ASSESSMENT OF GROUNDWATER CONTAMINATION BY HYDROCARBONS FROM GARAGES IN THE BIYEM-ASSI NEIGHBOURHOOD OF YAOUNDE

A thesis submitted in partial fulfilment of the requirements for the degree of Master of Engineering (MEng) in Environmental Engineering

Presented by:

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Academic year 2019-2020

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DEDICATION

This work is dedicated to my parents Prof. TAN Paul Vernyuy and Mrs. TAN Florence Fin Baye, who will stop at nothing to give me a proper education.

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ABSTRACT

Handling hydrocarbons in the form of petroleum products, solvents or even waste is a treacherous task. These substances, though beneficial and indispensable to the advancement of socio-economic activities, are environmentally unfriendly and so must be handled with care. One of the activities in Cameroon whose environmental impacts are overlooked is automobile repair. Automobile repair deals with the handling of hydrocarbons and yet in this sector, there is little regard for the impact of their activities. Garage waste is spilled directly on the ground and this is a potential threat to soil and groundwater. The main objective of this work therefore, was to assess contamination of the subsoil by hydrocarbons generated from automobile repair shops or garages and determine their potential for soil and groundwater contamination. The former was achieved by qualitative analysis of well waters located close to garages by gas chromatography. From these analyses, we were able to establish a link between subsoil contamination and garage effluents as we found some components of gasoline (most prominently; heptane and hexane) in the water. The latter was achieved by means of a modelling software, VS2DTI 1.3. We determined the intrinsic vulnerability of an approximation of the Yaoundé subsoil by simulating the movement of a contaminant in the subsoil over a period of 1year. At the end of the simulation, we found that an arbitrary contaminant could indeed percolate to the Yaoundé aquifer level. We came to the conclusion that garages ought to have a waste management plan because their effluents are an environmental hazard, polluting soil and groundwater and putting human health at risk. A remediation procedure was suggested (source removal) and measures for better management of garage effluents were prescribed.

Keywords: Hydrocarbons, Garages, Contamination, Waste, Groundwater.

RESUME

La manipulation des hydrocarbures sous la forme de produits pétroliers, solvants ou même sous forme de déchets et une tache laborieuse. Ces substances, bien qu'ils soient bénéfiques et indispensables à l'avancement des activités socio-économiques, ne sont pas écologiques et doivent être manipule avec soin. La réparation automobile comporte la manipulation des hydrocarbures et pourtant, peu d'attention est prêté à l'impact de leurs activités. Les déchets de garage sont déversés directement sur le sol, ce qui constitue une menace potentielle pour le sol et les eaux souterraines. Alors l'objectif principal de ce travail, était d'évaluer la contamination du sous-sol par des hydrocarbures provenant des ateliers de réparation automobile, aussi appelés garages, et déterminer leur potentiel pour la contamination des sols et eaux souterraines. Le premier objectif a été atteint par l'analyse qualitative des eaux de puits situées près des garages par spectrométrie de masse par chromatographie en phase gazeuse. Grace à ces analyses, nous avons établi un lien entre la contamination du sous-sol et les effluents des garages car nous avons trouvé certains composants de l'essence (principalement l'heptane et l'hexane) dans l'eau. Le second a été atteint par un logiciel de modélisation, VS2DTI 1.3. Nous avons déterminé la vulnérabilité intrinsèque du sous-sol de Yaoundé en simulant l'évolution d'un contaminant dans le sous-sol pendant une période de 1an. A la fin de la simulation, nous avons constaté qu'un contaminant arbitraire pouvait en effet percoler jusqu'au niveau de la nappe de Yaoundé. Nous sommes arrivés à la conclusion que les garages devraient avoir un plan de gestion des déchets car leurs effluents sont un danger pour l'environnement, polluant les sols et les eaux souterraines et mettant la santé humaine en danger. Une procédure de remédiation a été proposé et des mesures pour une meilleur gestion de effluents de garages a été prescrit.

Mots Clés: Hydrocarbures, Garages, Contamination, Déchets, Eaux-Souterraines.

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LIST OF ABBREVIATIONS AND ACRONYMS

- ## ABBREVIATIONS

AC   Air Conditioning

BSTFA   Bis- (Trimethylsilyl) -Trifluoroacetamide

BTEX   Benzene, Toluene, Ethylbenzene and Xylene

CIF   Cost, Insurance, Freight

CMD   Coefficient of Molecular Diffusion

CUY   Communaute Urbaine de Yaoundé

DCE   Dichloroethene

DNA   Deoxyribonucleic acid

DNAPL   Dense Non- Aqueous Phase Liquid

GCMS   Gas Chromatography, Mass Spectrometry

Kd   Equilibrium Dissociation Constant

Koc   Organic carbon to water partition coefficient

Kow   Octanol to water partition coefficient

LD   Longitudinal Dispersion

LNAPL   Light Non- Aqueous Phase Liquid

MINDHU   Ministère de l'Habitat et du Développement Urbain

MINEPDED   Ministry of Environment, Nature Protection and Sustainable Development

NAPL   Non- Aqueous Phase Liquid

PAH   Polycyclic Aromatic Hydrocarbons

PB   Propylbromide

PCB	Polychlorinated Biphenyl
PCE	Perchloroethene
PCN	Polychlorinated Naphthalene
PCV	Positive Crankcase Ventilation
PHE	Phenylalanine
POP	Persistent Organic Pollutants
RAC	Royal Automobile Club
SCDP	Société Camerounaise de Dépôts Pétroliers
SDG	Sustainable Development Goals
SNH	Société Nationale des Hydrocarbures
TCE	Trichloroethene
TD	Transverse Dispersion
UST	Underground Storage Tanks
VC	Vinyl Chloride
VOC	Volatile Organic Contaminant
WHO	World Health Organisation.

- **UNITS**

%	**percent**
°C	degree Celsius
d	days
g/l	grams per litre
gm^{-2}d^{-1}	grams per square metres per day
l/kg	litre per kilogram
m^3/h	cubic meters per hour
md^{-1}	metres per day
mg	milligram
ppm	parts per million
s	seconds
ug/l	micrograms per litre

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GENERAL INTRODUCTION

Industrialization is an inevitable part of development and it has led to the increased use and build-up of organic compounds. Major sources which are responsible for organic contaminants are anthropogenic activities which involve the use of fuels, solvents, and pesticides. Crude oil contamination is common due to its extensive use, unsustainable disposal methods and accidental spills. The automobile industry is very involved in this type of contamination especially automobile repair shops referred to from here on out as garages. Contamination caused by petroleum hydrocarbon is a matter of worry because they are harmful for various life forms. Crude oil and petroleum products form a waterproof film on water that prevents the oxygen exchange between environment and water causing damages to plants, animals, and human beings (Srivastava et al., 2019). Human beings in particular all around the world, depend on soil for provision of food and on groundwater as a source of water for various purposes. The Sustainable Development Goals (SDGs) established in 2015 took this into consideration as the sixth goal states "ensure availability and sustainable management of water resources and sanitation for all". More specifically, target 6.3 seeks to tackle the problem of groundwater pollution as it states "By 2030, improve water quality by reducing pollution, eliminating dumping and minimizing release of hazardous chemicals and materials, halving the proportion of untreated wastewater and substantially increasing recycling and safe reuse globally". SDG target 6.6. "By 2020, protect and restore water-related ecosystems, including mountains, forests, wetlands, rivers, aquifers and lakes" (United Nations, 2015). The focus in this work is a prerequisite to the achievement of this SDG as it is on evaluating the danger that hydrocarbons, specifically in the form of petroleum products and degreasing solvents originating from garages, pose to the soil and groundwater environment and by extension, to the exposed Cameroonian population.

The abundant presence and use of hydrocarbons on the national territory, coupled with the high concentration of garages in the suburban areas of Yaoundé and their mishandling of hydrocarbon waste leads us to ask the major question in this research which is;

Is the hydrocarbon pollution of Cameroonian soil and groundwater by garages a long-term hazard for the population?

The main objective of this work is to determine the extent and importance of soil and groundwater pollution by hydrocarbons generated from garages in Yaoundé. More specific objectives include;

- Predict the timeframe between hydrocarbon spill and groundwater pollution in order to demonstrate risk potential.
- Investigate groundwater for hydrocarbon contamination and suggest remediation methods adequate for the situation.

This thesis starts by stating the problem that led to this research as well as presenting the context in which the problem needs to be resolved. In first chapter, some concepts which are of great import to this work are defined. Next, an outline of the properties and importance of soils, groundwater and hydrocarbons are laid out, a connection between them is established and then, the problem is presented in the Cameroonian scenario, giving an overview of the industries linked to hydrocarbon production and usage and inevitably, pollution. In chapter 2, the area of study and research method are presented as well as the tools used for this research. This chapter closes with a presentation of the model and software used for data analysis. The results of the analyses conducted are laid out in Chapter three and their implications are discussed in depth. Subsequently, some recommendations and propositions are made followed by a general conclusion.

CHAPTER 1: LITERATURE REVIEW

Introduction.

This chapter begins with some concepts and definitions which are useful for the understanding of the document. Then, a general overview of soil and groundwater pollution, its sources, main actors and the fate of these contaminants in the subsoil. Next, we zoom in and observe the problem at a national level by looking at hydrocarbon pollution in Cameroon and Cameroon's policies regarding the subject. Next, we have a look at the industry the research focuses on; the automobile repair industry. We discover in what ways this industry contributes to the contamination of the subsoil and after that, impact of hydrocarbon contamination on human health. The chapter closes off with some notions of modelling and simulation which is a tool that is used in this research to determine the long-term risk of hydrocarbons, as well as some notions of remediation of contaminated sites.

1.1   CONCEPTS AND DEFINITIONS

i.   Pollution

Pollution is the addition of any substance (solid, liquid or gas) or any form of energy (such as heat, sound, or radioactivity) to the environment at a rate faster than it can be dispersed, diluted, decomposed, recycled, or stored in some harmless form (Pepper et al., 2019). It is the presence of a substance, either introduced or native, above the threshold level.

ii.   Contamination

According to Wikipedia, contamination is the presence of a constituent, impurity, or some other undesirable element that spoils, corrupts, infects, makes unfit, or makes inferior a material, physical body, natural environment. Contamination is the introduction of a substance which was not originally present to an environment.(Osman, 2014).

This definition differentiates contamination from pollution which are often used interchangeably. Contamination becomes pollution when regulatory threshold levels have been exceeded indicating that the biota present in the environment is in harm's way.

iii. Remediation

Environmental remediation deals with the removal of pollution or contaminants from environmental media such as soil, groundwater, sediment, or surface water. The technologies used to accomplish this could be biological, chemical, thermal or physical.

iv. Sustainability

Sustainability is a term that refers to the well-being of future generations and in particular with irreplaceable natural resources, as opposed to the gratification of present needs (Kuhlman & Farrington, 2010). It is supported by four pillars; the social aspect, economy, environment and more recently inter-culturalism. Within the context of soil and groundwater pollution and remediation, sustainability refers to the maintenance of healthy soil and groundwater systems which means incorporating environmental policies in the governance of economic and industrial activities.

v. Hydrocarbons

A hydrocarbon is an organic chemical compound composed exclusively of hydrogen and carbon atoms. Hydrocarbons are naturally-occurring compounds and form the basis of crude oil, natural gas, coal and other important energy sources (Fernando, 2021).

