

# **COMPARING TWO SAMPLE PREPARATIONS IN DIESEL ANALYTICS AND THE EFFECTS OF WEATHERING ON DIESEL**

Mira Ketola

Bachelor's thesis  
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Tampere University of Applied Sciences

**TAMPEREEN AMMATTIKORKEAKOULU**  
Tampere University of Applied Sciences

## ABSTRACT

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MIRA KETOLA: Comparing Two Sample Preparations in Diesel Analytics and the Effects of Weathering on Diesel.

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Petroleum hydrocarbons are the most common contaminant in Finland. That is why petroleum hydrocarbon analytics is developing continuously. The purpose of this study was to develop diesel fractions analytics by comparing Soxhlet extraction and ultrasonic extraction and determine the weathering effects on diesel. The first aim of this study was to find out which sample preparation has better repeatability and thus is more reliable. The second aim was to find out the chromatograms difference between Neste diesel and weathered free phase diesel.

In both cases the samples were measured with gas chromatography using a flame ionization detector. Sample preparation with ultrasonic extraction was made earlier in Diploma Thesis, when the treatments of soil were also made. Soil can be cleaned with different ways and in this thesis the soil was cleaned with hydrogen peroxide, a surfactant and a stabilizer.

In the qualitative part it can be seen that the Neste diesel and the weathered free phase diesel differ, so that the Neste diesel had peaks in higher retention time and the weathered diesel had peaks in lower retention time. In quantitative part the samples' results, which were compared to Neste diesel's standard curve, gave only half of the response what the results which were compared to the weathered free phase diesel's standard curve.

It can be concluded that the diesel is changing in soil by weathering and its long hydrocarbon chains are fractionated to smaller ones. The reference samples in Soxhlet extraction were quite similar, while in the ultrasonic extraction the replicates differed much more from each other, which leads to the conclusion that the Soxhlet-extraction has better repeatability than the ultrasonic extraction.

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Keywords: Petroleum hydrocarbon analysis, weathered diesel, GC/FID, Soxhlet extraction, soil remediation

## TIIVISTELMÄ

Tampereen Ammattikorkeakoulu  
Laboratorioala

MIRA KETOLA: Kahden esikäsittely menetelmän vertaaminen dieselanalytiikassa ja säästymisen vaikutukset dieselissä

Opinnäytetyö 45 sivua, liitteet 5 sivua  
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Suomessa hiilivedyt ovat yleisin maaperän pilaaja. Tämän vuoksi hiilivetyanalytiikkaa kehitetään jatkuvasti. Työn tarkoituksena oli kehittää diesel fraktioiden analytiikkaa vertaamalla Soxhlet-uuttoa ja uuttamista ultraäänen avulla ja selvittää säästymisen vaikutukset dieseliin. Tutkimuksen ensimmäinen tavoite oli selvittää, kummalla näytteen esikäsittelymenetelmistä oli parempi toistettavuus ja kumpi oli tämän vuoksi luotettavampi. Toinen tavoite oli saada selville Nesteen dieselin ja maassa vapaana faasina olleen dieselin kromatogrammien erot.

Kummassakin tapauksessa näytteet mitattiin kaasukromatografilla, jossa detektorina oli liekki-ionisaatiodetektori. Ultraäänihautteen esikäsittely oli tehty jo aikaisemmin diplomityönä. Siinä tutkimuksessa tehtiin myös eri puhdistukset maalle, joita tässä työssä tutkittiin. Maata voidaan puhdistaa eri tavoin ja tässä työssä maata oli käsitelty vetyperoksidilla, tensidillä ja stabilisaattorilla.

Kvalitatiivisesta osasta nähdään, että Nesteen diesel ja säästynyt, vapaana faasina ollut diesel eroavat toisistaan, kun Nesteen dieselin piikit ovat suuremmalla retentioajalla ja säästyneellä, vapaana faasina maassa olleella dieselillä ne ovat taas pienemmällä. Kvantitatiivisessa osassa Nesteen dieselin standardisuoraan verratut näytteet antoivat melkein puolet pienemmän vasteen kuin säästyneen dieselin standardisuoraan verratut näytteet.

Tuloksista voidaan päätellä, että diesel muuttuu maassa säästymisen seurauksena, jolloin öljyhiilivetyketjut muuttuvat pienemmiksi. Rinnakkaisnäytteet olivat melko samanlaiset Soxhlet-uuttoa käytettäessä, kun taas ultraääniuutossa ne erosivat toisistaan melko paljon, josta voidaan päätellä, että Soxhlet-uutossa toistettavuus on parempi.

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Avainsanat: Öljyhiilivetyanalytiikka, säästynyt diesel, GC/FID, Soxhlet-uutto, maan ennallistaminen

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## 1 INTRODUCTION

Petroleum hydrocarbons are widely studied, because of the harmful effect on soil. Contamination by petroleum hydrocarbons and the soil remediation are studied widely in Finland and the research is funded by private and public sector and also by the Soili program, which is a soil and groundwater restoration program for former service station and fuel distribution sites.

The work was made in the Department of Chemistry and Bioengineering in Tampere University of Technology. There has already been made a Diploma Thesis on this subject, studying treatments for soil, and also studying metals, soil pH, granularity and water and organic matter in soil.

The aim of this Bachelor thesis was to find out which of the sample preparations is the best. Results were compared to the previous study. There ultrasonic extraction was used in sample preparation while in this study the sample preparation was done by the Soxhlet extraction. There was also a question about the effects of weathering. The studied soil is from an old car depot in Tampere, where diesel has been contaminating the soil during the last 40 years as a result of car refueling and underground diesel tank leaks.

The thesis included a literature and an experimental part. In the literature part petroleum hydrocarbons, soil contamination and remediation and also analytical methods of hydrocarbons were reviewed. In the experimental part sample preparation with Soxhlet extraction and running the samples with GC/FID were studied.

## 2 LITERATURE REVIEW

### 2.1 Petroleum history

The word petroleum means rock oil because it occurs widely in the sedimentary rocks in the form of gases, liquids, semisolids and solids (Speight 2002, 10). It is believed that oil was formed 200-50 million years ago in the sea from remains of animals and plants. In nutritious waters there lived a lot of microscopic sea animals and plants at that time. After they had died they sank into seas' and lakes' oxygen-free basins. It accumulated mud and sand on top of them, which rivers had brought and so the remnants were buried still deeper. That organic matter and mud accumulated during the time over hundred meters layers, where the organic material remained from immediate destruction, namely chemical oxidation and organic destroyers. Complex chemical and physical processes changed the animal and plant remnants into crude oil and natural gas. It takes a long time, high temperature and pressure, oxygen-free conditions and formation for petroleum to be formed. Suitable bed of sedimentary rock were formed, while the new mud and organic matter in sediments pushed lower layers and shook them over millions of year's sedimentary rock. (Aatelo 1995, 13-14.)

When the sediments still grew thicker over time, they began to press the lower layers and the layers' water and oil droplets started to move under pressure. Fluids seek to gather in porous sand and limestone strata, because there was less pressure. (Aatelo 1995, 13-14.) Crude oil wells contain liquid oil as well as gas (Simanzhenkov & Idem 2003, 6).

### 2.2 Petroleum hydrocarbons and diesel

Petroleum is a naturally occurring mixture of hydrocarbons. It may also contain oxygen, nitrogen, sulfur, metals, principally nickel and vanadium, and other elements. (Speight 2002, 7; Clayton 2005, 248.) Crude oil is an oily, flammable liquid and it is occasionally found in springs or pools but is usually obtained from

beneath the soil by drilling wells (Gad 2005a, 377). Fluid hydrocarbons are called petroleum, which can be either liquid, e.g. crude oil, or gaseous (Selley 2004, 729-730). Overall, petroleum consists of hydrocarbons, asphaltenes, resins, paraffins, sulfur and ash. Hydrocarbons are divided in three main groups: paraffinic, naphthenic and aromatic hydrocarbons. (Simanzhenkov & Idem 2003, 5.) In some sources nitrogen, sulfur, oxygen (NSO) compounds are also counted in petroleum's main constituents (Farrell-Jones 2003, 133). The chemistry of the oil is determined by the nature, the quality and the thermal maturity of the source rock and the depositional environment of the kerogen which the oil formed (Clayton 2005, 248).

The most important fractions of petroleum are prepared by cracking or distillation and they are various hydrocarbon gases (butane, ethane and propane), naphtha of several qualities, gasoline, kerosene, fuel and lubricating oils, gas oil, paraffin wax and asphalt. Hydrocarbon gases, ethylene, butylene and propylene, are important industrial semi-finished products which are source of alcohols, ethylene glycols and monomers for a wide range of plastics, elastomers and pharmaceuticals. Benzene, phenol, toluene and xylene are also formed from petroleum. There are hundreds of other products, for example biosynthetically produced proteins, which are petroleum derived. (Gad 2005a, 377.)

Paraffinic hydrocarbons have the general formula  $C_nH_{(2n+2)}$  and they can be straight chains also known as normal (n) or branched chains or isomers of carbon atoms. The lighter, normal paraffins are found in gases and paraffin waxes and the isomer paraffins are usually found in the heavier fractions of crude oil. Paraffinic hydrocarbons are saturated compounds. The amount of paraffin varies from 2 to 50 percent in different crude oils. The carbon atoms in the paraffin molecule are connected by a covalent sigma ( $\sigma$ ) bond. (Simanzhenkov & Idem 2003, 5-6.)

Naphthenic hydrocarbons have the formula  $C_nH_{2n}$  and they are saturated compounds. Both paraffins and naphthenic hydrocarbons are relatively stable compounds. Naphthenic hydrocarbons make the biggest fraction of crude oil so their composition in oil can vary from 25 to 75 percent. Usually when the boiling

point of the fraction increases, the amount of naphthenes in crude oil fractions also increases, but heavy oils go vice versa. This is based on increasing the amount of aromatic compounds in heavy oils. (Simanzhenkov & Idem 2003, 7-8.)

Aromatic hydrocarbons are unsaturated cyclic compounds that react easily because they have carbon atoms that are lacking in hydrogen. All aromatics have at least one benzene ring, but they may also have two or more of the ring structures fused together. The majority of aromatics compounds have three or more benzene rings fused together, being so called polynuclear. The amount of aromatics varies from 15 to 50 percent in different crude oils. The highest amounts of aromatic hydrocarbons are typically found in naphthenic oils. (Simanzhenkov & Idem 2003, 9.) The examples of paraffins, naphthenic and aromatic hydrocarbons are present in Figure 1.

