppm in Hong Kong. The PAHs typically originated from vehicular emissions and cross border atmospheric deposition of PAHs may also be a significant source. Samples with very high concentration of PAHs were found sporadically (2% of collected samples).

While **Yu et al., (2006)**, studied the concentration, distribution, profile and the possible source of polycyclic aromatic hydrocarbons (PAHs) in soil were studied in Guiyu, an electronic waste (E-waste) recycling center, using primitive technologies in Southeast China. A total of 49 soil samples (0–10 cm soil layer) were collected from different locations throughout the Guiyu area between June and December, 2004. The results showed that 88.1% of the variance could be explained by three principal components. Principal component 1 explained 68.7% of the total variance, PC2 12.5%, and PC3 6.9%. The principal components were three distinct groups according to the number of aromatic rings. The first group contained Ane, Fle, Phe, Fla, Pyr, BaA and Chr, which were 3- and 4-ring PAHs. The second group contained BbkF, BaP, IcdP, DaA and BghiP, which were 5- and 6-ring PAHs. The third group included Nap, Any and Ant, which were 2- and 3-ring PAHs. According to the criteria established by **Maliszewska-Kordybach, (1996),** four classes of soil contamination were identified based on a total of 16 PAHs: non contaminated soil (<200 ppm), weakly contaminated soil (200–600 ppm), contaminated soil (600–1000 ppm) and heavily contaminated soil (>1000ppm). In general, Guiyu soil was weakly contaminated by PAHs.

Ye et al., in (2006), studied a total of 188 surface soil samples which were collected from different types of utilization soils in Tianjin area. Factor analysis and scatter point surface tension spine function interpolation were used to analyze types and spatial distributions of PAHs sources of surface soils in Tianjin area. The values of the concentrations of 16 priority PAHs in the surface soils of Tianjin and the standards for PAHs in soils were

high, and many of these values for PAHs in the surface soils of Tianjin were in excess of the reported standards for PAHs in soils and it was over 14 times higher than the value presented in standards. The results showed that most pollution sources were mixed sources including coal burning and petroleum spill. Mixed sources occupied 56.12%, 58.96%, 46.45% and 59.50% in farmland of wastewater irrigation, common farmland, wild land and city greenbelt, respectively. Other pollution sources such as vehicle emission, biogenic conversion, wood burning and natural gas combustion were also significant. The spatial distributions of pollution sources were closely related to geographic location, geographic condition and living habit of indigenes.

Amit and Ajay, (2006) studied the polycyclic aromatic hydrocarbons in surface soil was conducted at selected locations in Agra (semi-arid region of India) for a span of one year in order to ascertain the contamination levels. The concentrations of PAHs were measured at four locations in the city of Agra, which covers industrial, residential, roadside and agricultural areas. They found out that of the 16 EPA priority PAHs, 14 PAHs were found in the surface soils of Agra. The t-PAHs concentrations were found to be 13.72, 12.98, 9.37 and 6.73 ppm at industrial, roadside, residential and agricultural sites, respectively. The mean concentration of t-PAHs was 12.14 ppmfor all sites together. The industrial sites had the highest t-PAHs concentration followed by roadside, residential and agricultural site.

Ping et al., (2007), quantified the 16 (PAHs) in 30 soil profiles from the Yangtze River Delta Region, in east China. Relative concentrations of PAHs compounds with different benzene rings and ratios of fluoranthene to fluoranthene plus pyrene and benz(a)anthracene to benz(a)anthracene plus chrysene were used to identify the possible sources of soil PAHs. Total concentrations of 15 PAHs in topsoils ranged from 8.6 to 3881 ppm with an average of 397 ppm. Half of the soil samples were considered to be contaminated with PAHs (>200 ppm) and two sampling sites were heavily polluted by PAHs with concentrations >1000 ppm. Phenanthrene was found in soils below a depth of 100 cm in half of the sampling sites, but the detectable ratio of benzo(a)pyrene decreased sharply from 100% in topsoil to 0 in the 4^{th} horizon.

In general, PAHs from a petrogenic source have lower molecular weight (2- and 3-ring PAHs) with depletion of higher molecular weight (>3-ring) compounds, while pyrogenic sources are abundant in higher molecular weight compounds. Relative concentration values are commonly used to distinguish between combustion and petroleum sources. Relative values of PAHs with >3 benzene rings of more than 50% indicates a dominance of combustion and relative values of 2 and 3 benzene ring PAHs of >50% indicates a dominance of petroleum pollution.

I-7. Effect of Weathering on Hydrocarbon Pollutants Fingerprinting

Although the particular composition of a crude oil in its natural reservoir may be stable over geological time spans, its composition changes once it exposed to water, oxygen, sunlight, microorganisms and other factors. The sum of all physical, chemical and biological processes is known as *weathering.* Changes occur rapidly in the initial stages, but with diminishing speed as thermodynamic equilibrium with conditions in the environment are approached. When crude oil or petroleum products are accidentally released to the environment, they are immediately subject to a wide variety of weathering processes. These weathering processes can include (1) Evaporation, (2) Dissolution, (3) Microbial degradation, (4) Other processes such as dispersion and water-oil emulsification, photooxidation, adsorption onto suspended particulate materials and oil–mineral aggregation.

I-7-1. Evaporation

In the short term after a spill (hours to days), evaporation is the single most important and dominant weathering process, in particular for light petroleum products. In the first few days following a spill, the loss can be up to 70% and 40% of the volume of light crudes and petroleum products respectively. For heavy or residual oils the losses are only about 5-10% of the spilled volume **(Fingas, 1995).**

I-7-2. Dissolution

The amount of the oil hydrocarbons dissolving in water phase from oil slick largely depend on the molecular structure and polarity of a given oil component, and the relative solubility of the oil component in water phase versus its solubility in the oil phase. In general, the aromatic hydrocarbons are more soluble than aliphatic hydrocarbons and the solubilities increase as the alkylation degrees of alkylated benzene or PAHs decrease **(Samanta et al., 2002).** The lower molecular weight hydrocarbons are more soluble than the high molecular weight hydrocarbons in that class. Therefore, it can be readily understood why BTEX and lighter alkylbenzene compounds and some smaller PAHs compounds such as naphthalene are particulary susceptible to dissolution.

I-7-3. Biodegradation

Biodegradation of hydrocarbons by natural populations of microorganism represents one of the primary mechanisms by which petroleum and other hydrocarbon pollutants are eliminated from the environment **(Abalos et al., 2004).** It is a complex process, whose quantitative and qualitative aspects depend on the type, nature and the amount of the oil or hydrocarbon present, the ambient and seasonal environmental conditions (such as temperature, oxygen, nutrients, water activity, salinity and pH), and the composition of the autochthonous microbial community. Hydrocarbons differ in their susceptibility to microbial attack. In general, the degradation of hydrocarbons is ranked in the following order of decreasing susceptibility: n-alkanes > branched alkanes > low-molecular weight aromatics >light aromatic > high- molecular weight aromatics > polar compounds.

I-7-4. Photooxidation

It is considered to be another most important factor involved in the transformation of crude oil or its products released into the marine environment **(Samanta et al., 2002).** The photochemical degradation yields a great variety of oxidized compounds which are highly soluble in water.

I-7-5. Aggregation

Oil mineral aggregates **(OMA)** were found to result from interactions among the oil residues, fine mineral particle and seawater. **OMA** formation has now been identified as an important process that facilitates the natural removal of oil stranded in soils. **OMA** formation is enhanced by physical processes such as wave, energy, tides or currents. It has recently been noted that oil biodegradation may be enhanced by **OMA** formation **(Abalos et al., 2004).**

All these processes alter the chemical composition of spilled oil, making the unambiguous identification of the source of oil something of challenge.

I-8. Impact of Crude Oil on some Soil Properties

Many authors studied the relationship between some soil properties and its pollution with petroleum. When crude oil spilled onto soil, it is subjected to volatization the range of loss from this process reported to be 0.1% to nearly 40% **(Franke and Clark, 1974).**

El-Leboudi et al., in **(1985)** studied the effect of the petroleum by-products on the characteristic of alluvial soil. They used two petroleum by-products (acidic sludge and basic sludge) at rates of 0.5 and 1.5%. The pH values of the soil columns treated with acid sludge decreased by 0.2-.07 unit depending on the rate of applied acid sludge. While the basic sludge increased the pH values due to its relatively high content of sodium (1.3%). They also found that electrical conductivity EC values showed a positive response to the addition of acid sludge and basic sludge from petroleum by-product. They found that the higher the rate of the application, the higher the EC values.