1.2   SOIL AND GROUNDWATER POLLUTION

Groundwater is the most abundant source of freshwater and the most extracted raw material on earth. It represents about 97% of nonfrozen fresh water and the annual withdrawal rates amount to approximately 982 km^3/yr.(Boving & Kreamer, 2018). Because groundwater is generally more shielded from pollution than other exposed sources of freshwater such as lakes, ponds and streams, it is easier and less costly to treat. It is no surprise therefore, that groundwater is the source of drinking water for many people around the world especially in rural areas and increasingly in urban areas. Groundwater serves other purposes apart from drinking water. It supplies an estimated 38–42% of the global water used for irrigation, approximately 36% of the water resources needed for

households, and roughly 27% of the water needed for industry and manufacturing (Boving & Kreamer, 2018).

Soil is undoubtedly critical to the world. It is a non-renewable natural resource in human life time frame which supplies virtually all the food and fibre that sustains the human population and provides ecosystem services that support life. Almost 96 % of human food is obtained from the soil (Osman, 2014). It also provides a physical matrix, chemical environment, and biological setting for water, nutrient, air, heat exchange for organisms, as well as mechanical support for living organisms and their structures, including most of our buildings and other installations. Soils regulate exchange of material, energy, water, and gas within the lithosphere–hydrosphere–biosphere–atmosphere system (Osman, 2014).

Soil acts as a recycler of materials and as a purifier of water but as much as soil serves as a protective cover to groundwater, it is not pollution proof as it acts as a source and sink of pollutants (Osman, 2014). Soil itself is prone to contamination and when this happens, groundwater is exposed to contamination. Soils influence hydrological processes such as infiltration, percolation, drainage, streamflow, and surface as well as underground water storage. Reason why in case of contamination, it is just a matter of time before the contamination seeps from the soil to an aquifer and this is a function of the soil properties as well as the properties of the contaminant substance. Two physical properties that may affect fluid and contaminant movement through the subsurface environment are:

• porosity, which is the ratio of volume of void (pore) space to the total volume of material;

• and permeability, which is a measure of a soil's ability to transmit fluids. (Cole, 2017)

While soil is a very complex and heterogenous medium, we can generally say that an open, porous soil will allow contamination to migrate more rapidly, while a contaminated clay will have a slower propagation of the contaminant.

More often than not, the primary receptor of contamination is the vadose zone or unsaturated soil. The vadose zone is made up of three components; soil, air and water, reason why it is referred to as the unsaturated zone which could be contaminated to retention capacity. Contaminant travel in the vadose zone can occur in three ways:

1. Volatilizing into the air void and traveling as vapor;

2. Becoming dissolved into the soil moisture and/or into the infiltrating water and then traveling with the liquid;

3. Moving downward by gravity in the immiscible phase. (Mubashir, 2019).

In the case of the Non-Aqueous Phase Liquids, (NAPLs), there are two possible case scenarios depending on whether we are dealing with Light Non-Aqueous Phase Liquids, (LNAPLs) or Dense Non-Aqueous Phase Liquids, (DNAPLs). LNAPLs will travel down the vadose zone and settle on the water table due their immiscibility and density. This eases remediation and keeps the aquifer safe from contamination. The DNAPLs on the other hand sink down from the vadose zone through the aquifer which is the next receptor of contamination, made up of only soil and water. This leads to the creation of a plume in the aquifer which poses a major health issue. It sinks all the way and settles on the bed rock or clay layer (Bedient et al., 1999a).

There is a pressure on finite soil resources to meet the demands of increase in population for food, feed, fibre, and fuel which is likely to be intensified by several inter active factors. Some of these factors include: global warming, soil degradation, decline in fresh water supply along with pollution and contamination of water resources, urban encroachment and industrialization (Altieri & Nicholls, 2012). The last factor in particular can be considered a precursor factor as industrialization in particular usually precedes issues of global warming and pollution and contamination of water sources.

1.1.1 Sources And Types of Hydrocarbon Contamination

Pollution problems started in the industrial sector with the production of dyes and other organic chemicals developed from the coal tar industry in Germany during the 1800s (Bedient et al., 1999b). While to this day the industrial sector remains the main contributor to soil and ground water pollution, other sectors by extension such as transport, municipal and agricultural sectors now share the blame. Hazardous substances find their way to the soil with domestic, municipal, industrial, mining, and agricultural wastes as well as industrial and agrochemicals such as fertilizers and pesticides.

Hydrocarbons that we find in contaminated sites can be classified into petroleum fuels, oils or lubricants and solvents for degreasing. These reach the subsoil accidentally during spills from storage tanks or transportation vehicles and leakage from old, corroded and perforated underground storage tanks (USTs) and pipelines. In automobile repair shops they are released to the soil without care when cleaning and degreasing or changing parts. They may also reach the subsoil in less accidental ways such as discharge from landfills, open dumps and material stockpiles and surface impoundments (Bedient et al., 1999b). The different activities carried out in the afore mentioned economic sectors can be broken down and classified as shown in |Table 1.

Table 1: Types of Contamination Sources and Some Examples.

Source: Content extracted from (Bedient et al., 1999b)

	SOURCE TYPE	EXAMPLES
1	Sources designed to discharge substances	Subsurface percolation such as septic tanks. Injection wells.
2	Sources designed to store, treat and/or dispose of substances; discharge through unplanned release.	Above ground and underground storage tanks. Landfills, open dumps and material stockpiles. Surface impoundments.
3	Sources designed to retain substances during transport or transmission.	Pipelines. Materials transport and transfer.
4	Sources discharging as a consequence of other planned activities.	Mining and mine drainage. Fertilizer and pesticide applications. Irrigation practices.
5	Sources providing conduit or inducing discharge through altered flow patterns.	Production wells. Construction excavation.
6	Naturally occurring sources whose discharge is created and/or exacerbated by human activity.	Ground water-Surface water interactions. Natural leaching. Saltwater intrusion/brackish water upcoming.

Hydrocarbons have a range of physical and chemical properties that account for their hazardousness in soil and groundwater.

1.2.1.1 Physical Properties of Hydrocarbons.

From the standpoint of remediation, the more important physical properties are volatility, solubility in water, density, and kinematic viscosity (Cole, 2017).

Volatility is the tendency of a substance to vaporize at normal temperature and pressure. That is, to change state from liquid to gas without needing any alterations in the natural environment. Volatility has no defined numerical value but is described using vapour pressure. Hydrocarbons with high vapour pressures therefore, will have a significant vapor phase in the open spaces of the vadose zone (Cole, 2017).

Solubility is the ability of a substance referred to from here on out as solute, to dissolve in a solvent. Numerically speaking, it is the maximum amount of solute that can dissolve in a solvent at equilibrium. From a chemical point of view petroleum hydrocarbons are virtually insoluble in water. Solubility is approximately inversely proportional to molecular weight; lower molecular weight hydrocarbons are more soluble in water than higher molecular weight compounds. The maximum solubility of benzene in water for example is 1,750 μg/litre of water, or about 1,750 ppm. Unfortunately, that amount is sufficient to be harmful to human health and therefore, is unacceptable in groundwater (Cole, 2017).

Density is the mass of a unit volume of a substance or material. Hydrocarbons whose density are of relevance are NAPLs. LNAPLs will settle on the water table but will however form a plume over time in the direction of flow of the groundwater. DNAPLs on the other hand will settle on the bedrock meaning excavation for remediation will be deeper and more costly.

1.2.1.2 Biological Properties of Hydrocarbons.

The soil serves as a large sink for non-biodegradable molecules that persist in the environment (Langenbach, 2013). The main process which influences the fate of the pollutant in the soil is the adsorption capacity. Soils with high adsorption capacity can function as a filter, adsorbing residues which then become unavailable for the biosphere.

On the other hand, in soils of low adsorption capacity, pollutants remain bioavailable and can contaminate water, air, fodder plants, livestock and moving along the food chain up to humans. These pollutants are able to move in the environment in low concentrations over a long period of time, but through bioaccumulation they can have hazardous effects on the biota of the region

(Langenbach,2013).

Bioaccumulation occurs when concentrations in the biosphere become higher than those found in the surrounding environment. The uptake of persistent molecules to levels of high concentrations can have hazardous effects on flora and, through the food chain, on fauna and human health. Persistent molecules move into cells in higher concentrations than the surrounding environment through "Preferential partition". This is when there is a higher affinity between cell membranes and pollutants than other abiotic components of the environment (Langenbach, 2013).

Hydrocarbons come in four structural classes:

1. **Aromatic** - contain a benzene ring (most toxic) and are used in solvents and glues but also in paint and paint remover (Jeremy et al., 2020). Soluble aromatic hydrocarbons are associated with petroleum fuels and lubricants. The group includes benzene, toluene, ethyl benzene and various xylene isomers. They are commonly referred to as BTEX and are often associated with petroleum spills (Bedient et al., 1999b). Because of their high water-solubility, aromatic hydrocarbons dissolve readily in precipitation water and in this way penetrate into the groundwater and hence into drinking water supplies (Borowiec et al., 2008).

2. **Aliphatic**: Petroleum distillates found in polishes, lamp oils, and lighter fluid. They are practically water-insoluble, but low molecular-weight species have comparatively high vapor pressure which may enhance their ability to move in the gaseous phase through the unsaturated zone (Borowiec et al., 2008).

3. **Halogenated**: Could be fluorinated, chlorinated, or brominated, and are used for refrigeration (freon) and as insecticides and herbicides. Perchloroethylene (PCE) and Trichloroethylene (TCE) have been used in the cleaning industry particularly as degreasers in automobile repair shops. They are VOCs and also DNAPLs. They have a low solubility in water (TCE:1.070 g/L at 20°C and PCE: 150 mg/L at 25°C), they adsorb onto carbon (TCE: K_{oc} = 2.03-2.7 and PCE: K_{oc} = 2.2-2.7) (Carleton, 2016).

   TCE contamination exists in both vadose and saturated zones of the subsurface environment. Because of its density and low Koc, TCE will ultimately move downward in the vadose zone until an impermeable barrier is reached. Reductive dehalogenation of TCE

through natural or induced mechanisms may result in production of vinyl chloride (VC) which is a known carcinogen (Russell et al., 1992).

4. **Terpene** - found in turpentine and pine oil. Some of these hydrocarbons may be found in various mixed forms and used as an aerosol spray propellant.(Jeremy et al., 2020)

1.2.2 Fate Of Hydrocarbon Contaminants In The Subsoil

The distribution and concentrations of contaminants in ground water systems is strongly influenced by interactions between the contaminant and the physical, chemical, and biological components of the subsurface (Bedient et al., 1999b). These interactions determine the fate of the contaminants in the subsurface. In some cases, fate processes result in the alteration of the contaminants chemical structure ultimately resulting in the formation of non-hazardous compounds (Bedient et al., 1999b). This is also referred to as natural attenuation of contaminants and is the ideal scenario that is desired due to the fact that the environment is unharmed and the cost of remediation is zero. In other cases, the alteration of the contaminants chemical structure results in the formation of equally or more hazardous compounds. Other fate processes result in a phase change, without altering the compound's chemical structure. In either case, fate processes must be considered during the evaluation of contaminant transport to accurately describe or predict the behaviour of contaminants in ground water systems. The most common organic compounds found in the subsurface, including petroleum hydrocarbons (BTEX), chlorinated solvents (PCE, TCE), PCBs and PAHs are hydrophobic compounds and as such interact primarily with hydrophobic constituents of aquifer solids (Bedient et al., 1999b).

