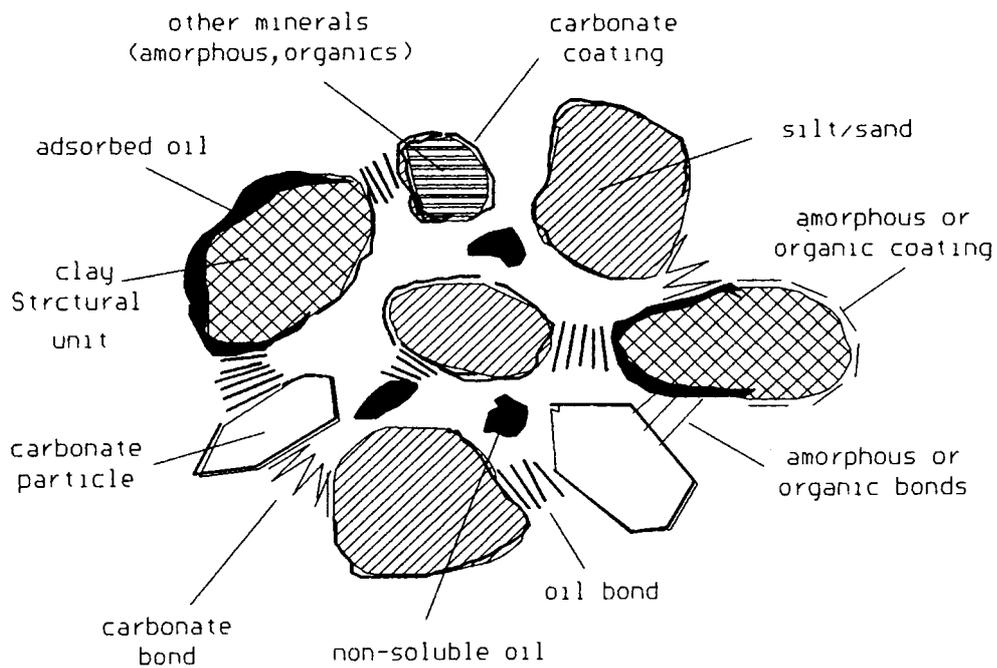


Methodology for In-situ Analysis of Soils, Contaminated with Cutting Fluids



Thesis for the completion of Masters of Science
In Applied Environment Measurement Techniques

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Abstract

The clean up of soils contaminated with cutting fluids is associated with several challenges, especially of analytical methodologies and data interpretation. Treatment technology and site remediation progress will lean heavily on analytical techniques that are accurate, reproducible and of real time value. Most of the existing analytical techniques for petroleum hydrocarbons especially cutting fluids are different for different group of hydrocarbons, moreover they are expensive and time consuming.

This study focuses on the development of methodology for the in-situ analysis of cutting fluids. The project was initiated and financed by Volvo Technical Development AB, Sweden which has shown their interest in the determination of cutting fluids in contaminated soils. Analytical techniques adopted for the project were; (1) photoionization detector, a screening technique for a wide range of volatile hydrocarbons; (2) Immunoassay, an efficient method to detect aromatic hydrocarbons; and (3) PetroFlag, a system for analysis of a wide range of all hydrocarbons especially heavy oils. The results of only one method could be used to decide the concentration levels of petroleum hydrocarbons, however combination of more than one technique for example PID and PetroFlag give a good idea of the concentration levels for a wide range of hydrocarbons. All of these analytical approaches are reliable, economical, and give real time values of the concentration levels in the field.

A part of the study was to investigate the mobility of soluble cutting fluids in saturated as well as in unsaturated soils. Cutting fluids containing a base of mineral oil and 30% - 85% water with some polar organic compounds were found to be highly mobile in the saturated soils. The high mobility of cutting fluids is attributed to the water-soluble constituents present in the cutting fluids. In the vadose zone oil can move as dissolved phase, non – aqueous phase liquid (NAPL), and gaseous phase. The NAPL stays in the unsaturated zone while the dissolved phase may move to the saturated zone with the rainfall and groundwater fluctuations. A higher flow rate may allow greater momentum to be transferred from the leaching water to the oil in the pore fluid, thereby providing more kinetic energy to reduce the interfacial between oil and water and hence poses a threat to the surrounding environment in the form of surface and groundwater contamination.

The environmental soil investigations were also performed at an old industrial site in Sweden to illustrate field analytical approaches for the characterization of complex petroleum hydrocarbon contaminants. Comparison of the field results and Swedish guideline values show higher concentration levels of aliphatic hydrocarbons at two locations of the site.

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Introduction

Recent discovery of contaminated land in many industrialized countries has resulted in major environmental concern with substantial social and financial implications. The uncontrolled disposal of complex hydrocarbons to the soil phase of the environment has resulted in the accumulation of oil constituents beyond the assimilative capacity of receiving soils (Hrudey et al, 1993). Contaminated soil has been actualized by new legislations and incidents at some sites as well as in connection to purchase of new production units. It is important to know the impact of human activities on surface and groundwater. The evaluation of potential risks to human health and environment that result from these releases, and the allocation of resources for the site remediation decision, relies increasingly on the results of assessment and characterization of the sites. These figures are valuable if there will be leaching of oil to soil. It is also important to develop functional methods of sampling and analysis ready to use when necessary.

Soil contaminated with petroleum hydrocarbon products as cutting fluids, poses a significant challenge for characterization and remediation programs that require rapid, accurate and comprehensive data in the field or laboratory. Oil based cutting fluids contain complex matrix of polar and non-polar petroleum hydrocarbons with a diverse range of physiochemical and toxicological properties. Organic contaminants in soil vary greatly in both space and time, and this variation depends on a host of factors specific to those particular sites of interest, including the nature of the soil, the behavior of the pollutants, its transport mechanism and the climates (Monge A., 1998). A proper knowledge of the various mechanisms of interaction between PHCs and soil surface is important in assessing the level of concentration and predicting their movement. Ongoing studies of organic compounds contaminated sites have highlighted that different types of organic compounds require different strategies for measuring and assessment in field and at chemical laboratories. Most of the existing analytical techniques, available give good results for the non-polar constituents of the cutting fluids, but analysis of the water soluble polar compounds is still a challenge for the environmental assessment of cutting fluids, especially in the field. Existing analytical techniques necessary for detailed account of contaminant's mass balance calculation are expensive and time consuming (Pollard et al., 1994). However calculations of mass balance of specific compounds of organic contaminants present in the soil media is beyond the scope of this project.

Cutting fluids require disposal once their efficiency is lost due to contamination and degradation, and waste management and disposal are major problems concerning environmental liability. The primary concern for this study is the significant negative effects in soils associated with use and waste disposal of cutting fluids. Back in the 1960s, people did not realize how dangerous spent cutting fluids could be, and therefore any treatment before disposal was not performed. In the present days, fluid disposal costs frequently exceed the cost of buying new fluids, when dilution factors are taking into account. In addition, water-soluble organic materials that do not respond well to either chemical or mechanical recycling techniques are often components of chemical and semi-chemical fluids. These materials ultimately can be a threat to the surrounding environment in the shape of soil and groundwater contamination (web ref. 1).

This study is performed in partial fulfillment of the requirements of international masters program “Applied Environmental Measurement Techniques”. The project has been initiated and financed by the department of Environment and Chemistry at Volvo Technical development AB, the study is focuses on the evaluation of economical analytical methodologies; for the in-situ determination of petroleum hydrocarbons products, especially cutting fluids. These field analytical methods should allow a rapid assessment of soils and can be used to direct further sampling and analysis to save time and resources. As a part of the study, an environmental soil investigation has been performed at an old industrial site located in Sweden.

The objectives of the project are to:

1. Introduce of a test and monitoring program for the field analysis, including screening techniques, as well as analytical methods that are accurate, reproducible and of real time value for cutting fluids.
2. To understand the movement of cutting fluid in soil media under saturated as well as unsaturated conditions.
3. Analysis of organic contaminants in soils at an old industrial area in Sweden, to illustrate field analytical approaches for the characterization of complex contaminants as cutting fluids.

Background Information

1. Cutting fluids

Cutting fluids are product of petroleum hydrocarbons, and play a significant role in machining operations and impact shop productivity, tool life and quality of work. They are widely utilized to optimize the process of machining operations such as turning, drilling, tapping, spot facing, fly cutting, seat forming, engraving, broaching, boring, grinding, milling and many other type operations. Cutting fluids are very efficient for rust retardancy; also they reduce friction at the tool chip interface for minimizing the heat (web ref. 1). The primary function of cutting fluid is temperature control through cooling and lubrication A cutting fluid's effectiveness depends on factors such as the method used to apply the cutting fluid, temperatures encountered, cutting speed, and type of machining process. The role of a cutting fluid as a coolant or lubricant is very sensitive to the cutting speed. For example, in high-speed cutting operations such as turning and milling where the tool-work interface is small, the cooling characteristic of a coolant is extremely important. Conversely, in low-speed cutting operations such as broaching, threading, and tapping, lubricity is more important since it tends to reduce the formation of a built-up edge (BUE) and improves surface finish (web ref. 2).

1.1 Main types of cutting fluids

The main types of cutting fluids fall into two categories based on their oil content

1. Oil-based fluids - including straight oils and soluble oils
2. Chemical fluids - including synthetics and semi synthetics

Straight oils are non-emulsifiable and are used in machining operations in an undiluted form. They are composed of a base mineral or petroleum oil and often contains polar lubricants such as fats, vegetable oils and esters as well as extreme

pressure additives such as chlorine, sulphur and phosphorus. Straight oils provide the best lubrication and the poorest cooling characteristics among cutting fluids.

Soluble oils (also called mixture fluid) are composed of a base of petroleum or mineral oil combined with emulsifiers and blending agents. The concentration of listed components in their water mixture is usually between 30-85%. Usually the soaps, wetting agents, and couplers are used as emulsifiers, and their basic role is to reduce the surface tension. They provide good lubrication and heat transfer performance. They are widely used in industry and are the least expensive among all cutting fluids.

Synthetic fluids contain no petroleum or mineral oil base and are instead formulated from alkaline inorganic and organic compounds along with additives for corrosion inhibition. They are generally used in a diluted form (usual concentration = 3 to 10%). Synthetic fluids often provide the best cooling performance among all cutting fluids.

Semisynthetics fluids (also called semi chemical) contain a lower amount of refined base oil (5-30%) in the concentrate. They are additionally mixed with emulsifiers, as well as 30-50% of water. Since they include both constituents of synthetic and soluble oils, characteristics properties common to both synthetics and water-soluble oils are presented.

1.2 Common additives used in cutting fluids

Fatty oil. (Metal wetting agent) This additive adds lubricity and makes oil “wetter” thereby lubricating and cooling the metal better than oil without this additive. This allows better, cleaner cuts and promotes longer tool life.

Sulfur. This additive performs an anti-wear function in cutting oils by forming a chemical bond between the cutting tool and work piece, thereby keeping the tool from coming in direct contact with the metal being cut. There are two types of sulfur additives, active and inactive. The inactive compound is used for cutting mild (low-carbon) steels and will not stain these softer materials. The active sulfur forms a stronger bond than the inactive but will stain soft metals. So, oil containing active sulfur is recommended for cutting and broaching the harder varieties of steel only. The object of this chemical bond is to promote longer tool life and to keep the tool from welding itself to the work piece under the severe temperatures created in many metal cutting operations

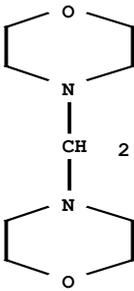
Synthetic metal wetting agent. This additive performs the same function as the fatty oil wetting agent; however, it has two distinct advantages. It will not turn rancid with age and it leaves the metal coated with a rust and corrosion inhibitor

Chlorine. This additive works in the same fashion as the sulfur additive and tends to complement the sulfur by strengthening the chemical bond (film) around the tool. Chlorine tends to be liberated to the atmosphere at elevated temperature; therefore chlorine additives are not particularly useful for extremely high temperature applications (web ref. 3).

1.4 Cutting fluid used in the project

The cutting fluid used in this project to spike the soil for the laboratory experiments is a product of Castrol, and the sample was provided by Volvo technology AB. The fluid is soluble in nature and used as emulsion with 30 – 85 % water content. It contains petroleum based mineral oil as a major constituent and some other more polar and water soluble hydrocarbons as shown in the Table 1.

Table 1 Compounds present in the cutting fluid

Chemical Name	Formula	%
Mineral oil	NIL (definition)	30
Poly(oxy-1,2-ethanediyl), -(9Z)-9-octadecenyl-hydroxy-, phosphate	$\text{HO} - \text{P} \begin{array}{c} \text{O} \\ \parallel \\ \text{OH} \end{array} - \text{OH}$ $\text{HO} \left[\text{C}_2\text{O} \right]_n \text{C}_8\text{H} = \text{C}_7\text{Me}$	1-5
N,N'-methylenebismorpholine		1-5
Ethanol, 2,2',2''-nitrilotris	$\text{HO} - \text{CH}_2 - \text{CH}_2 - \text{N} \begin{array}{c} \text{CH}_2 - \text{CH}_2 - \text{OH} \\ \\ \text{CH}_2 - \text{CH}_2 - \text{OH} \end{array}$	1-5
2-Aminoethanol	$\text{H}_2\text{N} - \text{CH}_2 - \text{CH}_2 - \text{OH}$	1-5
Poly(oxy-1,2-ethanediyl), -(9Z)-9-octadecenyl-hydroxy	$\text{HO} \left[\text{CF}_2 - \text{CF}_2 - \text{O} \right]_n \text{C}_8\text{H} = \text{C}_7\text{Me}$	1-5
Ethane-1,2-diol	$\text{HO} - \text{CH}_2 - \text{CH}_2 - \text{OH}$	1-5

Mineral oil is a complex petroleum product; it has no specific formula and the precise definition according to the European community legislation is “a complex combination of hydrocarbons obtained by treating a petroleum fraction with hydrogen in the presence of a catalyst. It consists of hydrocarbons having carbon numbers predominantly in the range of C20 through C50 and produces a finished oil of at least

100 SUS at 100°F (19cSt at 40°C). It contains relatively few normal paraffins. (TSCA)

2. Soil vadose zone

The geological profile of soil extending from ground surface to the upper surface of the principal water-bearing formation is called the vadose zone. The term “vadose zone” is preferable to the often-used term “unsaturated zone”, because saturated regions are frequently present in some vadose zones. The term “zone of aeration” is also often used synonymously (Holden P., et al, 2001). Generally the soil profile in the vadose zone is divided into horizons A, B, and C. these major horizons are further subdivided into sub horizons. A horizon starts from the surface, it contains large amount of humus material with vegetation roots and the color of this horizon is relatively darker than the horizons below. Thickness of A horizon varies from few cm to 1, 5 m. Below the A-horizon the relatively un weathered light color soil with platy or columnar structure is designated as B-horizon. It is rich in calcium and iron, secretion from upper layer. Thickness of B-horizon range from few cm to several meters. After B-horizon unconsolidated material of parent rock is present with least effects of weathering, called as C-horizon.

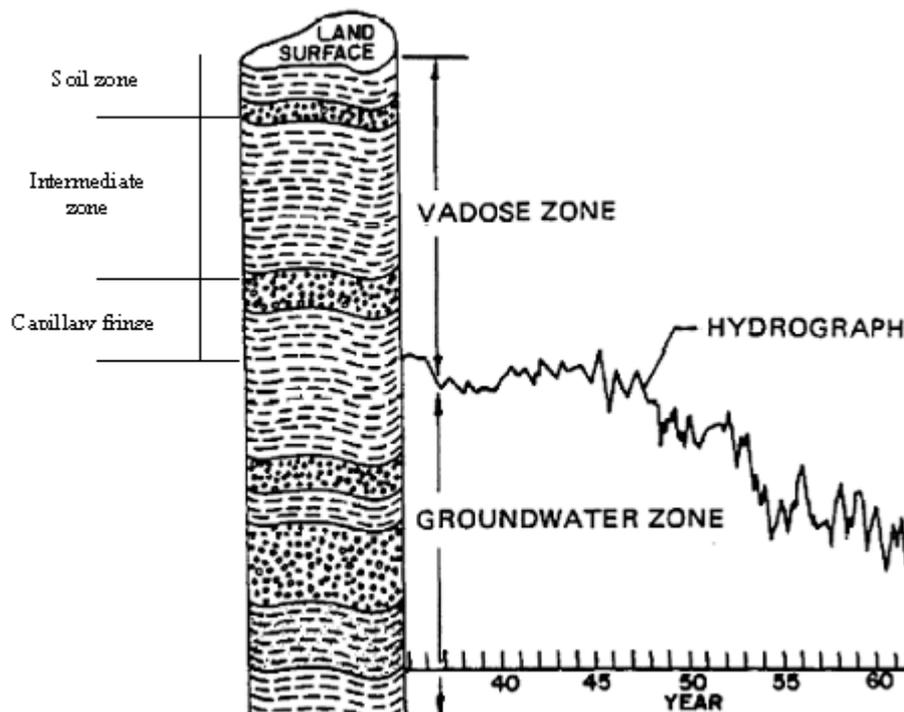


Figure 1 Schematic diagram of vertical profile of soil vadose zone (Pollard et al 1994)

The vadose zone is subdivided into three regions designated as: the soil zone, the intermediate vadose zone, and the capillary fringe. The surface soil zone is generally recognized as that region that manifests the effects of weathering of native geological material. The movement of water and chemical flow in the soil zone occurs mainly as unsaturated flow caused by in-filtration, percolation, redistribution, and evaporation. Water in the intermediate vadose zone may exist primarily in the unsaturated state, and in regions receiving little inflow from above, flow velocities may be negligible.