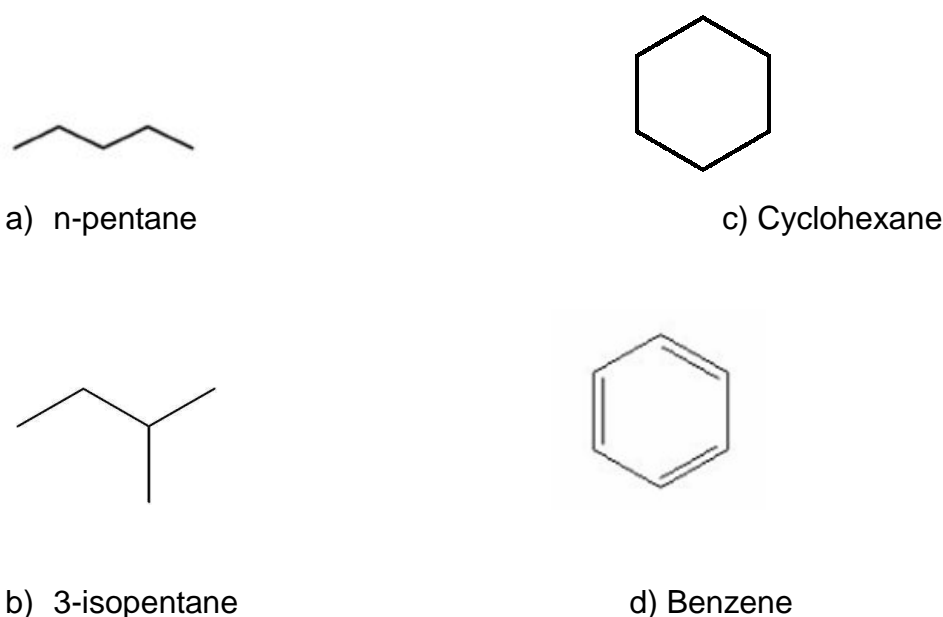


FIGURE 1. Constitutional formulas of some hydrocarbons: a) n-pentane is n-paraffin, b) 3-isopentane is iso-paraffin, c) cyclohexane is naphthenic and d) benzene is aromatic hydrocarbon (Farrell-Jones 2003, 134-135)

Asphaltenes and resins are dark substances that are soluble in aromatic solvents but not in paraffin solvents. Asphaltenes structures' have various types of heteroatoms present in crude oil. Asphaltenes are the most complex structures of all the petroleum compounds. (Simanzhenkov & Idem 2003, 9.)



They are a hard, friable and infusible powder. Resin is semisolid to solid ductile and adhesive material. (Gad 2005a, 377.)

Diesel fuel is a petroleum hydrocarbon mixture of branched-chain alkanes, cycloalkanes, aromatic compounds and sulfurized esters and it's produced by crude oil distillation. Its boiling points range from 163 to 357 °C. Diesel fuel number 1 is a straight-run middle distillate and it contains branched-chain alkanes, which are also known as paraffins, cycloalkanes or naphthenes, aromatics and mixed aromatic cycloalkanes. Diesel fuel number 1 contains less than 0.02 percent benzene and smaller amount of PAHs. It's primarily used in city busses. Diesel fuel number 2 or diesel fuel is a composition of straight-run and catalytically cracked streams; inclusive straight-run kerosene, straight-run middle distillate, hydrosulfurized middle distillate and light catalytically and thermally cracked distillates. Diesel fuel number 2 is similar to fuel oil number 2 formulation and it includes phenanthrene, fluoranthene, pyrene, benz(a)anthracene, chrysene and benzo(a)pyrene. It's used in railcars, trucks and boats. Diesel fuel number 4 also known as marine diesel fuel is the most viscous of all the diesel fuels and contains more of ash and sulfur. It may contain more than 10 percent of PAHs (Polycyclic Aromatic Hydrocarbons) content. Marine diesel fuel is used in marine vessels. (Gad 2005b, 19.)

In soil and in groundwater the diesel contamination is harmful because it evaporates really slowly and it is slowly degradable. In anaerobic conditions the diesel degradation is remarkably slow. Diesel is poorly soluble in water and it doesn't hydrolyze in water. It can permeate the soil and migrate to the groundwater's surface. (NEOT 2005.) Diesel is not accumulative because its  $\log K_{ow}$  is smaller than 3 and the  $\log K_{ow}$  means the octanol-water partition coefficient (NEOT 2005, EUR-Lex 2005). The higher the partition coefficient value is, the more liposoluble the compound is and the more closely it binds soil particles or plant roots (Forsbacka 1996, according to Sillanpää 2007, 8).

### 2.3 Soil, contamination and remediation

Each oil spill is unique, because it depends on the type of material spilled, the habitat in which the oil is spilled, its location and the weather conditions during and after the spill. For example the spreading and penetration of oil varies considerably depending on given location because of different soil types, which also means different grain size. (Fingas 2001, 175-176.)

In Finland there is geotechnical (GEO) classification for different soil types, which is based on grain sizes. There is also an ISO classification, which is used by European Union member countries. (Sassali 2008, 18.) The differences of GEO and ISO are shown in Table 1.

Table 1. Differences of ISO and GEO classification of soils (Sassali 2008, 18, edited)

Soil Types	Subtypes	GEO (acronym)	ISO (acronym)	GEO (grain size mm)	ISO (grain size mm)
Fine Soil	Clay	Sa	Cl	≤ 0,002	< 0,002
	Silt	Si	Si	> 0,002-0,06	> 0,002-0,063
	Fine	Si	FSi	> 0,002-0,006	> 0,002-0,0063
	Middle	Si	MSi	> 0,006-0,02	> 0,0063-0,02
	Coarse	Si	CSi	> 0,02-0,06	> 0,02-0,063
Coarse Soil	Sand	Hk	Sa	> 0,06-2,0	> 0,063-2,0
	Fine	Hk	FSa	> 0,06-0,2	> 0,063-0,2
	Middle	Hk	MSa	> 0,2-0,6	> 0,2-0,63
	Coarse	Hk	CSa	> 0,6-2,0	> 0,63-2,0
	Gravel	Sr	Gr	> 2,0-60,0	> 2,0-63
Very Coarse Soil	Fine	Sr	FGr	> 2,0-6,0	> 2,0-6,3
	Middle	Sr	MGr	> 6,0-20,0	> 6,3-20,0
	Coarse	Sr	CGr	> 20,0-60,0	> 20,0-63,0
	Rocks	Ki	Co	> 60-600	> 63-200
	Blocks	Lo	Bo	> 600	> 200-630
	Large Blocks	Lo	LBo		> 630

When petroleum products get to the environment, they undergo changes due to weathering effects such as evaporating, leaching, chemical oxidation and microbial degradation (Thompson & Nathanail 2003, 139). One of the most important elimination ways of petroleum products in soil is biodegradation, which means the change in form of compounds carried out by living creatures such as microorganisms. Natural attenuation is acting without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or ground water under favorable conditions. (USEPA 1999.)

Lack of individual, clearly distinguishable peaks is typical for old contamination. That's why the compounds are more difficult to identify. (Atlas 1981, according to Sillanpää, 2007, 9.) Oil contaminants or their derivatives might also form complexes with the humic substances of the soil or attach to reactive sites on the surface organic colloids and this has created new molecules that are not easily degraded. The longer the contaminant remains in soil, the more resistant it becomes to desorption and biodegradation. (Alexander 1994, according to Riser-Roberts 1998, 194.)

### 2.3.1 Statistics of contaminated land

There are about 2000 oil accidents in Finland every year. They usually occur in land and most of them are small leaks. About 160 leaks are more serious and should be reported to Finland's environment center's duty officer. (Finnish Environment Institute 2010.)

Lower reference value is set to the concentration level, which describes the most commonly an acceptable risk in ordinary land use. The upper reference value describes the maximum acceptable risk in less sensitive places like in industrial or warehouse areas. Both these reference values are based on either ecological or health risks. The threshold value of the harmful substance concentrations have been set to a level low enough, so that the environmental and health risks of the soil can be held insignificant, no matter where it is located or what it is used for. Harmful substance concentrations that are below

the threshold value should not cause a pollution risk for soil, groundwater or the environment. (Reinikainen 2007, 9.) In Table 2 reference values of different oil fractions are shown.

TABLE 2. Standard values: n-paraffin series in gas chromatograph analyses. (Finlex, 2007, edited)

Substance (symbol)	Threshold value mg/kg	Lower standard value mg/kg	Higher standard value mg/kg
Gasoline fractions (C <sub>5</sub> -C <sub>10</sub> )		100	500
Middle runnings (>C <sub>10</sub> -C <sub>21</sub> )		300	1000
Heavy oil fractions(>C <sub>21</sub> -C <sub>40</sub> )		600	2000
Oil fractions (>C <sub>10</sub> -C <sub>40</sub> )	300		

Soil is considered as contaminated if, due to human actions, it is found to contain substances that can pose damage to human health or nature, reduce the environment's attractiveness or service value or otherwise hurt public or private interests. The seriousness of the contamination of soil is affected by the quantity and quality of substances, in addition to the use of the contaminated area, its immediate surroundings and natural conditions. There are over 21 000 areas in Finland where soil may be contaminated, is known contaminated or has been remediated. All these are collected up in soils condition data system. It is maintained by the state's environment administration. (Finnish Environment Institute 2009.)

In the data system, targets are classified in four categories: functional, need of analysis, need of analyzing or cleaning or not needing cleaning targets. These partitions are showed in Figure 2. In the area of functional target the environmentally harmful substances are handled and stored. When the function has finished or it changes, the status of the soil should be clarified. (Finnish Environment Institute 2009.)

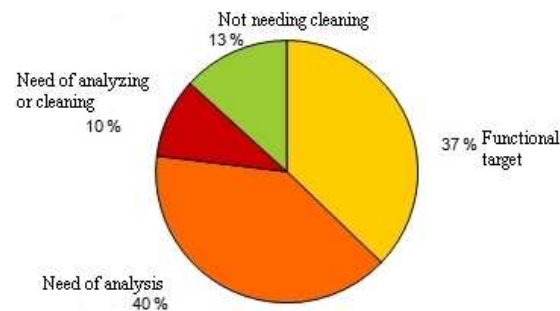


FIGURE 2. Data system's targets (Finnish Environment Institute 2009, edited)

The site needs to be analyzed, when it has been used for industry, dealing with environmentally harmful substances. Environmentally harmful substances could have ended up in the soil, though this is not always the case. The area is now no longer in industrial use. An investigation of the properties of the soil could be needed if the purpose of the area is changed, factors to do with contaminants are suspected, and the land is used for building on or is sold. (Finnish Environment Institute 2009.)

The quality of the soil is known to be lowered by harmful substances or wastes in the area that has to be analyzed or cleaned. The contamination level of the soil has to be analyzed, and the soil needs to be cleaned if needed. Before the cleaning is evaluated, there can be some restrictions on the land usage or the use of dug up soil masses on the land. If an area does not require cleaning, it means it has been cleaned to the authorities' standards or it is found not to be contaminated by the analysis. The area can still have restrictions on its use, if there are still harmful substances left in the soil. (Finnish Environment Institute 2009.)