PCE as a subsurface contaminant exists in two phases; PCE as a dense non-aqueous phase liquid (DNAPL) and PCE in the dissolved phase. The PCE may be introduced to the subsurface on dirt or gravel, which allows an easy pathway to the soil, or will travel directly, though untreated concrete and can even dissolve asphalt (Forensics, 2021).

The PCE in the pure or dissolved phase will travel in the direction of groundwater flow. In the case where the geology at a site will be such that the released materials will have a preferential pathway along a seam of sand for example, the spilled PCE will appear to have spread out. The fate and transport of the dissolved phase PCE plume in groundwater is also affected by other non-destructive and destructive processes. Some of these non-destructive processes include absorption

onto organic matter due to its Koc; dilution of PCE concentration by recharge of cleaner groundwater from upgradient and surface percolation of rainwater due to its solubility; and volatilization of the PCE from the groundwater plume in the vadose zone (Forensics, 2021). The DNAPL PCE on the other hand will migrate deep enough to where groundwater is encountered and a groundwater contamination plume is initiated. Much like is the case with TCE, a migrating DNAPL PCE plume will continue to travel into the saturated subsurface to a point where it will pool on an impermeable or less permeable geologic unit and continue to dissolve into the groundwater and spread more horizontally (Forensics, 2021).

One of the most important destructive processes working on PCE plumes both DNAPL and dissolved phase is called reductive dechlorination which occurs in the presence of naturally occurring subsurface microbes available in saturated spaces. The dechlorination or degradation process produces the following daughter products; TCE, cis-1,2-dichloroethylene (cis-DCE), trans-1,2-dichloroethylene (trans-DCE), and vinyl chloride (VC). The daughter products can be as dangerous to human health and the environment as PCE in some cases, more dangerous (Forensics, 2021).

TCE contamination exists in both vadose and saturated zones of the subsurface environment. Because of its density and low K_{oc}, TCE will ultimately move downward in the vadose zone until an impermeable barrier is reached. Once in the vadose zone, TCE can become associated with soil pore water, enter the gas phase because of its Henry's constant, or exist as nonaqueous phase liquid (NAPL). This implies that upward or downward movement of TCE can occur in each of these three phases, thereby increasing areal extent of the original spill in both the vadose and saturated zones. Nonaqueous phase concentrations of TCE which are large enough to overcome capillary forces will move downward from the vadose zone into the aquifer. Once the water table is penetrated, lateral flow may be mediated by the regional ground-water flow. Due to its high density, the movement of free-phase TCE is directed vertically until lower permeability features are encountered. The vertical movement of TCE through an aquifer is determined by geological properties of the aquifer material such as granular size of sand or clay lenses. TCE will tend to pool near these impermeable features. Water passing over and around these pools solubilize TCE and spread it throughout the aquifer. Once an impermeable layer is encountered, horizontal movement will occur (Bedient et al., 1999b). Reductive dehalogenation of TCE through natural or

induced mechanisms in the subsoil may result in production of vinyl chloride (VC) which is a known carcinogen.

When **petroleum compounds** such as crude oil are released into the environment, the compounds undergo physical, chemical, and biological changes collectively referred to as weathering. The degree to which various types of petroleum hydrocarbons degrade under these changes depends on the physical and chemical properties of the hydrocarbons. Less than 5 percent of crude oil will dissolve in water. Aromatic hydrocarbons, especially BTEX, tend to be the most water-soluble fraction of crude oil and other petroleum compounds. Benzene is 10 times more soluble than ethylbenzene or xylenes and is the most water soluble of the BTEX compounds (Williams et al., 2006). BTEX compounds also are the most volatile of the aromatic compounds and are considered to be VOCs and hence will disperse in the pores of the vadose zone. BTEX compounds have the lowest soil organic carbon sorption coefficients (Koc) of the most common aromatic hydrocarbons. Benzene is considered to be highly mobile in soil, toluene, moderate to highly mobile in soil, and xylenes moderately mobile in soil with Kocs of 59, 182 and 363 to 407 l/kg respectively. Benzene often is the main ground-water contaminant of concern at petroleum release sites because of its high toxicity and mobility as compared to other petroleum hydrocarbons (Williams et al., 2006).

Biodegradation is a major weathering process of crude oil and an important natural attenuation process. Rates of biodegradation vary with different microbial populations, hydrocarbons, and geochemical and hydrological conditions present in the subsurface. Nearly all soils and sediments have populations of bacteria and other organisms capable of degrading petroleum hydrocarbons. Resistance to biodegradation typically increases as the molecular weight of the hydrocarbon increases (Williams et al., 2006).

1.3 HYDROCARBON POLLUTION IN CAMEROON

Cameroon like any other country is in the pursuit of socio-economic development and achieving this requires industrialization. As previously stated, industrialization and urbanization are the primary push factors that encourage activities that require the use of hydrocarbons of all sorts. Cameroon is involved both upstream and downstream oil and gas operations. According to an article by (Kramer, 2020), Upstream oil and gas production and operations identify deposits, drill

wells, and recover raw materials from underground. They are also often called exploration and production companies. Downstream oil and gas operations are represented by refiners of petroleum crude oil and natural gas processors, who bring usable products to end users and consumers such as diesel, natural gas, gasoline, heating oil, lubricants, pesticides, pharmaceuticals, and propane. Finally, midstream operations link the upstream and downstream entities and constitute transportation and storage services of resources such as pipelines and gathering systems, oil refineries, petroleum product distributors, petrochemical plants, natural gas distributors, and retail outlets. Cameroon's main upstream company is the National Hydrocarbons Company (Société Nationale des Hydrocarbures, SNH). Table 2 illustrates the companies involved in the different stages of the oil and gas supply chain in Cameroon.

Table 2: Companies and Their Position in the Oil and Gas Supply Chain.

Upstream	Elf, Perenco, and Pecten International, CMS Nomeco, Phillips Petroleum, Trophy Petroleum, Euroil Cameroon, Mobil Producing Cameroon, Globex and Kelt Cameroon.
Midstream	SCDP
Downstream	Ola Energy Cameroon,

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Clearly therefore, Cameroon is rich in the petroleum resource and has the means of manipulation at all stages. It is inevitable then, that some accidents occur at any stage of these manipulations that result in the contamination of the subsoil and even surface waters.

1.4   CAMEROON'S POLICY ON POLLUTION OF SOIL AND GROUNDWATER.

The main institution responsible for managing the environment in Cameroon is the Ministry of Environment, Nature Protection and Sustainable Development, (MINEPDED). Cameroon has a range of national legislative and regulatory texts which relate to protecting the environment. Some of these, address the ways in which environmental impact assessments are to be conducted, in order to identify the potential risks of a project (such as the construction of an oil refinery) to environmental and human well-being and identify measures to eliminate and/or mitigate these risks. Others address the legal framework for water, including provisions relating to its conservation, management and the protection of public health (American Journal of Sociology, 2014). They assign responsibility to legal persons involved in activities which have the potential to degrade the soil and subsoil.

The legislative foundation for addressing environmental issues in Cameroon is the Law No. 96/12 of August 5, 1996, relating to environmental management. In Article 17, it states that "the promoter or owner of any development, labour, equipment or project which may endanger the environment owing to its dimension, nature or the impact of its activities on the natural environment shall carry out an impact assessment"(Savira & Suharsono, 2013). In Article 36 is more specific to the protection of the soil and subsoil as it states that "the soil and sub-soil as well as the limited renewable or non-renewable resources contained therein, shall be protected against any forms of degradation and jointly managed rationally by the competent Administrations."(Savira & Suharsono, 2013). Another law which relates more directly to the protection of groundwater is the Law No. 98/005 of April 14, 1998 on the water regime. In Article 4, it prohibits any actions likely to alter the quality of ground water, underground water or seas, or to damage public health, or aquatic and underwater flora and fauna. Similarly, Article 6 of this law states that any natural or legal person who owns an installation likely to lead to water pollution must take measures to reduce or eliminate these effects. The main implementing Decree of the Law relating to the water regime is Decree No. 2001/165/PM of May 8, 2001 establishing measures to protect ground and underground water against pollution. In article 3, it prohibits Spills, flows, discharges, infiltrations,

burial, spreading, direct or indirect deposits in water, of any solid, liquid or gaseous matter and, in particular, any industrial, agricultural or atomic waste liable to alter the quality of groundwater, harm the quality health, comfort and of life of the residents. It goes further to prohibit the release of oils, lubricants and other materials resulting from the cleaning and maintenance of motor vehicles, combustion machines and other similar devices.(Republic of Cameroon, 2001)

While Cameroon has ratified several laws and established decrees and orders to ensure the protection of the soil and subsoil, their implementation is still deficient.

1.5   THE AUTOMOBILE REPAIR INDUSTRY IN CAMEROON

1.5.1 Status Quo Of the Automobile Industry

The automotive sector is growing fast and 95% is fuelled by imported old pre-owned vehicles, while the new vehicles market is still very little with new vehicles share of annual new registrations stable around 5% of total, with only around 3.000 units sold per year.(*Focus2move*, 2017).

1.5.2 Factors Influencing the Growth Of The Automobile Repair Industry.

Wikipedia defines a vehicle breakdown as the mechanical failure of a motor vehicle in such a way that the underlying problem prevents the vehicle from being operated at all, or impedes the vehicle's operation so much, that it is very difficult, nearly impossible, or else dangerous to operate. This, and the fact that motor vehicles are machines that require regular maintenance is the main reason for the existence and growth of the automobile repair industry. According to Wikipedia, in 2014, The Royal Automobile Club (RAC) attended almost two million breakdowns in the United Kingdom. While such general statistics are not obtainable for Cameroon and Yaoundé in particular due to the fact that such records are not kept, the proliferation of automobile repair shops is an indication of their necessity. The following factors are responsible for the growth of the automobile repair industry.

1.5.2.1 Nature Of Automobiles.

Motor vehicles are the main means of transportation for people and goods in this day and age. For human safety and efficiency of time spent on the road, it is imperative that these vehicles should be in good condition. Motor vehicles are complex machines made of several parts that all need to be in good condition for the vehicle to be in good condition. This is the reason why maintenance milestones are set for vehicles; in order to make sure that all these parts are in good shape. Most mechanics still recommend the so-called 30-60-90 service interval, which puts your car in the shop for scheduled maintenance at 30,000 miles, 60,000 miles, and 90,000 miles (Cheapism, 2021). Although these milestones are not set in stone, they are a good average set to check things like battery, cables, transmission fluid and power steering, coolant, tires , oil, air filter, fuel filter, fluids, spark plugs and breaks etc (Cheapism, 2021).