Perched groundwater, however, may develop in the interstitial deposits of regions containing varying textures. Such perching layers may be hydraulically connected to small stream channels so that, respectively, temporary or permanent perched water tables may develop. Alternatively, saturated conditions may develop as a result of deep percolation of water from the soil zone during prolonged surface application.

The base of the vadose zone, the capillary fringe, merges with underlying saturated deposits of the principal water-bearing formation. This zone is characterized by the nature of geological materials and by the presence of water under conditions of saturation or near saturation. (Bendient. 1994)

The capillary rise varies inversely with the pore size of the soil and directly with the surface tension. In general, the thickness of the capillary fringe is greater in fine materials than in coarse deposits.

Vadose zone plays an important role in the fate and movement of the organic contaminants. Most of the physiochemical processes like; adsorption, absorption, advection, dispersion and diffusion take place in the vadose zone. Nature of the gravity drainage of both water and non aqueous phase liquids in the saturated and unsaturated condition is different. As water and oil are immiscible, the movement of oil from pore spaces is difficult if they are already filled with water. However the fluctuations of groundwater and different pore sizes have significant effects on this movement. A prolonged draughty period can result in dropping water table while a rainy season can result in the increase of water table. Similarly drainage of the contaminant from the large pore size is easier than the smaller sizes pores. The sources and transport mechanism of organic contaminants is discussed in further sections.

2.1 Sources of soil pollution

The term soil contamination can have different connotations because anthropogenic sources of contaminants have affected virtually every natural ecosystem in the world; a commonly held view is that contamination occurs when the soil composition deviates from the non-contaminated composition (Monge A. 1998).

The pollution problem started in the industrial sector in 1800s in Germany. In the 1900s the variety of chemicals wastes increased drastically from the production of steel and iron, lead batteries, petroleum refining and automobile industries. The World War II era unshared in massive production of wartime products that required use of organic compounds for example polychlorinated solvents, polymers, plastic, paints and wood preservatives without having knowledge of their environmental consequences that resulted in severe accidents later.

Now-a-days, large quantities of organic compounds are being manufactured by industry, government agencies, agriculture and municipalities. These organic compounds have created a great potential for soil as well as groundwater contamination. The organic compounds released in the soil can be divided into categories: fuels and derivatives (BTEX), PAHs, alcohols and ketones; halogenated aliphatics(trichloroethylene), halogenated aromatics and polychlorinated biphenyls (Bedient B. et al, 1999).

United States EPA has reported more than 30 potential sources of organic contaminants in the soil. Major sources of pollution spilled during the last decades, can be categorized into the following groups.

Underground storage tanks

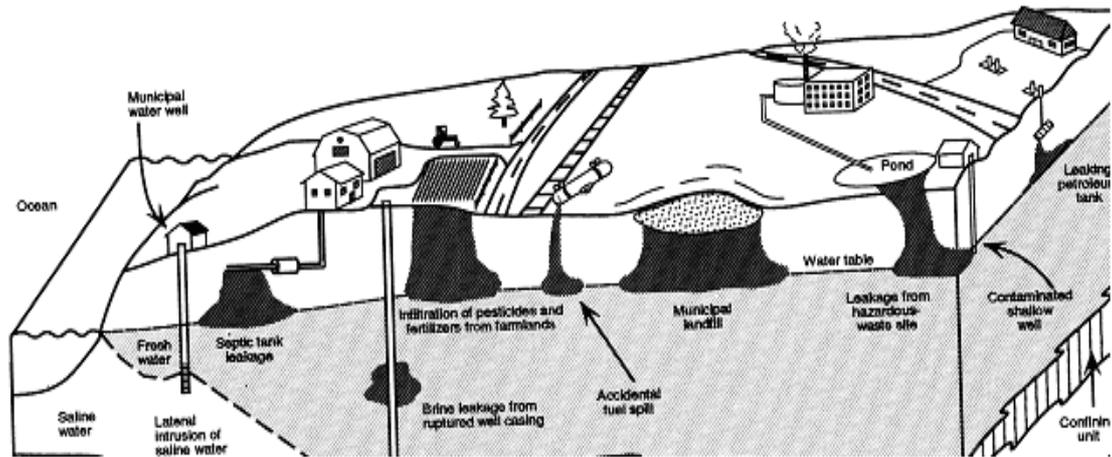


Figure 2 Contamination of soil as well as groundwater by different sources

- Atmospheric deposition
- Surface water and sediments
- Landfill nearby
- Agricultural waste
- Radioactive contamination
- Land application and mining
- Industrial wastes and Spills

2.1.1 Underground storage tanks

Nearly one out of every four underground storage tanks in the United States may now be leaching, according to U.S Environmental Protection Agency (Planas, 1996). These tanks are used by small and large industries, agriculture, governmental agencies and private homes for storage of products. In general fuels, oils, hazardous chemicals and solvent and chemical waste products are stored in below ground tanks.

Underground tanks can leach due to internal or external corrosion of the metal. Leach can occur through holes in the tank or associated piping and valves. The steel tanks are being replaced by fiberglass tanks but faulty piping and subsequent leach still occur. The leaching chemicals contaminate the soil and in case of porous media the plum reach the water table.

2.1.2 Landfills

Modern landfills are built with elaborate leach prevention system, but most, particularly the older ones are simply large hole in the ground filled with waste and covered with dirt. They were designed to reduce the air pollution and unsightly trash that accompanied open dumping and burning, landfills became the disposal method for every conceivable type of waste. However, many may poorly designed and are leaching liquids or leachates, which have contaminated surrounding, soil and shallow

ground water. Modern landfills have a leachate collection system to control the migration of contaminants so they can be collected and transported off-site to a treatment plant. A landfill must have a properly designed and constructed liner to minimize migration of the pollutants.

2.1.3 Surface water and sediments

Surface impounds are often called pits, ponds, or lagoons. Ranging in size from a few square feet to several thousand acres, surface impounds serve as disposal or temporary storage sites for hazardous or non hazardous wastes. They are designed to accept purely liquid waste, or mixed solid and liquid that separate in the impoundment. These surface impoundments are commonly used by municipal wastewater and sewage treatment operations. Water from surface impoundments may be discharged to streams and lakes. Many surface impoundments are found to leach and create large contaminated zones in the subsurface. Most industrial sites where contamination occurred have one or more impoundments located on the site.

2.1.4 Agricultural waste

During the last decades pesticides were identified as a source of pollution in the soil and groundwater but now it is a major source in several countries. Pesticides have been widely used for many purposes for example weed control, insecticides, fungicides, and defoliant. United States EPA has identified 50,000 different pesticides products composed of 600 active ingredients. They are used in agricultural fields, golf courses, lawns and gardens, roadsides, parks, home foundations and in wood products. Fertilizers from agriculture can also provide a major source of elevated nutrient level in the subsurface. Nitrogen, Potassium and Phosphorous are three basic fertilizers, Nitrogen is the most mobile in the soil and leach to the ground water but the phosphorous is not very mobile.

The production of millions of tons of manure by agricultural sources contaminates, soil and underlying aquifers with Nitrogen, bacteria, viruses, hormones and salts. The most obvious threat stems from animal feedlots, where dense livestock populations are confined to small areas. Agricultural sources of contamination to the soil have been generally ignored under hazardous waste legislation, but as urban sprawl continues to expand into former agricultural areas, especially in developing countries, the pesticides and nitrates may become important in the future. (Bedient B. et al, 1999).

2.1.5 Land application and mining

The land application involve spreading waste sludge and wastewater generated by public treatment works, industrial operations such as papers, pulps and textile mills, tanneries and canneries, livestock farms, and oil and gas exploration and extraction operations. Wastewater is applied primarily by a spray irrigation system, while sludge

from wastewater plant is generally applied to the soil as a fertilizer. Oily wastes from refining operations have been land formed in soil to broken down microbes. If properly designed land application recycle nutrients and waters to the soil and aquifer.

2.1.6 Radioactive contamination

Since the World War II the massive production of radioactive isotopes and nuclear warhead has been accompanied by increasing concern about environmental and health affects (Bedient B. et al, 1999). The legacy of Cold War has been a nuclear weapons complex that spreads form one coast to the other, and include some of the most contaminates sites of the world.

Radionuclides are unstable isotopes of elements, including fission and products of heavy nuclei such as Uranium and Plutonium and naturally occurring isotopes such as C-14. Large quantities of radioactive wastes have been produced by the nuclear weapons industry in the U.S and other countries actively involved in this field. The potential sources occur in Uranium mining and milling, fuel fabrication, power plant operation, fuel reprocessing and waste disposal. The health hazards associated with radioactive leaks from the soil are well known but the risks are difficult to asses at low levels of exposure.

2.1.7 Accidental spills

Accidental spills are not very common source of soil contamination but whenever it happens it causes a high concentration of pollutants in the soil. The spills are more often for organic copmounds during the processing and transportation. The spillage moves under the transport mechanism or suffer other transformations and can travel in the unsaturated zone and under the water table as well, and create the risk of the health of humans, animals, or plants; damage to buildings or structures on the soil; contamination of ground waters, or surface waters in contact with the contaminated soil (web ref. 4).

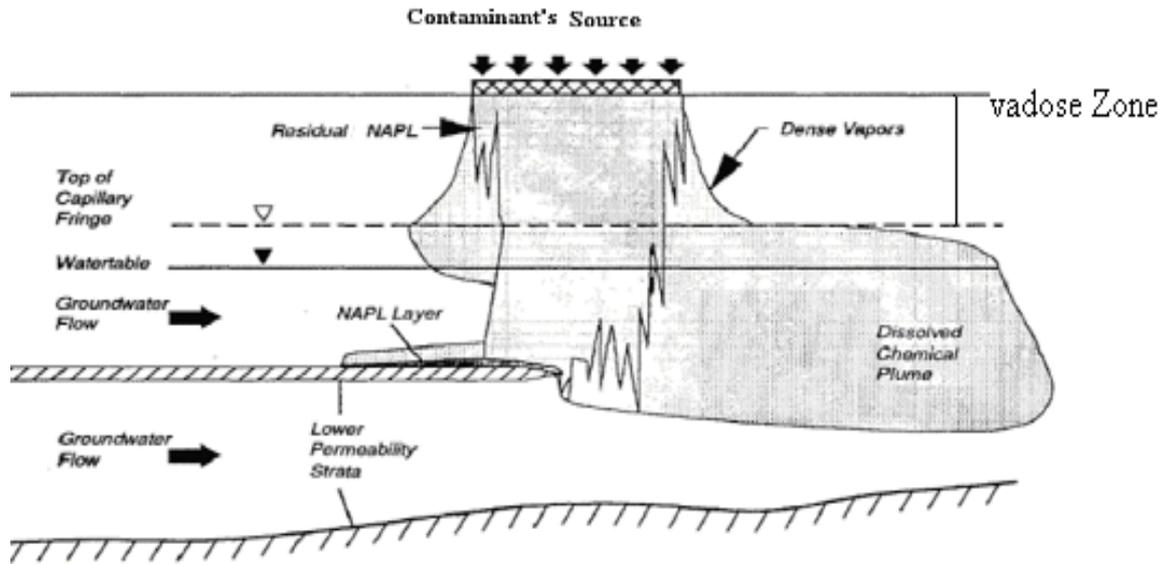


Figure 3 Transport of soluble oils into the subsurface illustrating the distribution of the NAPL, the dense vapors, and the dissolved chemical plume (Pollard 1994).

3. Transport of organic contaminants in the soil

Soil and other solids are complex materials that may support a range of transport mechanism for the organic compounds present in cutting fluids. A proper knowledge of various mechanisms of interaction between oil, water and soil surface is important in predicting the transport mechanism and long-term behavior of cutting fluid in the soil. An individual soil grain is an extraordinarily heterogeneous mixture of minerals and natural organic matter (Bendient et al 1999). The mineral surfaces are dominated by polar or ionic functional groups capable of interacting with polar or ionic contaminants. The natural organic matter is generally hydrophobic material that tends to exclude water and other highly polar molecules. This fraction of soil occurs typically where non-polar/hydrophobic molecules associate.

The transport of emulsified cutting fluids (mixture of mineral oil and water with blending agents) in the vadose zone can be a product of the gravity, hydraulic gradient of ground water, and capillarity. The capillary transport is due to the suction of the porous media, the oil is moving under the tension force active above the capillary zone (Fitter, 1993). Under the capillary forces, within the pore fluid of soil, oil can exist in three separate phases: dissolved, liquids (non-aqueous phase liquids "NAPL") or gaseous. The capillary forces are important in fine soils with low water content. However, a high amount of water in the soil can be a barrier for the insoluble products. As the aromatic and aliphatic compounds have lower density than the water, they will be above the water film as NAPL without any significant penetration into the saturated zone. The hydrocarbons spills can move horizontally due to capillary forces and hydraulic gradient. Figure 3 gives a demonstration of the movement of oil in the vadose zone.

Non-aqueous phase liquids (NAPLs) are defined as separate phase product that are either lighter than water (LNAPL) such as normal gasoline that can float on the water surface or denser than water (DNAPL) such as chlorinated solvents. Some of them are volatile and of environmental concern. They frequently enter groundwater systems after they have been spilled on the surface and pass through the unsaturated zone. These contaminants flow through the unsaturated zone, a portion of the liquid remains behind in fingers at residual saturation, in pools of material on small heterogeneities, or above the capillary fringe (Palmer et al, 1989).

Since the mineral oil consists of large molecules with long chain lengths, it is expected that the primary mode of interaction in mixture of soil and water through vadose zone, will be via Van der Waal's attraction forces. As the number of contact points between the oil and soil particle surface increase, in addition to the Van der Waal's interactions, significant binding interactions of alkyl groups (oil) with surface oxygen or hydroxyls (soil or water) and exchangeable cations will also occur. A schematic picture of the interactive mechanisms involved is shown in the fig 4.

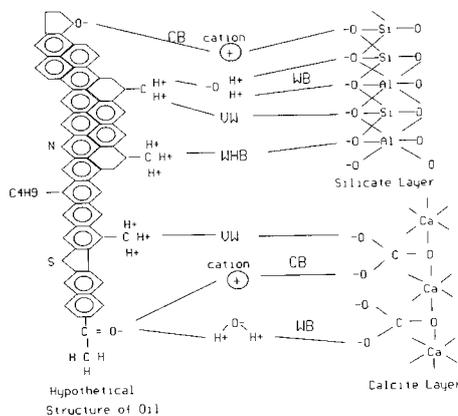


Figure 4 A schematic diagram of the interactive mechanisms involve in oil-soil-water mixture VW is Ven der Waal's attraction, WHB is weak hydrogen bonding, WB is water bonding, and CB is cation bridging (Source Young R., et al, 1994)

3.1 Physiochemical processes controlling the Transport Pathways

The hydrocarbons that remain in the unsaturated zone are an important source of contamination because they are dissolved by the passing recharge water, and by the passing ground water as the water table rises. Such sources of contamination can last for many years and contaminate large volumes of groundwater. On the other hand the water soluble component of the contaminant are washed out readily and reach the groundwater if the strata is permeable enough. This phenomenon is called advection. However, in addition to this pathway, contaminants can also be transported through diffusion and dispersion, adsorption, biodegrading, chemical reaction and volatilization. These transport pathways may spread the contaminants over much broader areas. To get the idea of the transport of dissolved contaminants and the design of optimal remediation schemes, require knowledge of the physiochemical processes that control transport pathways.