The adsorption of vapour hydrocarbons from the synthetic kerosene source on different Mediterranean soils, red sandy clay, arid brown silt loam and clay were studied by **(Yaron et al., 1989).** The kerosene used consisted of 20% aromatic components (m-xylene, n-butylbenzene) and 80% aliphatic component (n-decane, n-dodicane). The most influential parameter in the adsorption desorption processes was the moisture content which

was examined over the range from oven dry to 1 bar water pressure (70% field capacity). It was found that the highest adsorption values were on the arid silty loam soils, having the following order of adsorption n-decane > m-xylene > n-butylbenzene > n-dodecane. **Acher et al., (1989)** also studied the adsoption of petroleum vapour by a Mediterranean red sandy clay with different moisture content (0.0, 0.8, 4.0 and 8.0% w/w). The soil was contaminated with vapour and/or liquid containing 5 kerosene components. The vapour adsorption was found to be dependent on the vapour concentration of each component (except for n-decane), and on the moisture content. The increase in the soil moisture content increases the rate and depth of kerosene downward penetration. However the vapour movement stooped at 4% moisture and upward liquid movement at 12% moisture content.

Raymond et al., in **(1992)** found that the pH of sites received oil sludge increased and that was properly due to the buffer capacity of the applied sludge. They showed that after three years of very high application rate (5.25%) for the sites, the pH continued to remain higher (pH 6.7) than the control soil (pH 5.7). They evaluated also the cation exchange capacity CEC, and the soil temperature as a result of application of contaminates to an old field site in Tompkins country. They found that with higher application 5.25%, the CEC decreased from 20.2 to 13.5cmol/kg and the soil temperature increased by 1-5°C.

Amadi et al., in **(1996)** studied the properties of a tropical rain forest soil after 17 years of oil spillage. They showed that pH of contaminated soil (heavy impact and moderate impact) varied from acidic (pH 4.0) to near neutral (pH 6.0). They showed that the CEC of a tropical rain forest soil after 17 years of oil spillage decreased from 5.48 cmol/kg at a heavy impact zones to 4.64 cmol/kg at a moderately impact zones.

I-9. Heavy Metals (HM) in Soil

Heavy metals are natural components of the environment, but are of concern because they are being added to soil, water, air in increasing amounts. Some for example copper, manganese and zinc are micronutrients (trace element) which are essential in small amounts for plant and animal life. They can, however, be harmful if

they are taken up by plants or animals in large amounts, as can other heavy metals not known to be essential nutrients. Toxicity of trace metals follow the general trend that an under supply leads to a deficiency, sufficient supply result in optimum conditions, but an oversupply result in toxic effect and lethality in the end as shown in Fig. 6.

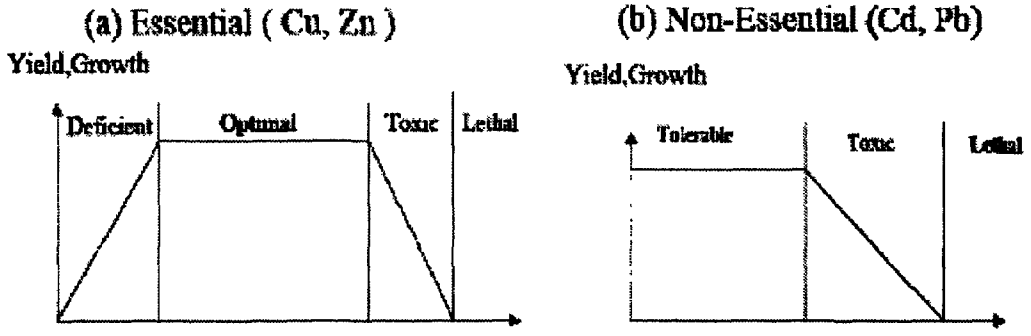


Fig. 6: Essential and non-essential trace element for plants.

The term heavy metals refer to the metals with a density greater than a certain value 5 or 6 g/cm^3. This term often refers to the metals discharged by industry in which lead, chromium, arsenic, zinc, mercury, cadmium, copper and nickel are discharged and representing the greatest hazard to soil, plant and animal.

Soil consists of a mixture of weathered minerals and varying amounts of organic matter, soils can be contaminated as a result of spills or direct contact with contaminated waste streams such as airborne emissions, process solid wastes, sludges, or leachate from waste materials. The solubility of metals in soil is influenced by the chemistry of the soil and groundwater **(Evans, 1989 and Sposito, 1989).**

Factors such as pH, ion exchange capacity, and complexation / chelation with organic matter directly affect metal solubility.

The fate and transport of a metal in soil and groundwater depends significantly on the chemical form and speciation of the metal **(Allen et al., 1991).** The mobility of metals in ground-water systems is hindered by reactions that cause metals to adsorb or precipitate and /or chemistry that tends to keep metals associated

with the solid phase and prevent them from dissolving. These mechanisms can retard the movement of metals and also provide a long-term source of metal contaminants **(NRC, 1994)**. Metals undergo similar reactions in a number of aspects, the extent and nature of these reactions varies under particular conditions.

I-9-1. Sources of heavy metal pollution

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment **(U.S.EPA, 1992).**

The nine major metal-waste producing industries are:
1-Metal coating (plating and metal finishing) industry segment includes operation such as electroplating, anodizing, electroless plating, chemical conversion, coating etching, printed circuit board, manufacturing and milling.
2-Smelting and refining of nonferrous metals.
3-Paint, ink and associated products.
4-Petroleum refining.
5-Iron and steel manufacturing.
6-Photographic industry.
7-Leather tanning.
8-Wood preserving.
9-Battery manufacturing.

The extraction of metal ores causes generally a multi elemental contamination of the environment **(Dudka and Domy, 1997). Vega et al., (2004),** found that open cast mining causes serious environmental impact like the destruction of natural soils and the extraction of important volumes of materials. This causes the formation of new soils, on the accumulated wastes of the mine.

Davydova, (2005), concluded that heavy Metals (HMs) can exert detrimental effects on human health and on the environment. Their ecotoxicological properties are generally well known. As regards urban atmosphere, motor vehicles (Pb) and industry (V, Ni, Cr, Cd) exert the greatest influence; water, soil, vegetation. Regarding the environmental aspects of contamination of big cities by HMs (via petroleum and fractions burning), it is useful to know

that about 30 elements have been found in crude oil, they include V, Ni, Mo, Zn, Co, Mn, Cu, Hg and Pb. Although lead is present in petrol in minor portions (10^{-7} % mass), Pb in the form $Pb(C_2H_5)_4$ and $Pb(CH_3)_4$ is still being introduced to fuels in many countries for antiknock improvement. HMs, especially Ni, V, and Pb attracted considerable attention in view of their sharp toxicity.

Heavy–metal ions are toxic pollutants. Some of these are cumulative poisons capable of being assimilated, stored, and concentrated by organisms that are exposed to low concentrations of these substances for long periods or repeatedly for short periods. Eventually, the building of the metal in tissues is sufficient to cause noticeable physiological effects. Heavy metals are the main hazardous nondegradable substances in the environment. One of the side effects of the progress of civilization is growing consumption of heavy metals and their growing concentration in the environment and human organisms. The concentration of lead in bones of present day man is 1500 times higher than that of man from Bronze Age **(Aleksandrowicz and Duda, 1988).**

(Karin et al., 2006) found that much attention has been given to remediation of point-source polluted sites with regard to potential health risks for children. However, because of diffuse pollution and long-range atmospheric deposition, soil contaminant levels are generally increased in urban areas compared to their rural counterparts, even in areas located away from any point sources of pollution. Intake of urban soil can thereby result in significant amounts of the child's daily metal intake.

Battaglia et al., (2007), found that the concentration of heavy metals in natural soils is usually low, although industrial wastes deposited on soil, the use of fertilizers and atmospheric fallout increase their concentrations. Metals are usually associated with various soil components (speciation) depending on their origin and their interaction with the reactive surface of soil components. Usually remediation methods applicable to soils contaminated with metals are based on two approaches: removal/extraction of the heavy metals from the matrix by electrokinetic and/or "washing" processes which are characterized by high costs and laborious management or reduction of metal mobility with "in situ", but in this work, in order to reduce the concentration of bioavailable

this work, in order to reduce the concentration of bioavailable forms of metals in contaminated soils they have began a study based on the treatment of metal polluted soils with paper mill sludges.