Soil can be contaminated locally in accidental or by slow leakage, as a consequence of normal action's environmental emission. In Figure 3 different industries that cause pollution are shown, found the in data system. The distribution of different substances that are contaminating soil in is shown in Figure 4. Most common contaminations are petroleum hydrocarbons and heavy metals or both together. (Finnish Environment Institute 2009.)

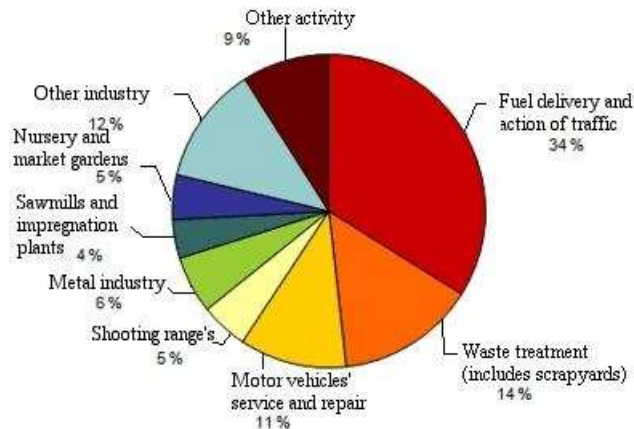


FIGURE 3. Different origins of contamination (Finnish Environment Institute 2009, edited)

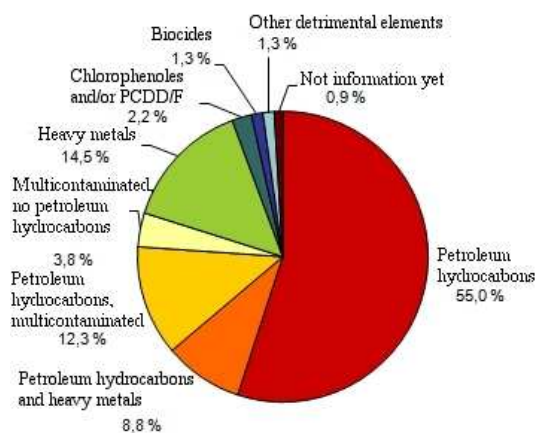


FIGURE 4. Substances that contaminate soil (Finnish Environment Institute 2009, edited)

In Figure 5 and 6 expenditures for cleaning contaminated areas in European countries are shown. There are the annual expenditures per capita (Figure 5) and the comparison of private and public expenditures are divided in some European countries (Figure 6). Values on top indicate total annual management expenditure in million euros. (EEA 2007a,b)

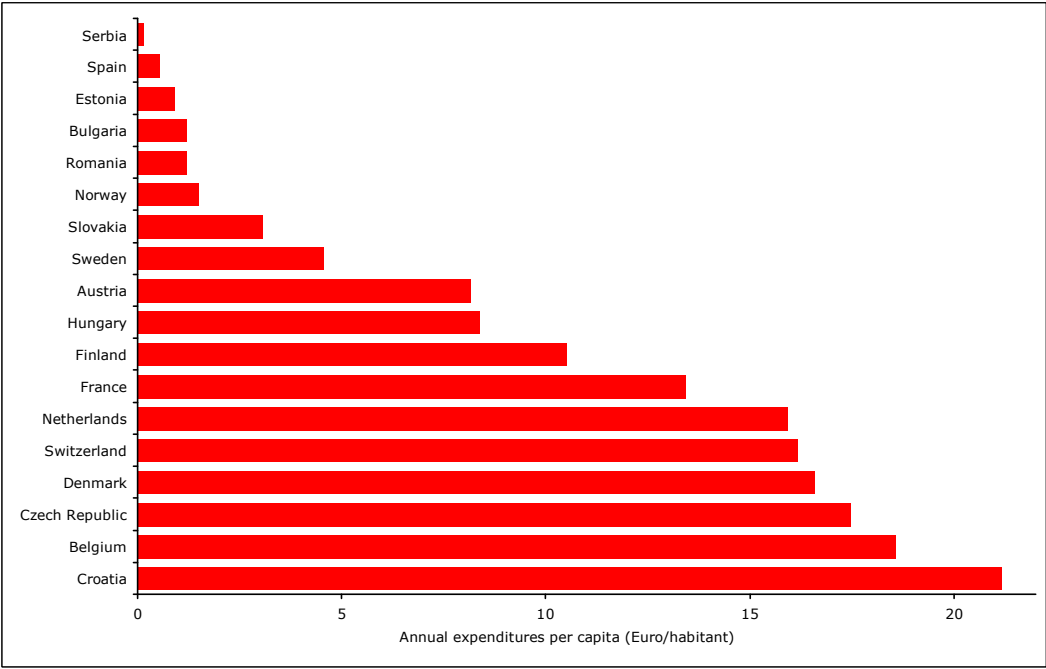


FIGURE 5. Annual national expenditures for management of contaminated sites (EEA 2007a)

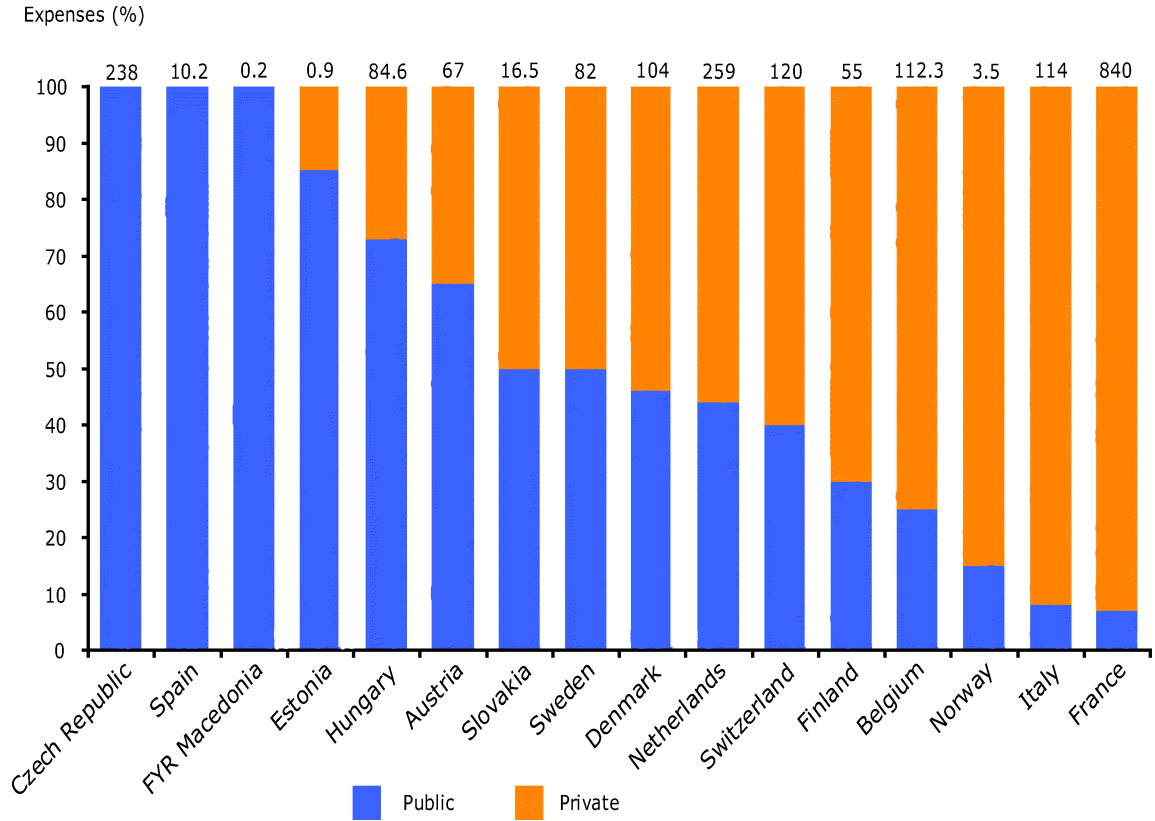


FIGURE 6. Estimated allocation of public and private expenditures for management of contaminated sites (EEA 2007b)

### 2.3.2 Soili program

Soili is a soil and groundwater restoration program for old service station and fuel distribution sites. Soili is based on a 1996 agreement between the Ministry for the Environment, the Finnish Oil and Gas Federation and the Association of Finnish local and Regional Authorities. (Finnish Oil and Gas Federation 2010.)

The Oil Industry Service Center Ltd is responsible for the implementation of Soili. The deadline for participation in the funded part of the program was 2005. Almost 700 applications were received by that date. By the end of 2009, all sites had been investigated and an estimated 100 sites are planned to be restored. The program is heading for completion by the end of 2014, according to the decision by the Finnish Oil and Gas Federation board. (Ministry of the Environment 2010, 10.)

### 2.3.2 Remediation of contaminated soil

Oil spills in the subsurface are difficult to clean up. These spills can be difficult to locate and without knowledge of the geology of the area it can be difficult to predict the movement of the oil. In these cases the oil must be contained and its movement stopped or slowed. There are a lot of methods that can be used in the oil contamination. The most appropriate method for oil spill depends on the type of oil spilled and the soil at the site. In table 3 the cleaning methods for subsurface spills are shown. (Fingas 2001, 186-187.)



TABLE 3. Clean up methods for subsurface spills

(\*) -acceptable or recommended,

(+) -can be use under certain circumstances,

(-) -only marginally acceptable

Product type in soil type	Hydraulic Measures	Interceptor Trench	Soil Venting	Soil Excavation	Recovery Wells
Gasoline in sand or mixed till	+	*	+	*	*
Gasoline in loam or clay	*	*	-	*	+
Diesel in sand or mixed till	+	*	-	*	*
Diesel in loam or clay	+	*	-	*	+
Light crude oil in sand or mixed till	+	*	*	*	*
Light crude oil in loam or clay	*	*	-	*	*
Heavier oils in sand or mixed till	*	*	-	*	-
Heavier oils in loam or clay	*	*	-	*	-

The hydraulic measures are flooding, flushing, sumps and French drains. These methods are most effective in permeable soils and with no adhesive oils. Depending on the land use, it may be acceptable that all these methods leave residual material in soil. In flooding water is used either directly to the surface or to an interceptor trench in order to float out the oil. Flushing means that the oil is flushed with water into a sump, recovery well or interceptor trench. A sump or deep hole should be dug in permeable soil, which is above an impermeable layer of soil. This method can be used in soil, which is contaminated with light fuel. A French drain is a horizontal dike, which is placed under the

contamination. There is fuel and also often water pumped out. Though this is effective in permeable soils, French drains are expensive and difficult to install. (Fingas 2001, 187.)

Interceptor trenches are dug vertical from the spill or there where the spill is flowing. They are dug just below the depth of the groundwater so that oil flows on top of the water into the trench. Both the water and oil are pumped out of the trench and to ensure that the flow will continue. These trenches are good if groundwater is very close to the surface and soil above the water is permeable. (Fingas 2001, 187.) An interceptor trench is shown in Figure 7.