Some major physiochemical processes are given below:

3.1.1 Advection

Advection represents the movement of a contaminant with the flowing ground water according to the seepage velocity in the pore space. It is defined as

$$v_x = -\frac{k}{n} \frac{dh}{dl} \quad [3-1]$$

It is important to realize that the seepage velocity is equal to the average linear velocity of the contaminant in the porous media, and is the correct velocity for use in governing solute transport scenario. The average linear velocity v_x is equal to the Darcy's velocity divided by effective porosity, n , associated with the pore spaces through which water can actually flow. This velocity is less than the microscopic velocities of water molecules moving through individual flow paths. So the one-dimensional mass flux due to advection is equal to the product of flow and concentration of solute in the soil media (Bendient. et al, 1999).

3.1.2 Diffusion and dispersion

Diffusion is a micro-scale process, which cause spreading due to concentration gradient. Diffusive transport can occur in the absence of velocity, and is important where the relatively impermeable soil is present on the surface for example clay or silty clay. Mass transport in the soil due to diffusion in 1-D can be described by Fick's first law of diffusion.

$$f_x = D_d \frac{\partial C}{\partial x} \quad [3-2]$$

where f_x is mass flux ($M/L^2/T$)

D_d is diffusion coefficient (L^2/T)

dC/dx is concentration gradient ($M/L^3/L$)

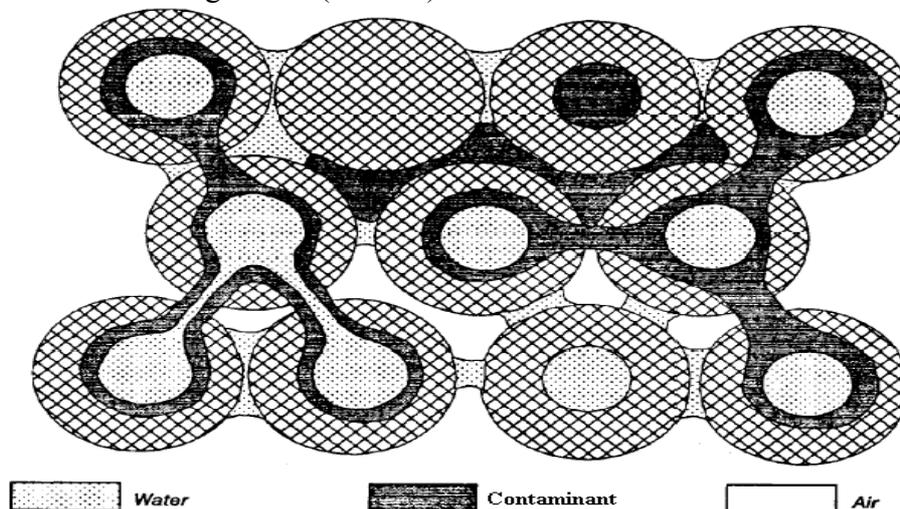


Figure 5 Movement of contaminant showing movement under diffusion and dispersion mechanism. (pollard et al, 1994)

Dispersion is caused by the heterogeneities in the medium that create variation in flow velocities and flow paths. This variation can occur due to friction with in single pore channel, due to velocity difference from one channel to another, (figure 5) or due to variable path lengths. Mass transport due to dispersion can also occur normal to the

flow. This transverse dispersion is caused by driving flow path in the porous media that cause mass to spread literally from the main direction of flow.

3.1.3 Sorption

The association of dissolved or gaseous contaminant with a solid material is called sorption. In the vadose zone the solid of interest are soil particles and typically the contaminants are in the dissolved phase. The term sorption encompasses two more specific processes referred to as **adsorption** and **absorption**. Adsorption is the association of contaminant with the surface of solid particle.

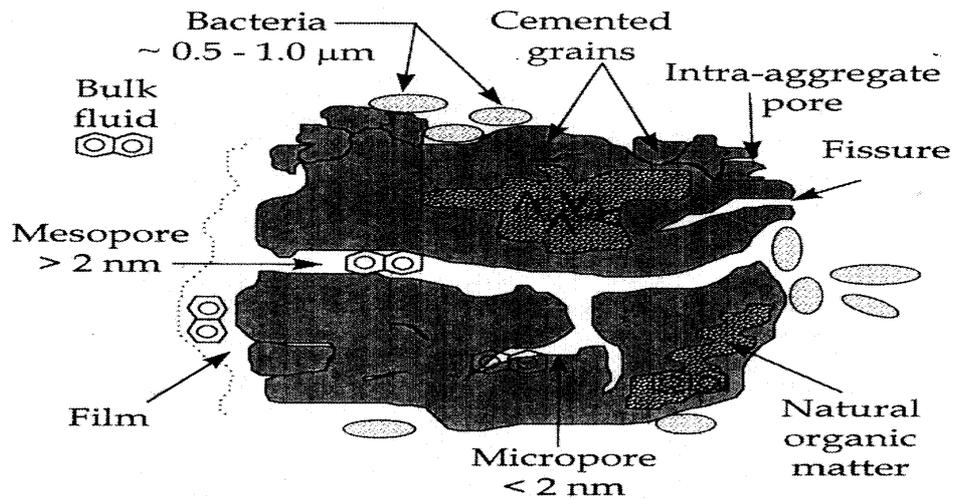


Figure 6 Schematic of soil grain Sorption (Bendient. et al, 1999).

Absorption is the association of contaminant with in the solid particle. Incase case of hydrocarbons; it is often difficult to distinguish between adsorption and absorption, since both may occur simultaneously. At least three different situations can be speculated that can co-exist in soil-oil-water mixture: 1) Oil may adsorb onto the surface of the soil constituents, 2) oil may form bond which link (aggregate) some of the soil particles and cause retention of oil in the soil and, 3) oil may exist separately in the soil pore space. When hydrocarbons are spilled on the soil, nonpolar or hydrophobic contaminants interact primarily with hydrophobic constituents of the soil media, while ionic or polar material interact with charged mineral surfaces. In either case, the extent to which sorption may occur is influenced by the chemical properties of both sorbent and the sorbate (Figure 6)

Adsorption is described by the adsorption coefficient K_d . The ability of a compound to be absorbed by the soil is characterized by the adsorption coefficient. There are empirical results indicating that soils with higher content in organic matter than 1% adsorb some more amount of any contaminant agent. The K_d value can be obtained by knowing the amount of organic matter present in the soil (K_{oc}) (Canter, 1996)

$$K_{oc} = (K_d / f_{oc}) \quad [3-3]$$

K_d is the adsorption coefficient and f_{oc} is the organic matter present calculated by the octane-water coefficient (K_{ow}). K_{ow} represents the distribution of of a chemical between octanol and water in contact with each other at equilibrium conditions:

$$K_{ow} = \text{Concentration in octanol} / \text{concentration in aqueous phase.}$$

K_{ow} has been measured in the laboratory for many chemicals and is readily available parameter. Measured values of K_{ow} for organic chemicals have been found as low as

10^{-3} and as high as 10^7 (Bendient. et al, 1999). K_{ow} values of some hydrocarbons of concern are given in the Table 2.

The K_{oc} values can be calculated in different ways:

There exists several empirical correlation between K_{oc} and Octane-water coefficient(K_{ow}). For instance

$$10 \text{ polyaromatic hydrocarbons} \quad \text{Log } K_{oc} = \text{Log } K_{ow} - 0.21 \quad [3-4]$$

$$\text{Miscellaneous Organic} \quad K_{oc} = 0.63 K_{ow} \quad [3-5]$$

Table 2 Octane-water coefficient (K_{ow}) (Canter, 1996).

Compound	Log K_{ow} (mean)	Log K_{ow} (std)
Alkanes and alkenes		
Methane	1,09	No data
Ethane	1,81	No data
Propane	1,13	No data
Pentane	3,39	
Aromatics		
Benzene	2,01	0,45
Naphthalene	3,32	0,35

Taken into consideration the contaminants solubility in water according to the following relation:

$$\text{Log } K_{oc} = 0.44 - \text{Log } S \quad [3-6]$$

S is the contaminant's solubility in water.

The partition coefficient (K_d) can be defined by following equation.

$$k_d = \frac{[A]_{solid}}{[A]_{aqueous}} \quad [3-7]$$

A is the concentration of contaminant in either phase

There are also other chemical mechanisms responsible of the adsorption process, such as Van der Waal's interactions, hydrophobic binds, hydrogen bond, charge transference or ionic exchange.

3.1.4 Biotransformation and biodegradation

It is a complete conversion of a contaminant to mineralized end product (i.e., CO_2 , H_2O and salts) through metabolism by living organism. In soil the organism that carry this process are bacteria indigenous to the system. In some cases, metabolic activity change the chemical form of the contaminant but does not result in the mineralization. The metabolism of soil and groundwater contaminants is an extremely important end process since it has the potential to impact the fate of all organic contaminants, and is a process that has the potential to yield nonhazardous products. It is a complicated process due to the diversity of bacteria that may be involved, and range of metabolic processes that can be expressed. Studies have shown total petroleum hydrocarbons

(TPH) in different oily soils showed that 90% of the alkanes and monocyclic saturates and 50-70% of aromatic compounds (<C₄₄) were degraded (Mohamed, et al, 1992)

3.1.5 Volatilization

Near a spill of organic contaminant especially hydrocarbons, a four-phase system exists. The phases include (1) the aquifer matrix, (2) the residual soil water, (3) the NAPL, and (4) the air-filled pore space (Figure 4-3). A volatile NAPL partitions from the NAPL phase into the gas phase where it then can be transported to other portions of the unsaturated zone. The vapor pressure of a particular contaminant, P_k, in the gas phase can be calculated from Raoult's Law:

$$P_k = X_k P_k^0 \quad [3-8]$$

Where x_k is the mole fraction of component k in the NAPL and P_k⁰ is the vapor pressure above the pure component. For example, if the NAPL is gasoline, the partial pressure on benzene, one of the many components of gasoline, is the mole fraction of benzene in the gasoline times the ideal vapor pressure above pure benzene. The concentration of the gas in the soil atmosphere can be calculated from the ideal gas law:

$$(n/V)_k = P_k / (RT) \quad [3-9]$$

Where n is the number of mole of component k, V is the volume of gas, T is the kelvin temperature, and R is the gas constant.

3.1.6 Gas-phase transport

The movement of the contaminants in the gas phase of the unsaturated zone can be described by performing a mass balance on a volume of aquifer:

$$D \frac{\delta^2 C}{\delta x^2} - v \frac{\delta C}{\delta x} = \frac{\delta C}{\delta t} \pm RXN \quad [3-10]$$

Where v is the groundwater velocity (L/T), D is the dispersion coefficient (L²/T), C is the concentration of the dissolved constituent (M/L³), t is time, and RXN represents a general chemical reaction term or the retardation factor which depend on the bulk mass density, porosity and partition coefficient (K_d). The first term in equation 3-9 describes the net advective flux of the contaminant in and out of a volume of the aquifer; the second term describes the net dispersive flux of the contaminant. The first term on the right-hand side of the equation describes the change in concentration of the contaminant in the water contained within the volume of aquifer, the second term on the right-hand side represents the amount of contaminant that may be added or lost to the groundwater by chemical or biological reaction. If there is no reaction term, then the equation describes the transport of a conservative, nonreacting tracer such as chloride or bromide (Palmer et al, 1989).

3.2 Factors influencing the distribution of organic contaminants in soil

The contaminant distribution is a function of hydrogeological properties of soil as well as the initial concentration of the contaminant, contaminant phase, and volatility of the compound. These parameters are described as permeability coefficient, Diffusive properties of soil and adsorption by the soil.

Permeability coefficient

It is related to how easy a liquid can propagate through the soil, it depends on the shape and size of the pores and adsorptive properties of soil grains. Low permeability soils are clays and silt having saturated hydraulic conductivity below 10^{-5} cm/s

Diffusive properties of soil

It relates to the movement of a solute in water from higher concentration to low concentration (Fitter1993). Where the soil is highly permeable the diffusion is negligible but dominates in the soil having low permeability like clay and silt etc.

Water solubility

The amount of the contaminants dissolved and transported by the water is indicated by the water solubility. The higher solubility of the contaminant the higher concentration of this product in the aqueous phase, and the component with lowest density will be adsorbed to the soil grains.

Density and viscosity

This property influences the mobility and location of the final non-aqueous phase. If non-aqueous phase is lighter than the water, the contaminant will situate over the water table. On the other hand, if it is heavier than the water. this pollutant will penetrate through the soil towards the impermeable layer. The detection and soil remediation depend on the location of the contaminant in reference to the water table (Callabo de Roa 1996)

Vapour pressure and density of vapour phase

Vapour pressure is defined as the pressure exerted by the vapour phase of a pure compound. Vapour pressure gives the relative volatility of the compound. The density of the vapour pressure indicates whether a gas will rise or sink in the atmosphere. It is related to equilibrium vapour pressure, the molecular weight of the gas, and the temperature (Fitter, 1993).

3.2.6 Grain size effect

The size of soil particles is very important in the spatial distribution of the contaminants. The relationship between horizontal and vertical propagation velocity and internal spatial extension along those two directions depends on the soil permeability, which is a function of soil's texture, water content and chemical composition of a blend present in the soil. For instance a low velocity blend penetrates into the sand more quickly and spread area is smaller (Pons et al., 1992).

If 1 m³ kerosene is poured over 10 m² of coarse sand, the final penetration depth will be of 20 m. If the same spill is discharge over the fine or medium sand the depth will be 6.7 m. If the medium is clay it will penetrate to only depth of 2.5 m. The time propagation is the same for the three examples (Pons et al., 1992; Monge., 1998).

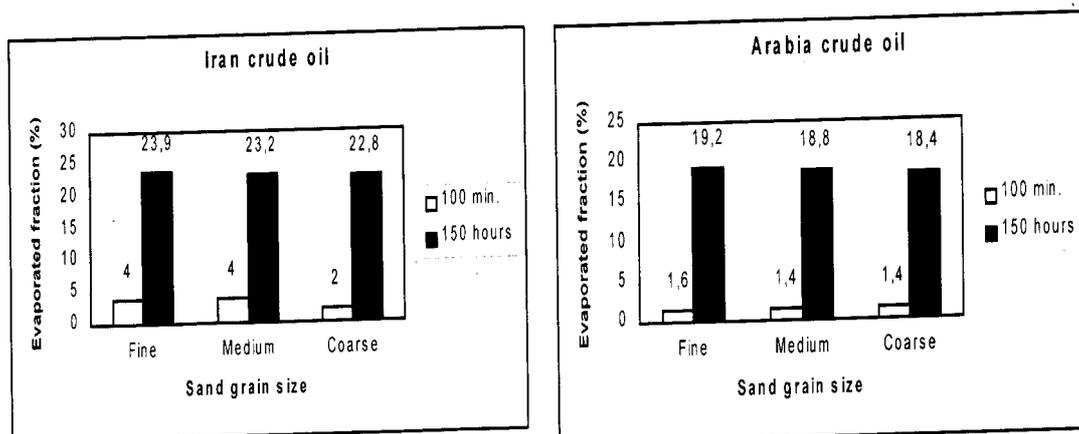


Figure 7 Evaporation of Iran and Arabia crude oils (Monge. 1998).

The grain size is important in the case of evaporation calculation of the volatile content spilled on the soil. For example, spilled occurred over a fine sand will evaporate more than medium or coarse sand. Since the permeability of coarse sand is high, the large amount of hydrocarbons will percolate downward.

A study of evaporation rates of crude oils in different soil performed by Bergueiro et al., 1988, shows the results presented in the Figure 7. The wind speed of 5,8 m/s at 15⁰C was set for experimental condition. The evaporation was measured after 100 minutes and 150 hours on heavy crude oils (Monge., 1998).

4. Field analytical techniques

In evaluating the effects and to be able to take decision about remedial action for organic contaminants especially petroleum hydrocarbons, selection of the appropriate analytical method is essential. The study of soils contaminated with organic contaminants is associated with several challenges, especially of analytical methodologies and data interpretation. Organic contaminants, especially petroleum product comprise a vast continuum of hydrocarbons from short chain aliphatic and simple aromatic hydrocarbons in gasoline to kerosene, diesel and heavy oils to lubricant oils or vaseline, each gradation with increasing carbon chains and complexity. Properties of these hydrocarbons vary and composition of the hydrocarbons is of environmental concern. Treatment technology and site remediation progress will lean heavily on analytical techniques, that are accurate reproducible and, of real time value. There are several methods currently available for the analysis of organic contaminants. These field analytical techniques contain screening as well as in-situ analytical methods. Screening methods provide an indication of the presence or absence of a particular chemical or chemical class of concern, or provide an indication of whether the chemical or chemical class of concern is above or below a predetermined threshold. Screening methods provide relative concentrations for chemical classes, but rarely provide chemical specific information (EPA/625/R-93/003b, May 1993). Field analytical methods include all chemical analysis methods capable of providing chemical-specific quantitative data in the field or in non-laboratory setting. Field analytical and screening techniques can be classified as:

Portable: Require no external power source, are compact and are rugged enough to be carried by hand in the field.