I-9-2. Oil pollution as source of heavy metals

The growth of the petroleum industry in Egypt and the marketing of petroleum products have resulted in the pollution of the environment by oil spills involving blowouts, leakages from tanks or tanker trucks, and dumping of waste petroleum products **(Ogoke, 1996)** The effects of such oil spills on the environment, human, livestock, wildlife, aquatic life, crop, and soil have been documented. Heavy metals are often mixed with organic pollutants in contaminated sites **(Adeniyi and Afolabi, 2002).**

Petroleum hydrocarbons and heavy metals can impact soil ecosystems sufficiently to result in significant losses in soil quality. Their negative impact results from their toxicity to biological processes catalyzed by soil microorganisms. Field studies of contaminated soils have demonstrated that elevated loadings of these contaminations can result in diminished microbial biomass, reduced viable bacterial population densities, inhibition of organic matter mineralization as well as decreased leaf litter decomposition and mycorrhizal infection of clover (Trifolium sp.) roots **(Koomen et al., 1990 and Kelly and Tate, 1998).** Remarkable accumulations of petroleum hydrocarbons and heavy metals have been observed in organisms found in contaminated soils. These have their attendant toxicological and health implications as the pollutants find their way into the complex food chain. Bioremediation techniques using plants and microorganisms have been widely applied in cleaning up petroleum hydrocarbon and heavy-metals-polluted soils as most contaminants are usually transformed via natural processes to innocuous compounds **(Geller et al., 2000).** However, the degree of soil decontamination using bioremediation techniques depend largely on the nature and levels of heavy metals and petroleum hydrocarbons present in the soil **(Marwood et al., 1998).**

It was noted noted with interest that the appearance of mixtures of non-ionic organic contaminants NOCs and heavy

instance, industrial enterprises, such as coking plants, have resulted in the simultaneous accumulation of PAHs and heavy metals with high concentrations in surrounding soils **(Gao et al., 2005).** It has been known that NOCs mainly interact with soil organic matter, and heavy metallic cations can also be complexed by the organic molecules in soil solids or released into soil solution **(Gao et al., 2005).** Thus it can be postulated that the presence of heavy metals in soil may play an important role in the sorption of NOCs by soils. However, little information is available on the sorption of NOCs including PAHs by soils contaminated with heavy metals **(Gao et al., 2006).**

I-9-3. Heavy metals found in contaminated sites

I-9-3-1. Lead

The primary industrial sources of lead (Pb) contamination include metal smelting and processing, secondary metals production, lead battery manufacturing, pigment and chemical manufacturing, and lead-contaminated wastes. Widespread contamination due to the former use of lead in gasoline is also of concern. Lead released to groundwater, surface water and land is usually in the form of elemental lead, lead oxides and hydroxides, and lead metal oxyanion complexes **(Smith et al., 1995).** Lead occurs most commonly with an oxidation state of 0 or +II. Pb(II) is the more common and reactive form of lead and forms mononuclear and polynuclear oxides and hydroxides.

Under most conditions Pb^{2+} and lead-hydroxy complexes are the most stable forms of lead **(Smith et al., 1995).** Low solubility compounds are formed by complexation with inorganic (Cl^-, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}) and organic ligands (humic and fulvic acids) EDTA and amino acids **(Bodek et al., 1988).** Lead carbonate solids form above pH 6 and PbS is the most stable solid when high sulfide concentrations are present under reducing conditions. Most lead that is released to the environment is retained in the soil **(Evans, 1989).** The primary processes influencing the fate of lead in soil include adsorption, ion exchange, precipitation, and complexation with sorbed organic matter. These processes limit the amount of lead that can be transported into the surface water or groundwater. The relatively volatile organolead compound

tetramethyl lead may form in anaerobic sediments as a result of alkyllation by microorganisms **(Smith et al., 1995)**.

The amount of dissolved lead in surface water and groundwater depends on pH and the concentration of dissolved salts and the types of mineral surfaces present. In surface water and ground-water systems, a significant fraction of lead is undissolved and occurs as precipitates ($PbCO_3$, Pb_2O, $Pb(OH)_2$, $PbSO_4$), sorbed ions or surface coatings on minerals, or as suspended organic matter.

Health Effects: Carcinogenic or teratogenic Neurotoxic, irreversible brain damage, cumulative poison to humans, gastrointestinal disturbance, tenderness and it causes also gradualparalysis in muscles, specifically arms and impairment of haemoglobin.

I-9-3-2. Chromium

Chromium (Cr) is one of the less common elements and does not occur naturally in elemental form, but only in compounds. Chromium is mined as a primary ore product in the form of the mineral chromite, $FeCr_2O_4$. Major sources of Cr contamination include releases from electroplating processes and the disposal of chromium containing wastes **(Smith et al., 1995)**.

Cr(VI) is the form of chromium commonly found at contaminated sites. Chromium can also occur in the (+III) oxidation state, depending on pH and redox conditions. Cr (VI) is the dominant form of chromium in shallow aquifers where aerobic conditions exist. Cr(VI) can be reduced to Cr(III) by soil organic matter, S^{2-} and Fe^{2+} ions under anaerobic conditions often encountered in deeper groundwater. Major Cr(VI) species include chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) which precipitate readily in the presence of metal cations (especially Ba^{2+}, Pb^{2+} and Ag^{+}). Chromate and dichromate also adsorb on soil surfaces, especially iron and aluminum oxides. Cr(III) is the dominant form of chromium at low pH(<4). Cr^{3+} forms solution complexes with OH^-, Cl^-, F^-, CN^-, SO_4^{2-}, and soluble organic ligands. Cr(VI) is the more toxic form of chromium and is also more mobile. Cr(III) mobility is decreased by adsorption to clays and oxide minerals

below pH 5 and low solubility, above pH 5 due to the formation of $Cr(OH)_{3(s)}$ **(Chrotowski et al., 1991).**

Chromium mobility depends on sorption characteristics of the soil, including clay content, iron oxide content and the amount of organic matter present. Chromium can be transported by surface runoff to surface waters in its soluble or precipitated form. Soluble and unadsorbed chromium complexes can leach from soil into groundwater. The leachability of Cr(VI) increases as soil pH increases. Most of chromium released into natural waters is particle associated, and ultimately deposited into the sediment (**Smith et al., 1995**).

Health Effects: Trivalent chromium may be nutritionally essential with a safe and relative innocuous level of 0.2 mg/day. Hexavalent chromium has a deleterious effect on the liver, kidney and respiratory organs with hemorrhagic effects, chromium was classified as highly carcinogenic to human and animal. Damage and irritate nose, lungs, stomach, and intestines.

I-9-3-3. Zinc

Zinc (Zn) does not occur naturally in elemental form. It is usually extracted from mineral ores to form zinc oxide (ZnO). The primary industrial use for Zinc is as a corrosion-resistant coating for iron or steel (**Smith et al., 1995**).

Zinc usually occurs in the +II oxidation state and forms complexes with a number of anions, amino acids and organic acids. Zn may precipitate as $Zn(OH)_{2(s)}$, $ZnCO_{3(s)}$, $ZnS_{(s)}$, or $Zn(CN)_{2(s)}$. Zinc is one of the most mobile heavy metals in surface waters and groundwater because it is present as soluble compounds at neutral and acidic pH values. At higher pH values, zinc can form carbonate and hydroxide complexes which control zinc solubility. Zinc readily precipitates under reducing conditions and in highly polluted systems when it is present at very high concentrations, and may coprecipitate with hydrous oxides of iron or manganese (**Smith et al., 1995**).

Sorption to sediments or suspended solids, including hydrous iron and manganese oxides, clay minerals, and organic

matter, is the primary fate of zinc in aquatic environments. Sorption of zinc increases as pH increases and salinity decreases.

Health Effects: Essential element in many metallo-enzymes, aids wound healing, toxic to plants at higher levels.