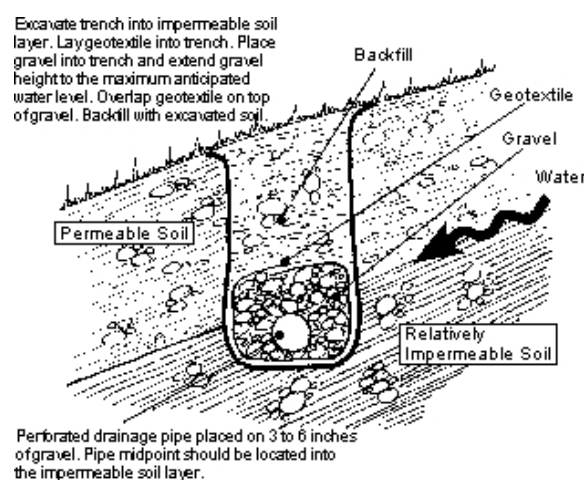


FIGURE 7. Interceptor trench (Department of ecology, State of Washington)

Soil can be vented, when vapours are released from permeable soil above a subsurface spill. This can be used, if contaminant is gasoline and also in case of very light crude oils in warm climates. Heavier oils don't evaporate enough so this method is not good for them. Venting can be passive or active. In passive venting vapors are released through their own natural vapor pressure. In active venting air is blown through the soil and/or drawn out with a vacuum pump. The vapours are removed later from air to prevent air pollution. Soil venting is also enhancing biodegradation. (Fingas 2001, 188.)

Especially in urban areas, where human safety is an issue, a commonly used cleaning up technique is excavation. Particularly in urban areas the vapors from gasoline are dangerous. Vapors can travel through the soil and explode if ignited and those vapours can also penetrate into houses and buildings, forcing evacuation of the area. To prevent these situations, oil contaminated soils are

often quickly dug and treated or packaged for disposal in a landfill. Realization of excavation is depending on the size of the spill and prevailing conditions at the site. (Fingas 2001, 188.)

A recovery well is drilled or dug to the depth of the water table so that the oil is on top of the groundwater and both the water and oil are flowing to the well like in the interceptor trench. Sometimes the water table is lowered by pumping so that the recovery of the oil is sped up and the area of the collection zone is increased. From the well the oil is recovered with a pump or a specially designed skimmer. (Fingas 2001, 188-189.)

There are lots of different chemical treatments. Organic substances can be degraded by indirect electro-oxidation, where oxidation agent is Co(III). This oxidation agent is used because of the high redox potential of the Co(III)/Co(II) redox couple, where redox potential is 1,808 V. Organic carbon is ultimately transformed to CO<sub>2</sub> and to a small amount of CO. There is also chemical extraction like heap leaching and liquid or solid contactors, which can also be used in the treatment of excavated, contaminated soil. Chemical extraction has been employed on a pilot scale for remediation soil contaminated with PAHs by applying the Resource Conservation Company solvent extraction process. (Riser-Roberts 1998, 11.)

Hydrogen peroxide oxidation, which is also called Fenton treatment, is one of the most successfully used chemical treatments for contaminated soil. The Fenton treatment is able to remediate chlorophenols, polycyclic aromatic hydrocarbons, diesel and transformer oil contaminated soil. Oxidation with hydrogen peroxide can happen directly and/or through the generation of free radicals. The last one relies on the degradation of hydrogen peroxide catalyzed by most ions of transition metals (Fe, Cu, Zn, etc.) and by natural minerals of those metals (hematite, goethite, and etcetera) present in soil. The basic reaction is:  $\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{OH}^- + \text{OH}^* + \text{Fe}^{3+}$ , where OH\* means free radical. Chemical oxidation can be applied both *in situ* and *ex situ*. (Goi, Trapido, Kulik 2009, 185.)

The Fenton treatment has many advantages. It is quite fast, because it takes only days or weeks. The contaminants are treated *in situ*, converted to innocuous and natural occurring compounds like  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{O}_2$ , halide ions. Positioning the reagent up on the contaminant serves to eliminate the possibility of contaminant vertical movement except due to the act of vertical injection itself. This is often a concern in other remediation treatments. As a favorable side effect aerobic biodegradation of contaminants can benefit from the presence of oxygen released during hydrogen peroxide degradation. It can be electrochemically generated *in situ*, which may further increase the economic feasibility and effectiveness of this process for treated contaminated sites. Natural iron oxide minerals, like hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ), goethite ( $\alpha\text{-FeOOH}$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ) and ferrihydrite, present in soil can catalyze hydrogen peroxide oxidation of organic compounds. This treatment of contaminant soil wouldn't hence require addition of soluble iron catalyst. (Goi et. al 2009, 186.)

Disadvantages are the need for controlling pH in some cases and difficulties to supervise *in situ* heat and gas production. The efficacy of this treatment may be limited by low soil permeability, incomplete site delineation, subsurface heterogeneities, and highly alkaline soil where carbonate ions remove free radicals. (Goi et. al 2009, 186.)

Stabilization refers to the chemical changes to the hazardous constituents in a contaminated soil, including converting the constituents into a less soluble, mobile, or toxic form. (Wilk) In this study the stabilizer was  $\text{KH}_2\text{PO}_4$ .

Surfactants, also known as surface active agents, are a class of natural and synthetic chemicals that promote the wetting, solubilization, and emulsification of various types of organic chemicals like petroleum hydrocarbons, which can be removed about 93 percent by adding surfactant. This is more effective than just water washing. (Riser-Roberts 1998, 82.)

The limitations, side effects and high expense of traditional cleaning up technology has stimulated interest in unconventional alternatives like the use of hydrocarbon-degrading microorganisms for cleaning up of contaminated soils and groundwaters. (Riser-Roberts 1998, 29-30.) One of these is

hydrocarbonoclastic bacteria (HCB) strain, which was found recently, because of bacteria genome analysis. These bacteria degrade hydrocarbons through metabolism and biosurfactant production. (Terra Nova)

#### 2.4 Analytical methods of hydrocarbons

The most common and simplest form of analysis is to measure how much petroleum is in soil. This kind of analysis is due to a value known as total petroleum hydrocarbon (TPH). The TPH analysis can be obtained in many ways, including extracting the soil or evaporating a solvent such as hexane and measuring the weight of the residue that is presumed to be oil. (Fingas 2001, 62.)

There are lots of methods for analyzing crude oil and its derivatives, chromatography being probably the oldest and most important. In these analyses gas (GC), high performance liquid (HPLC) and thin layer (TLC) chromatography can be used. In gas chromatography the mobile phase is gas, and in HPLC and TLC it is liquid. GC and HPLC can be used for quantitative and qualitative analyses. TLC can only be used for qualitative analysis. In GC there are also different detectors, which can be used in determination, such as the flame ionization detector (FID) or mass spectrometer (MS). (Simanzhenkov & Idem 2003, 73-74, 83, 97-98, 107.)

Hydrocarbons can also be analyzed with spectroscopic methods. These methods include infrared spectroscopy, Raman spectroscopy, colorimetry and photometry, fluorescence and phosphorescence spectroscopy, atomic absorption and emission spectroscopy and x-ray spectroscopy. (Simanzhenkov & Idem 2003, 112, 127, 131, 136, 139, 144.)

The biggest problem in contaminated soil analysis is the wide range of matrices like clay, peat, limestone, sandstone, steel slag, waste materials and demolition debris. It can be difficult to ensure that unacceptable biases don't disturb the analysis by arising for the small percentage of samples. It is also difficult to make the sample homogenous when grinding and sub-sampling coarse soils or other inhomogeneous materials. (Thompson & Nathanail 2003, 14, 44.)

#### 2.4.1 Extraction

There are different extraction methods, such as Soxhlet, ultrasonic extraction, accelerated solvent extraction, microwave, thermal extraction and static headspace and purge and trap also known as dynamic headspace. (Farrell-Jones 2003, 142-145.)

Soxhlet (Figure 8) is solid-liquid extraction. It is for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges and wastes. It is applicable to the isolation and concentration of water-insoluble and slightly water soluble organics in preparation for a variety of chromatographic procedures.(USEPA, 1996, 1.) In this extraction the fresh solvent is continuously refluxed through the finely divided sample contained in a porous thimble and a siphon system removes the extract back into the refluxing solvent (Reeve 2002, 144). It is recommended to dry the soil because water affects the polarity of the solvent and can also prevent contact between the solvent and the matrix. Crushing will also assist the extraction process. (Farrell-Jones 2003, 142-143.) The advantage of this procedure is continuous extraction by fresh solvent, while the disadvantage is that the compound extracted is kept at the boiling point of the solvent for a prolonged period. (Dean J. et. al 2002, 106.) One of the major drawbacks is that it sometimes extracts unwanted substances also (Farrell-Jones 2003, 142-143). The process is repeated usually 12 to 16 hours depending on substances. (Farrell-Jones 2003, 142-143; Reeve 2002, 144.) The solvent is chosen so that the solid is dissolving in the solvent and the impurities are not. (Sella 2007).

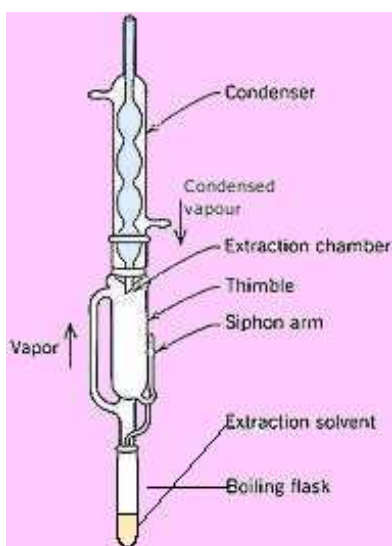


FIGURE 8. Soxhlet extractor (Technology Loading, 2010, edited)

In this work Florisil® is used for cleanup of the samples. It's used for clean pesticide residues and other chlorinated hydrocarbons and also for the separation of nitrogen compounds from hydrocarbons and aromatic compounds from aliphatic-aromatic mixtures and other similar applications for use with fats, oils, and waxes. Florisil® is also considered to be good for separations of steroids, esters, ketones, glycerides, alkaloids, and some carbohydrates. (USEPA 2007, 1.)

#### 2.4.2 Gas chromatography

Compound is applicable for being analyzed for gas chromatography (GC), if it can evaporate without degrading. (Jaarinen & Niiranen 2005, 207-208.) In GC the mobile phase is gas and stationary phase is generally a cross-linked silicone polymer, coated as a thin film on the inner wall of the fused silica capillary ( $\text{SiO}_2$ ). (Dean, Jones, Holmes, Reed, Weyers, Jones 2002, 211.) Because in GC the separation is based on different steam pressures and the solubility in the stationary phase of compounds, it is called partition chromatography. Every compound has it's own retention time, which depends on how easily that compound evaporates. They elute usually in boiling point order, but the stationary phase's polarity can change the order. (Jaarinen & Niiranen 2005, 183.)