Fieldable: Require limited external power, are compact and are rugged enough to be transported in small van or pick-up.

Mobile: Are small enough to carry in a mobile laboratory, which is feasible for most analytical instruments although power consideration can be a limitation.

However standards by which the sensitivity, precision, and accuracy of field screening techniques are measured are those obtained in fixed-base laboratories.

Field measurement devices may be categorized as quantitative, semi quantitative, and qualitative. A **quantitative measurement device** measures hydrocarbon concentrations ranging from its reporting limit through its linear range. The measurement result is reported as a single, numerical value that has an established precision and accuracy. A **semi quantitative measurement device** measures TPH concentrations above its reporting limit. The measurement result may be reported as a concentration range with lower and upper limits. A **qualitative measurement device** indicates the presence or absence of PHCs above or below a specified value (for example, the reporting limit or an action level).

4.1 Field analysis versus analytical laboratory

Key advantages of field analytical techniques include:

1. Results can be obtained within hours compared to the normally 20 to 40 days required for laboratories, which allows for more rapid definition of the scope of contamination and allows the optimal selection of permanent monitoring locations.

2. Lower cost per sample (commonly one-tenth of lab. Cost) allows for more detail characterization of contaminant distribution and reduces the overall cost.
3. The techniques are best suited for preliminary site characterization, emergency remedial actions and monitoring of remediation activities.

Some general disadvantages of field analytical techniques includes:

1. Application of analytical QA/QC procedures is more difficult in the field.
2. Generally less sophisticated instrumentation and have generally higher detection limits and lower precision and accuracy compared to the laboratories analysis.
3. The data may be more liable to challenge by litigation.

The following sections address various methods for analyzing the soil samples in the field, employed for the project.

4.2 Photo ionization detector (PID)

PID is a portable nonspecific, vapor/gas detector employing the principle of photo ionization to detect a variety of chemical compounds, both organic and inorganic. The PID is a useful general survey instrument at hazardous waste sites. A PID is capable of detecting and measuring real-time concentrations of many organic and inorganic vapors. A PID is similar to a flame ionization detector in application; however, the PID has somewhat broader capabilities in that it can detect certain inorganic vapors and also can be used in combination with gas chromatography for detecting specific compounds.

Conversely, the PID is unable to respond to certain low molecular weight hydrocarbons, such as methane and ethane that are readily detected by FID instruments.

4.2.1 Principle and method summary

The PID employs the principle of photo ionization. The analyzer responds to most vapors that have an ionization potential less than or equal to that supplied by the ionization source, which is an ultraviolet (UV) lamp. Photo ionization occurs when an atom or molecule absorbs a photon of sufficient energy to release an electron and form a positive ion. This will occur when the ionization potential of the molecule in electron volts (eV) is less than the energy of the photon. The sensor is housed in a probe and consists of a sealed ultraviolet light source that emits photons with an energy level high enough to ionize many trace organics, but not enough to ionize the major components of air (e.g., nitrogen, oxygen, carbondioxide). The ionization chamber exposed to the light source contains a pair of electrodes, one a bias electrode, and the second the collector electrode. When a positive potential is applied to the bias electrode, an electro-magnetic field is created in the chamber. Ions formed by the adsorption of photons are driven to the collector electrode. The current produced is then measured and the corresponding concentration displayed on a meter, directly, in units above background. Several probes are available for the PID, each having a different eV lamp and a different ionization potential. The selection of the appropriate probe is essential in obtaining useful field results. Though it can be calibrated to a

particular compound, the instrument cannot distinguish between detectable compounds in a mixture of gases and, therefore, indicates an integrated response to the mixture (web ref. 5)

Three probes, each containing a different UV light source, are available for use with the photovac. Energies are 9.5, 10.2, and 11.7 eV. All three detect many aromatic and large molecular hydrocarbons. The 10.2 eV and 11.7 eV probes, in addition, detect some smaller organic molecules and volatile halogenated hydrocarbons. The 10.2 eV probe is the most useful for environmental response work, as it is more durable than the 11.7 eV probe and detects more compounds than the 9.5 eV probe. Gases with ionization potentials near to or less than that of the lamp will be ionized. These gases will thus

be detected and measured by the analyzer. Gases with ionization potentials higher than that of the lamp will not be detected. Ionization potentials for various atoms, molecules, and compounds that could not be present in the cutting fluids are given in Table 3.

Table 3 Volatile hydrocarbons detectable with Photovac

Compound	Ionization Potential (ev)
Benzene	9,53
Cyclohexane	10,50
Cyclopentane	10,52
Dicyclopentadiene	9,82
Dimethylaniline	8,24
n-Heptane	10,07
Methylcyclohexane	11,25
Naphthalene	8,10
n-Nonane	n.p.
n-Octane	9,19
Toluene	8,82
o-Xylene	8,56
m-Xylene	8,56
p-Xylene	8,45

The ionization potential of the major 5 components of air, oxygen, nitrogen, and carbon dioxide, range from about 12.0 eV to about 15.6 eV and are not ionized by any of the three lamps.

While the primary use of the PID is to get quantitative results, it can also be used to detect certain contaminants, or at least to narrow the range of possibilities. Noting instrument response to a contaminant source with different probes can eliminate some contaminants from consideration instance, a compound's ionization potential may be such that the 9.5 eV probe produces no response, but the 10.2 eV and 11.7 eV probes do elicit a response (web ref. 6).

4.2.2 PID instrument limitations

1. The PID is a nonspecific total vapor detector. It cannot be used to identify unknown

substances; it can only roughly quantify them.

2. The PID must be calibrated to a specific compound.
3. The PID does not respond to certain low molecular weight hydrocarbons, such as methane and ethane. In addition, the PID does not detect a compound if the probe has a lower energy than the compound's ionization potential.
4. Certain toxic gases and vapors, such as carbon tetrachloride and hydrogen cyanide, have high ionization potentials and cannot be detected with a PID.
5. They measures concentration from about 1-2000ppm, although the response is not linear over this entire range. For example, if calibrated to benzene the response is linear from about 0-600 units above the background. This means the PID reads a true concentration of benzene only between 0 and 600. Greater concentrations are detected at a lower level than the true value.
6. This instrument does not give response if it is exposed to precipitation.
7. This instrument cannot be used for headspace analysis where liquids can inadvertently be drawn into the probe (web ref.5)
8. The response of PID varies greatly with the nature of the volatile organic compound. While the PID response to halogenated volatiles and aromatics may be fairly similar between similar compounds, the PID response to alkanes may be lower by an order of magnitude or more. As a result, knowledge of the site-specific contaminants of concern will be essential to successful application of this procedure (web ref. 6).

4.3 Immunochemical techniques

Immunoassay is an analytical technique useful for the separation, detection and quantitation as both organic and inorganic analytes in diverse environmental and waste matrices. Immunoassay methods are used to produce two types of quantitative results: 1) range-finding or screening results indicative of compliance with an action level, and 2) assay values (www.epa.gov test method 4000). These techniques are in the framework of wet analytical chemistry and may be called as enzyme immunoassay (EIA), enzyme linked immunosorbent assay (ELISA), radioimmunoassay (RIA) or fluorescence immunoassay. Out of these techniques EIA is used to analyze benzene, toluene, xylene (BTX), PCB, PCP, cocaine, heroin, and pesticides.

4.3.1 Method selection consideration

Immunoassay test products use an antibody molecule to detect and quantitate substance in a test sample. These testing products combine the specific binding characteristics of an antibody molecule with a detection chemistry that produces a detectable response used for interpretation. In general antibody molecules specific for the method's intended target are provided at a predefined concentration (web ref. 7). Immunoassay testing products have a quantitative basis, and produce a signal that is dependent on the concentration of the analyte present in the sample. For environmental immunoassay methods, the signal produced is exponentially related to the concentration of the compounds present.

EIA methods use enzymes to develop chromogenic response and are termed as enzyme immunoassays. This technique involves the use of antibodies reagents that

react with the analyte of interest to produce reaction that can be analyzed calorimetrically and are a recent development for the trace organic analysis. EIA is the best-suited techniques for the primary screening where only a few contaminants are of interest. EIA kits are very simple rapid and inexpensive. It has potential for specific field tests for a large number of toxic organics with very low detection limits up to ppb. Assays that generate a chromogenic response are analyzed photometrically, and use the principle of Beer's Law (Absorbance= Extinction Coefficient* Concentration* path Length) to determine the concentration of analyte in the sample.

4.3.2 Interferences

Non-target analytes may bind with the antibody present, producing a false-positive result. These non-target analytes may be similar to the target analytes, or may be chemically dissimilar to co-contaminants.

Some test products have designated temperature ranges for operation. When these products are used, all tests must be performed within specific operating temperature limits, or else false negative/positive results may exceed performance claims.

4.3.3 Advantages and limitations

The two key features of the immunoassay technology are the rapid turn-around time for results and the portability and ease of use of the kits. These rapid analytical solutions can lead to substantial savings in time and expenses when applied to environmental projects. The kits are prepared to be used by nonchemists with minimal training. These capabilities have enabled environmental professionals to shorten the time frame in which site assessment and remediation projects are completed, saving up to 50% of the project costs and reduce the owner liability.

The immunoassay technology is generally specific in its detection capabilities, thereby prohibiting detection of broad groups of compounds (i.e., the immunoassay detects PCBs but not all chlorinated compounds). However, the antibody might recognize a compound chemically very similar to the target compound, causing false positive results. The analysis can also be affected by specific matrix conditions. For example, analyte recovery for analytes such as PCBs and PAHs can be affected by excessive soil moisture. Also, percent levels of oil can result in false positive results.

Immunoassay technology is not applicable for all classes of small, environmentally significant molecules (e.g., long chain aliphatic hydrocarbon compounds and most metals). Temperature extremes can affect test results; the operational temperature ranges are typically between 40° and 100°F. Immunoassay kits have a limited shelf life (between 1 month to 1 year) dependent upon the vendor development and enzyme conjugate stability (web ref. 7)

4.4 PetroFLAG™ System

The PetroFLAG™ System is a field measurement device capable of providing quantitative TPH measurement results. Measurements made using the PetroFLAG Systems are based on emulsion turbidimetry. Turbidimetry may be described as measurement of the attenuation, or loss in intensity, of a light beam as the beam

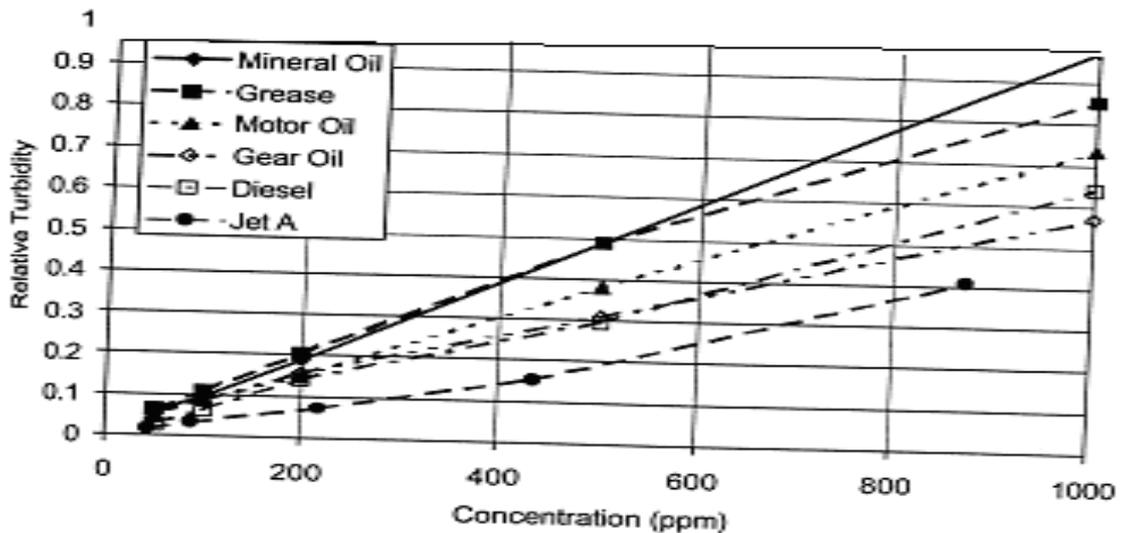


Figure 8 Relative intensity data for common analytes (Dexil corporation, 1999).

passes through a solution with particles large enough to scatter the light. Emulsion turbidimetry involves measurement of the light scattered by an emulsion (in an emulsion, one liquid is stably dispersed in a second, immiscible liquid). The relationship between the amount of light scattered (turbidity) and the concentration of the emulsion may be expressed as shown in Equation 5-1.

$$T = kbc \quad [5-1]$$

Where

T = Turbidity

k = Proportionality constant

b = Light path length (centimeter)

c = Concentration of emulsion (milligram per liter [mg/L])

Unlike other field screening techniques this technique does not target specific compounds such as BTEX or PNAs that may be a part of hydrocarbon mixture. Because of its broad linear response, PetroFLAG kit can be used on a wide range of hydrocarbons analytes including fuels, lubricants, hydraulic fluids and greases. This makes PetroFlag kit useful as fast, low cost general screening tool for the hydrocarbons, as well as for the quantitative determination of hydrocarbons in the soil samples, while provide the user with real time data for onsite decision making. PetroFlag system is most sensitive to heavier hydrocarbon such as mineral oils and greases and less sensitive to the lighter more volatile hydrocarbon fuels. The PetroFlag responses to some typical hydrocarbon contaminants are plotted in Figure 8.

The PetroFLAG system extracts PHCs in soil using a proprietary organic solvent mixture composed of alcohols, primarily methanol. The device also uses a proprietary developer solution that is polar in nature and acts as the emulsifying agent. The developer solution also contains water and surfactants that stabilize the emulsion. The PetroFLAG system can be used to measure the petroleum products listed in Table 4 the device does not distinguish between aromatic and aliphatic hydrocarbons and it responds to compounds in the C8 until C36 carbon range. Method detection limits (MDL) for the device are also listed in Table 4 and range from 10 mg/kg for hydraulic fluid to 1,000 mg/kg for weathered gasoline. In addition, Table 4 lists the device's

response factors, which are based on mineral oil. The response factors range from 2 for weathered gasoline to 10 for transformer oil, indicating that the instrument is more sensitive to transformer oil than weathered gasoline. If no information is available regarding the type of contamination in a sample, use of an average response factor of 5 is recommended (web ref. 8).

Table 4 PetroFLAG™ system method detection limits and response factors for petroleum products (web ref. 8, and 9).

Petroleum Product	Method Detection Limit (milligram per kilogram)	Response Factor
Mineral oil	15	10
Transformer oil	15	10
Grease	15	9
Hydraulic fluid	10	8
Transmission fluid	19	8
Motor oil	19	7
No. 2 fuel oil	25	7
No. 6 fuel oil	18	6
Diesel	13	5
Gear oil	22	5
Low-aromatic diesel	27	4
Pennsylvania crude oil	20	4
Kerosene	28	4
Jet A fuel	27	4
Weathered gasoline	1,000	2

The Petro-FLAG test is easily performed at the contaminated sites where a variety of sampling strategies are to be used. The test is useful at sites requiring lateral and vertical definition of soil contamination plume throughout the vadose zone, including the sites that are being drilled and sampled or excavated and sampled prior to the collection of expensive laboratory confirmation samples.

The Petro-FLAG test is well suited for use at large sites where a grid-sampling plan is strategy of choice. It will help to economically locate and define the extent of the soil contamination, locate and define hotspot. This could help to save unnecessary drilling and sampling costs and equipment relocation costs caused by waiting for laboratory analytical data, and allow more area to be tested thus reducing the possibility of future liability caused by failing to identify contaminated areas (T.B Lynn et al, 1994).

4.4.1 Interferences

This method is considered a screening technique because of broad spectrum of hydrocarbons it detects. It cannot distinguish between co-extracted naturally occurring hydrocarbons and petroleum hydrocarbons. The PetroFlag has also been shown to be susceptible to interference from vegetable oils. It is anticipated that co-extracted naturally occurring oils from vegetative material would be one of the most probable positive interferants found in the field. Therefore in situations where the soil contain a high organic content is suspected, the background level outside the spill site should be determined (T.Lynn et al, 1994).