I-9-3-4. Cadmium

Cadmium (Cd) occurs naturally in the form of CdS or $CdCO_3$. Cadmium is recovered as a by-product from the mining of sulfide ores of lead, zinc and copper. Sources of cadmium contamination include plating operations and the disposal of cadmium-containing wastes (**Smith et al., 1995**). The form of cadmium encountered depends on solution and soil chemistry as well as treatment of the waste prior to disposal. The most common forms of cadmium include Cd^{2+}, cadmium-cyanide complexes, or $Cd(OH)_2$ solid sludge (**Smith et al., 1995**).

Hydroxide ($Cd(OH)_2$) and carbonate ($CdCO_3$) solids dominate at high pH whereas Cd^{2+} and aqueous sulfate species are the dominant forms of cadmium at lower pH (<8). Under reducing conditions when sulfur is present, the stable solid $CdS_{(s)}$ is formed. Cadmium will also precipitate in the presence of phosphate, arsenate, chromate and other anions, although solubility will vary with pH and other chemical factors.

Cadmium is relatively mobile in surface water and ground-water systems and exists primarily as hydrated ions or as complexes with humic acids and other organic ligands (**Callahan et al., 1979**). Under acidic conditions, cadmium may also form complexes with chloride and sulfate. Cadmium is removed from natural waters by precipitation and sorption to mineral surfaces, especially oxide minerals, at higher pH values (>pH 6). Removal by these mechanisms increases as pH increases. Sorption is also influenced by the cation exchange capacity (CEC) of clays, carbonate minerals, and organic matter present in soils and sediments. Under reducing conditions, precipitation as CdS controls the mobility of cadmium (**Smith et al., 1995**).

I-9-3-5. Copper

Copper (Cu) is mined as a primary ore product from copper sulfide and oxide ores. Mining activities are the major source of copper contamination in groundwater and surface waters. Other sources of copper include algicides, chromated copper arsenate (CCA) pressure treated lumber, and copper pipes.

Solution and soil chemistry strongly influence the speciation of copper in ground-water systems. In aerobic, sufficiently alkaline systems, $CuCO_3$ is the dominant soluble copper species. The cupric ion, Cu^{2+}, and hydroxide complexes, $CuOH^+$ and $Cu(OH)_2$, are also commonly present. Copper forms strong solution complexes with humic acids. The affinity of Cu for humates increases as pH increases and ionic strength decreases. In anaerobic environments, when sulfur is present $CuS_{(s)}$ will be formed.

Copper mobility is decreased by sorption to mineral surfaces, Cu^{2+} sorbs strongly to mineral surfaces over a wide range of pH values **(Dzombak and Morel, 1990).** The cupric ion (Cu^{2+}) is the most toxic species of copper. Copper toxicity has also been demonstrated for $CuOH^+$ and $Cu_2(OH)_2^{2+}$ **(LaGrega et al., 1994).**

I-9-3-6. Nickel

Source and occurrence of nickel (Ni) that it isn't found in nature as a pure metal, it occurs in sulfides, arsenides, antimonides, oxides and silicates, while in ores associated with iron. Nickel salts are soluble in water, it is used in alloys and for plating because of its resistance to oxidation, also used in making stainless steel, ceramics, special batteries, electronics, and space applications.

Health Effects: It is essential element for animals, nickel has low toxicity comparable to zinc, manganese, and chromium, and it doesn't accumulate in tissues.

I-9-3-7. Manganese

The biogeochemistry of Mn in soils is very complex due to the following observations: Mn can exist in several oxidation states, Mn oxides can exist in several crystalline or

pseudocrystalline states, the oxides can form coprecipitates with Fe oxides, Fe and Mn oxides exhibit amphoteric behavior and interact both with cations and with anions, and oxidation–reduction reactions involving Mn are influenced by a variety of physical, chemical, and microbiological processes. Therefore, Mn adsorption is more complicated as it forms insoluble oxides in response to pH conditions. Adsorption has been found to increase with increasing pH **(Willett and Bond, 1995).**

I-9-4. Influence of soil properties on mobility of heavy metals

Chemical and physical properties of the contaminated matrix influence the mobility of metals in soils and groundwater. Contamination exists in three forms in the soil matrix: solubilized contaminants in the soil moisture, adsorbed contaminants on soil surfaces, and contaminants fixed chemically as solid compounds.

The chemical and physical properties of the soil influence the form of the metal contaminant, its mobility, and the technology selected for remediation **(Gerber et al., 1991).**

I-9-4-1. Physical properties

Particle size distribution can influence the level of metal contamination in a soil. Fine particles (<100 μm) are more reactive and have a higher surface area than coarser material. As a result, the fine fraction of a soil often contains the majority of contamination. The distribution of particle sizes with which a metal contaminant is associated can determine the effectiveness of a number of metal remediation technologies, e.g., soil washing **(Dzombak et al., 1994).**

Soil moisture influences the chemistry of contaminated soil. The amount of dissolved minerals, pH and redox potential of the soil water depends on the soil moisture content. Soil structure describes the size, shape, arrangement and degree of development of soils into structural units. Soil structure can influence heavy metals mobility by limiting the degree of contact between groundwater and the heavy metals.

I-9-4-2. Chemical properties

The presence of inorganic anions (carbonate, phosphate, and sulfide) in the soil water can influence the soil's ability to fix metals chemically. These anions can form relatively insoluble complexes with metal ions and cause metals to desorb and/or precipitate in their presence. Soil pH values generally range between 4.0 and 8.5 with buffering by Al at low pH and by $CaCO_3$ at high pH (**Wild, 1988**). Metal cations are most mobile under acidic conditions where anions tend to sorb to oxide minerals in this pH range **(Dzombak and Morel, 1987).** At high pH, cations precipitate or adsorb to mineral surfaces and metal anions are mobilized.

The presence of hydrous metal oxides of Fe, Al and Mn can strongly influence metal concentrations because these minerals can remove cations and anions from solution by ion exchange, specific adsorption and surface precipitation **(Ellis and Fogg, 1985 and Dzombak and Morel, 1987).**

Sorption of metal cations onto hydrous oxides generally increases sharply with pH and is most significant at pH values above the neutral range, while sorption of metal anions is greatest at low pH and decreases as pH increases. Cation exchange capacity (CEC) refers to the concentration of readily exchangeable cations on a mineral surface and is often used to indicate the affinity of soil for uptake of cations such as metals. Anion exchange capacity (AEC) indicates the affinity of soils for uptake of anions, and is usually significantly lower than the (CEC) of the soil. In addition to hydrous oxides, clays are also important ion exchange materials for metals **(Sposito, 1989).** The presence of natural organic matter (NOM) has been shown to influence the sorption of metal ions to mineral surfaces. NOM has been observed to enhance sorption of Cu^{2+} at low pH, and suppress Cu^{2+} sorption at high pH **(Tipping et al., 1983 and Davis, 1984).**

Organic matter, particularly humic materials, can complex metals and affect their removal from solution **(Ali and Dzombak, 1996).** Humic materials contain carboxylic and phenolic functional groups that can complex with metal ions.

I-9-5. Movement of heavy metals in soil profiles

The factors which influence the downward movement in soil profile are essentially that already modulot bioavailability.

Soil pH considered to be the most important factor controlling the metal movement in soil profiles **(Emmerich et al., 1982)**. Although stability of metal-ligand complexes increases as soil pH increases resulting in decline movement of heavy metals **(Naidu and Herter, 1998)**. It was reported that soil pH values affecte on precipitation and dissolution process **(White and Chaney, 1980)**.

Certain elements are much more sensitive to the changing in soil pH, which reflected in their leachability. Thus Ni, Zn, and Cd tend to be affected strongly by soil pH, whereas Cu, Pb and Cr are little affected by soil pH conditions **(Bolton, 1975)**.

Welch and Chaney, (1987) found that the soil texture also influenced the downword movement of heavy metals. They mentioned that the movement of heavy metals was corrected positively with coarse fraction content and negatively with fine fractions. And these results were similar to the results of **(El-Gendi et al., 1997)** who mentioned that the high permeability of sandy soils facilitates the downword movement of heavy metals.

However, many other authors showed that the movement of heavy metals is not affected by the soil texture. **Dawis and Freites, (1970)** reported that the movement of Cd, Cr, Zn, Cu and Ni in sandy soils equals that movement of these elements in calcareous soils.

The influence of volume water applied to soil through irrigation processes or by rainfall on movement was also studied. **Welch and Chaney, (1987)** stated that there was no evidencethat the rainfall was associated greatly with the movement of the heavy metals. However, **El-Gendi et al., (1997)** reported that volume of water applied to irrigate the contaminated soils was positively contributed to the movement of heavy metals.