In GC the sample is fed through a gas tight septum into the hot injector. There the sample evaporates and traverses through the column to the detector. Column is inside the oven, where temperature is controlled during the run. The temperature of the column is an important factor, because it contributes to the evaporation of compounds. After the column compound is moved to the detector, which detects compounds and gives a signal to the computer. (Jaarinen & Niiranen 2005, 183-184.) The diagram of GC is shown in Figure 9. In this thesis the detector was flame ionization detector.

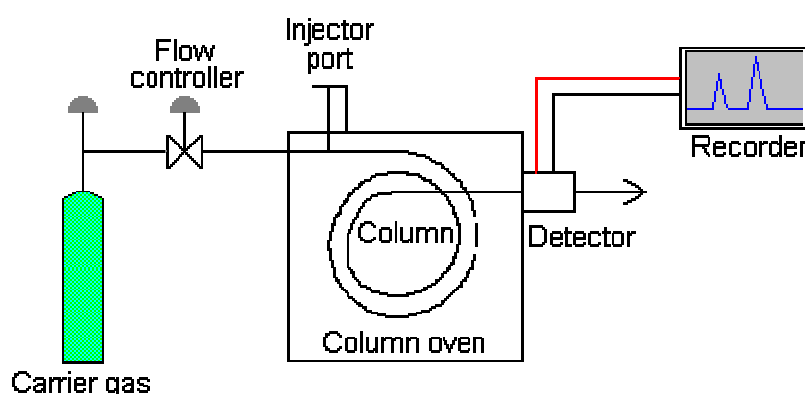


FIGURE 9. Diagram of a gas chromatograph (Sheffield Hallam University)

#### 2.4.3 Flame ionization detector

Flame ionization detector (FID) is particularly useful for the analysis of a wide range of organic molecules. (Dean et. al 2002, 215). When a compound is analyzed, it is eluting from the end of the column, mixed with hydrogen and burned in synthetic air. The use of synthetic air is necessary to ensure clean burning of the hydrogen and the component analyzed. (Simanzhenkov & Idem 2003, 82-83.) The hydrogen flame has a potential more than 100 V applied across it. Most organic compounds, on passage through the flame, produce ions and electrons that create a small current across the electrodes and this is amplified for measurement purposes. The flame ionization detector is very sensitive, which means that it is typically down to 0,1 pg and it has a linear response over a wide concentration range. (Dean et. al 2002, 215.) A diagram of FID is presented in Figure 10. Dynamic ranges of different detectors are



shown in Figure 11, where it is seen that the FID has the largest linear dynamic range.

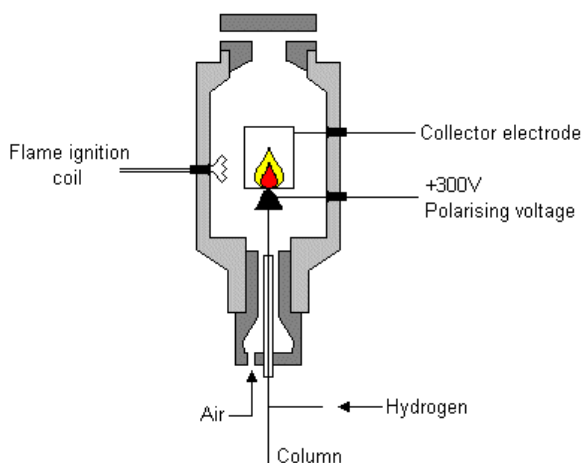


FIGURE 10. Diagram of a FID (Sheffield Hallam University. n.d.)

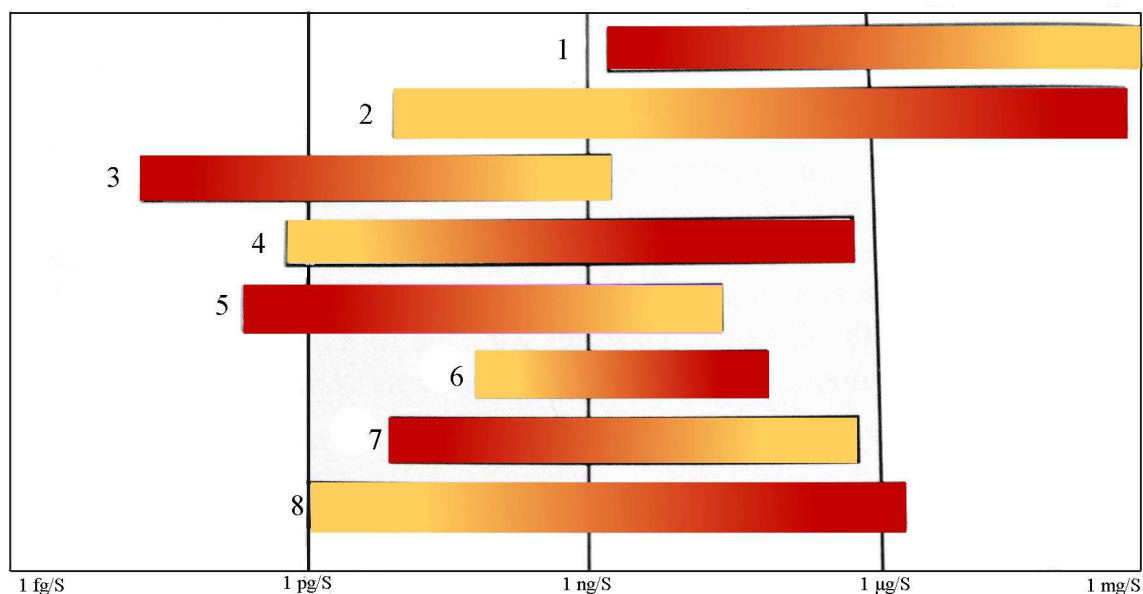


FIGURE 11. Dynamic ranges of different detectors (Simanzhenkov & Idem 2003, 82, edited)

- 1- thermal conductivity detector
- 2- flame ionization detector
- 3- electron trap detector
- 4- nitrogen/phosphor thermo ionic detector for nitrogen compounds
- 5- nitrogen/phosphor thermo ionic detector for phosphor compounds
- 6- flame photometric detector for sulfur compounds
- 7- flame photometric detector for phosphor compounds
- 8- photo ionization detector
- S- attitude of the signal

#### 2.4.4 Internal standard method

Internal standard is a compound which will produce a chromatographic peak close to the analyzing compound, but it is still distinguishable from analyte. An exactly known amount of the standard is added to a fixed volume of the unknown solution and to each of the external standard solutions. (Reeve 2002, 99.) The quantity of the element analyzed is variable, but the concentration of the internal standard is kept the same in all samples. The calibration in the method of internal standard is based on the assumption that the analyte and the internal standard signals values are directly proportional to concentration. (Jaarinen & Niiranen 2005, 21-22.) The internal standard should be chemically similar to the test substance or substances. A disadvantage is that it may be difficult to fit an internal standard peak into a complex chromatogram. (Dean et. al 2002, 224.) Any variation in injection volume would show up in a change in peak area of internal standard. The normalization is calculated with formula, which is seen in Figure 12. (Reeve 2002, 99.)

$$\frac{\text{peak area}}{\text{internal standard peak area}} \quad \text{versus concentration}$$

FIGURE 12. Formula of internal standard method (Reeve 2002, 99.)

### 3 MATERIALS AND METHODS

#### 3.1 Materials

The contaminated area has had bus traffic's depot activity since early 1960's. The contamination has happened in a long-term consequence of depot activity, possible old leaking oil tanks and overfills. The site is located in industrial area in Tampere and it isn't in groundwater zone. Studied soil consists of silt and sand with granule size 0,002-2 mm according to geotechnical classification. This means that the soil is both permeable and impermeable. (Pirkanmaa Regional Environment Centre 2009.)

The used commercial diesel was from Neste. It is sulphur-free diesel, which has a cloud point of 0 °C and the cold-filter plugging point (CFPP) is -10 °C. (Neste oil, 2011.) The weathered diesel was light non-aqueous phase liquid, which means that it was in ground on free phase form. Florisil® is activated magnesium silicate, which is a highly selective adsorbent. It is a trademark of U.S. Silica Company. (Material Harvest 2008.) The internal standard was n-hexatriacontane (C36) and its concentration was 100 mg/l. It is a hydrocarbon with 36 carbon atoms. In Soxhlet extraction the solvent was hexane.

#### 3.2 Methods

In this thesis Soxhlet-extraction was used in sample preparation. The samples were analyzed with GC/FID. The internal standard method was used because it minimizes the errors in sample preparation.

##### 3.2.1 Soxhlet extraction and samples treatment

The concentration of hydrocarbons in the range between C10 and C40 was measured with the GC-FID method according to modified ISO 9377-2. To start with, sample must be prepared for GC by an extraction technique. The soil must

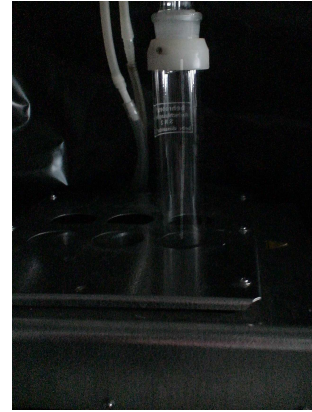
be dried (Figure 13a) so that the water doesn't convert the results. Soxhlet-extraction was chosen because it is automatic and easy and it is quite cheap, because it uses solvent only 50 ml per sample. It separates fractions quite well, while the solvent is chosen properly.

Every sample was extracted three times so there were three reference samples. 5 grams of soil was weighted into the thimble and the exact weight was written down. 50 ml of hexane was measured with graduated glass and it was added into the solvent tube (Figure 13b) and an extraction tube (Figure 13c) was put over it. The thimble was put into the extraction tube (Figure 13d). The condenser (Figure 13e) was put over the extraction tube. Then tubes were heated (Figure 13f) in 150 °C for 16 hours. The whole apparatus is shown in Figure 13g. After that the remaining hexane was measured with measuring glass and 5 ml was taken with automatic pipette in a tube. Subsequently Florisil was added about spatula tip; the tube was shaken and let it normalize. With a needle and a syringe the liquid phase was taken out and filtered through 0.2 µm filter (Phenex™) in another tube. 0,5 ml of sample were added into vial with 0,5 ml of internal standard. After that it was put in freezer waiting for analyzing.

The heater was Behrotest TRS 200 and Soxhlet's glass equipments were made by Behr. Thimbles were Whatman's extraction thimbles the size of which was 22 x 80 mm.



a)



b)



c)



d)



e)



f)



g)

FIGURE 13. Soxhlet extraction's materials and equipments a) Samples, b) Solvent tube, c) Extraction tube, d) Thimble, e) Condenser f) Heater and g) The Whole apparatus

### 3.2.2 Gas chromatograph

The GC was PerkinElmer's Clarus 500 in TUT. The chromatographic column was a 30 m x 0.25 mm ID HP-5ms capillary column. The analytical run was programmed to hold 40 °C for 3 minutes, and then increase from 40 °C to 330 °C at a rate of 10 °C/min, and then held for 5 min at 330 °C. The carrier gas was helium with a velocity of 1ml/min. The range of the retention time was from 3 to 37 min.