1.5.2.2 State of Cars.

The state of cars accounts greatly for the growth of the car repair business. On the roads of Yaoundé, one can find cars of all states. From brand new to so old that they should not be driven anymore. The older the vehicle, the more prone it is to breakdowns and generally they require more frequent maintenance than new vehicles. Cameroonians opt for these used vehicles for a few reasons;

i. **Low Cost Price**: Second-hand cars are generally cheaper than brand new cars. Cameroon is a middle-income country and hence its inhabitants generally cannot afford brand new cars which are more expensive.

ii. **Low Import Tax**: Cameroon custom duties on cars depend on the condition of the cars, their age, as well as their horsepower and cylinder capacity. Vehicles with engines of less than 2000 cc are subject to a 58% tax while vehicles with engines of 2000 cc or greater are subject to a 77% tax (Rrichards, 2019). Therefore, it is only sensible for Cameroonians to prefer vehicles with low engine capacity. Also, tax is assessed on the CIF value of the car. (Cost, Insurance, Freight), i.e., the total value of the car, plus the cost of shipping insurance and the cost of the shipping itself. Given the high taxes, it's therefore paramount to the middle class to keep the cost of the used vehicle as low as possible when importing into Cameroon.

iii.   **Availability of Spare Parts**: Cameroonians opt to purchase cars whose parts can be found easily in the event of necessity for replacement. According to Isidore Biyiha, General Manager of the customs one stop shop in Douala, Toyota vehicles are the most imported into Cameroon (*Cameroon, First Automobile Market in Central Africa - Business in Cameroon*, n.d.), in particular the Toyota Yaris, Hilux, Avensis and Rav 4 all enjoy robust sales. Toyota is closely followed by Mercedes and the spare parts for these vehicles are available and easily obtainable.

While all cars are prone to breaking down sometimes due to malfunction or lack of care, just like the human body, cars are subject to failures due to age. Some failures common with old cars include: gear box problems, electrical problems, clutch failure, break failure and engine failure. The latter is usually due to overheating caused by damaged or broken thermostat, dirty or low coolant level, non-functioning cooling fan, failed radiator hose, internal or external coolant leaks, defective radiator cap. For this reason, there are repair shops dotted all over the town with a concentration in the residential areas.

1.5.2.3 State of roads.

According to (Mteboh, 2011), not up to 20% of roads in Cameroon were asphalted by 2011 and today, the improvement is not sufficient. Roads are constructed and within a few years or in critical cases, a few months, the roads begin to develop potholes. The asphalt which is often just a thin layer is eroded in heavy rains. However, even properly built roads are not designed to withstand the load of heavy-duty trucks. Road damage from one 18-wheeler is equivalent to the impact of 9,600 cars. A fully loaded tractor-trailer weighs 80,000 pounds, 20 times more than a typical passenger car at 4,000 pounds, hence the wear and tear caused by the truck is exponentially greater. This degradation is further amplified when such trucks are overloaded which is often the case. Therefore, having trucks on local roads instead of on interregional highways contributes greatly to the deplorable state of our roads (Murphy, 2017). Bad roads damage cars greatly and cause them to require more than regular maintenance. According to (IMart, 2020), some car parts that suffer greatly from the effects of bad road are:

Tyres: Tyres are major receivers of brunt damages from driving on rough roads. A pothole can damage tyres badly. If also, alignment is off, that will affect the way the tyres wear and

significantly reduce the lifespans of the tyres. One tyre may begin to wear off more than the others, therefore, increasing the chance of a flat tyres or even a blowout.

Wheels: If a wheel is bent, it won't roll smoothly. More so, the airtight seal between the tire and the wheel could be compromised. Rough roads damage wheels, if there is a visible damage, that wheel will most likely need to be replaced.

Alignment: As mentioned above, when the car alignment is off, it affects the way tyres wear off and reduce it's lifespan, thereby increasing the chances of a flat tyre or even a blowout. Bad roads can easily affect a car's alignment.

Suspension: A vehicles suspension system is responsible for the car's ability to balance. Driving consistently on bad roads can really affect the suspension. If a vehicle's suspension develops a fault, the car bounces or sways more than usual and this could be very hard to control or steer, even when at low speed.

1.5.3 Activities Carried Out in Automobile Repair Shops and Their Associated Substances.

Chemicals are an inevitable aspect of automobile repair. The activities carried out in the course of a day necessitate the use of and or encounter with toxic substances. Some of these activities and their associated chemicals include;

i. **Cleaning Parts**: There are many ways in which cars get oil on the engine. Under the hood of a car, one will find that there is engine oil, Air Conditioning (AC) compressor oil, and power steering fluid. Over time, most engines will develop some kind of leak. It could be a small leak from the head cover gasket or a cracked Positive Crankcase Ventilation (PCV) valve. It could also be spilled when filling the oil. Also, most car engines are open to the road on the underside allowing dirty, oily water and dust to splash and blow up into the car from underneath. Over the years very small amounts of oil and dirt just build up in this way therefore the older the car, the thicker the layer of grease (if not cleaned regularly) (JPhi, 2016). Dust, dirt, grease, and oxidation contamination can cause corrosion, slipping hazards, overheating, increase electrical resistance in contact areas, and many other issues

(TechSpray, 2021). It is usually when one of such incidents has occurred that a car is taken to the repair shop.

Oil sludge accumulates in areas where the lubricating oil works. Oil sludge can be hazardous to the health of an engine as it reduces the effectiveness of the oil, keeps the oil from dissipating heat properly, and reduces the sheer volume of the oil in the engine. In this case an engine flush cleaner is used to remove oil sludge (Bjornstad, 2017).

Cleaning car parts is often synonymous to degreasing which is accomplished with the help of degreasers. Degreasers are cleaners designed to remove grease, oils, cutting fluids, corrosion inhibitors, handling soils. Degreasing solvents are commonly packaged as an aerosol for convenience. Aerosols have the added advantage of providing a forceful spray that creates agitation and penetrates all the crevices of the part. Water-based degreasers are common in a trigger sprayer, or gallon or drum containers for immersion or batch system cleaning (TechSpray, 2021).

N-Propyl Bromide (nPB), TCE and PCE are highly toxic chemicals commonly used in degreasers to provide cleaning performance in a non-flammable formula. Once released into the environment, these chlorinated solvents pass quickly into soil and groundwater, where they are slow to break down and biodegrade. In other words, they are persistent.

ii. **Lubrication**: Motor oil, transmission fluid, gear oil, and grease are common lubricants that are used to reduce friction between parts, remove heat (i.e., act as a coolant), and act as a sealing liquid. In the course of performing this task of lubrication or changing out lubricant, oil often gets spilled on the ground. The most common lubricating oils are crude oil distillate fractions. Lubricating oils are composed of 80–90% petroleum hydrocarbon distillate which usually contains paraffinic or naphthenic compounds (Sullivan, 2005). Owing to their low water-solubility but high saturated vapour pressure, naphthene can contaminate both soils and groundwater. They vaporize mainly to the soil air in the vadose zone (Borowiec et al., 2008).

1.6 IMPACT OF HYDROCARBONS ON HUMAN HEALTH AND THE ENVIRONMENT.

The focus on the impact of hydrocarbons on human health has mostly been with regards to air pollution. Globally, the majority of air pollution is generated by the combustion of fossil fuel (coal, diesel fuel, gasoline, oil, and natural gas) for electricity production, heating, transportation, and industry (Perera, 2018). Fossil fuel combustion accounts for most of the global air pollution, generating 85% of airborne respirable particulate pollution along with PAHs, nitrogen and sulfur dioxides, mercury, and volatile chemicals that form ground-level ozone (O_3) (Perera, 2018). All of these are associated with adverse health effects. According to the World Health Organisation (WHO), ambient air pollution accounts for an estimated 4.2 million deaths per year due to stroke, heart disease, lung cancer, acute and chronic respiratory diseases. Also, the main of the driver of air pollution which is combustion of fossil fuels is a major source of greenhouse gas emissions which cause global warming.

However, hydrocarbons also affect human health and the environment via soil and groundwater pollution. Environmental contamination by hydrocarbons and petroleum products constitute nuisance to the environment due to their persistent nature and tendency to spread into ground and surface waters (Abioye, 2011). The growth of the automobile industry has contributed significantly to the increased use and dependency on hydrocarbons in the form of fuel, motor oil, lubricants etc.

BTEX compounds can enter the human body not only through the inhalation of vapour but also from the soil and skin exposure through the ingestion of contaminated crops or water. When in the human body, they are acutely toxic and have noticeable effects on human health, including headaches, dizziness and irritation to the mucous membranes. Benzene is a known carcinogen and neurotoxin with proven links between long-term exposure and leukaemia (Njobuenwu & Ukpaka, 2017).

Some PAHs, but not all, are acutely toxic, mutagenic, or carcinogenic. Some PAH metabolites bind to DNA, RNA and proteins; the resulting adducts may cause damage directly to cells and also have teratogenic or carcinogenic effect (Sataloff et al., 2001). Evidence arose from occupational studies on workers exposed to mixtures containing PAHs, and further long-term studies have demonstrated an increased risk of bladder and gastrointestinal, cancers (Istrate et al., 2018)

1.7 NOTIONS OF MODELLING AND SIMULATION

1.7.1 Definition

Mathematical models are an abstraction of the environmental system and they are based on our understanding of the physical principles that govern the system. The purpose of mathematical model building and modelling is to simulate the behaviour of the environmental system being modelled. Models are built to represent the system behaviour in a controlled computational environment (Aral, 2010). Simulation models are a special subset of mathematical or physical models that allow the user to ask "what if" questions about the system. Changes are made in the physical conditions or their mathematical representation and the model is run many times to simulate the impacts of the changes in the conditions (Carson, 2005).

1.7.2 Elements of a Model.

In its mathematical formulation, a model is comprised of five main elements:

- **External variables**

External variables are factors outside the scope of a system or experiment that however, have an impact on the system. Assumptions may be made about these external variables in order to predict what would change in the system given external influence on a system;

- **State variables**

These are variables that can be measured and describe the state or the conditions of the system under study. The selection of state variables is crucial for the structure of the model. However, these are usually evident variables;

- **Mathematical equations**

They are used to represent biological, chemical and physical processes. They describe the relationship between state variables and external variables. A singular process may be found in different environmental systems and contexts, reason why an equation may be used in more than one model;

- **Parameters**

Parameters are components of mathematical equations that characterize different aspects of a system. They may be variable in time and space or constant or constant for a specific system;

- **Universal constants.**

They are physical constants of wide application and frequent occurrence in physical formulas such as the speed of light ©, or planck's constant (h).