On the other hand, the influence of the number of the years and quantity of contamination application on the movement of the heavy metals was also studied. **Damondy et al., (1983)** reported that Cu was particularly mobile in the silt loam soil amended with 150-300 ton/ha. **Dowdy et al., (1991)** reported that the application 765ton/ha of sludge over a period of 14years, Cd and Zn were only accumulated in the upper layer of the soil (32-51cm).

The influence of the organic matter on the movement of heavy metals was studied by many authors, **(Arzahanova and Yelpat, 1980)** studied the form of which some heavy metals migrate. They observed that, for example, Cu and Pb migrate mainly in collidal phase, while Zn migrates mainly in truly soluble form. **(El-Gendi, 2003)** mentioned that the pattern of the Pb distribution within the soil profile was mainly attributed to the organic matter content. Like wise Pb, the distribution of Cu was closely associated with the organic matter content.

In contrast, **Welch and Chaney, (1987)** mentioned that no relations were observed between the organic matter content and the movement of the heavy metals.

In the northern Campine in Belgium, **Horckmans et al., (2007),** mentioned that large areas are contaminated by heavy metals such as Zn and Cd due to the metal industry. In the sandy soils, the heavy metal adsorption/attenuation in the spodic horizon represents the main retention mechanism of leached pollutants from the contaminated topsoils. The pH-dependent behavior of the elements in these spodic horizons was tested by pH test experiments and compared to sandy loam soils. Extractions with $CaCl_2$ 0.01M and EDTA 0.05M provided a further insight into the binding mechanisms. The results indicate that organic matter is the main factor responsible for the mobility of Cd, Zn and Ca in the spodic horizons. The binding of elements is not very strong, and highly dependent on pH. A slight decrease in pH can cause a significant release of metals from the spodic horizons, with up to 60% of Cd and 90% of Zn being released within a 1.5 unit change in pH (starting from the naturally occurring pH). This pH change can happen rapidly in these soils, due to the low buffering capacity, and is realistic given the acidification in Flanders. For the sandy loam soils, a pH decrease of 3 units is needed to release 40% of Cd

20% of Zn, and the acid neutralization capacity was exhausted more gradually, suggesting that slower buffering mechanisms took place. For the sandy loam soils, Cd retention is mainly governed by organic matter, while for Zn other factors such as the clay minerals also play an important role. Despite the high potential mobility and pH dependence of the heavy metal retention in the spodic horizons, the actual risk for groundwater pollution is limited. For the diffusely contaminated areas, where traditional remediation is not an option, spodic horizons may therefore contribute to a natural attenuation of the soil contamination.

Camobreco et al., (1996) studied the relative mobility of some heavy metals through soil columns and observed that their mobility may ranked as follow Cd > Zn > Cu > Pb, while **Morera at al., (2001)** arranged the mobility in the following order Zn = Cd =Ni > Pb > Cu.

The leachability of heavy metals could be attributed to the chemical form of the metal present in the soil and to its removal form of each metal according to **El-Gendi., (2003),** and ranked the relative mobility of heavy metals starting from the highest Co > Cd > Cu > Zn > Pb. And he mentioned that the mobility index for the industrial polluted soil was higher for Zn (28.2%), than that for Pb (20.1%).

Anxiang et al., (2005) investigated the time effect on the fractionation of Cu, Zn, Pb, and Cd in three typical Chinese soils. A total of 500 ppm of Cu, Zn, Pb and 2.5 ppm of Cd were added to soils as nitrates. Metals in the incubated soils were fractionated from 3 h to 8 weeks by the sequential extraction procedure, in which the metal fractions were experimentally defined as exchangeable, carbonate-, Fe–Mn oxide, organic matter-bound and residual fractions. Results showed that the changes of Cu, Pb and Zn in fraction distribution were biphasic by an initial rapid step followed by a slow one. Metals in exchangeable fraction were increased in the first 3h, and then decreased, such decrease could be stimulated by a diffusion equation and the decrease rate followed the order Pb>Cu>Zn>>Cd. Metals bound to Fe–Mn oxides and organic matter increased consistently in the 8-week incubation. There were almost no changes for the metals in the residual fraction. After 3h incubation most of Cd added to soils

presented in the exchangeable fraction. The content of Cd in each fraction changed slightly in the 8-week incubation. Soil pH played an important role in metal fraction distribution patterns. Jiangxi soil, with low soil pH, tended to keep more metals added in exchangeable fraction and the changes of metals in each fraction were not as remarkable as in other two soils. High organic matter content resulted in the increased organic matter-bound fraction.

Lister and Line, (2001) concluded that the chemical properties of the sludge (pH value, buffer capacity, organic matter content, carbonates and silicates contents) favour the heavy metals sorption in a more or less stable form and to change chemical soil parameters such as soil pH and organic carbon content. The aim was to obtain changes in heavy-metal speciation towards more stable forms by acting on the pH and organic matter content. Effectively, it was found that in pulptreated soils the availability of zinc and manganese for plants decreases and that this effect is negatively correlated to the pH increase.

Barry and Sposito, (1988) used a one dimensional convection–dispersion equation to describe solute transport in soils. In miscible displacement experiments, a mixture of $4mgl^{-1}$ $CdCl_2$, 20 ppm $NiCl_2$, and 60 ppm $ZnCl_2$ was leached from top of the column and the effluent was collected in increments with the aid of a fraction collector. The retardation factor (R) calculated from the least squares method was close to the R value observed from breakthrough curves. The R value showed the trend: Cd>Zn>Ni, indicating the rate of metals transport in red soils: Ni>Zn>Cd.

I-10. Establishment of Remediation Goals

The physical and chemical form of the metal contaminant in soil or water strongly influences the selection of the appropriate remediation treatment approach. Information about the physical characteristics of the site and the type and level of contamination at the site must be obtained to enable accurate assessment of site contamination and remedial alternatives.

Once the site has been characterized, the contamination in the groundwater and soil should be characterized to establish the type, amount, and distribution of contaminants across different

media and the desired level of each contaminant in soil and groundwater must be determined. This is done by comparison of observed contaminant concentrations with soil and ground-water quality standards for a particular regulatory domain, or by performance of a site-specific risk assessment.

To obtain good representing samples there some parameters should be taken:

Soil Sampling: Before any chemical analysis can be performed, it is very important to obtain a good representative soil sample for the soil under investigation, and it is not a simple task. Frequently sampling errors are commonly much greater than analytical errors.

Time of Sampling: Normally, sampling instructions do not specify a particular time of sampling, although seasonal cycles in soil test parameters are present. Generally the best time to take samples is in midsummer to early fall, when seasonal effects are minimal. Some workers recommend taking soil samples at the same time plant tissue is being collected for analysis, normally during mid /or late summer **(Kim, 2005)**

Samples Preservation: After the samples collection, care must be taken to avoid contamination and to prevent the occurrence of further chemical and biochemical reactions. The sample must be preserved as much as possible in its original condition, and it is necessary to maintain the properties and the identity of the sample at all stages of sample preparation.

Air drying is the most accepted procedure of sample preservation. Additionally, a sample should not be allowed to stay moist for extended periods of time. Soil aggregates should be broken carefully to accelerate the drying procedure. Chemical and biochemical reactions in air-dry soils are reduced to a minimum, although these reactions are still possible sources for errors. To accelerate the drying process, samples may be placed in a forced draft of moving air, but not in heated air. The temperature must not exceed 35°C because drying at elevated temperatures may cause drastic changes in the physical, chemical, and biological characteristics of the soil sample **(Hesse, 1972).**

Contamination of samples because of adsorption of gases is a frequently overlooked source of error. Samples should be dried and stored in airtight containers as soon as possible to avoid adsorption of NH_3, SO_3, and/or SO_2 gases in the laboratory. They must be protected from contamination with dust, including radioactive particles, and a variety of gases, as mentioned above. Containers should be clean and should be composed of materials that will not contaminate the sample. Glass jars, plastic containers, or waxed card-board containers are suitable for this purpose. The storage room should be well-ventilated and kept at low temperatures and low relative humidity. The stored samples can be used for analysis at a later date. Standard or certified reference samples are usually preserved in this way for checking after two to four years.