Samples were taken from the freezer and put in GC's stand. The places of the samples in stand were written in sequence and the method was made in computer. When all was ready, the GC was put on. When all the samples had been run, the results were analyzed.

### 3.2.3 Treatments of soil

In Diploma Thesis the Fenton treatment for contaminated soil was made using  $\text{H}_2\text{O}_2$  (0,05, 0,10 and 0,15 M) and 0,1 % surfactant (soap) and 0,2 g/l stabilizer ( $\text{KH}_2\text{PO}_4$ ). Sample numbers and the treatment methods are shown in Table 4.

Table 4. Treatments for soil (Peltola 2010, 48, edited)

$\text{H}_2\text{O}_2$ concentration	Only $\text{H}_2\text{O}_2$	$\text{H}_2\text{O}_2$ + surfactant	$\text{H}_2\text{O}_2$ + stabilizer
0,05 M	1	3	6
0,10 M	2	4	7
0,15 M	5	8	9

## 4 RESULTS

The results were calculated using chromatograms' areas, which were integrated from retention time 9 to 28. This integration was made manually and it was used in standards and samples.

### 4.1 Qualitative results

In Figure 14 the difference of Neste diesel (a) and weathered free phase diesel (b), which was in soil are shown. When diesel is a long time in ground, its big fractions cut in smaller fractions, which is seen in Figure 14 a and b. While the highest peak in the Neste diesel's chromatogram is at time value 17.40, in oil well diesel it is 13.25. In Appendix 1 Neste diesel and weathered free phase diesel chromatograms are shown in the same picture. There is also seen that though these standards have the same concentrations, the oil well curve's area is bigger than that of the Neste diesel. The peak of the internal standard is marked in both chromatograms.

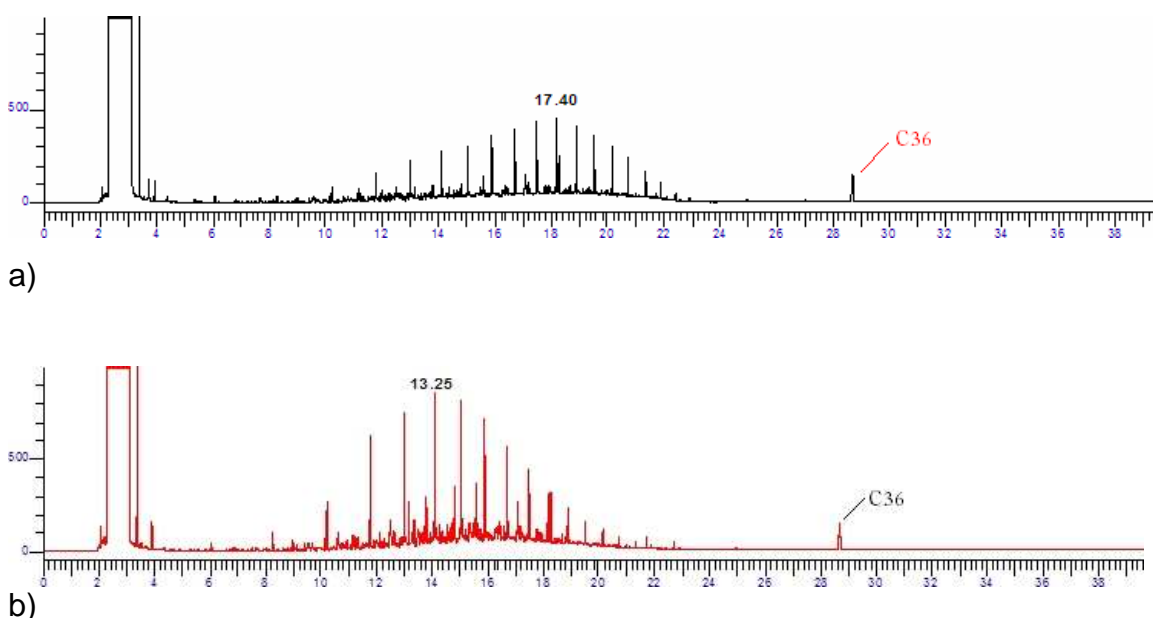


FIGURE 14. Difference of a) commercial and b) weathered free phase diesel's chromatograms

## 4.2 Quantitative results

All the results are shown in Appendix 2. There are also the areas of the standards, internal standards and samples. There are standard curves and aggregate of sample's results. The treatment's results from previous thesis are shown in Appendix 3.

### 4.2.1 Standard curve

In Figure 15 the standard curve of Neste diesel is shown, where the correlation coefficient is 0,9951. In Figure 16 is the standard curve of weathered free phase diesel whose correlation coefficient is 0,9776. In the Neste diesel's standard curve the standard 2 was discarded, because of its vial was scant after deep-freezing. The curve's formula was used for calculation of samples, shown in Appendix 2.

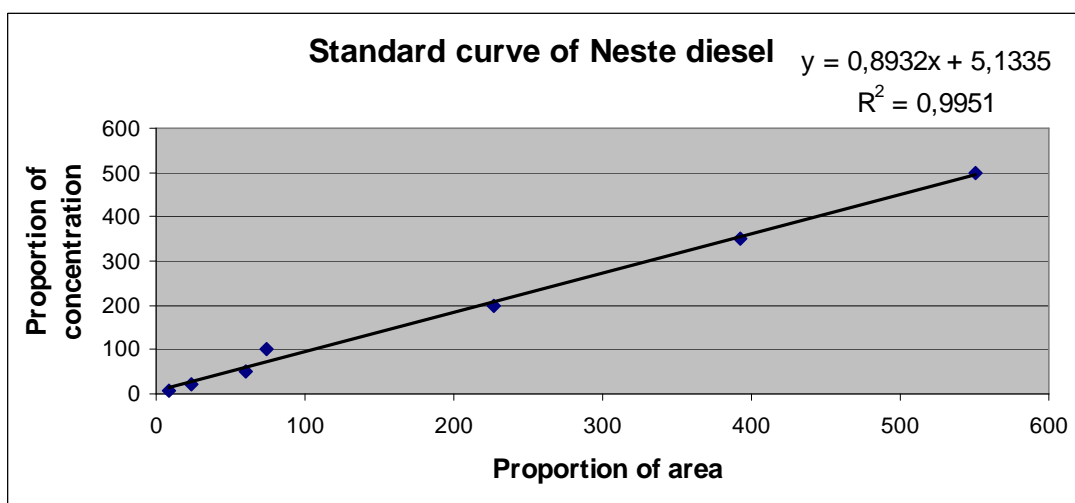


FIGURE 15. Standard curve of Neste diesel



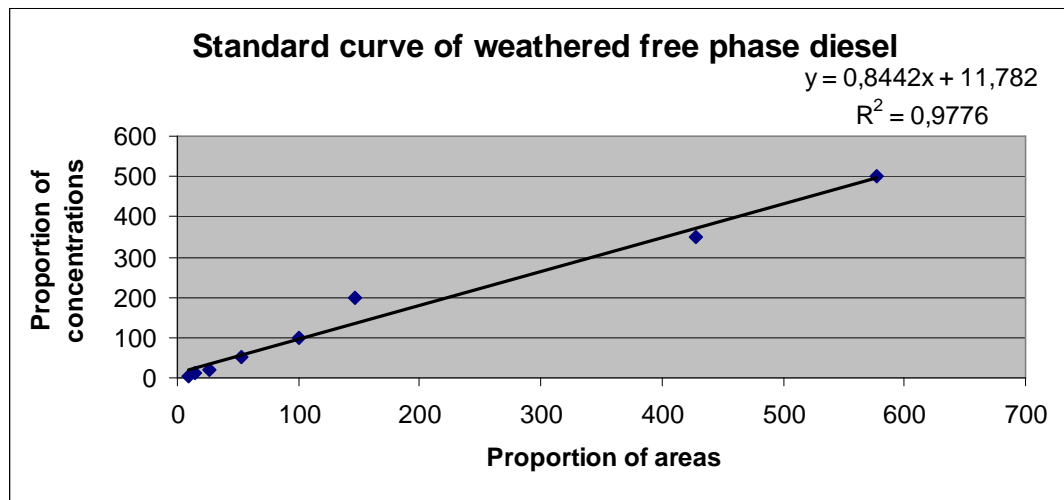


Figure 16. Standard curve of weathered free phase diesel in soil

#### 4.2.2 Samples

In Table 5 it is seen that when the samples are compared to the Neste diesel's standard curve, concentrations are almost only half of the concentrations, which samples have when they are compared to the weathered diesel's standard curve. The variation of samples is shown in Figure 17.

Table 5. Samples results

Sample	Average diesel mg/kg	Average weathered diesel mg/kg
1	46877,15	80038,25
2	39797,04	74073,84
3	62399,74	99856,39
4	48867,92	83810,09
5	33446,39	68244,13
6	47969,29	84458,12
7	49444,76	84344,27
8	48961,25	83180,63
9	47133,55	84278,20

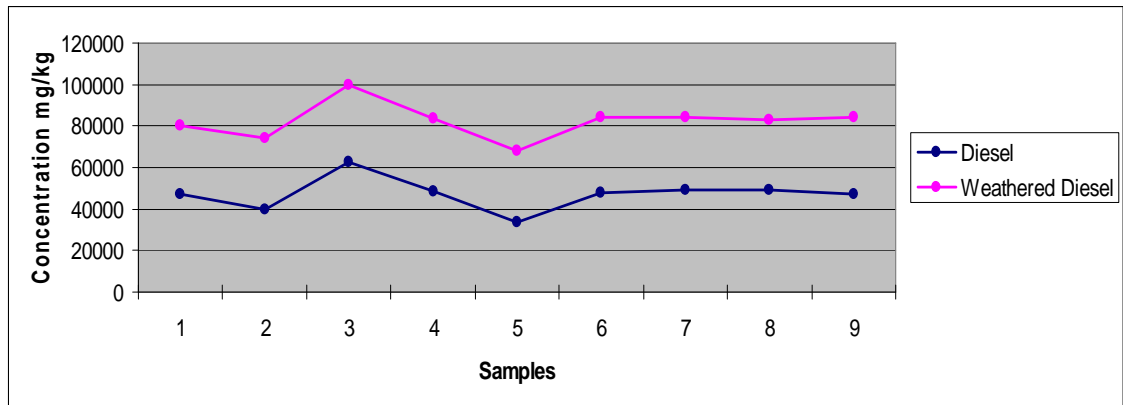


FIGURE 17. Diagram of concentration of diesel and weathered diesel in the numbered samples

## 5 CONCLUSIONS

The aim of this study was to determine the effects of weathering, and to compare two sample preparations in diesel analytics and find out which has better repeatability. Thesis considered of qualitative and quantitative parts. In the qualitative part the effects of weathering in chromatograms are shown and in the quantitative part weathering effects and comparison of sample preparations are shown.