Materials and methods

1 Soil sampling

The soil samples were collected from two different places in the Mölndal area. For the first site sampling was done near the Sisjön centrum using PVC sampling tube of one meter in length and 8 cm in diameter. The soil was moved from the sampling tube into an airtight glass jars according to the depth profile recovered from the tube. The second sample was taken as a composite sample separately for horizon A and B from the working site of NCC near the Mölndal station. This sample was collected in diffusion less plastic bags and was transferred into glass jars after arrival to the laboratory.

These sampling sites were selected on the basis of the soil textural class (sandy Loam) shown by the soil map of Mölndal area (SGU Ser Ae nr 96, 6B Kungsbacka NV). The same texture class is present in the soil of the case study area. The two sampling locations are marked with a star in figure 9.

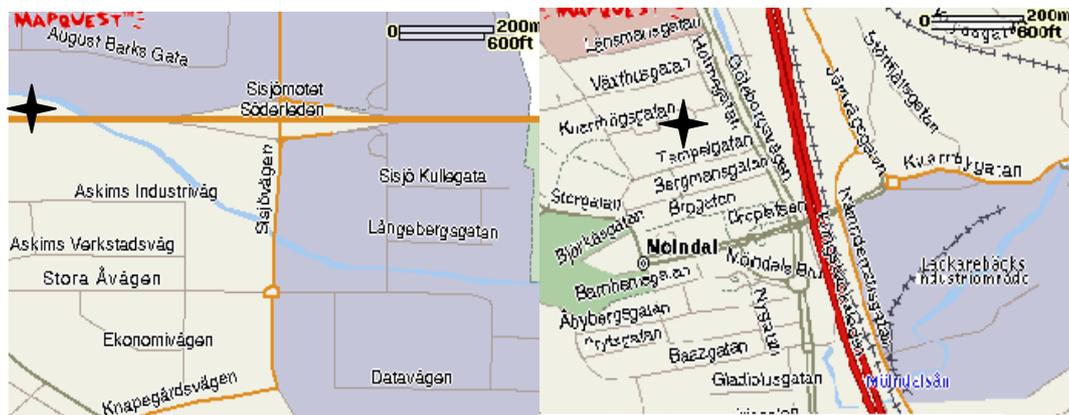


Figure 9 Locations of sampling sites in the Mölndal area (web ref. 8).

2 Soil sampling at the old industrial site

During the environmental soil investigations of the old industrial area in Sweden, samples were collected from the five locations. Out of these five locations four locations were within the project area of investigation as shown in the Figure 10. Location five was outside that area; the sample was taken to compare the background values of the parameters to be investigated in the study. Almost whole project area is covered with asphalt pavement. Sampling location 1, 3, and 4 are on the right bank of the watercourse. Location 2 is at the small grassland made between the asphalt pavements.

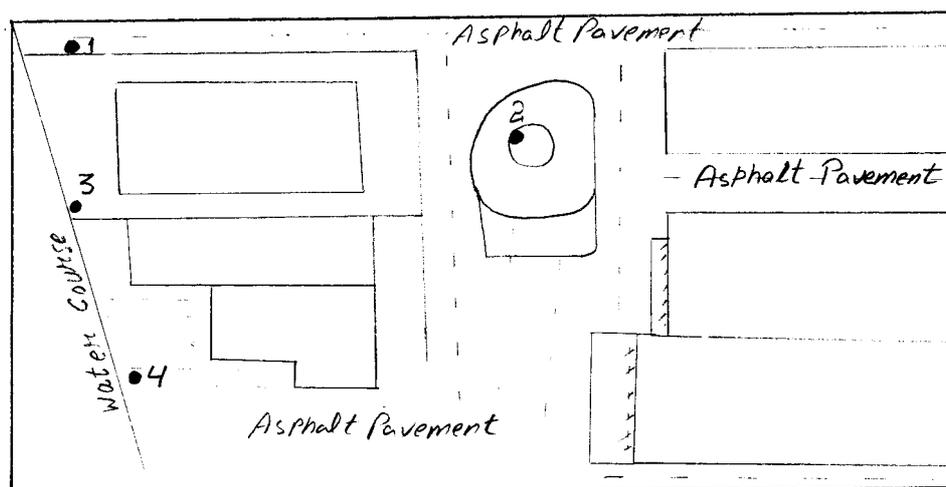


Figure 10 Sketch of sampling locations at an old industrial site in Sweden.

3 Experimental

Two experiments were designed for the laboratory. The object of these soil experiments was to check the validity of the analytical techniques used for soil samples contaminated with cutting fluids, and to get an idea of the transport mechanism of the polar as well as non-polar compounds present in the cutting fluids in two different scenarios. In the first experiment, the soil was kept unsaturated to stimulate controlled conditions, but in the column-leaching test saturated conditions were proposed to simulate more realistic environmental conditions. A description of these two experiments is given below.

4 Cylinder- unsaturated

The object of the experiment was to verify the validity of the analytical techniques used for organic contaminants in the soil samples and to get an idea of the transport of cutting fluid in unsaturated soil media. For this first experiment a glass cylinder of 10 cm in diameter and 50 cm in length was used. 2 kg of soil was spiked with 16 ml of a 12% solution of cutting fluid to get a total concentration of approximate 1000ppm. The soil was kept in the glass cylinder for 8 weeks at room temperature. The total length of the soil column in the cylinder was 35 cm. The cylinder was covered with aluminum foil to reduce the process of photodegradation. After 8 weeks samples were collected at different depths by pressing a tube of smaller diameter than the glass cylinder, into the soil.

5 Soil column experiment

Evaluation of the potential leaching of organics compounds to soil can be performed by several approaches. For this EPA standard method 1311 give the guideline for toxicity characteristic leaching procedures (TCLP). This method is designed to

determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphase wastes under anaerobic conditions (web ref. 11). As the nature of the soil being discussed in this project is different, as we are dealing with upper horizons (A and B) of soil profile. Both of these horizons contain oxygen and thus can not follow TCLP for this type of experiment. The column-leaching test was designed to simulate more realistic environmental conditions. The object of leaching experiment of soil column was to get an idea of the transport mechanism of the polar as well as non-polar compounds present in the cutting fluids.

The testing apparatus consists of a glass leaching columns. The Column was 0.75 m tall and 8 cm in diameter. The column contained soil (passing #4 sieve) with a known concentration of cutting fluid, 1000 ppm. The soil was kept in the glass column, and the profile of the column contained 50 cm of soil divided into two horizons (A&B), with a thin filter of medium sand at the top and bottom of the soil column. The filter was applied for the uniform distribution of fluid in the soil. A leachate collection port was fixed at the bottom of the column to collect the dripping of fluid from the column outlet.

5.22 ml of the cutting fluid with 1500 ml of distilled water was added on the soil at the inlet of the column to get the total concentration of approximate 1000 ppm. The calculations of this added amount were done by the following formulas

$$m_{cf} = m_s \cdot c_w / c_{cf} \quad [5-1]$$

Where:

m_{cf} is mass needed of the cutting fluid

c_w is the wanted concentration i.e 1000mg/kg=1000ppm=0,001%.

m_s is the mass of soil= 5,362 kg=5362 g.

The mass of the cutting fluid calculated from the equation 5-1 is used in the formula

$$v_{cf} = m_{cf} / \delta_{cf} \quad [5-2]$$

Where:

v_{cf} is the volume of the cutting fluid in ml.

m_{cf} is the mass calculated from equation 5-1

δ_{cf} is the density of the cutting fluid= 1,027g/l.

After addition of the cutting fluid, the column was left for 42 days to get an idea of the movement of the chemicals with time at several depths. Unfortunately the dripping collected in the sample port at the column outlet was not large enough in volume to make any analysis using immunoassays and PetroFlag kits. The analyses were performed only for soil samples collected from the column.

6 Analysis procedure for the soil samples

For the soil samples collected from the Mölndal area as well as from the area of the case study, the following parameters were tested:

6.1 Particle size analysis

Particle size analysis was conducted using the method described in the ASTM method D, 1140-54, method for particle size analysis of soils. The sieving was carried out using an electric sieving machine, having stainless steel sieves with mesh width sizes 4,760 mm, 2,0 mm, 1 mm, 0,05 mm, 0,025 mm, 0,0125 mm, and a residue of grains

<0.125 mm. The sieving results are reported as the mass percent of soil within the respective fractions (Borg G., 1985).

6.2 Soil moisture content

The moisture content of the soil samples was performed according to the ASTM test method D2216, method-determining moisture content for soils. Approximately 50 g of soil was taken and weighed in ceramic crucible. The soil was heated in oven at 105 C° for 8 to 12 hours until constant weight. The soil was weighed again and mass loss in gram percent w/w was calculated (Borg G., 1985).

6.3 Determination of mass loss of ignition

Approximately 50 g of dried soil sample was taken in a ceramic crucible and was weighed carefully. It was heated in an electric furnace at 500 C° for 6 hours. The sample was cooled in desiccators and weighed. The mass loss in gram and percent was calculated (Borg G., 1985).

6.4 Soil pH

The pH of soil samples was analyzed using distilled water. For pH measurement 20 g of dry soil (< 2mm) was transferred in 200 ml plastic container. About 70 ml of distilled water was added in the container and the lid was screwed. The containers were placed on a shaking table and shaken well for one hour. After one hour the containers were removed from the shaking table and left for few hours to settle sand grains. The pH was calculated putting directly the electrode of pH meter in to the container (McLean, E.O. 1987).

7 Procedures for the screening and analysis of organic contaminants in the soil

The analysis procedures for the screening of organic contaminants in the soil samples were performed using photo ionization detector and wet chemistry analytical techniques, Immunoassay and PetroFlag system. A description of these analytical techniques is given below.

7.1 Screening procedure with PID

The screening of soil samples was performed with the Photovac 2020 PID. The specification of the instrument used are given in the Table 5.

For the screening of soil samples in the field the EPA standard method 3815 "Screening of solid samples for volatile organics" was followed with some modification. Method 3815 suggests the use of glass vials with about 5 g of sample but the quantity of the sample can be changed depending on the field conditions. In the environmental soil investigations, soil is normally put into diffusion tight plastic bags (Rilsan-bag). About 100-200 g of soil was taken and left with air in the bag (about the same volume in all bags), the bags were folded and swirrelled and tighten with plastic tape to control the emission of VOC. The Rilsan bag is almost completely diffusion tight for the volatiles. Readings were taken after 2-3 hours and after 24

hours. It should be interesting to find out correlations between time elapsed and diffusion through these bags.

Table 5 Specifications of PID used in the project (web ref. 12).

Model	Photovac 2020
Detector	Instant on photo ionization detector with standard 10.6eV UV lamp
Operating Temperature Range	0°C to 40°C (32°F to 105°F)
Operating Humidity Range	0 to 100% relative humidity (non-condensing)
Operating Concentration Range	0.5 ppm to 2000 ppm isobutylene equivalent
Response Time	Less than 3 seconds, to 90%
Accuracy	± 10 % or ± 2 ppm, whichever is greater

7.2 Analysis procedure with Immunoassay

The analysis of soil samples to find the total petroleum hydrocarbon concentration (TPH) was performed using EPA standard method 4030 “Soil screening for petroleum hydrocarbons by Immunoassay”.

The analyses were performed using Ensys™ Petro Soil test kit, 7042301, produced by SDI (Strategic Diagnostic Inc) USA (web ref 13). The EnSys Petro Test System includes antibody-coated test tubes containing monoclonal antibodies, which are produced using m-xylene as the antigen. The enzyme conjugate used to produce color is composed of m-xylene as the target compound and horseradish peroxidase as the enzyme. The washing step is made with a dilute detergent solution. Color development is achieved using hydrogen peroxide as the substrate and tetramethylbenzidine (TMB) as the chromogen. The stop solution added to terminate color development is 0.5 percent sulfuric acid. A differential spectrophotometer that emits light in the visible range of the electromagnetic spectrum at 450-nm wavelength is used to measure the absorbance of the sample extract and of a reference standard containing 3 mg/L m-xylene during color measurement. The concentration of PHCs in the sample extract is then determined by comparing the absorbance readings associated with the sample extract and the reference standard.

The analysis consists of two parts; extraction of the analyte and assay procedure.

7.2.1 Sample extraction

All analysis of soil samples begins with an extraction step, where the contaminants are extracted by a solvent. The extraction of soil sample with the immunoassay method was done with the methanol. 20 g of the soil sample were collected in extraction container (plastic), and 20 ml of 100% methanol was added. The container was shaken well for one minute and then left for 3-4 minutes until a liquid solvent layer was observed. The upper layer containing the contaminant was separated using a bulb pipette. This extract was filtered by special filter supplied with the extraction kit.

7.2.2 Assay procedure

The samples obtained from the filtered extract were diluted using 140 μl and 540 μl of methanol. First dilution ampoule is to test the sample for 10 ppm and second dilution ampoule is the test the sample for 100 ppm. There was no intermediate dilution ampoule. 60 μl of sample was applied in the first dilution ampoule (140 μl) and then same volume from first to second ampoule (540 μl). From each ampoule 60 μl mixture of sample and dilution methanol was transferred to the corresponding conjugate tubes, which contain 1.25 ml of buffer solution. The schematic diagram of dilution process is shown in Figure 11.

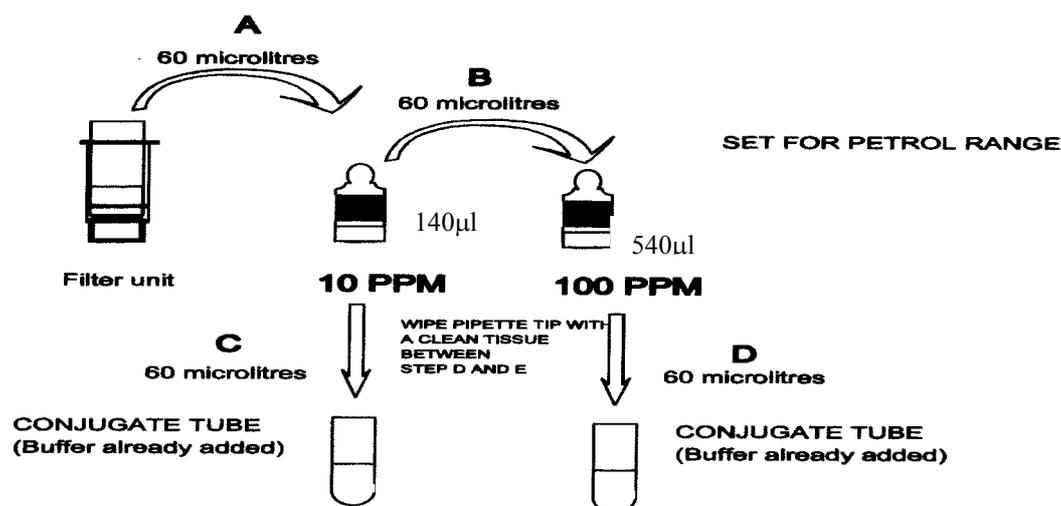


Figure 11 Schematic diagram of dilution process for TPH kit.

After the dilution process, the antibody-coated tubes were fit firmly on the conjugate tubes and shaken 2/3 times. The conjugate tubes were thrown away and antibody tubes were kept for ten minutes for the incubation. After the completion of incubation the samples in the antibody tubes were vigorously shaken out to the waste containers and tubes were washed with the wash solution. After washing the 200 μl of “substrate A” was applied in the tube followed by start solution labeled as “substrate B. After 2.5 minutes of the reaction 200 μl stop solution containing sulphuric acid was applied to stop the reaction. The color of the tubes were interpreted visually as well as with differential photometer. The color produced is inversely proportional to the concentration.

7.3 Analysis procedure with PetroFlag system

The PetroFLAG™ test kit, is a quantitative device manufactured by Dexsil® Corporation (Dexsil®). It is based on emulsion turbidimetry. Measuring TPH in soil using the PetroFLAG™ test kit involves the following three steps: (1) extraction, (2) filtration and emulsion development, and (3) turbidity measurement and calculation of the TPH concentration.

7.3.1 Extraction

Extraction of 5-10 samples consists of following procedure:

10 grams (± 0.1 gram) of the each soil sample was weighed, and placed in a polypropylene tube. To extend the quantification range for the samples containing very high concentration of PHCs 1g sample were analyzed. One breaktop vial of extraction solvent was poured into the tube, and the tube was capped. The timer was set to 5 minutes, and the tube was shaken for 15 seconds or until the sample is fully wet. Shaking was continued for the tube intermittently for a minimum of 4 minutes, and then let to stand for 1 minute.