Certain analyses however require the use of soil samples in their original moisture status, eg, pesticide residue, NH_4^+, and NO_3^- determination. Samples collected for the microbial process, are often suggested to be analyzed as soon as they have been sampled, when it is not possible, they may be stored moist at -40°C. Soils with high microbial activity need to be preserved at a sufficiently low temperature and preferably in darkness in order to prevent condensation and growth of algae **(Kim, 2005).**

Soil samples preserved in the moist state should not be stored for extended period of time. If storage for a day or two is required, the samples are kept in airtight containers, placed at temperatures of 10°C or lower, in the dark in order to prevent algae's growth. Redox reactions and recrystallization may occur during storage, and some of the original moisture content is lost, which appears as condensation on the inner walls of the containers of plastic bags.

Samples Crushing and Grinding: Through mixing requires that the sample should be crushed and ground to particles of uniform size. Large aggregates are reduced by crushers, and the crushed sample is then further reduced by grinding. Care should be taken not to break the individual soil minerals during the process. The purpose of grinding is to reduce heterogeneity and to provide maximum surface area for physical and chemical reactions. Various devices are used for crushing and grinding. The choice of

equipment depends on four factors, the amount of sample to be crushed, the degree of fineness to be obtained, the concentration that can be tolerated, and the analysis in question.

Crushing soil aggregates can be done by using jaw crushers, hardened steel mortars, or rocking boards. Jaw crushers are used for crushing large aggregates, steel mortars are used for smaller aggregates.

Samples Sieving: It is an essential part of homogenizing the sample after its grinding. In the past, a 0.5-mm sieve was used for this purpose, but currently a 2-mm sieve is preferred. The fraction passing a 2-mm sieve is collected and stored as a stock sample.

It is also believed that the soil fraction >2 mm represents more accurately the total soil volume than do the finer sieve size fractions. However, sieves finer than 2 mm are, of course, also employed. The different sand fractions are obtained by sieving through sieves of finer sizes, and where microanalysis requiers the use of a very small amount of sample, the stock sample (<2 mm fraction) can be subsampled, ground, and screened through a 1-mm or 0.5-mm sieve. The fraction <0.5 mm, preferred in modern microanalysis. Resistant soil minerals are often accumulated in the coarse size fraction and are discarded by sieving with finer sieves. Results obtained by analyses of samples passing different sieves are not necessarily comparable. The soil fraction >2 mm is usually discarded in soil chemical analysis. These materials are not soil constituents, but are rock fragments which may produce soil constituents after weathering.

Samples Size: When a very large sample is taken and processed, it may be necessarey to reduce the amount of the sample for ease of storage and handling. The mixture obtained by grinding and sieving must be reduced in size and subsampled for analysis can properly identify the soil characteristic under investigation. This objective requires that every particle have an equal chance of being subsampled. It can be done by two ways, the first is the mechanical sample splitting where reduction in size or sample splitting can be performed with a mechanical sample splitter, such as a riffle sampler, by which the sample is automatically divided in

half by a series of chutes **(Willard and Dhiel, 1943 and Hesse, 1972).** This process can be repeated as many times as necessary. The second type is the Quartering where the sample is usually reduced in size by quartering. The sample is spread uniformly over a sheet of paper or plastic and divided into four equal portions, 1, 2, 3,4. Portions 2 and 3 are collected and thoroughly mixed, whereas the remainder is discarded. This process of quartering can be repeated as many times as necessary until the right size of sample is attained.

I-11. General Remediation Approaches for Heavy Metals

Several technologies exist for the remediation of metals-contaminated soil and water. These technologies are contained within five categories of general approaches to remediation: isolation, immobilization, toxicity reduction, physical separation and extraction. These are the same general approaches used for many types of contaminants eg. hydrocarbons in the subsurface **(LaGrega et al., 1994)**. As usually the case is, combinations of one or more of these approaches are often used for more cost-effective treatment of a contaminated site.

I-11-1. Isolation

Isolation technologies attempt to prevent the transport of contaminants by containing them within a designated area. These technologies can be used to prevent further contamination of groundwater when other treatment options are not physically or economically feasible for a site. Contaminated sites may also be isolated temporarily in order to limit transport during site assessment and site remediation **(Conner, 1990).**

I-11-2. Capping

Capping systems are used to provide an impermeable barrier to surface water infiltration to contaminated soil for prevention of further release of contaminants to the surrounding surface water or groundwater. Capping provides a range of design options that includes simple single-layer caps and more complex multilayer systems **(U.S.EPA, 1991 and Rumer and Ryan, 1995).**

1995). Design selection depends on site characteristics, remedial objectives and risk factors associated with the site. A variety of materials are available for use in capping systems and choice of materials is site specific because local soils are often incorporated into parts of the cap. Synthetic membranes such as high-density polyethylene are also available for incorporation into capping systems.

I-11-3. Subsurface barriers

Subsurface barriers may be used to isolate contaminated soil and water by controlling the movement of groundwater at a contaminated site. These barriers are designed to reduce the movement of contaminated groundwater from the site, or to restrict the flow of uncontaminated groundwater through the contaminated site (**Rumer and Ryan, 1995**). Vertical barriers are commonly used to restrict the lateral flow of groundwater. For effective isolation of the contaminated matrix, the barrier should extend and key into a continuous, low-permeability layer, such as clay or competent bedrock, below the contaminated area (**U.S.EPA, 1991 and Rumer and Ryan, 1995**). If an impermeable layer is not available, a ground-water extraction system must be used to prevent transport of contaminants under the barrier. Vertical barriers may be installed upstream, downstream, or completely surrounding the site and are often implemented in conjunction with a capping system to control surface water infiltration.

Slurry walls are the most common type of vertical barrier due to their low relative cost. The use of slurry walls can be limited by the topography, geology and type of contamination at the site, while technologies for the construction of horizontal barriers would enable control of the downward migration of contaminants by lining the site without requiring excavation of the contaminated matrix.

I-11-4. Immobilization

Immobilization technologies are designed to reduce the mobility of contaminants by changing the physical or leaching characteristics of the contaminated matrix. Mobility is usually decreased by physically restricting contact between the

contaminant and the surrounding groundwater, or by chemically altering the contaminant to make it more stable with respect to dissolution in groundwater. The aqueous and solid phase chemistry of metals is conducive to immobilization by these techniques. A variety of methods are available for immobilization of metal contaminants, including those that use chemical reagents and/or thermal treatment to physically bind the contaminated soil or sludge. Most immobilization technologies can be performed ex situ or in situ. In situ processes are preferred due to the lower labor and energy requirements, but implementation in situ will depend on specific site conditions **(Conner, 1990).**

I-11-5. Solidification / stabilization

Solidification and stabilization (S/S) immobilization technologies are the most commonly selected treatment options for metals-contaminated sites **(Conner, 1990).** Solidification involves the formation of a solidified matrix that physically binds the contaminated material. Stabilization, also referred to as fixation, usually utilizes a chemical reaction to convert the waste to a less mobile form. The general approach for solidification/stabilization treatment processes involves mixing or injecting treatment agents to the contaminated soils. Inorganic binders, such as cement, fly ash, or blast furnace slag, and organic binders such as bitumen are used to form a crystalline, glassy or polymeric framework around the waste. The dominant mechanism by which metals are immobilized is by precipitation of hydroxides within the solid matrix **(Bishop et al., 1982 and Shively et al., 1986).**

Solidification / stabilization (S/S) technologies are not useful for some forms of metal contamination, such as species that exist as anions (e.g., Cr(VI) and arsenic) or metals that don't have low-solubility hydroxides(e.g. mercury). S/S may not be applicable at sites containing wastes that include organic forms of contamination, especially if volatile organics are present. Mixing and heating associated with binder hydration may release organic vapors. Pretreatment, such as air stripping or incineration, may be used to remove the organics and prepare the waste for metal stabilization/solidification **(Smith et al., 1995).**

The application of S/S technologies will also be affected by the chemical composition of the contaminated matrix, the amount of water present, and the ambient temperature. These factors can interfere with the solidification/stabilization process by inhibiting bonding of the waste to the binding material, retarding the setting of the mixtures, decreasing the stability of the matrix, or reducing the strength of the solidified area.