1.7.3 The modelling process.

It is impossible to include all sub-processes affecting the behaviour of a complex system. This is why a common feature of all models is that they are all based on the "concept" of simplification of the environmental system they are built to represent. This simplification, referred to as a conceptual model, may be achieved either by reducing the dimensionality of the system, eliminating less important processes that govern or affect the system, or by introducing simplified definitions for the parameters and variables that are used to describe the system (Aral, 2010). The process we generally go through on a modelling project is represented by Figure 1.
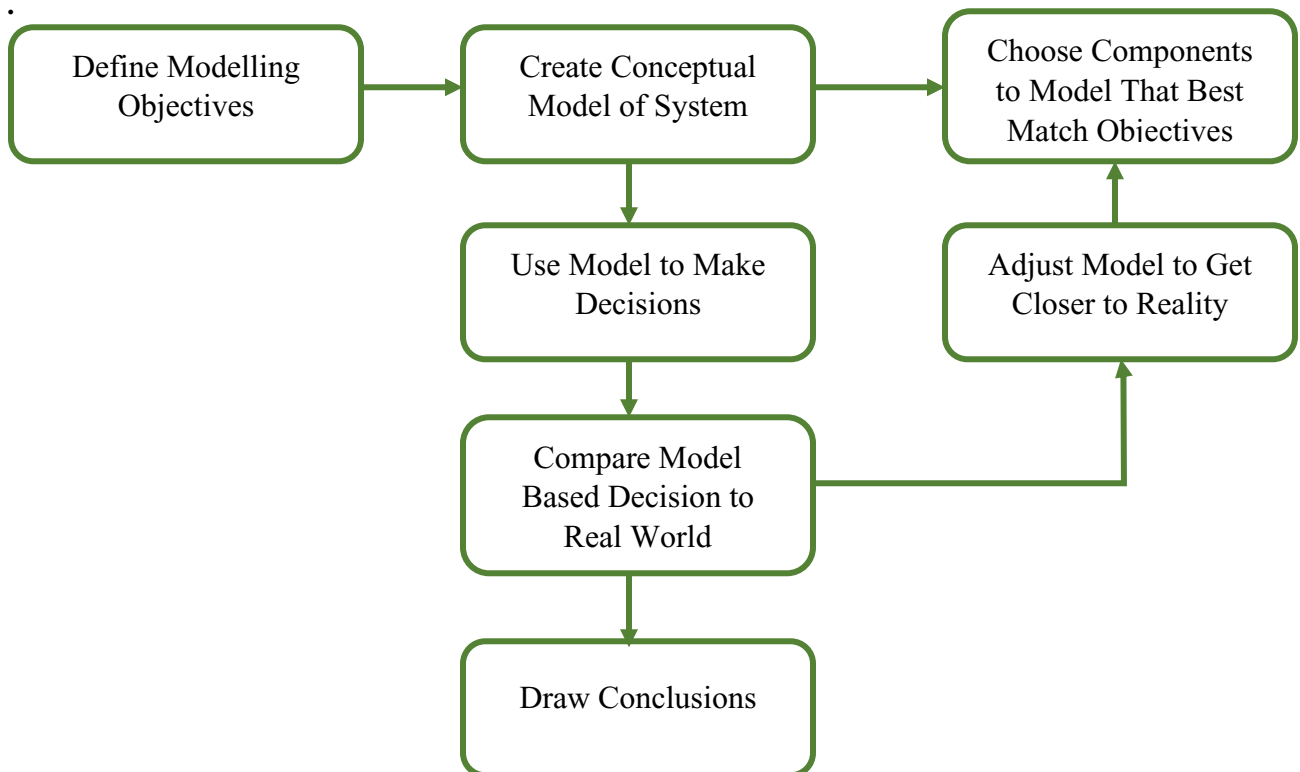
Figure 1: Modelling Procedure (Carson, 2005)

Mathematical models, unlike direct field observations and laboratory scale tests, are not very useful in the problem recognition stage of an environmental pollution problem. However, they are very useful tools in gaining control and finding solutions to our problems. They are cost effective and can be easily set up to test "what if" scenarios associated with a remedial application or a contamination problem (Aral, 2010).

Some important aspects of the modelling process include:

- **Verification**

A model is said to be verified if it behaves in the way in which the modeler wants it to behave. Verification is a test of the internal logic of the model. It is important to ensure that the inter relations between components is logical and consistent;

- **Sensitivity analysis**

The purpose of a sensitivity analysis is to identify the most sensitive components of the model, that is, the sensitivity of a variable to a given parameter. A sensitivity analysis determines the outcome of changes in the parameters of a process;

- **Calibration**

Calibration is an attempt to find the best possible accord between calculated and observed data by modifying certain parameters;

- **Validation**

This is the process of determining the degree to which a simulation model and its associated data are an accurate representation of the real world from the perspective of the intended uses of the model. This is an objective test of calibrated parameters with a set of independent data.

In our specific case, we will be creating a model to simulate and quantify the groundwater vulnerability of the Yaoundé soil. Groundwater vulnerability refers to the potential level of groundwater contamination, which is controlled by natural attenuation processes occurring in the unsaturated zone, from the source of pollution to the saturated zone of the aquifer and it depends on three principal processes:

i. The flow velocity of water and fluid pollutants through unsaturated and then saturated zones of the aquifer;

ii. Residual concentration of fluid pollutants at the groundwater table, which identifies the capacity of the unsaturated zone to attenuate its initial concentration; and

iii. Decrease in the pollutant concentration in the saturated zone by advective dispersion, diffusion, and geochemical processes (Fusco et al., 2020).

Given that attenuation processes in the unsaturated and saturated zones also depend on the type of pollutant, groundwater vulnerability is usually subdivided into intrinsic and specific vulnerability. Intrinsic vulnerability of an aquifer is considered as its capability to receive, convey, and attenuate a generic pollutant through the unsaturated and saturated zone depending on the geological, hydrological, and hydrogeological features of both. On the other hand, specific vulnerability is related to specific contaminants by considering their peculiar physical and chemical properties, with the associated attenuation processes occurring in the unsaturated and saturated zones (Fusco et al., 2020).

1.8 NOTIONS OF REMEDIATION OF CONTAMINATED SITES.

According to the Environmental Protection Act of 1990, a contaminated land is "Land which appears to the local authority in whose area it is situated, to be in such a condition, by reason of substances in, on or under the land that:

a) significant harm is being caused or there is a significant possibility of such harm being caused or;

b) significant pollution of controlled water is being caused, or there is significant possibility of such pollutions being caused."

It goes ahead to define the term "possibility of significant harm" as the risk posed by one or more relevant contaminant linkage(s) relating

to the land. It comprises:

(a) "The estimated likelihood that significant harm might occur to an identified receptor, taking account of the current use of the land in question;

(b) The estimated impact if the significant harm did occur i.e., the nature of the harm, the seriousness of the harm to any person who might suffer it, and (where relevant) the extent of the harm in terms of how many people might suffer it."

Having defined clearly a contaminated site therefore, we may now go ahead and define environmental remediation. The environmental protection act of 1990 defines remediation as

"(a) the doing of anything for the purpose of assessing the condition of

- the contaminated land in question; or
- any controlled waters affected by that land; or
- any land adjoining or adjacent to that land;

 (b) the doing of any works, the carrying out of any operations or the taking of any steps in relation to any such land for the purpose of

- Preventing or minimising, or remedying or mitigating the effects of, any significant harm (or significant pollution of controlled waters), by reason of which the contaminated land is such land or;
- Restoring the land or waters to their former state or;

 (b) the making of subsequent inspections from time to time for the purpose of keeping under review the condition of the land or waters."

1.8.1 Classification of treatment techniques.

There are several techniques that may be employed to remediate a contaminated site. They may be classified in several ways either according to mode of application or processes involved. The technologies involved may be contaminant or site specific. Remediation can be achieved by contaminated soil removal, contaminant removal, containment, stabilization/solidification, transformation, or different combinations of these mechanisms. It may also be necessary to apply these technologies in combination to achieve remediation goals, in particular, for cases of contamination by multiple contaminants (Yeung, 2010). Some classifications of remediation techniques include:

➤ Passive or Active Systems

Active systems engage in some affirmative action to remove contaminants from soil or water. The alternative is passive systems, which is usually accomplished by normal flushing processes occurring over time.

➤ Source Control or Plume Control
➤ In-Situ or Ex-Situ

The in-situ technologies involve applying chemical, biological, or physical processes to the subsurface to degrade, remove, or immobilize contaminants without removing the bulk soil. Ex-situ technologies on the other hand involve treatment of excavated contaminated soil bulk.

➤ Physical, Chemical, Biological or Thermal Treatments

Treatment techniques may either employ physical techniques, chemical, biological or thermal techniques. Also, a combination of these techniques may be used depending on the nature of specific contaminated site.

Remediation may also be classified based on the mode of transfer of contaminants in the subsoil. Whether the contaminants undergo phase transfer or degradation in the subsoil or both, will influence the choice of remediation technique.

1.8.2 Types of remediation.

We will discuss types of remediation based on the physical, chemical, biological and thermal classification.

a) Biological Treatments.

They include;

i. Biopile

This treatment involves the piling of petroleum-contaminated soils into piles or heaps and then simulating aerobic microbial activity by aeration and the addition of minerals, nutrients, and moisture. Heat and pH can also be controlled to enhance biodegradation (Khan et al., 2004).

ii.   Bioreactors

This is an ex-situ biological treatment which is accomplished by combining the excavated soil
with water and other additives. In this system the bacteria selected for breaking down the
contaminant is also added. The excavated soil is treated in a controlled bioreactor where the slurry
is mixed to keep the solids suspended and the microorganisms in contact with the contaminants.
After the process is completed, the slurry is dewatered and treated soil disposed (Khan et al., 2004).

iii.   Bioventing and Biosparging

The bioventing process injects air into the contaminated media at a rate designed to maximize in
situ biodegradation and minimize or eliminate the off-gassing of volatilized contaminants to the
atmosphere. Biosparging on the other hand, involves pumping air and nutrients into the saturated
zone. Bioventing pumps the air only into the unsaturated or vadose zone (Khan et al., 2004).

iv.   Landfarming

Landfarming is an above-ground remediation technology that reduces the concentration of
petroleum constituents present in soils through processes associated with bioremediation. This
technology usually involves the spreading of excavated contaminated soils in a thin layer (no more
than 1.5 m) on the ground surface of a treatment site and stimulating aerobic microbial activity
within the soils through aeration and/or the addition of nutrients, minerals, and water/moisture,
bacteria, which have been selected for their success in breaking down hydrocarbons, are frequently
added to the soil to achieve speedy degradation (Khan et al., 2004).

b) Physical-Chemical Treatments.

They include;

i.   Soil venting

It involves the installation of vertical and/or horizontal wells in the area of soil contamination. Air
'blowers' are often used to aid the evaporation process. Vacuums are applied through the wells
near the source of contamination to evaporate the volatile constituents of the contaminated mass
which are subsequently withdrawn through an extraction well. Extracted vapours are then treated
(commonly with carbon adsorption) before being released into the atmosphere (Khan et al., 2004).

ii.   Soil washing

Soil washing uses liquids (usually water, occasionally combined with solvents) and mechanical processes to scrub soils. Solvents are selected on the basis of their ability to solubilize specific contaminants, and on their environmental and health effects(Khan et al., 2004).

iii.   Air Sparging

It involves injecting atmospheric air, under pressure, into the saturated zone to volatilize groundwater contaminants and to promote biodegradation by increasing subsurface oxygen concentrations. The injected air forms channels through the contaminated plume as it flows upwards through the saturated zone and into the vadose zone. .The injected air volatilizes the contaminants in the flow channels and transports them to the vadose zone where they are either biodegraded or removed (Khan et al., 2004).

iv.   Reactive barriers

These are treatment walls that are installed underground to treat the contaminated groundwater found at hazardous waste sites. Treatment walls rely on the natural movement of water to carry the contaminants through the wall structure. As contaminated groundwater passes through the treatment wall, the contaminants are either trapped by the treatment wall or transformed into harmless substances that flow out of the wall(Khan et al., 2004)

c) Thermal Treatments.