7.3.2 Filtration and emulsion development

The solvent extraction from the polypropylene tube containing the soil and extraction solvent was poured into the syringe barrel. Care was taken to stop soil to enter the syringe, as too much soil might plug the filter. First a few drops of the extract from the filter were discard into a waste container, and then the extract was filtered into the vial containing developer solution. The extract was added into the vial one drop at a time until the meniscus just enters the vial neck. The vial was shaken for 10 seconds. Then the timer was set to 10 minutes, and the vial let to stand. During the 10-minute period, an emulsion associated with the hydrocarbons in the extract is developed.

7.3.3 Turbidity measurement and calculation of TPH concentration

After the 10-minute development period, the vial was placed in the turbidimeter, which was calibrated using a blank and a single calibration standard. The samples were analysed with the response factor of 10 (for mineral oil) and 5 (for diesel fuel). When the vial is placed in the turbidimeter, the TPH reading of the sample extract is displayed on the turbidimeter as mg/kg (ppm) TPH in soil on a wet weight basis. In certain circumstances, the water content of the soil and analyte carbon number range may require a correction factor to account for soil-water content (web ref. 8). To correct the TPH concentration in mg/kg, on a wet weight basis for solvent dilution associated with the moisture content of a given soil sample, the following formula is used

“mg/kg TPH after correcting for solvent dilution = mg/kg TPH before correcting for solvent dilution x (100 + percent moisture)/100.”

Results and Discussion

The experimental program consisted of two parts. The first part involved determination of properties of the soil samples, cylinder-unsaturated soil experiment and soil column leaching experiment. In the second part, environmental soil investigations at an old industrial site in Sweden were analyzed using the same analytical approaches that were used in the laboratory experiments. Brief description of the results of all experiment is given in following section.

1 Selected parameters of soils

Particle size analysis was performed to calculate hydrogeological properties of the soils being used in the project. Textural class of the soil is shown in figure 12. The values of hydraulic conductivity (K), and bulk density were calculated using a grain size distribution curve shown in Table 6.

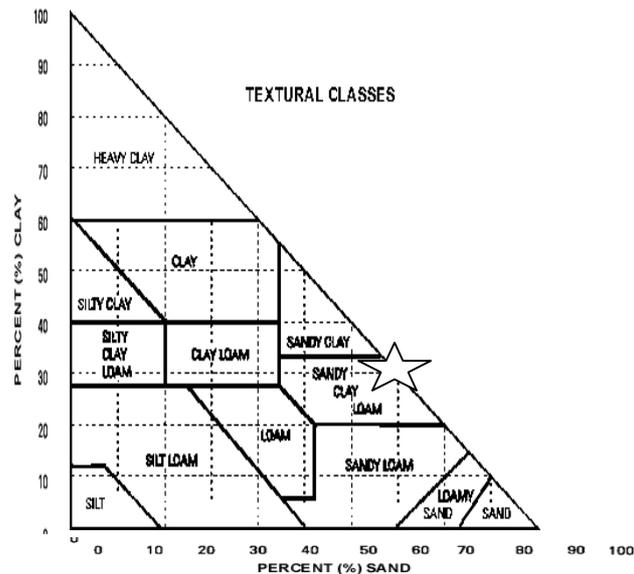


Table 6 Hydrogeological properties of the soil samples:

Sand %	74,5
Clay %	25
Silt %	0,5
Texture	Sandy Clay Loam
Bulk density	1,44g/cm ³
Hydraulic conductivity (K)	0,37 cm/hr

Figure 12 Textural class of the soil.

Particle size plays an important role in the mobility and fate of organic contaminants in soil. Colloidal particles exhibit the largest sorption capacity, with a diameter of 10^{-6} to 10^{-3} mm. High clay content results in the lower permeability of the soil, it allows the fluid to stay more in the vadose zone. This will cause complex bonding mechanism in the soil-oil-water mixture. The sorption capacity decreases with increasing size, and particles larger than 2 mm in diameter especially do not affect the soil sorption capacity (J. Tölgyessy, 1993).

One of the first operational parameters that were investigated in the laboratory experiments was the moisture content of the soil samples. Moisture content plays an important role in the efficiency and must be considered in the measurement of oil contents of soils. Water may cause oil-in-water emulsion that makes the extraction difficult, which ultimately makes the extraction efficiency low (O'Shay et al; 1994). The moisture content of the soil samples are given in Table 7. For all the samples

containing high moisture content (> 30%w/w for immunoassay and >15%w/w for PetroFlag), appropriate correction was applied for different analytical methods.

The results of pH and loss of ignition are also given in Table 7. There is no significant influence of pH of soil on the detection efficiency of the analytical approaches applied. However pH less than 4 affects the bonding mechanism of the hydrocarbons with the soil particles. With decreasing pH the adsorption process is increased and bioactivity is decreased. All the samples had pH in the range of 6-7.

Table 7 Selected properties of soil samples.

Sample No.	Moisture content (w/w%)	pH*	Mass Loss of ignition (%)
Lab. Ex1	8%	5,9	9%
Field Samples			
1	10	6,67	1,17
2	10,2	6,90	5,34
3	26	6,44	7,56
4	29,4	6,56	7,36
5	20,8	6,50	10,35
6	24,4	6,54	11,21
7	6,8	6,93	1,71
8	6,2	7,05	1,49
9	13,8	6,76	3,9

Mass loss of ignition was calculated to get an estimation of the organic contents present in the soil samples. The presence of calcium carbonate in the soil may somewhat affect the result due to slight decomposition of carbonate, thereby giving a larger mass loss than caused solely by the incineration of the organic remains. Furthermore, with a high content of clay minerals in the soil, there may also be a slight decrease in mass due to loss of chemically bound water in the clay minerals, but with negligible significance (Swedish EPA report 4639).

2 Response of photoionization detector (PID) for the soil samples

Photoionization detector is basically used for the air monitoring operations, as it gives the real time values. Use of this analytical method for screening of soils is a new approach. The preliminary objective of this screening is to check the volatile content of the soil samples. The results of PID for the laboratory experiments as well as of environmental soil investigations of old industrial site are given below.

2.1 Cylinder – unsaturated

The results of the experiment are given in Figure 13 and Table 8. The values were measured with both glass jar (250ml) and Rilsan bags. The concentration of the volatiles is higher for the sample No. 2, 3, 4 and 5 for depth ranging from 10 cm to 25 cm. The spiked value for the 12% solution in this experiment was 1000 ppm. The cutting fluid was added on the surface of the soil column in the glass cylinder. In the upper layer low result show the evaporation of the volatile content with time but its

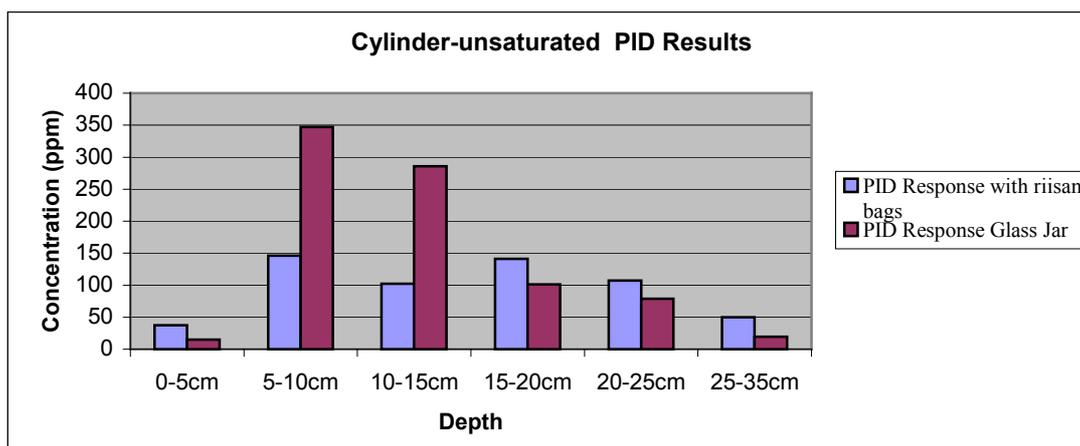


Figure 13 PID response for the soil samples of cylinder-unsaturated

Table 8 PID Values of volatile contents at different depths

Sample No	Depth	BkGd	Sample (glass jar)	Sample (Rils.Bags)
1	0-5cm	5.5	15	37,2
2	5-10cm	4.5	347	146
3	10-15cm	0.1	286	102
4	15-20cm	0.0	101	141
5	20-25cm	0.0	79	107
6	25-35cm	0.0	19,3	49,8

presence at lower depth shows movement of the cutting fluid in unsaturated soils. The movement of hydrocarbons in this case can be partially related to the sorption (adsorption and absorption) of organic contaminants with soil particles. However in the unsaturated soil at room temperature the volatilization rate is very high as compared to the saturated conditions that result in lower volatile content values by PID.

The relative higher values for the samples with glass jars are due to the small air volume in it. The PID suction capacity is about 300 ml/min, it consumes all the air readily, and as a result a sharp response curve is seen and then suddenly nothing. On the other hand Rilsan bags have a larger volume of air, but the response curve is not as sharp as with the glass jar. The results with rilsan bags are more reliable because of their larger volume, as the instrument has more time to reach the average of values it has calculated in a specific span of time.

2.2 PID results of soil-column leaching experiment

The results of soil column leaching experiment are shown in the Figure 14. The soil used for this project contains about 65 ppm of background value. Background value is obtained by the analysis of blank sample from the same sampling site. All the samples show relatively higher values of volatile content. For the samples 2, 4 and 5 the PID response is almost equal to the spiked value. Which shows the high mobility of cutting fluids in the saturated media. Moreover higher response of photoionization detector for these samples shows the reliability of the instrument for the soils containing high moisture content. On the bases of the results obtained from this

experiment, we can say that the response of PID is very good up to the moisture content 30 % w/w.

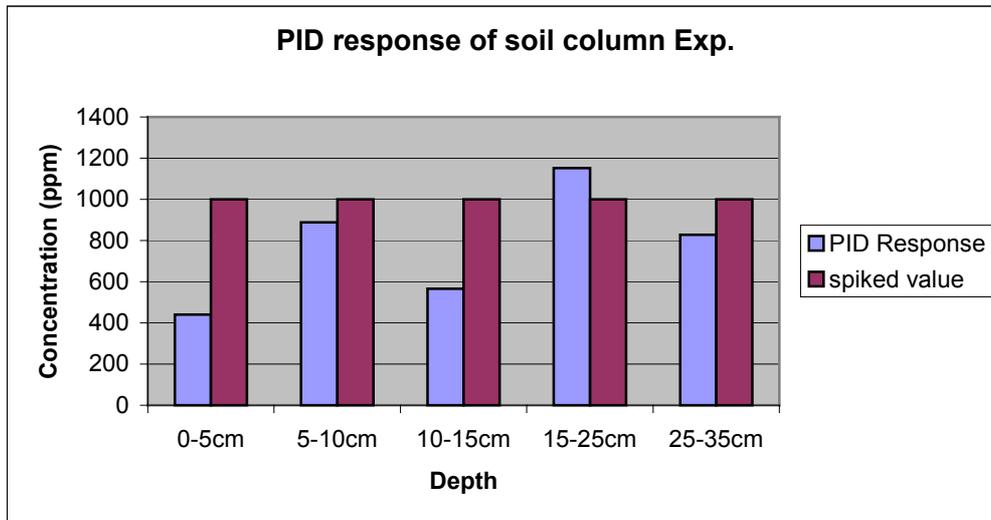


Figure 14 Evaluation of samples with PID at different depths in the soil column.

Table 9 PID Results of Column Experiment.

Sample No	Depth	Conc.(ppm)	Spiked value
1	0-5cm	440	1000
2	5-10cm	889	1000
3	10-15cm	566	1000
4	15-25cm	1152	1000
5	25-35cm	828	1000

2.3 PID Results of field measurements at the old industrial site

Screening of the samples collected from the field was conducted after 4 hours in the Rilsan bags and after two days to find out correlations between time elapsed and diffusion in these bags. The response of PID after 4 hours is shown in Figure 15. The concentration at location 2 and 4 are higher than at location 5, which is a location outside of the project area. This sample was collected to check the general background value in the area. Location 2 is near the car parking and the higher value in the upper layer is probably due to the presence of light fuel hydrocarbons such as benzene, toluene and xylene. The values of volatile content at this location are almost the same after 4 hours and after 48 hours. There could be the following explanations of this fact.

1. The value of PID reading for location 2 is almost the same for the 4 hour reading and 48 hours reading i.e. 63,3 and 60. But the values of other locations are higher after 48 hours. The explanation for location 2 is that it may contain only lighter hydrocarbons (for example gasoline). Aliphatic hydrocarbons with longer chain molecules may not be present. This explanation could be verified by the results of petroFlag analysis for this location. The value with response

- factor 5 is high as compared to the value with response factor 10, which is confirmed by the absence of heavy oil present in the samples of location 2.
2. There may be a leakage of air during the storage and packing of the sample in the rilsan bag that results in almost equal value of volatile content after 4 hours and 48 hours.
 3. Polyaromatic hydrocarbons released from the car exhaust are degraded soon by the reaction with NO₂ and ozone present in the air. For example toluene has a half-life time of two days and xylene has half-life of only a few hours (Roger N 1994). This could be the explanation for the reason why the value of volatile content after 48 hours is almost same as after 4 hours.

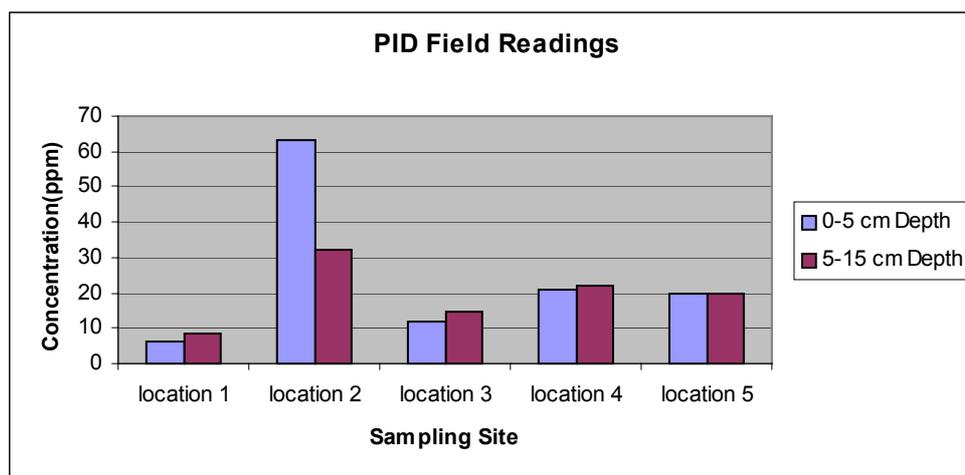


Figure 15 PID response in the field after 4 hours in Rilsan bags.

Table 10 Field measurement of PID After 4 hours in Rilsan Bags

Sample ID	Conc. [ppm] At 0-5cm	Conc. At 5-15cm
Location 1	6,1	8,7
Location 2	63,3	32,2
Location 3	11,8	14,6
Location 4	21	22
Location 5	20	20

The concentration of volatiles after 48 hours storing in Rilsan bags, are very high as compared with the first results. In two days the Rilsan bags probably saturated with volatile content. Location 3, and 4 shows very high values. Location 4 is close to the old operational industrial site, and higher values at especially location 4 can be related to the old industrial contamination in the soil. However only the results of PID can not be used to decide that a sample or site is free of volatile contaminants. Rather it is a procedure to decide the number and size of samples to be collected for further quantitative VOC analysis.

Generally, in a mixture of soil and petroleum hydrocarbons (at temperature up to 30°C), it is expected that the volatilization rate will be lower, due in parts to adsorption of some of the oil to soil particle surfaces and also to low Henry's constant of the petroleum hydrocarbons fraction with long chain molecules. However higher temperature results in higher vapor pressure, lower viscosity, and higher aqueous

solubility of the oil and thus, an increase in the volatilization of the petroleum hydrocarbons (Raymond et al, 1994).