I-11-6. Vitrification

The mobility of metal contaminants can be decreased by high-temperature treatment of the contaminated area that results in the formation of various materials, usually an oxide solid. During this process, the increased temperature may also volatilize and/or destroy organic contaminants or volatile metal species (such as Hg) that must be collected for treatment or disposal. Most soils can be treated by vitrification and a wide variety of inorganic and organic contaminants can be targeted. Vitrification may be performed ex situ or in situ, although in situ processes are preferred due to the lower energy requirements and cost.

Typical stages in ex situ vitrification processes may include excavation, pretreatment, mixing, feeding, melting and vitrification, off-gas collection and treatment, and forming or casting of the melted product. The energy requirement for melting is the primary factor influencing the cost of ex situ vitrification. Different sources of energy can be used for this purpose, depending on local energy costs. In situ vitrification (ISV) involves passing electric current through the soil using an array of electrodes inserted vertically into the contaminated region. Each setting of four electrodes is referred to as a melt. If the soil is too dry, it may not provide sufficient conductance and a trench containing flaked graphite and glass frit (ground glass particles) must be placed between the electrodes to provide an initial flow path for the current **(Buelt and Thompson, 1992).**

I-11-7. Toxicity and/or mobility reduction

Chemical and/or biological processes can be used to alter the form of metal contaminants in order to decrease their toxicity and/or mobility.

I-11-7-1. Chemical treatment

Chemical reactions can be initiated that are designed to decrease the toxicity or mobility of metal contaminants. The three types of reactions that can be used for this purpose are oxidation, reduction, and neutralization reactions.

Chemical oxidation changes the oxidation state of the metal atom through the loss of electrons. Commercial oxidizing agents are available for chemical treatment, including potassium permanganate, hydrogen peroxide, hypochlorite and chlorine gas. Reduction reactions change the oxidation state of metals by adding electrons. Commercially available reduction reagents include alkali metals (Na and K), sulfur dioxide, sulfite salts, and ferrous sulfate. Changing the oxidation state of metals by oxidation or reduction can detoxify, precipitate, or solubilize the metals **(NRC, 1994).**

Chemical neutralization is used to adjust the pH balance of extremely acidic or basic soils and/or groundwater. This procedure can be used to precipitate insoluble metal salts from contaminated water, or in preparation for chemical oxidation or reduction.

Chemical treatment can be performed ex situ or in situ. However in situ chemical agents must be carefully selected so that they do not further contaminate the treatment area. The primary problem associated with chemical treatment is the nonspecific nature of the chemical reagents. Oxidizing/reducing agents added to the matrix to treat one metal will also target other reactive metals and can make them more toxic or mobile **(NRC, 1994).** Also, the long-term stability of reaction products is of concern since changes in soil and water chemistry might reverse the selected reactions.

I-11-7-2. Biological treatment

Biological treatment technologies are available for remediation of heavy metals-contaminated sites. These technologies are commonly used for the remediation of organic contaminants and are beginning to be applied for metal remediation, although most applications to date have been at the bench and pilot scale **(Schnoor, 1997).** Biological treatment exploits natural biological processes that allow certain plants and

microorganisms to aid in the remediation of metals. These processes occur through a variety of mechanisms, including adsorption, oxidation and reduction reactions, and methylation **(Means and Hinchee, 1994).**

Bioaccumulation

Bioaccumulation involves the uptake of metals from contaminated media by living organisms or dead, inactive biomass. Active plants and microorganisms accumulate metals as the result of normal metabolic processes via ion exchange at the cell walls, complexation reactions at the cell walls, or intra- and extracellular precipitation and complexation reactions. Adsorption to ionic groups on the cell surface is the primary mechanism for metal adsorption by inactive biomass. Accumulation in biomass has been shown to be as effective as some ion exchange resins for metals removal from water **(Means and Hinchee, 1994).**

Phytoremediation

Phytoremediation refers to the specific ability of plants to aid in metal remediation. Some plants have developed the ability to remove ions selectively from the soil to regulate the uptake and distribution of metals. Most metal uptake occurs in the root system, usually via absorption, where many mechanisms are available to prevent metal toxicity due to high concentration of metals in the soil and water. Potentially useful phytoremediation technologies for remediation of metals-contaminated sites include phytoextraction, phytostabilization and rhizofiltration **(U.S.EPA, 1996).**

Phytoextraction

Phytoextraction employs hyperaccumulating plants to remove metals from the soil by absorption into the roots and shoots of the plant. A hyperaccumulator is defined as a plant with the ability to yield 0.1% chromium, cobalt, copper or nickel or 1% zinc, manganese in the aboveground shoots on a dry weight basis. The aboveground shoots can be harvested to remove metals from the site and subsequently disposed as hazardous waste or treated for the recovery of the metals **(Means and Hinchee, 1994).**

Phytostabilization

Phytostabilization involves the use of plants to limit the mobility and bioavailability of metals in soil. Phytostabilizers are characterized by high tolerance of metals in surrounding soils but low accumulation of metals in the plant. This technique may be used as an interim containment strategy until other remediation techniques can be developed, or as treatment at sites where other methods would not be economically feasible **(Means and Hinchee, 1994).**

Bioleaching

Bioleaching uses microorganisms to solubilize metal contaminants either by direct action of the bacteria, as a result of interactions with metabolic products, or both. Bioleaching can be used in situ or ex situ to aid the removal of metals from soils. This process is being adapted from the mining industry for use in metals remediation. The mechanisms responsible for bioleaching are not fully defined, but in the case of mercury bioreduction (to elemental mercury) is thought to be responsible for mobilization of mercury salts **(Means and Hinchee, 1994).**

I-12. General Remediation Approaches for Oil Pollution

Remediation of soils contaminated with hydrophobic contaminants is always a challenge for soil and environmental scientists, because hydrophobic molecules often bind tightly to soil particles making them inaccessible to low cost remediation solutions and necessitating the use of costly capital energy, chemical and/or physical treatment. Polycyclic aromatic hydrocarbons (PAHs), which are made up of only carbon and hydrogen, are ubiquitous contaminants in soils and are well known for their toxic, carcinogenic, and mutagenic effects **(Tao et al., 2004).** Most PAHs are hydrophobic with high boiling and melting points and possess low water solubility and electrochemical stability. Therefore, they can exist and be accumulated in soils for a long time.

Solvent extraction is an effective method for removal of PAHs from contaminated soils at a number of superfund sites. Vegetable oil, a natural non-toxic, cost-effective, and biodegradable extractant, was considered as a less hazardous solvent for use in the extraction of hydrophobic contaminants from soils by some scientist **(Pannu et al., 2004).**

Gong et al., (2006), found that sunflower oil can be used as a promising agent to remove more than 90% total PAHs from MGP soils with total PAHs concentrations between 1000 and 5000 ppm. Regeneration and reuse of the oil in the process are quite essential for effective application of vegetable oil to extract PAHs contaminants from soils. Thus, a method for subsequent removal of the extracted PAHs from the oil is necessary. It was proved that vegetable oil has an advantageous to be used as a non-toxic, cost-effective and biodegradable solvent to extract polycyclic aromatic hydrocarbons (PAHs) from contaminated soils for remediation purposes. Activated carbon adsorption of PAHs from vegetable oil was used in soil remediation. The results revealed the effectiveness of using activated carbon as an adsorbent to remove PAHs from vegetable oils for reemployment of the oil in remediation. Adsorption capacity was dependent on the initial concentrations of the PAHs in the vegetable oil, the higher the concentrations, the more PAHs adsorbed. Batch adsorption exhibited a better performance as compared to column adsorption, as vigorous shaking provided more contact and more adsorption sites. More than 90% of PAHs in the vegetable oils were removed when suitable amount of activated carbon was used in the batch adsorption. Total PAHs removals from oils in the column adsorption experiments were in the range of 68.1–93.5% **(Gong et al., 2007).**

Chemical oxidation is quite widely studied method for the treatment of soils and slurries including refractory compounds. The effect of ozonation for the degradation and kinetics of soil contaminated with PAHs has been studied by **(Miller and Olejnik, 2001).** For removal of PAHs, ozonation is a good alterative. Due to the molecular structures of PAHs, they react very fast with ozone. The ozone (O_3) is attacking and degrading aromatic organic pollutants in the aqueous phase, which broke the hydrophobic PAHs into more simple, soluble and biodegradable form via

aromatic ring cleavage and/or via hydroxylation of the aromatic rings due to radical reactions. pH has a great influence on the ozonation of PAHs in the liquid media. The rate of PAHs disappearance is usually decreased when the pH is increased. In direct ozone reactions each PAH molecule needs two ozone molecules to disappear, but intermediate compounds can consume much more ozone **(Haapea and Tuhkanen, 2006).**

The effects of surfactants on the washing of crude oil contaminated soils have been reported by **(Urum et al., 2004)**. Sodium dodecyl sulfate (SDS) was evaluated as surfactants for treating petroleum hydrocarbon contaminated soil through soil washing. He concluded that the enhancement of crude oil removal using the surfactant solutions was more effective for the non weathered soils than for the weathered soils. The crude oil removal from both the weathered and nonweathered contaminated soil samples by SDS was within the same experimental repeatability range of ±6%.