The main thermal treatment is called thermal desorption and is a technology of physical separation based on heating the contaminated soil to volatilize water and organic contaminants. This implies that it only works for volatile contaminants.

These techniques may be used in conjunction with one another to address the specific problems of a contaminated site.

Conclusion.

Subsoil contamination by hydrocarbons and petroleum products constitute nuisance to the environment due to their persistent nature and tendency to spread into ground and surface waters. The growth of the automobile industry has contributed significantly to the increased use and dependency on hydrocarbons in the form of fuel, motor oil, lubricants. BTEX compounds are of

particular importance as they are highly water soluble, volatile, adsorb onto organic carbon and are frequently found in petroleum products. For this reason, this is the group of substances that we will investigate for in the next chapter. We will also seek to determine the long-term risk that such contamination poses by means of modelling and simulation.

CHAPTER 2: MATERIAL AND METHODS

Introduction

This chapter begins by presenting the region of study, bringing out in detail, its location, climate, relief, hydrogeology, vegetation and fauna, demography and economy in order to bring out the physical context in which the work was carried out. The research methods employed which comprised of qualitative analysis of well water samples and modelling and simulation as well as the material used to facilitate the processes, are described explicitly.

2.1 PRESENTATION OF STUDY AREA.

This work was carried out in Yaoundé (Centre Region) of Cameroon, precisely in Biyem-Assi which is a subdivision municipality of Yaoundé VI.

2.2 LOCATION OF STUDY AREA

It is the capital of Cameroon and chief town of the Centre region; situated between latitudes 3° 45' 50" and 3° 59' 55" North and longitudes 11° 22' 40" and 11° 30' 25" East at an elevation of about 760 m above sea level. Located 300 km from the Atlantic Ocean and surrounded by 7 hills, Yaoundé belongs to the Mfoundi Division of the Centre region and measures a total surface area of 183km2.It is surrounded:

- to the West, by the district of Nbankomo and to the North West by the Lekié Division;

- to the East, by the Mefou-Afamba Division;

- to the South, by the Mefou-Akono Division;

- and to the North, by the Okala District (Kewir, 2019).

2.3   DESCRIPTION OF BIOPHYSICAL ENVIRONMENT

2.3.1 Climate

Yaoundé experiences the classical guinea equatorial climate with four seasons as follows:

- long dry season (November to March);
- long rainy season (March to June);
- short dry season (July to August);
- short rainy season (September to November).

It receives an average annual rainfall of about 1700mm and experiences an average annual temperature of 25°C, with record high temperatures reaching 36°C and record low temperatures going down to 14°C Unlike other equatorial settlements, the climate of Yaoundé is moderated by relief and continentality. It is set amidst many hills and mountains altering the patterns of wind circulation, rainfall and temperature. Thus, compared with settlements like Douala and Limbe, located at a similar latitude, Yaoundé has a milder climate.(Ngala Ndi et al., 2015)

2.3.2 Relief

According to CUY & MINDHU, (2008), the relief of the town of Yaoundé is rough and dominated by hills alternating with valleys thus, shaping the area into domes and basins structure. Morphologically, the city is located largely in the Mfoundi watershed. There are four types of terrains:

- low slope ridges whose land is easily constructible;

- amenable hills whose slopes vary from 5 to 15%;

- hills difficult to develop with a slope greater than 15%;

- flooded valley bottoms generally of slopes less than 5%.

From these terrain types, two large areas emerge; non constructible areas which include areas with a slight slope (less than 5%) whose valley bottoms are usually floodable, and areas of steep slopes characterized by permanent erosion and landslide sites. Constructible or buildable areas are often sites with slopes between 5 and 15%.(Kewir, 2019)

2.4   HYDROGEOLOGY

Yaoundé is located in the South Cameroonian Plateau (average altitude 750 m) and dominated by smooth rocky hills (>800 m) with large convex slopes relayed by large swampy valleys (<700 m) of different widths (ranging from 50 to 150 m). About 90% of the Cameroon area is occupied by Precambrian basement rocks and the rest by sedimentary formations. The aquifers of these metamorphic formations (gneiss, migmatite, schist, etc.) are exploited through wells and boreholes for the supply of drinking water to the populations of rural and urban areas (Ruano et al., 2016). The differing hydraulic characteristics of the confining layers give rise to two aquifer levels. A perched aquifer in the iron crust whose permeability promotes rapid infiltration into areas where it is protected from erosion. An aquifer of alterite whose lower part composed of very weathered rock and relatively healthy blocks facilitate the circulation of water. Rates obtained in this aquifer are approximately 1 m^3/h (Ruano et al., 2016).
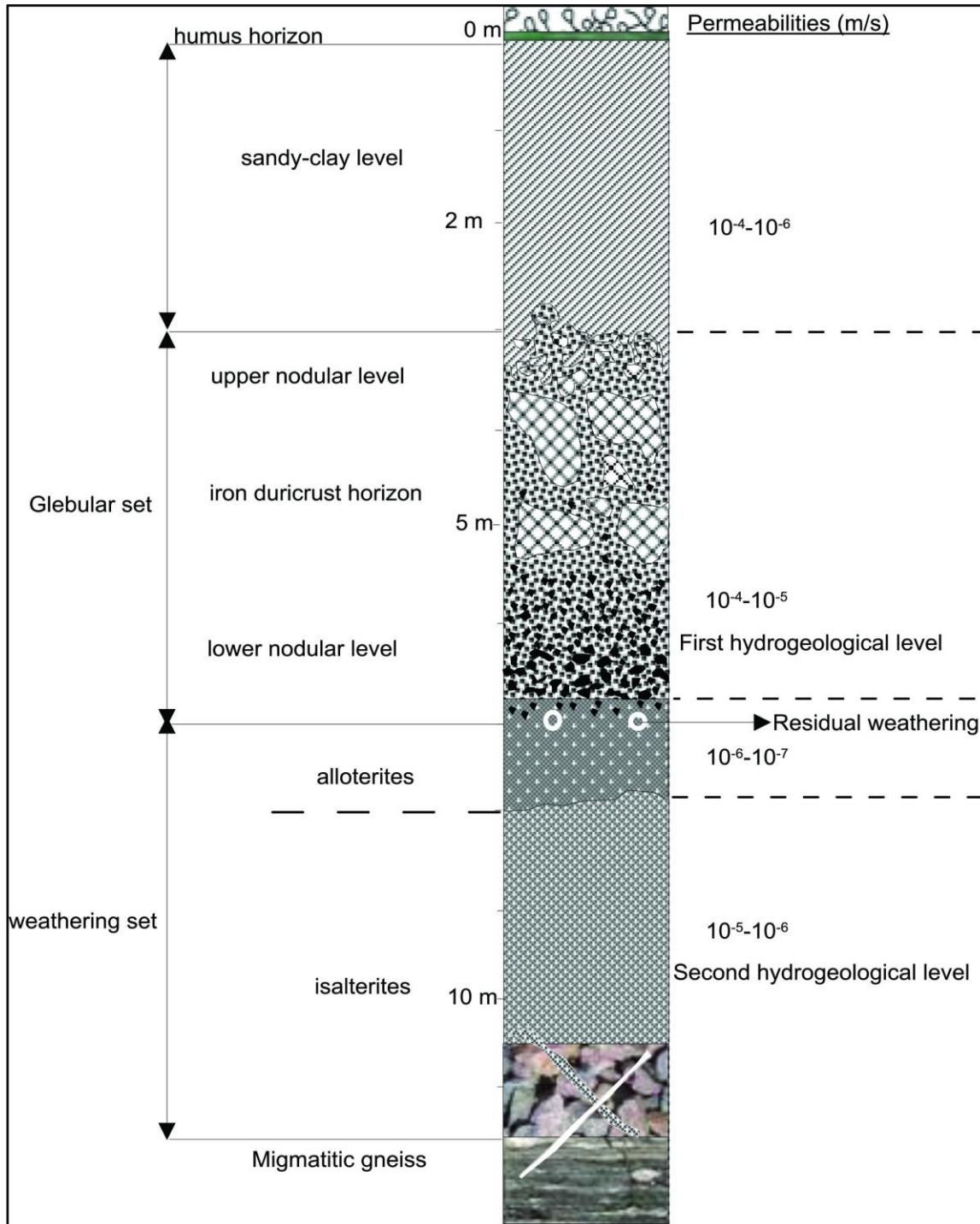
Figure 2 Graphic representation of the Yaoundé soil profile by (Ruano et al., 2016)

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2.4.1 Vegetation And Fauna

Yaoundé is part of the western sector of the Southern Cameroon Plateau. The area is characterized by gentle rolling chains of hills, and numerous valleys and wetlands; this varied physical landscape permits a combination of streams, hydromorphic soils and a great variety of plants and Fauna. This area is found in the heart of the Equatorial evergreen forest where forest vegetation is supposed to cover every square meter of the domain. The area is also in a tropical domain where the sun is constantly overhead and with high atmospheric humidity.(Kewir, 2019)