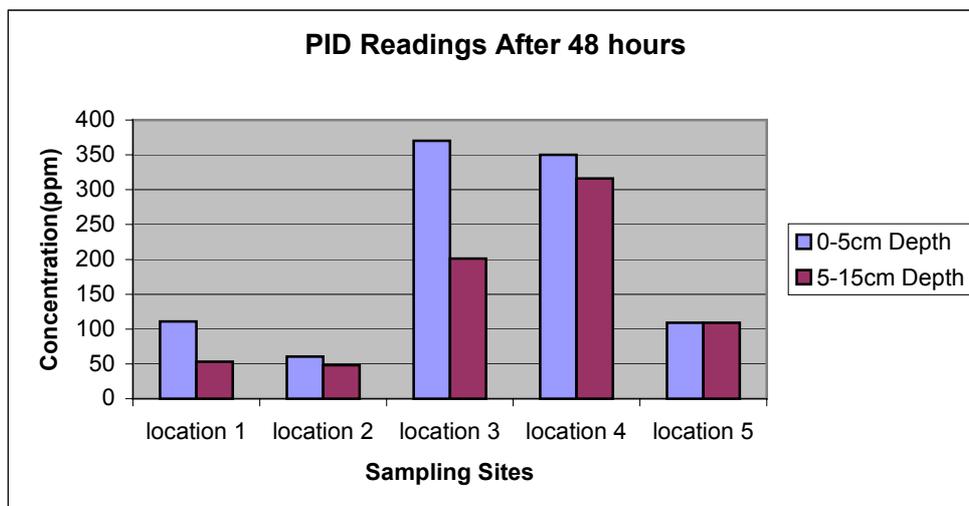


Figure 16 PID response for the field samples after 48 hours

Table 11 Field measurement photoionization detector after two days in Rilsan bags

Sample ID	Conc. [ppm] At 0-5cm	Conc. At 5-15cm
Location 1	111	53
Location 2	60,6	48
Location 3	370	201
Location 4	350	316
Location 5	109	109

3 Results of PetroFlag System

3.1 Unsaturated-cylinder

The results of the soil analysis with petroFlag are given in Figure 17. Background value is the value obtained from the blank soil sample and the spiked value is the known concentration of the cutting fluid that is added in the cylinder. The results are only for the response factor 10 (for mineral oil). Concentration of total petroleum hydrocarbon is very high for the samples 1 and 6. Sample 1 is from the upper layer of the cylinder, which contains roots of vegetation and, other humus materials.

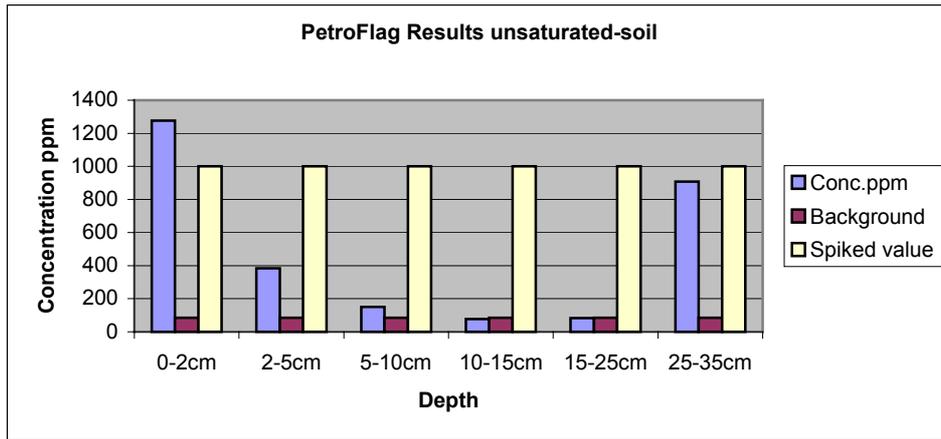


Figure 17 Results of the soil analysis with petroFlag

Table 12 Concentration of TPH calculated with PetroFlag system

Sample	Depth	Conc. ppm
Sample 1	0-2cm	1276
Sample 2	2-5cm	384
Sample 3	5-10cm	150
Sample 4	10-15cm	77
Sample 5	15-25cm	83
Sample 6	25-35cm	907
Blank		65

The glass cylinder is closed from the bottom and there are no chances of further movement of oil. We can assume that the oil is accumulated at the bottom of the cylinder, which results in very high concentration of TPH. PID is sensitive to volatiles and that is probably the reason, why it could not detect the longer chain molecules present at the bottom of the cylinder. Presence of oil concentration higher than the background value in the middle of the cylinder shows that at least two different situations can co-exist: (1) oil may exist separately in the soil pore and the soil particles, and (2) oil may adsorb on the surface of the soil constituents.

3.2 Soil column experiment

The results of soil column leaching experiment are shown in the Figure 18. The samples were analyzed both for the response factor 5, for diesel oil and 10 for the mineral oil. The analysis was performed only for the soil samples, as we could not get enough leachate to make any water analysis. Actual spiked values for this experiment was 1000 ppm while the background value of the soil was 65 ppm.

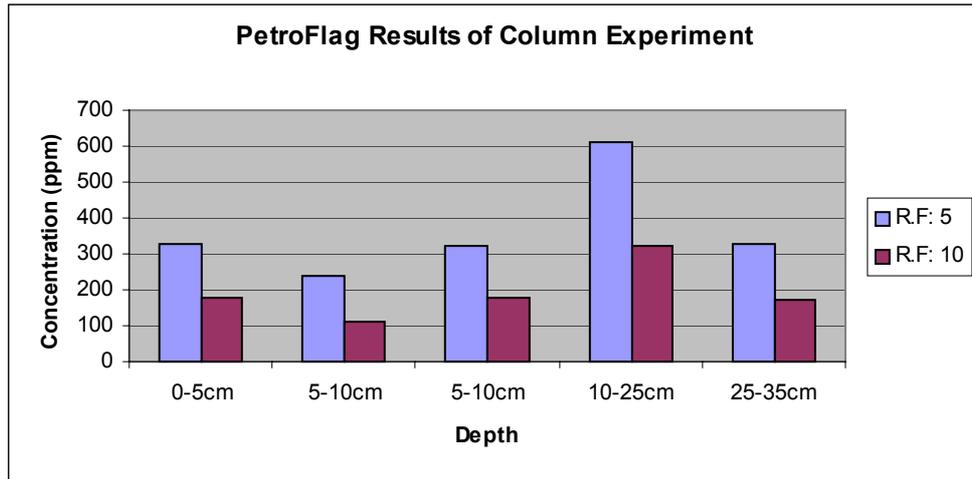


Figure 18. Results of the soil analysis of column experiment with petroFlag

Table 13 Concentration of TPH calculated for column experiment

Sample	Depth	Conc. (ppm), R.F:5	Conc.(ppm) R.F:10
1	0-5cm	330	180
2	5-10cm	240	110
3	5-10cm	320	180
4	10-25cm	610	320
5	25-35cm	330	170

In this experiment the cutting fluid was added from the inlet of the soil column, diluted in nanopure water so a soil-oil- water mixture was formed. The soil contains high clay content, which increases retention time of the contaminants in the column. The surface-active constituents of soil such as organics, amorphous materials and hydro-silicate minerals (clay minerals) significantly enhance its interaction with oil. In turn, one expect that within the pore fluid of soil, oil can exist in three separate phases: dissolved, liquid (non-aqueous phase: NAPL), or gaseous. The appropriation of each situation will depend on the interacting constituents and conditions leading to the development of soil-oil-water mixture (Mohamed, et al, 1992).

Since the mineral oil present in the cutting fluid consists of large molecules with long chain lengths, it is expected that the primary mode of interaction will be via van der Waal's interactions, significant binding interaction of alkyl group (oil) with surface oxygen or hydroxyl (soil or water). Hypothetical presentation of soil-oil-mixture is shown in Figure 19.

If the retention of the cutting fluid in the vadose zone is compared for the two scenarios (unsaturated and saturated) presented in the laboratory experiments. It is obvious that the oil retains more in the saturated conditions because of the low permeability of soil – oil mixture. A higher flow rate may allow greater momentum to be transferred from leaching water to the oil in pore fluid, thereby providing more kinetic energy to reduce the interfacial tensions between the oil and water. This may enhance the mobility of a large portion of the oil in pore fluid (Mohamed, et al 1992). In the natural conditions, it is expected that the effects of rainfall and groundwater fluctuation would provide the opportunity of migration of oil from the stabilized soils,

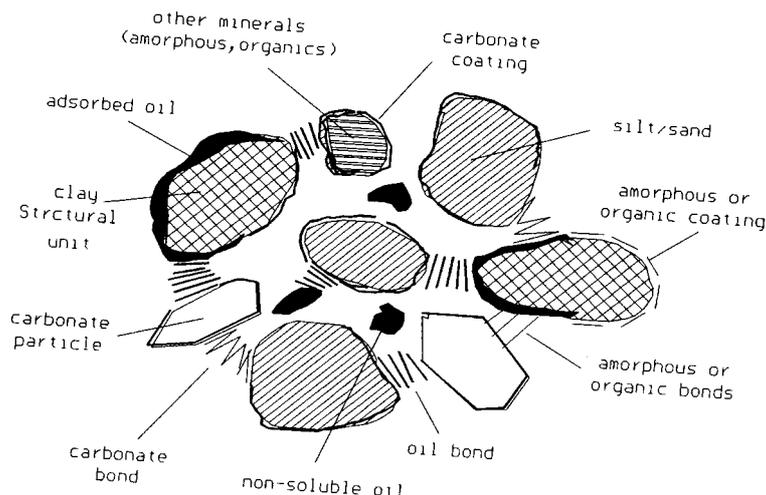


Figure 19 Hypothetical presentation of soil-oil-mixture (Raymond et al 1994).

and poses a threat to the surrounding environment in the form of surface and ground water contamination (Raymond et al 1994).

3.3 Measurements of TPH with PetroFlag system at an old industrial site

During the field investigation of soil at Old industrial site, each sample was analyzed with both response factor 5 and 10. During in-situ analysis sample from the locations 1, 2, 4 and 5 were found highly wet with moisture content >30% w/w. The results obtained by PetroFlag system were corrected using the formula.

“mg/kg TPH after correcting for solvent dilution = mg/kg TPH before correcting for solvent dilution x (100 + percent moisture)/100.”

Corrected results for the response factor 5 and 10 are shown in the Figure 20 and 21. Analysis for the diesel oil shows the presence of higher content of TPH in the upper layer at almost all locations. The whole project area is an urban area and high values may be due to traffic or transported soils. A study done at Chalmers University of Technology shows the presence of semivolatile PAH at 1m depths in ditched along E20 highway at Partille, but concentration of long chain aliphatic compounds present in the lower layer can not be related to the traffic.

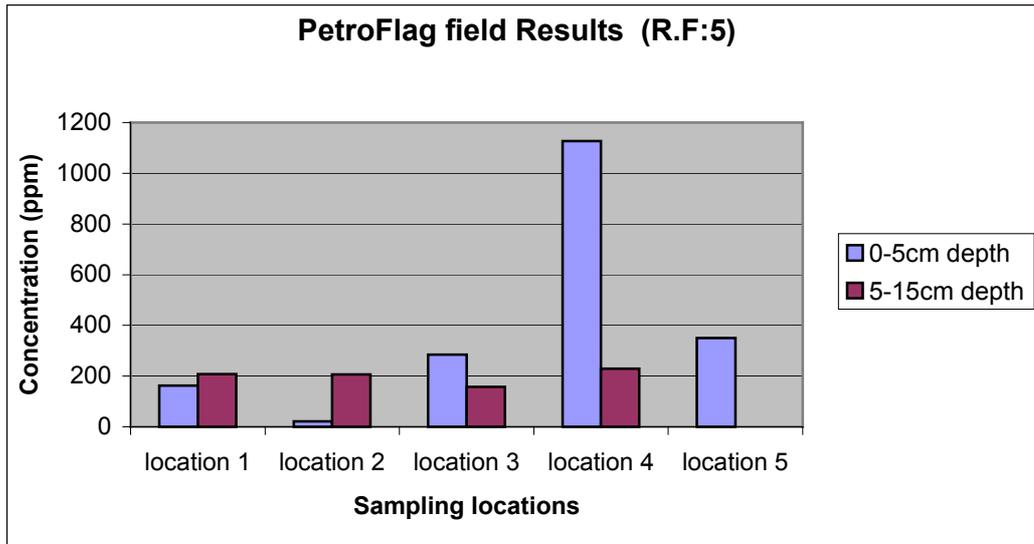


Figure 20 Corrected results of the soil analysis of field measurement with petroFlag

Table 14 Concentration of TPH calculated for field measurements.

Sample ID	Conc. [ppm] At 0-5cm	Conc. At 5-15cm
Location 1	163	208
Location 2	21	207
Location 3	285	158
Location 4	1127	229
Location 5	350	

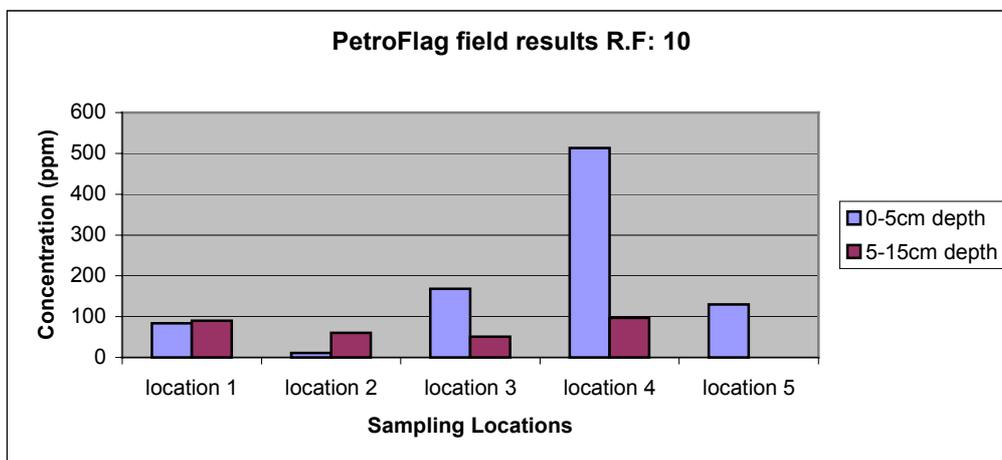


Figure 21 Corrected results of the soil analysis of field measurement with petroFlag

Table 15 Concentration of TPH calculated for Field measurements (R.F: 10)

Field Measurement Response factor: 10 after correction for mc		
Sample ID	Conc. At 0-5cm	Conc. At 5-15cm
Location 1	84	90
Location 2	11	60
Location 3	168	51
Location 4	513	97
Location 5	130	

Results obtained with response factor 10 confirm the same trend of concentration in two layers of soils of the project area. The petroFlag system gives the aggregate response for all hydrocarbons present in the soil samples, analysis with different response factors give the relative concentration for a group of compounds.

Location 4 seems to have very high concentration of TPH, confirmed with response factor 5 and also with the results of screening test with PID. As already mentioned this location is very close to the old industrial operational site. On the basis of the results above we can easily relate the soil pollution present at this location to the old industrial operations. Sampling location 5 shows the consistent values with all techniques, but the location 2 shows higher values for only light fuel hydrocarbons.

The results of the above experiments cannot be used to get an idea about the mobility of the petroleum hydrocarbons in the project area, because the whole area contains fill material, which varies in texture at places. However if we consider the natural soil type (sandy loam) of the project area, oil transport from the soil due to rainfall is expected to be low because of the low aqueous solubility of the soil, its high structural form and relatively low permeability of soil-oil mixture. One can assume that the rapid reduction of oil concentration in the lower layer can be attributed to the removal of soluble and lighter fractions of petroleum hydrocarbons present in the soil pore fluid.

4 Results of Immunoassay analysis

Immunoassay technique was used in the environmental soil investigation of all the samples laboratory experiments as well as in the field investigations. This technique is basically designed to measure a large portion of the aromatic hydrocarbons but only a few of the aliphatic hydrocarbons in the C₆ through C₂₂ carbon range (web ref. 7).

As described in previous chapter, this system does not generate qualitative results. The semi quantitative results produced by the device only indicate whether the PHC concentration in a sample extract is above or below a particular level. For this project these levels were selected as 10 ppm and 100 ppm. The section below will give the results of the immunoassay analysis of the project.