In the qualitative part it is seen that the Neste diesel and weathered diesel differ, while the free phase diesel which has been a long time in soil is fractionated from long hydrocarbon chains to shorter by weathering. There is also seen that the weathered free phase diesel has a bigger area in its curve than diesel's curve although they have the same concentration. This is due to fractionating, as the smaller fractions evaporate and the bigger ones degrade to smaller, so the middle fractions are then larger.

The standard curves of Neste diesel and weathered diesel were both quite good, because correlation coefficients were for Neste diesel 0,9951 and for weathered diesel 0,9776. In the quantitative part the samples which were compared to the Neste diesel's standard curve have only half of the concentration than when the samples were compared to the weathered diesel's standard curve. This will affect the choice of the standards, because it is changing the results so much.

In this study, where soil sample preparation was made by Soxhlet extraction, the reference samples were quite similar, which is seen in Appendix 2. In ultrasonic extraction the reference samples differed significantly, so it may be inferred that Soxhlet extraction has better repeatability than ultrasonic extraction.

The samples can be studied with GC/MS in further research, as there is interest to find out what the difference in diesel and weathered diesel in soil is in hydrocarbon level. The hydrocarbons may be quite different in those compounds.

## REFERENCES

- Aatelo M. (toim.) 1995. Lähteiltä tuotteiksi- öljyn tie. Kemianteollisuus ry, taloudellinen tiedotustoimisto, Suomen Muoviteollisuusliitto ja Öljyalan keskusliitto
- Alexander M. 1994. Biodegradation and Bioremediation. Academic Press. San Diego, CA.
- Atlas, R. M. 1981. Microbial Degradation of Petroleum Hydrocarbons: an Environmental Perspective. Microbiological Reviews 45 (1), 180-209.
- Clayton C. 2005. Petroleum Geology/ Chemical and physical Properties. Elsevier, 248-260.
- Dean J., Jones M., Holmes D., Reed R., Weyers J., Jones A. 2002. Practical Skills in Chemistry. United Kingdom, Harlow: Pearson Education Limited
- Department of ecology, State of Washington. Groundwater Interceptor Drains. Read 1.12.2010.  
<http://www.ecy.wa.gov/programs/sea/pubs/95-107/groundwater.html>
- EEA. 2007a. Annual national expenditures for management of contaminated sites.  
<http://www.eea.europa.eu/data-and-maps/figures/annual-national-expenditures-for-management-of-contaminated-sites-eur-per-capita>
- EEA. 2007b. Estimated allocation of public and private expenditures for management of contaminated sites. <http://www.eea.europa.eu/data-and-maps/figures/estimated-allocation-of-public-and-private-expenditures-for-management-of-contaminated-sites-by-country>
- EUR-Lex. 2005. Official Journal of the European Union, Commission decision 26.4.2005 establishing ecological criteria and the related assessment and verification requirements for the award of the Community eco-label to lubricants. L 118/26-34
- Farrell-Jones J. 2003. Petroleum hydrocarbons and polyaromatic hydrocarbons. In work
- Fingas M. 2001. The basics of oil spill cleanup. Florida, Boca Raton: CRC Press LLC.
- Finnish Environment Institute. 2009. Maaperän pilaantumisen syyt ja esiintyminen Suomessa. Updated 10.12.2009. Read 13.9.2010.  
<http://www.ymparisto.fi/default.asp?contentid=307132&lan=fi&clan=fi>
- Finnish Environment Institute. 2010. Öljy- ja kemikaalivahinkojen torjunta. Read 6.9.2010. <http://www.ymparisto.fi/default.asp?contentid=220831&lan=fi>

Finnish oil and gas federation. 2010. SOILI-ohjelma.  
<http://www.oil-gas.fi/index.php?m=12&id=32>

Finlex. 2007. Valtioneuvoston asetus maaperän pilaantuneisuuden ja puhdistustarpeen arvioinnista: maaperän haitallisten aineiden pitoisuuksien kynnys- ja ohjearvot. Liite, N:o 214. 743-746

Forsbacka, A. 1996. Öljy-yhdisteiden biologinen hajoaminen ja saastuneen maan biosaneeraus. Helsingin kaupungin ympäristökeskuksen julkaisu 2/96. Helsingin kaupungin ympäristökeskus. Helsinki.

Gad S. 2005a. Petroleum hydrocarbons. Elsevier, 377-379

Gad S. 2005b. Diesel Fuel. Elsevier, 19-22

Geological Survey of Finland. Maalajien luokitus. Read 6.9.2010.  
<http://www.gsf.fi/aineistot/mp-opas/maalajiluokitus2.htm>

Goi A., Trapido M., Kulik N. 2009. Contaminated Soil Remediation with Hydrogen Peroxide Oxidation. World Academy of Science, Engineering and Technology 52/2009, 185-189

ISO 9377-2. 2000. Water quality - Determination of hydrocarbon oil index, Part 2: Method using solvent extraction and gas chromatography. International Standard

Jaarinen S., Niiranen J. 2005. Laboratorion analyysitekniikka. Helsinki: Edita. 5. reformed edition

Material Harvest. 2008. Florisil® for Column Chromatography. Read 15.2.2011.  
[http://www.materialharvest.com/welcome/silica\\_products/florisil\\_chromatology.html](http://www.materialharvest.com/welcome/silica_products/florisil_chromatology.html)

Ministry of the Environment. 2010. Öljysuojarahaston tilinpäätös vuodelta 2009. Helsinki.

NEOT (North European Oil Trade Oy). 2005. KTT Diesel.  
[http://www.agrimarket.fi/Liitetiedostot/Docs/KTT\\_Dieseloljy.pdf](http://www.agrimarket.fi/Liitetiedostot/Docs/KTT_Dieseloljy.pdf)

Neste oil. 2011. Neste diesel -0/-10. Read 18.3.2011.  
<http://www.nesteoil.com/default.asp?path=1,41,535,547,557,5465>

OEHHA (Office of Environmental Health Hazard Assessment). 2007. Health Effects of Diesel Exhaust.  
[http://www.oehha.org/public\\_info/facts/dieselfacts.html](http://www.oehha.org/public_info/facts/dieselfacts.html)

Peltola L. 2010. Site characterization of a diesel contaminated soil and the assessment of the designed remediation strategy. Tampere University of technology. Master of Science Thesis.

Pirkanmaa Regional Environment Centre. 2009. Päätös pilaantuneen alueen puhdistamisesta. Given 17.6.2009. PIR-2005-Y-675-114

Reinikainen J. 2007. Maaperän kynnys- ja ohjearvojen määrittäminen perusteet. Helsinki: Edita Prima Oy. Suomen ympäristö 23/2007,

Riser-Roberts E. 1998. Remediation of petroleum contaminated soils. United States of America, Florida: CRC Press LLC

Sassali J. 2008. Geoteknisestä maaluokituksesta euroluokitukseen. Teknillinen korkeakoulu. Engineering and Architectural Department. Construction and environmental engineering. University of Technology. Bachelor's Thesis.

Sella A. 2007. Classic Kit: Soxhlet extractor. RSC (Royal Society of Chemistry). Read 16.2.2011. <http://www.rsc.org/chemistryworld/Issues/2007/September/ClassicKitSoxhletExtractor.asp>

Selley R. 2004. Petroleum Geology. Encyclopedia of Physical Science and Technology. 729-740

Sheffield Hallam University. n.d. Gas chromatography. Read 31.1.2011. <http://teaching.shu.ac.uk/hwb/chemistry/tutorials/chrom/gaschrom.htm>

Simanzhenkov V., Iden R. 2003. Crude oil chemistry. Marcel Dekker

Speight J. 2002. Handbook of petroleum product analysis. Hoboken, New Jersey: John Wiley & Sons.

Technology loading. 2010. Soxhlet Extractor. Read 18.3.2011. <http://www.technologylodging.com/tag/soxhlet-extractor/>

Terra Nova. Terra Nova's Remediation Technology. Read 5.1.2011. <http://www.terranoabiobiosystems.com/science/remediation-technology.html>

Thompson K., Nathanail C. (edited) 2003. Chemical Analysis of Contaminated Land. Blackwell Publishing.

USEPA (United States Environmental Protection Agency). 2007. Method 3620C Florisil Cleanup. Read 8.3.2011. <http://www.epa.gov/wastes/hazard/testmethods/sw846/pdfs/3620c.pdf>

USEPA (United States Environmental Protection Agency). 1999. Monitored natural attenuation of petroleum hydrocarbons. U.S. EPA remedial technology fact sheet. EPA/600/F-98/021. 1-3.

USEPA (United States Environmental Protection Agency). 1996. Method 3540C Soxhlet extraction. Read 8.3.2011 <http://www.epa.gov/wastes/hazard/testmethods/sw846/pdfs/3540c.pdf>