2.5   SOCIAL AND ECONOMIC ENVIRONMENT

2.5.1 Demography

Yaoundé has a population density of about 19126/km2.(Kewir, 2019). The current metro area population of Yaoundé in 2021 is **4,164,000**, a **4.31% increase** from 2020.(*Yaoundé, Cameroon Metro Area Population 1950-2021 | MacroTrends*, n.d.). The graph shows the total population estimation of Yaoundé with projections up to 2035.
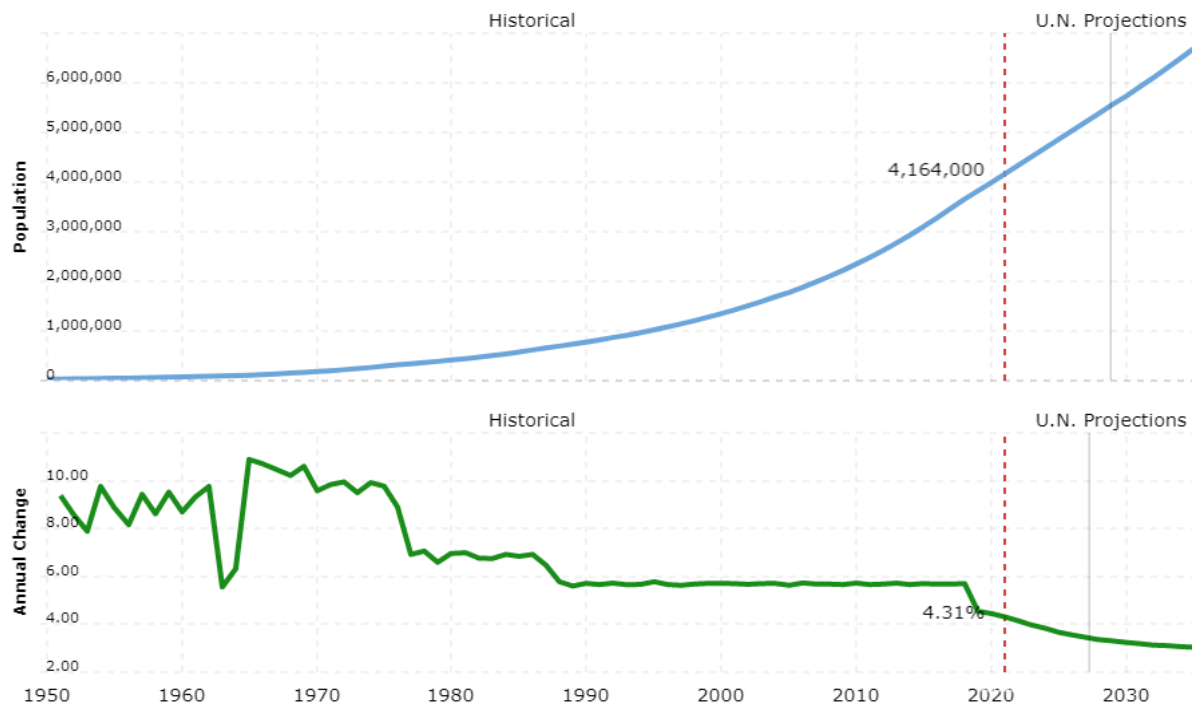

Figure 3: DEMOGRAPHY OF YAOUNDE WITH PROJECTIONS UP TO 2035

2.5.2 Economy

Most of Yaoundé's economy is centred around the administrative structure of the civil service and the diplomatic service. Due to these, Yaoundé has a higher standard of living and security than the rest of Cameroon. Major industries in Yaoundé include tobacco, dairy products, beer, clay, glass goods and timber transformation units whose implantation is facilitated mainly by the town's proximity to the source of raw material. It is also the regional distribution centre for coffee, cocoa, copra, sugar cane and rubber. Local residents mostly engage in urban agriculture like poultry farming and fish cultivation (Kewir, 2019).

2.6   MATERIAL.

The following tools and materials, were employed in order to carry out this work.

- A phone camera to take pictures in the field;

- The application "MAPS.ME" was used as a navigation guide and for taking geographical coordinates of sites visited during the data collection phase;

- The software "VS2DTI" was used for modelling and simulation of flow in porous media;

- The software "Mendeley" for citations and references;

- A laptop computer for registering the work;

2.7   METHODS.

In order to attain the objective of this work, both quantitative and qualitative research methods were used.

2.7.1 Collection Of Secondary Data.

This stage involved the consultation of documents such as books, dissertations and thesis, journals, articles, and web pages on and about the subject matter to obtain information which could not have been gotten otherwise from the field. Some such information included; information concerning generalities of soil and groundwater pollution in general and hydrocarbon pollution in particular, Cameroon's policies on handling of hydrocarbons, the adverse effects of hydrocarbon pollution on public health and the environment, as well as a description of the geographical environment and the socio-economic situation of our zone of study.

2.7.2 Collection Of Primary Data.

2.7.2.1 Case Study

A case study was used in order to get a better appreciation of the potential impact of repair shop spills on the environment. The main criterion that guided the choice of selection was the proximity between the well and the repair shop. A total of five wells were sampled for qualitative analysis.
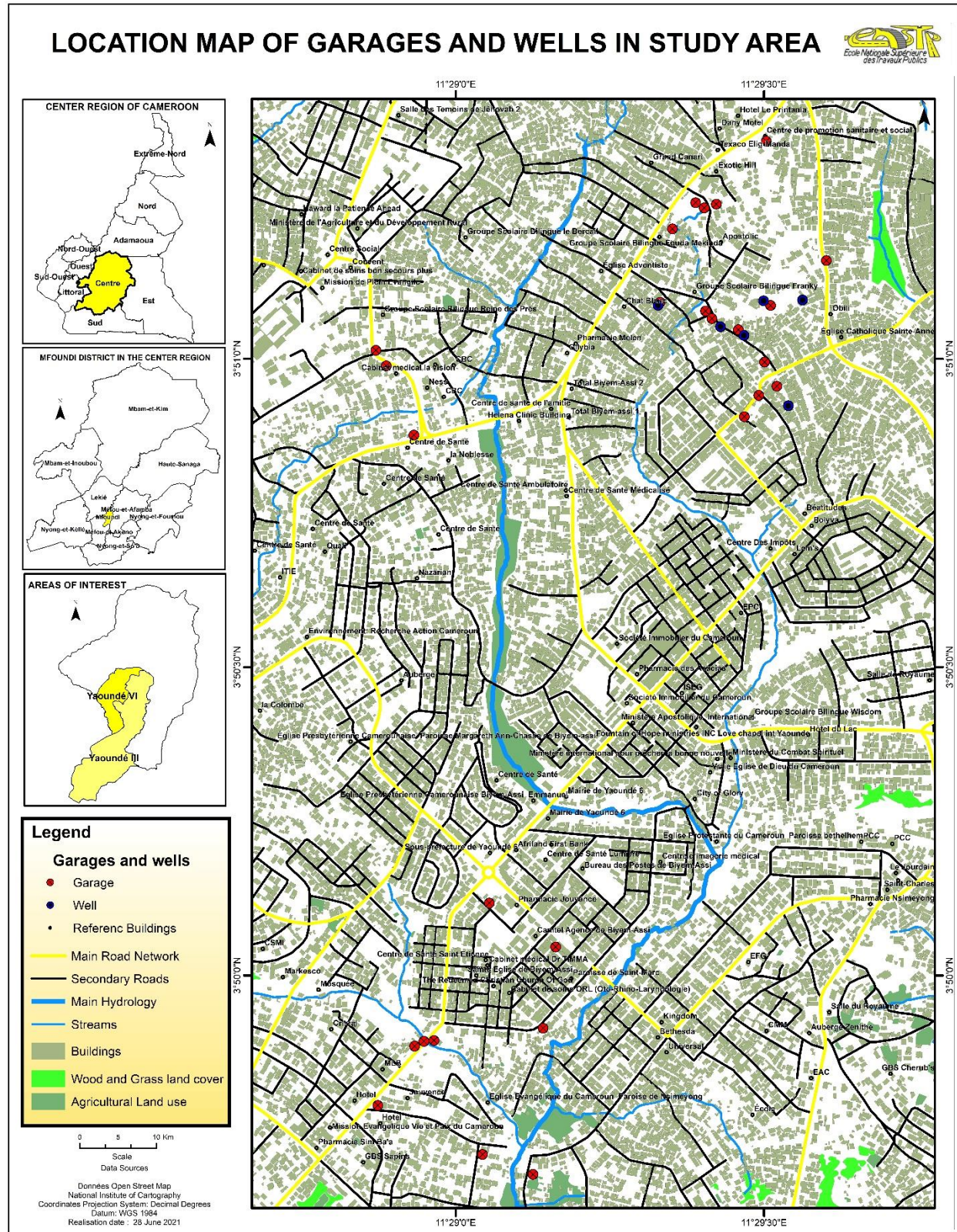
Figure 4: Location Map of Garages and Wells in Study Area, Biyem-Assi. (Map by Tan Sangnyuy)

2.7.2.2 Methodology for qualitative analysis of water sample: Detection of Alkanes, Aromatic Hydrocarbons and Polycyclic Aromatic Hydrocarbons.

MATERIALS

- Separating funnel
- Glass funnel
- Stopper
- Clamp stand
- Conical flask
- Measuring cylinder
- Spatula
- Centrifuge

METHODS

Groundwater Sampling

For each well, two 300ml groundwater samples were collected into clean glass bottles. One, to be tested for saturated and aromatic hydrocarbons and the other for putative metabolites. The sample for metabolites was acidified immediately to pH < 2 with 50% HCl to preserve said putative acidic metabolites (Gieg & Suflita, 2002). The other sample on the other hand did not require any preservation.

For each sample a new and clean sampling container and sampling material was used as it is important to take the sample as 'cleanly' as possible. The following procedure was employed:

1) Fill the sampling container completely with unfiltered water. Do not allow the sample container to overflow to prevent dilution of the preservative.
2) Close the sampling container securely and shake the solution mildly.
3) Mark the sampling container.
4) Samples do not have to be kept cool after sampling (when using a preservation solution) (Wittebol & Dinkla, 2015).

Sample Preparation.

The sample was prepared by liquid-liquid extraction using a separating funnel. Typically, two or three repeat extractions are required with fresh organic solvent to achieve quantitative recoveries. For one-step liquid–liquid extractions, equilibrium dissociation constant, k_d, must

be large, i.e., >10, for quantitative recovery (>99%) of the compound in one of the phases. The following procedure according to   (Sataloff et al., 2010) was employed.

1) Set up the clamp stand and place the separating funnel securely on the clamp and the conical flask directly beneath it.

2) Using a glass funnel to avoid spillage, pour 100ml of groundwater sample into the separating funnel (Wittebol & Dinkla, 2015).

3) Using the same glass funnel, add 100ml of water immiscible organic solvent (We used isooctane in our case and used 50ml of groundwater sample and 50ml of organic solvent due to limited amount of organic solvent).

4) Close the separating funnel with the stopper, take it out of the clamp and shake gently at first then vigorously to achieve homogeneity. By placing the stoppered end of the separating funnel into the palm of the hand an inversion of the funnel can take place. This process is repeated for approximately 1–2 min (inverting the separating funnel approximately 5–6 times). Open the stoppered end regularly during this step to release pressure. (Sataloff et al., 2010)

5) Place the separating funnel back on the clamp and allow the mixture to settle for approximately 5mins.

6) When two stable phases are observed, open the tap and let out the bottom phase (aqueous phase) into the conical flask.

7) Open the stopper and let out the top phase (organic phase) into another conical flask from the top (Sataloff et al., 2010).

Sample Clean up

1) Use 4 ml of organic phase for clean-up.

2) Using a spatula, add 150 mg of magnesium sulphate ($MgSO_4$) to the mixture to dry out any water left in it thereby concentrating the organic compounds.

3) Stir or swirl the solution and set aside to settle for a couple of minutes. If the solution is dry then there still should be fine drying agent still visible.

4) If instead, thick clumps of hydrated $MgSO_4$ precipitate are observed at the bottom of the flask, add a little more drying agent.

5) If the solution is dry, then remove the drying agent by centrifugation (Shannon, 2010).

Sample Preparation for Metabolites (Acid Succinates)

Detection of petroleum hydrocarbon metabolites, that is acid succinates, necessitates the derivatization of the succinates. This is done in order to bring down their boiling point. During derivatization, functional groups are modified in order to increase analyte stability and volatility. This prevents the absorption of succinic acid on the injector, allows the compound to volatize into the gas chromatograph column and normalizes the peak heights and area of the chromatograms. The derivatizate used here was - bis- (trimethylsilyl) -trifluoroacetamide (BSTFA (≥99.9 %) Supelco, USA).