Furthermore, an appreciable amount of waste crude oil generated during field operation can be collected in a waste pit (Group Gathering Stations, GGS) **(Gogoi et al., 2003)**. Thermal treatment of petroleum contaminated soil (PCS) is considered expensive process and is suspected to cause air pollution. Land farming is another technique where the contaminated soil could be mixed with clean desert sand to reduce the hydrocarbon concentration to less than 5% by weight **(McCarthy et al., 2004).**

The photooxidation is considered to the most important factor involved in the transformation of crude oil or its products released into the soil **(Samanta et al., 2002)**. The photochemical degradation yields a great variety of oxidized compounds which are highly soluble in water

I-13. Impact of Heavy Metals on Bioremediation of Petroleum Contaminated Soil

Oil pipelines leakage and accidental oil spills are common problems in petroleum industry resulting into contamination of soils. An oil spill can cause not only hydrocarbon contamination but also heavy metals contamination into the surrounding

subsurface and groundwater, posing a threat to the environment and to human health **(Jamrah et al., 2007).** Many metallic compounds occur in petroleum in extremely small concentrations, such as inorganic salts, metal soap, and organic metal-complex compounds. Petroleum-contaminated soil (PCS) is a mixture of sand, slit, clay and petroleum products. Disposal of PCS in waste dumping sites is not considered an option because of the lack of proper design and control of dumping in Egypt which poses a continuous threat of further contamination to the soil. Major metal contaminants in petroleum oil commonly include aluminum (Al), sodium (Na), iron (Fe), nickel (Ni) and vanadium (V), with frequently smaller amounts of magnesium (Mg), tin (Sn), barium (Ba), zinc (Zn), molybdenum (Mo), calcium (Ca), copper (Cu), manganese (Mn), lead (Pb), chromium (Cr), and titanium (Ti). Vanadium and nickel are the most abundant metallic constituents of crude petroleum, sometimes reaching thousand of parts per million.

They are primarily present in porphyrin complexes and other organic compounds. Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the environment. They are known or suspected to be genotoxic or carcinogenic and have been classified as priority pollutants **(Chung et al., 2007).** Persistence of PAHs in the environment linked to their general recalcitrance, binding to the soil matrix and low water solubility, make them non-bioavailable to PAHs-degrading organisms **(Guo et al., 2005).**

Microbial communities play important roles in soil because of the many functions they perform in nutrient cycling, plant symbiosis, decomposition, and other ecosystem processes **(Nannipieri et al., 2003).** Large heavy metals (HM) contents in soil are of concern because of their toxicity to soil microorganisms and impairment of ecosystem functions **(Frey et al., 2006).** Most of studies reported reduced soil microbial activities and microbial biomass, inhibition of organic matter mineralization and changes in microbial community structure following application of HM to the soil **(Shen et al., 2006).** The hazard posed by HM in soil is suggested to be a function of their relative mobility and bioavailability which are dependent on soil characteristics such a pH, mineralogy, texture, and organic matter content as well on the source and quantities of HM in the soil **(Lofts et al., 2004).** In consequence these sites become inhospitable and just those

microorganisms able to tolerate the high concentration of petroleum hydrocarbons and heavy metals can survive. Thus, the bioprospection of these natural selected organisms represents an important strategy in order to obtain agents for bioremediation processes **(Castro-Silva et al., 2003).**

Along with deciding whether or not a site should be remediated using on site treatment or in situ treatment, it is necessary to decide the bioremediation options needed to be employed. Three types of bioremediation are predominant in the industry today **(Kaplan and Kitts, 2004):** natural attenuation (soil's natural ability to degrade the contaminant), biostimulation (adding nutrients to improve the natural biodegradation rate) and bioaugmentation (addition of a microbial consortium from selected species previously isolated from a contaminated soil plus nutrients). Biostimulation is the most recommended method **(Olaniran et al., 2006).** Various studies have been carried out to determine the effect of biostimulation on biodegradation of hydrocarbons in HM and oil polluted soils **(Braddock et al., 1999 and Aislabie et al., 2006).** Biostimulation treatment includes the addition of nitrogen, phosphorous, surfactant, adjustment of pH for the proliferation of indigenous microorganisms, hence speeding up the bioremediation process **(Bento et al., 2005).**

Heavy metals (HM) exposure has, since the last century, been known to affect microbial growth and survival **(Sokhn et al., 2001 and Oliveira and Pampulha, 2006).** An extensive literature is available on the effects of HM on microbial populations and microbial processes, such as litter decomposition and carbon mineralization. However little is known about the effect of heavy metals on the degradation of recalcitrant hydrocarbons, such as PAHs. Some HM are thought to be essential for oil-degrading microorganisms while others are known to be toxic. Whereas some metals, such as copper, are essential for bacteria and fungi in trace amounts, high concentrations are known to be toxic. The addition of copper to the soil significantly inhibits soil respiration, nitrogen mineralization and nitrification **(Atagana, 2006).** Long-term exposure to heavy metals (Cu, Ni and Zn) has been found to alter microbial structure **(Chaerun et al., 2004).** However, tolerance and adaptation of microorganisms to heavy metals are common phenomena, and the presence of tolerant fungi and bacteria in

polluted soils has frequently been observed **(Deighton and Goodman, 1995).** The negative effects of HM on soil microbes and soil microbial processes means that their presence in contaminated soils can potentially limit the bioremediation of organic pollutants, the influence of HM on PAHs degradation in polluted soils has only recently emphasized **(Baldrian et al., 2000).** It is well documented that the presence of heavy metals can inhibit a broad range of microbial processes including methane metabolism, growth, nitrogen and sulfur conversions, dehalogenation, and reductive processes in general. Metals may inhibit pollutants biodegradation through interaction with enzymes directly involved in biodegradation (e.g., pollutants-specific oxygenases) or through interaction with enzymes involved in general metabolisms. In either case, inhibition is mediated by the ionic form of the metal **(Sandrin and Maier, 2003).** Biosurfactant was reported to decrease heavy metal toxicity in polluted sites and enhance biodegradation efficiency **(Sandrin et al., 2000).**

Since indigenous microorganisms at spill sites may be exposed to these heavy metals (HM), which may affect their growth and ability to degrade crude oil and PAHs, finding microorganisms having combination of the genetic systems encoding the production of biosurfactant, degradation of PAHs and resistance to HM is one of the approaches to the creation of multifunctional strains for bioremediation of soils co-contaminated by organic pollutants and heavy metals.

When bioremediation technique is applied, application of precise and reliable methods for the evaluation of pollutants biodegradation process is necessary. Some of the currently used methods include: Enumeration, isolation and identification of strains with potential for hydrocarbons degradation **(Chaineau et al., 2005).** Along with the above mentioned, the literature sources outline compounds effective for the evaluation of biodegradation such as, n-alkanes and isoprenoids biomarkers (pristane, Pr and phytane, Ph), naphthalenes, phenanthrenes and dibenzothiophenes **(Wang et al., 1998).**

Cu, Mn, Ni and Zn were selected for this study as they occur widely in the natural environment and have many uses in industrial applications. They have been identified as co-

contaminants in hydrocarbon-contaminated soils **(Riis et al., 2002 ; Wong et al., 2005 and Atagana, 2006)**. Although they are essential elements at trace concentrations, at higher concentrations they are known to be toxic, impacting microbial growth, morphology and biochemical activities as a result of adverse interactions with cellular components **(Olaniran et al., 2006).** Phenanthrene was selected as the target hydrocarbon in this study as it is prevalent in petroleum products, and has been previously used as a model compound for determining biodegradation potential in contaminated soils **(Sokhn et al., 2001 and Wong et al., 2005).**