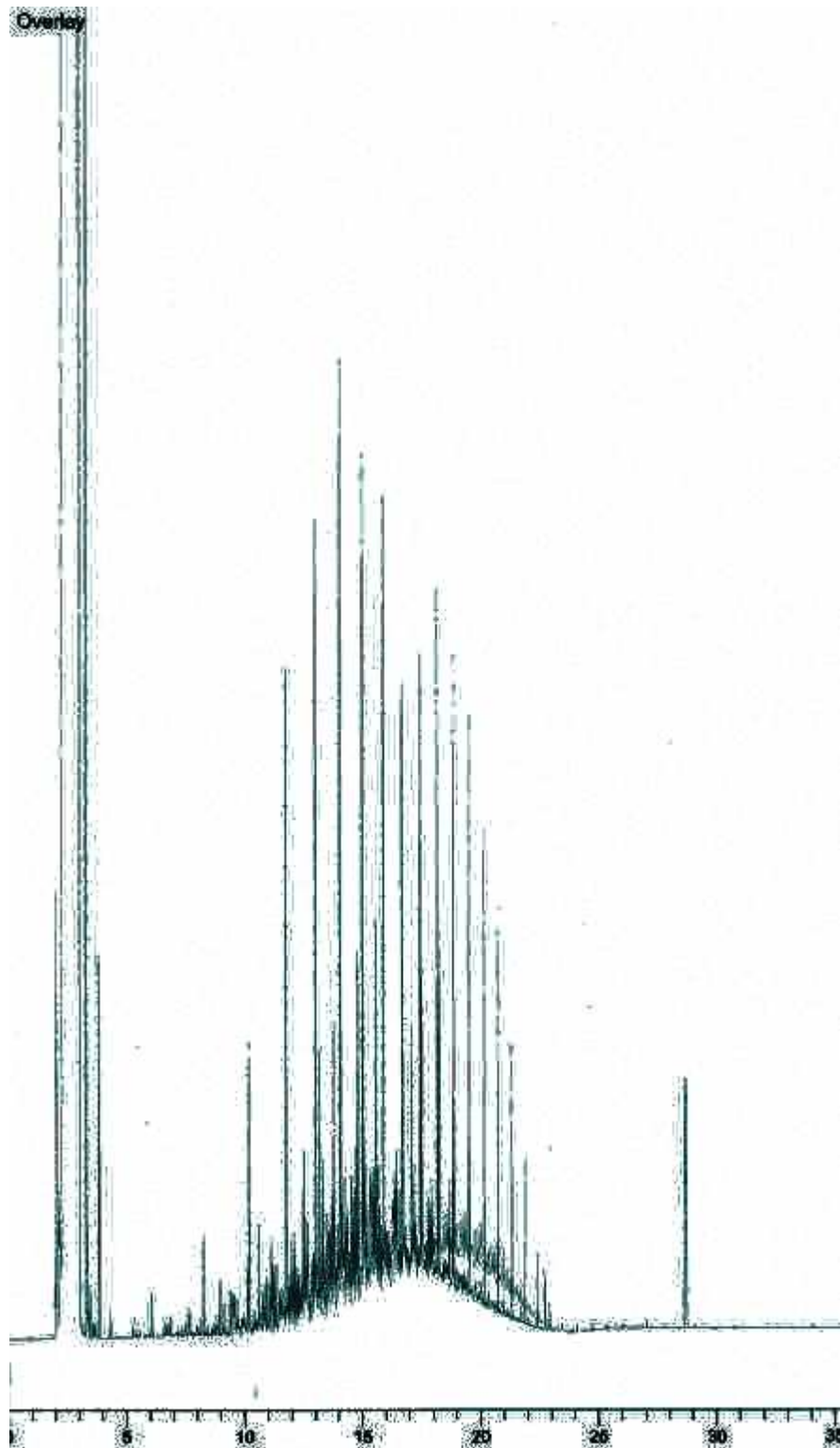
Wilk C. n.d. Applying Solidification/Stabilization for Sustainable Redevelopment of Contaminated Propert. Read 6.1.2011.  
[http://www.pollutionengineering.com/PE/Home/Files/PDFs/PCA\\_SS-Whitepaper.pdf](http://www.pollutionengineering.com/PE/Home/Files/PDFs/PCA_SS-Whitepaper.pdf)



## APPENDICES

## APPENDIX 1

## DIESEL AND OIL WELL IN THE SAME CHROMATOGRAM



The weathered diesel is the left curve and the right curve is Neste diesel

## AREAS AND CONCENTRATIONS OF

## APPENDIX 2:

1(3)

## STANDARDS AND SAMPLES

St.	Whole area	IS-area	Proportion of whole area and IS-area	Conc. g/l	IS C g/l	Conc/ IS C	NB
di1	3438720,81	406430,33	8,46078788	0,567	0,1	5,67	
di2	9617352,53	5291,41	1817,540604	1,027	0,1	10,27	<b><u>was scant</u></b>
di3	9819270,25	423499,90	23,1860037	2,013	0,1	20,13	
di4	23525583,37	389085,44	60,4637978	5,142	0,1	51,42	
di5	29696474,53	398407,55	74,53793115	10,029	0,1	100,29	
di6	96381937,67	425474,75	226,5279847	20,052	0,1	200,52	
di7	168000000	428631,08	391,9454464	35,049	0,1	350,49	
di8	241000000	437826,07	550,4468932	50,035	0,1	500,35	
ow1	3529654,80	406118,85	8,691186829	0,555	0,1	5,55	
ow2	5382319,50	378146,47	14,23342521	1,032	0,1	10,32	
ow3	9479174,35	357369,52	26,52485402	2,022	0,1	20,22	
ow4	22281996,52	356061,27	62,57910758	5,009	0,1	50,09	
ow5	40266527,96	402755,08	99,97770347	10,027	0,1	100,27	
ow6	56152312,48	382078,79	146,9652699	20,007	0,1	200,07	
ow7	174000000	406557,86	427,9833626	35,029	0,1	350,29	
ow8	208000000	360782,19	576,5251328	50,008	0,1	500,08	

## APPENDIX 2: 2(3)

Sample	Whole area	IS-area	Proportion of whole area and IS-area
1,1	2766435,74	652881,72	4,237269409
1,2	2589281,89	576459,18	4,491700332
1,3	2405231,58	524674,32	4,584237285
2,1	454256,36	380987,74	1,192312278
2,2	1554203,66	378874,94	4,102154817
5,1	497560,02	343569,85	1,448206296
5,3	477590,20	388717,66	1,228630055
3,1	3057619,49	412975,28	7,403880179
3,2	2555516,32	485694,24	5,261574278
3,3	2566309,06	477340,45	5,37626564
4,1	1557455,06	377212,38	4,128854573
4,2	1824089,06	426531,67	4,276561832
4,3	2834402,48	618728,67	4,581010413
8,1	3057619,19	737841,01	4,144008192
8,2	1738691,60	391306,41	4,443299562
8,3	1854125,53	366629,97	5,057212126
6,1	2176090,90	484191,41	4,494278203
6,2	1558781,52	446129,60	3,49401053
6,3	3708988,64	1059384,80	3,501077833
7,1	2265917,03	501361,92	4,519523601
7,2	2009516,50	459918,96	4,369283884
7,3	1925501,31	429827,01	4,479712222
9,1	2307972,28	711186,32	3,245242794
9,2	1882148,02	518164,39	3,632337645
9,3	1853822,34	525941,19	3,524771163

## APPENDIX 2: 3(3)

Sample (kg)	Volume (l)	$y = 0,8932x + 5,1335$	$y = 0,8442x + 11,782$	Diesel	Oil well
0,005047	0,028	8,918229036	15,35910284	49,47601851	85,20831356
0,005032	0,024	9,145486736	15,57389342	43,62350823	74,28668232
0,005048	0,026	9,228140743	15,65201312	47,53192664	80,61974345
0,005008	0,025	6,198473326	12,78855002	30,94471178	63,8444297
0,005063	0,028	8,797544682	15,2450391	48,64937613	84,30325368
0,005001	0,026	6,427037864	13,00457576	33,41324598	67,60891997
0,005025	0,027	6,230912365	12,81920949	33,47952913	68,87933459
0,005020	0,033	11,74664578	18,03235565	77,21590984	118,5346672
0,005010	0,026	9,833138145	16,22382101	51,03127643	84,19715885
0,005056	0,030	9,93558047	16,32064345	58,95204092	96,8373457
0,005000	0,029	8,821392904	15,26757903	51,16407884	88,55195838
0,005008	0,024	8,953325028	15,3922735	42,90816523	73,76636194
0,005093	0,029	9,225258501	15,64928899	52,5315144	89,1119582
0,005015	0,025	8,834928117	15,28037172	44,04426955	76,1763765
0,005095	0,030	9,102255168	15,53303349	53,59206623	91,45506736
0,005095	0,026	9,650601871	16,05129848	49,24742859	81,91045346
0,005028	0,023	9,147789291	15,57606966	41,84632823	71,25233242
0,005011	0,035	8,254350205	14,73164369	57,65821602	102,9033507
0,005023	0,027	8,260662721	14,73760991	44,4033234	79,21868753
0,005014	0,024	9,17033848	15,59738182	43,89822154	74,66434573
0,005034	0,029	9,036144365	15,47054946	52,05152284	89,11606829
0,005057	0,029	9,134778957	15,56377306	52,38453426	89,2524063
0,005061	0,031	8,032150863	14,52163397	49,20105058	88,95246857
0,005088	0,026	8,377903984	14,84841944	42,8158238	75,88381434
0,005031	0,030	8,281825603	14,75761182	49,38378647	87,99832134

## LIISA'S RESULTS

## APPENDIX 3

Diesel Area [ $\mu\text{V}\cdot\text{s}$ ]	C36 Area [ $\mu\text{V}\cdot\text{s}$ ]	Ad/Ais	average Ad/Ais	reduction %	Treatment for soil sample
1023724	28234	36,258554	36,2	0,0	Sand original
1006714	27878	36,111414			Sand original
10497	0.000000			x	[H <sub>2</sub> O <sub>2</sub> ] 0.05 M
8214	0.000000			x	[H <sub>2</sub> O <sub>2</sub> ] 0.05 M
1195507	23620	50,614183		-39,9	[H <sub>2</sub> O <sub>2</sub> ] 0.10 M
723182	27513	26,285102		27,4	[H <sub>2</sub> O <sub>2</sub> ] 0.10 M
5660	0.000000			x	[H <sub>2</sub> O <sub>2</sub> ] 0.05 M + surfactant 0.1 %
947186	36806	25,734554		28,9	[H <sub>2</sub> O <sub>2</sub> ] 0.05 M + surfactant 0.1 %
643704	25420	25,322738		30,0	[H <sub>2</sub> O <sub>2</sub> ] 0.10 M + surfactant 0.1 %
462477	32749	14,121866		61,0	[H <sub>2</sub> O <sub>2</sub> ] 0.10 M + surfactant 0.1 %
6725	0.000000			x	[H <sub>2</sub> O <sub>2</sub> ] 0.15 M
636703	27879	22,838086		36,9	[H <sub>2</sub> O <sub>2</sub> ] 0.15 M
627594	27391	22,912416		36,7	[H <sub>2</sub> O <sub>2</sub> ] 0.05 M + stab KH <sub>2</sub> PO <sub>4</sub> 0.2 g/l
668081	27221	24,542853		32,2	[H <sub>2</sub> O <sub>2</sub> ] 0.05 M + stab KH <sub>2</sub> PO <sub>4</sub> 0.2 g/l
959521	27482	34,914526		3,5	[H <sub>2</sub> O <sub>2</sub> ] 0.10 M + stab KH <sub>2</sub> PO <sub>4</sub> 0.2 g/l
633753	35463	17,870823		50,6	[H <sub>2</sub> O <sub>2</sub> ] 0.10 M + stab KH <sub>2</sub> PO <sub>4</sub> 0.2 g/l
808941	29099	27,799615		23,2	[H <sub>2</sub> O <sub>2</sub> ] 0.15 M + surfactant 0.1 %
564168	29059	19,41457		46,3	[H <sub>2</sub> O <sub>2</sub> ] 0.15 M + surfactant 0.1 %
				x	[H <sub>2</sub> O <sub>2</sub> ] 0.15 M + stab KH <sub>2</sub> PO <sub>4</sub> 0.2 g/l
				x	[H <sub>2</sub> O <sub>2</sub> ] 0.15 M + stab KH <sub>2</sub> PO <sub>4</sub> 0.2 g/l

The average reduction for diesel fragments in percent

Concentration	Only H <sub>2</sub> O <sub>2</sub>	+Surfactant 0.1 % (5 ml/5 l)	+Stabilizer KH <sub>2</sub> PO <sub>4</sub> 0.2 g/l (1 g/5l)
0.05 M	1 X	3 28,1	6 34,4
0.10 M	2 27,4	4 <b>45,5</b>	7 27,1
0.15 M	5 36,9	8 34,8	9 X