4.1 Unsaturated-cylinder

The results of soil samples analyzed with immunoassay for the unsaturated-cylinder experiment are given in the Table 16. Samples 1, 2, 3, 6, and 7 show the presence of aromatic hydrocarbons in the range between 10 ppm and 100 ppm. Sample 4 and 5 show the presence of aromatic hydrocarbons even less than even 10 ppm. If we look

Table 16 Immunoassay results of unsaturated-cylinder experiment

Sample ID.	Depth	10ppm Test			100ppm Test			Agreement
		>10	<10	Value	>100	<100	Value	
Standard 1								Acceptable
Sample 1	0-2cm	•		-0,04		•	0,66	
Sample 2	2-5cm	•		-0,2		•	0,24	
Sample 3	5-10cm	•		-0,44		•	0,22	
Sample 4	10-15cm		•	0,32		•	0,4	
Standard 2								Acceptable
Sample 5	15-25cm		•	0,27		•	0,36	False +
Sample 6	25-35cm	•		-0,33		•	0,17	
Sample 7	Blank	•		-0,04		•	0,06	

at the results of PID and petroFlag for the samples of depth 15-25 cm, they show relatively higher values of TPH as compared to the results of immunoassay for the same depth. It shows the presence of very small fraction of aromatics in the cutting fluid used to spike the soil samples.

4.2 Immunoassay results of soil column experiment

The results of soil analysis with immunoassay techniques for the soil column experiment are given in the Table 17. All samples show presence of aromatic hydrocarbons less than 10 ppm. Only sample 3 has concentration of aromatics even less than 10 ppm, it is interesting to remind that at this depth PID and petroFlag techniques show higher concentration of TPH. The blank soil sample also gives the concentration less than 10 ppm.

Table 17 Immunoassay results of soil column leaching experiment

Sample ID.	Depth	10ppm Test			100ppm Test			Agreement
		>10	<10	Value	>100	<100	Value	
Standard 1								Acceptable
Sample 1	0-5cm	•		-0,15		•	0,24	
Sample 2	5-10cm		•	0,06		•	0,15	False +
Sample 3	10-25cm	•		-0,01		•	0,15	
Standard 2								Acceptable
Sample 4	25-35cm	•		-0,12	•		-0,16	
Sample 5	Blank		•	0,24		•	0,06	

4.3 Immunoassay results of field measurements

The results of field samples analyzed with immunoassay are given in the Table 18. All of the samples show less than 10 ppm of aromatic hydrocarbons. Immunoassay gives best results for the soil samples having moisture content up to 30% w/w. Some samples were found with high moisture content so excess moisture was removed by

Table 18 Immunoassay results of field measurements

Sampling Sites	Depth.	10ppm Test			100ppm Test			Agreement
		>10	<10	Value	>100	<100	Value	
	Standard							Acceptable
Location 1	0-5 cm		•	0,32		•	0,29	
	5-15 cm		•	0,39		•	0,19	
Location 2	0-5 cm		•	0,37		•	0,29	
	5-15 cm		•	0,91		•	0,49	
Location 3	0-5 cm		•	0,37		•	0,65	
	5-15 cm		•	0,55		•	0,67	
Location 4	0-5 cm		•	0,12		•	0,42	
	5-15 cm		•	0,16		•	0,45	
Location 5	0-5 cm		•	0,55		•	0,83	
	5-15 cm		•	0,41				

putting the soil on a paper towel. The towel was wrapped around the soil and water was pressed out for a few minutes. After that the soil sample was left with the moisture content <30 %. The amount of soil required for the analysis was taken out from the center of the soil ball.

The results obtained for aromatic hydrocarbons by laboratory method agree with the field results of immunoassay technique. However this technique is ideal if prior knowledge of contaminants and expected level of concentration is available.

5 Comparison of the results with the results of GC/MS

Three soil samples were analyzed with GC/MS technique from SGAB analytica Sweden. The results obtained from the commercial lab are shown in the Figure 22.

Sample 1 is from the old industrial site at location 4, sample 2 from the 0-5 cm depth of soil column experiment and sample 3 a blank with soil used for the laboratory experiments. Table 19 shows the results of all these samples with the techniques used in the project. Sample 1 and 2 show higher values with PetroFlag and PID and less than 10 ppm concentration of aromatics. The same pattern is observed in the results obtained by GC/MS. The results obtained from the laboratory do not give the concentration of total petroleum hydrocarbons but they give the detailed information about the specific compounds or group of compounds.

Provnummer		0016653	0016654	0016655
Beteckn 1		1	2	3
Beteckn 2				
TS 105°C	%	96.0	77.2	98.4
glödförlust	mg/kgTS	1.0	4.2	4.8
alifater >C ₅ -C ₈	mg/kgTS	<10	<10	<10
alifater >C ₈ -C ₁₀	mg/kgTS	<10	<10	<10
alifater >C ₁₀ -C ₁₂	mg/kgTS	<10	<10	<10
alifater >C ₁₂ -C ₁₆	mg/kgTS	<10	<10	<10
alifater >C ₅ -C ₁₆	mg/kgTS	<20	<20	<20
alifater >C ₁₆ -C ₃₅	mg/kgTS	22	26	<10
		-----	-----	-----
aromater >C ₈ -C ₁₀	mg/kgTS	<1.0	<1.0	<1.0
aromater >C ₁₀ -C ₃₅	mg/kgTS	<1.3	<1.3	<1.3
		-----	-----	-----
bensen	mg/kgTS	<0.01	<0.01	<0.01
toluen	mg/kgTS	<0.05	<0.05	<0.05
etylbenzen	mg/kgTS	<0.05	<0.05	<0.05
summa xylener	mg/kgTS	<0.05	<0.05	<0.05
summa TEX	mg/kgTS	<0.08	<0.08	<0.08

Figure 22 Results of the soil samples analyzed with GC/MS.

Table 19 Results of the samples with the techniques used in the project.

Sample ID	PID	PatroFlag (R.F 10)	Immunoassay
1	350	513	<10 ppm
2	440	330	<10 ppm
3	65	85	<10 ppm

The field methods give an aggregate idea about the compounds or group of compounds so exact comparison of the values of any specific compound is not possible. However, the general trend is that results obtained in the field measurements are matching with the laboratory methods. For example the field analysis with immunoassay give value less than 10 ppm for aromatics, and this result show same trend <1.3 ppm in all of the samples. Similarly PetroFlag give very high response for total hydrocarbons for sample 1 and sample 2, and results of GC/MS analysis also show an increase in aliphatic hydrocarbons. These results indicates that the concentration of total petroleum hydrocarbons is quite high in these samples.

6 Comparison of field results with Swedish guideline values

Swedish environmental protection agency suggests the guideline values for the specific compounds or group of compounds of hydrocarbons, but it does not give the guideline values for total petroleum hydrocarbons present in the soil. Table 20 gives the Swedish guideline values levels in polluted soils for the groups of compounds studied in this project. Comparison of the results from the soil analysis of the old industrial site is presented in the figures 23 and 24. These figures also give an overview of the results obtained by different techniques. The figures show guideline values of aliphatic and aromatic hydrocarbons shown in the Table 21 and Table 22.

Table 20 Swedish guideline values for levels in polluted soils (source www.environ.se)

Compounds	Mg/kg dry substance
Aliphatic hydrocarbons	
C6-C16	100
C17-C35	100
Aromatic hydrocarbons	
Sum of toluene, ethylbenzene and xylene	10
C9-C10	40
C11-C35	20
Organic substances	
Benzene	0.06
Toluene	10
Ethylbenzene	12
Xylene	15
Carcinogenic PAHs (sum of 7)	0.3
Other PAHs (sum of 9)	20

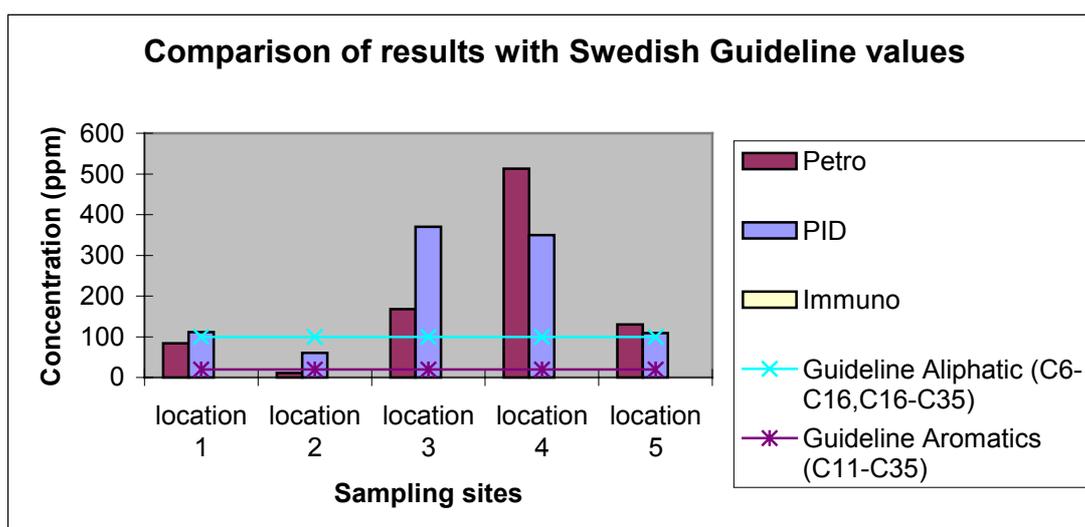


Figure 23 Comparison of the measured results with Swedish guideline values for the field samples 0-5 cm depth.

Note: Value of immunoassay results is < 10 ppm for all locations.

Table 21 Comparison of the measured results with Swedish guideline values for the field samples 0-5 cm depth.

Sample ID	PetroFlag	PID	Immunoassay	Guideline aliphatic	Guideline aromatic
Location 1	84	111	<10	100	20
Location 2	11	60,6	<10	100	20
Location 3	168	370	<10	100	20
Location 4	513	350	<10	100	20
Location 5	130	109	<10	100	20

The results of petroFlag analysis for this comparison are selected for the response factor 10 (for heavy oils). For the PetroFlag results the guideline for aliphatic hydrocarbons can be followed as the results given below for heavy oils. Location 3 and location 4 shows the concentration of aliphatic hydrocarbons higher than the Swedish guideline values for polluted soils. The immunoassay analysis of all soil samples shows less than 10 ppm concentration, which indicates that all samples contain aromatic hydrocarbons less than the Swedish guideline values.

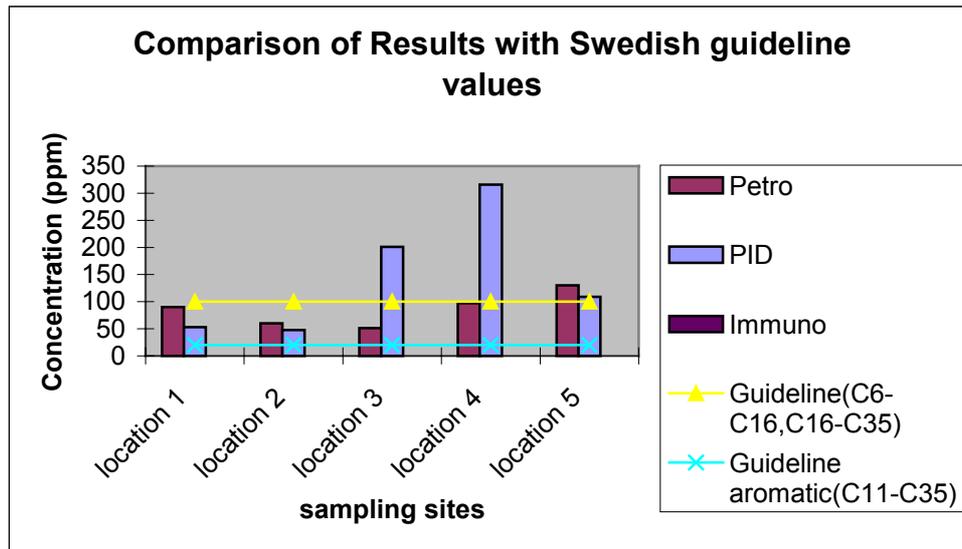


Figure 24 Comparison of the measured results with Swedish guideline values for the field samples 5-15 cm depth.

Note: Value of immunoassay results is < 10 ppm for all locations.

Table 22 Comparison of the measured results with Swedish guideline values for the field samples 5-15 cm depth.

Sample ID	PetroFlag	PID	Immunoassay	Guideline aliphatic	Guideline aromatic
Location 1	90	53	<10	100	20
Location 2	60	48	<10	100	20
Location 3	51	201	<10	100	20
Location 4	97	316	<10	100	20
Location 5	130	109	<10	100	20

Conclusions

Soil contaminated with complex petroleum hydrocarbon products is a growing problem in all industrialized countries, and poses a significant challenge for characterization and remediation programs that require rapid, accurate and comprehensive data in the field or laboratory.

This study demonstrates the usability of field analytical equipments for soils contaminated with petroleum hydrocarbons especially cutting fluids containing heavy oils and emulsions. The field analytical instruments used in this study give the concentration of the group of compounds such as more volatile hydrocarbons as gasoline, high molecular weight diesel range hydrocarbons, total petroleum hydrocarbons, aromatic hydrocarbons, and higher molecular weight aliphatic hydrocarbons. These field equipments allow the rapid assessment of soils and can be used to direct further sampling and analysis to save time and resources.

Photoionization detector used in this study effectively determines the concentration of volatiles present in the soil samples. However the results of PID can not be used to decide the level of concentration of VOC in the soil sample because some time PID can not detect low molecular weight hydrocarbons, such as methane and ethane. Rather it is a procedure to decide the number and size of samples to be collected for further quantitative VOC analysis. Combination of PID and any other field analytical method for example PetroFlag system gives a good idea of the level of concentration of any specific group of petroleum hydrocarbons present in the soil samples.

Because of its broad linear response range the PetroFLAG test kit can be used on a wide variety of hydrocarbon analytes. The PetroFLAG kit does not only test for specific compounds such as aromatics, rather all hydrocarbons. However the results of A-horizon of soil profile of laboratory experiments in this study indicate that the accuracy of TPH measurement using the petroFlag system may be significantly impacted by naturally occurring oil and grease.

Immunoassay has been found to be an efficient and prompt technique to measure a large portion of the aromatic hydrocarbons but only a few of the aliphatic hydrocarbons as the absorbance results are converted to petroleum fuel product equivalent for only aromatic hydrocarbons. The spectrophotometer is not designed to account for more than one type of PHCs that may present in the extract. However this technique is ideal only, if prior knowledge of contaminants and expected level of concentration is available. By increasing number of detection standards we can get very precise results but this will ultimately increase the cost of investigations.

The study of soil-oil-water mixture in saturated and unsaturated conditions suggests that high aqueous mobility of the cutting fluids and the surface activity of the soil contribute to oil retention in the vadose zone. From these experiments we could only prove that the mobility of non-polar constituents of the cutting fluid to the lower depth of column in saturated condition. Soluble oil based cutting fluids contain polar constituents as well that can result in the higher mobility of the fluid with the rainfall and groundwater fluctuations. A higher flow rate may allow greater momentum to be transferred from the leaching water to the oil in the pore fluid, thereby providing more kinetic energy to reduce the interfacial between oil and water, and hence poses a threat to the surrounding environment in the form of surface and groundwater contamination.

The environmental soil investigations with the three methods; PID, petroFlag, and immunoassy of old industrial site in Sweden suggest the higher concentration levels of petroleum hydrocarbons especially heavy oils at sampling locations 4 and 3 respectively which may be a threat to the groundwater and surface water resources in that the area.

Future Recommendations

This project is not a starting point in the research of contaminated soils, rather this piece of work is inspired by the existing research about the in-situ analytical techniques. This study can serve as a tool in the economical environmental soil investigations in the field to get real time results. Given below are some suggestions that could be considered for the study of contaminated soils by the similar techniques.

1. A major priority in the future research should be focused to evaluate the response of all the analytical techniques for different textural classes of soil. This will give an idea about the extraction efficiency of the analytical methods
2. The analysis of soil samples with clay content more than 30% are found to be difficult to extract with PetroFlag extraction solvent. On the basis of the experiment performed in this project, it is recommended to use 1g of soil sample instead of 10g, and then multiplying the obtained concentration with 10.
3. Immunoassay is evolving as a promising technique to the analysis of aromatic hydrocarbons in the soil samples. It would be of value to establish correlation between reading of the differential photometer and the actual absorbance.
4. It would be useful to have a better idea of the movement of more polar constituents of the cutting fluid with more sophisticated analytical techniques.
5. More precise and extensive investigation is necessary for a detailed account of the extent of contamination at the old industrial area investigated in Sweden. The investigation should not be focused only for petroleum hydrocarbons but also on persistent organic pollutants and heavy metals, as these substances can stay for years in soil and sediments.

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