Samples were capped and heated at 70 ºC to convert the targeted analytes to their trimethylsilyl derivatives.

Derivatization was conducted in a well-ventilated area.

The following derivatization protocol was followed:

Derivatization Protocol.

Materials

- Oven
- 2 ml Reaction Vial with cap
- Syringe

Procedure

- Using a syringe, inject 1ml of organic phase in reaction vial
- Using another syringe, inject 0.5ml of BSTFA
- Cap tightly and mix well
- Place in oven and heat at 70°C for 15 minutes
- Cool to room temperature (Thermo Scientific, 2008).
- Inject 1 µL of mixture in gas chromatograph.

Characteristics and Settings of Gas Chromatograph.

The capillary column was 30 m long, 0.25 mm outer diameter and 0.25 μm liquid-stationary phase thickness with a liquid stationary phase (5 % diphenyl and 95 % polysiloxane). Carrier gas of chromatography – helium. Succinates were identified by comparison with database mass spectra of compounds or analysing ions characteristic of mass spectra. For the identification of compounds, a computer used the mass spectra measured by standard compounds. The spectrum of analytes was selected for comparison by a computer estimating the probability of the presence of the provided compounds.

- The oven temperature was programmed from 45 °C for 2 min, then 16 °C/min to 250 °C for 1 min, then 50 °C/min to 315 °C and held constant for 5 min.
- The injector temperature was set at 280 °C
- Injection mode splitless (1 min), injection volume was 1 μL, split ratio 1:20 and the ion source voltage 70 eV.
- Mass spectra scan range of m/z 40–500 amu with mass scan time 0.2 seconds, interface temperature 280 °C (Jarukas et al., 2018).

2.7.3 Modelling And Simulation

In order to attain one of our objectives, which was to project the effects of continuous pollution of the soil and subsoil into the environment, the software VS2DTI was used - The VS2DI package, which is developed and maintained by USGS (https://www.usgs.gov/software/vs2di-version-13) contains all the tools that a user needs to create, run, and view results for a simulation of flow and transport through variably saturated porous media (Lappala et al., 1987). The entire subsoil system and all its components are very complex and hence it is impossible to include all sub-processes. Therefore, as aforementioned, the system had to be simplified by creating a conceptual model.

2.7.3.1 The Conceptual Model

A common feature of all numerical models is that they are all based on the simplification of the environmental system they are built to represent. The simplification, which is referred to as a conceptual model (Figure 5), was achieved in our case by

- Reducing the dimensionality of the system. The model was reduced to two dimensions in the x and z planes. It runs for 10.5 m in the z axis and 18m in the x axis.
- Eliminating less important processes that govern or affect the system such as transpiration and by considering only the intrinsic vulnerability of the aquifer, that is, the aquifer's capability to receive, convey, and attenuate a generic pollutant through the unsaturated and saturated zone depending its geological, hydrological, and hydrogeological features.
- Introducing simplified definitions for the parameters and variables that are used to describe the system. In particular, simplifying the layers of the Yaoundé soil profile (Table 3), into textural classes as follows

Table 3: Soil Layers and Their Corresponding Textural Classes.

Soil layer	Depth	Textural Class
Sandy Clay	0 m – 3 m	Sandy Clay
Glebular Set	3 m – 7 m	Sandy loam
Alloterites	7 m – 8 m	Clay CP
Isalterites	8 m – 10.5 m	Medium Sand
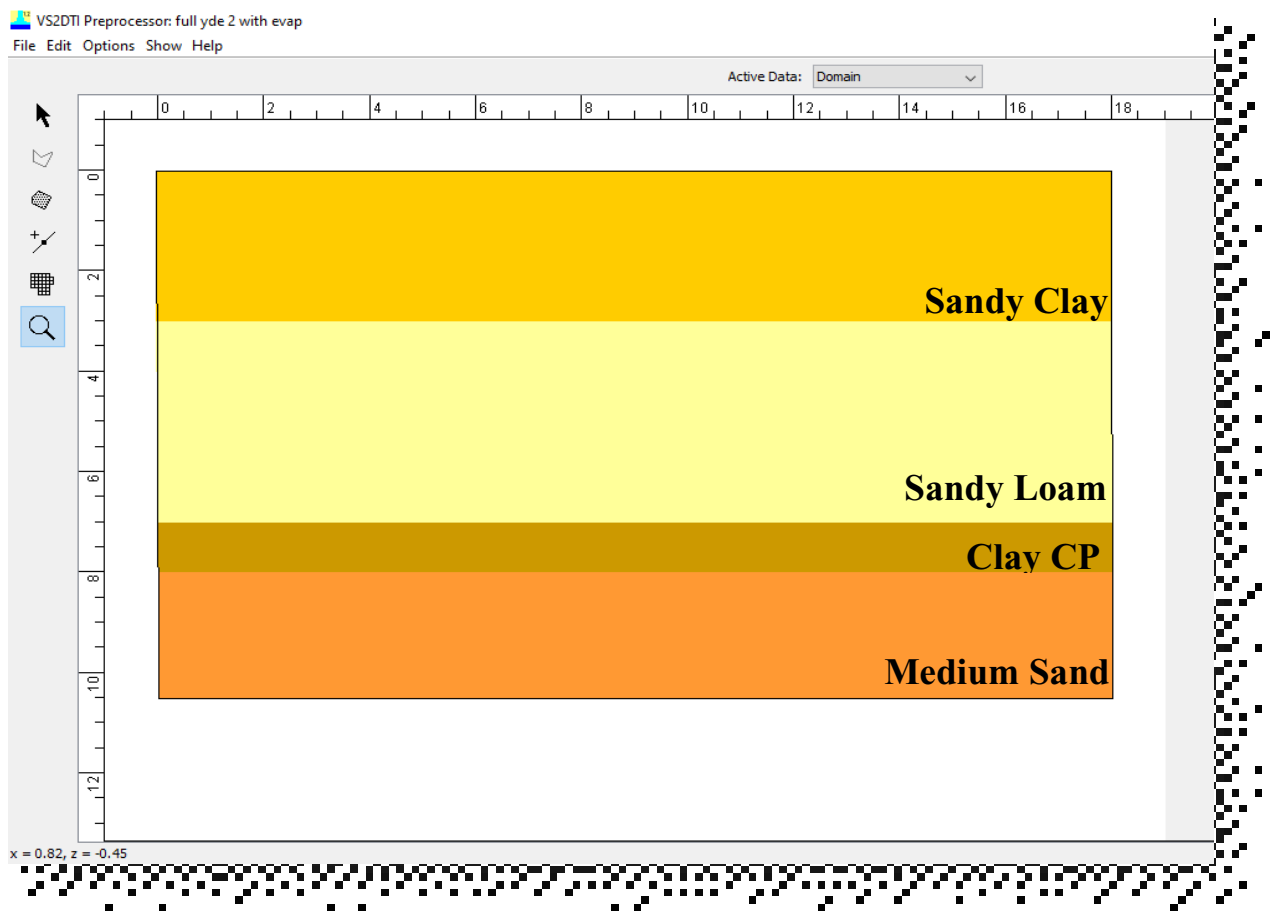
Figure 5: Textural Classes of Soil Model

These approximations were made based on the similarity in soil properties such as porosity and specific storage.

Table 4: Main Properties of Soils Used in the Model.

Name	Sandy Clay	Sandy loam	Clay CP	Medium Sand
Saturated Khh	0.029	0.7	0.048	400
Specific Storage	1E-4	1E-4	1E-4	1E-4
Porosity	0.38	0.496	0.38	0.375
Retention Moisture Content (RMC)	0.1	0.15	0.068	0.02

2.7.3.2 The simulation

The simulation was made to run over a period of one year, alternating between rainy and dry periods. The meteorological data was used was obtained from (Weather Atlas, 2020) as shown in Table 5.

Table 5: Average Annual Rainfall Data for Yaoundé from (Weather Atlas, 2020)

Month	Number of rainfall days	Amount of rainfall (mm)	Humidity (%)
January	3	19	79.5
February	4	42.8	79.5
March	12	124.9	81
April	14	171.3	82
May	17	199.3	84
June	14	157.1	85
July	11	74.2	85.5
August	12	113.7	86
September	20	232.3	85.5
October	23	293.6	85
November	11	94.3	82
December	3	18.6	79

Simulating both flow and contaminant transport, the boundary conditions were set as follows:

- **The lateral boundaries:** The flow boundary condition for the lateral boundaries was a fixed total head value corresponding to a level of the water table at -3.1m below the land surface, in agreement with typical hydrogeologic setting of the study area. As for the transport boundary conditions, the specified concentration of contaminant on the land surface was set to 0g.d^{-1}. The lateral boundary conditions remained unchanged throughout the entire simulation.

- **The lower boundary:** The conditions at this boundary were kept constant throughout the simulation as well. That is: no flow across boundary (q=0).
- **The top boundary:** The flow conditions were specified as alternating wetting phases representing rainy periods (Table 6) and a dry phase representing the days without rain. The wetting periods or rainy periods were characterised by the upper boundary condition of the model domain set as vertical flux entering through the ground surface. Variable daily rainfall values were obtained by using the data in table above and the following formula:

$$\text{Specified flux into domain} = \frac{Amount\ of\ rainfall\ (m)}{Number\ of\ rainfall\ days\ (d)}.$$

In addition to that, the inflow of contaminant was specified at a maximum value of $1 \text{gm}^{-2}\text{d}^{-1}$ for every rainfall period.

Table 6: Wetting Periods and Corresponding Flux into Domain.

Period length (d)	Specified flux into domain (m/d)
3	0.0063
4	0.01
12	0.01
14	0.012
17	0.012
14	0.011
11	0.0067
12	0.0095
20	0.012
23	0.0128
11	0.0086
3	0.0062

The drying periods on the other hand were characterised by evaporation. The evaporation parameters were as follows;

i. **Pressure Potential of Atmosphere (HA)**, [L]: Computed using the Kelvin equation which is given by;

$$HA = \frac{R \times T \times \ln(ha)}{Mw \times g} \quad \text{where}$$

R = universal gas constant = 8.314 J.mol^{-1}. K^{-1}

T = temperature in degrees Kelvin

h_a = relative humidity of atmosphere = 71 %

M_w = molecular weight of water = 18 g.mol^{-1}

g = acceleration due to gravity = 9.8 m.s^{-2}

ii. **Potential Evaporation (PEVAL)**, [L]/[T]: which we obtained from literature. According to (Guenang et al., 2016) the value is approximately equal to 1100 mm/year (0.003 m/d)

iii. **Surface resistance (SRES)**: 1/[L]. The value was set to the reciprocal of the depth of the top node. The depth of the top node is equal to the depth of the first grid element of the model.

Depth of top node = 0.2 m. Therefore, SRES = 5 m^{-1}

Figures 6 to 9 show the windows in the VS2DTI software in which alternation between rainy and
dry periods were specified, the specific evaporation parameters, the boundary conditions for the
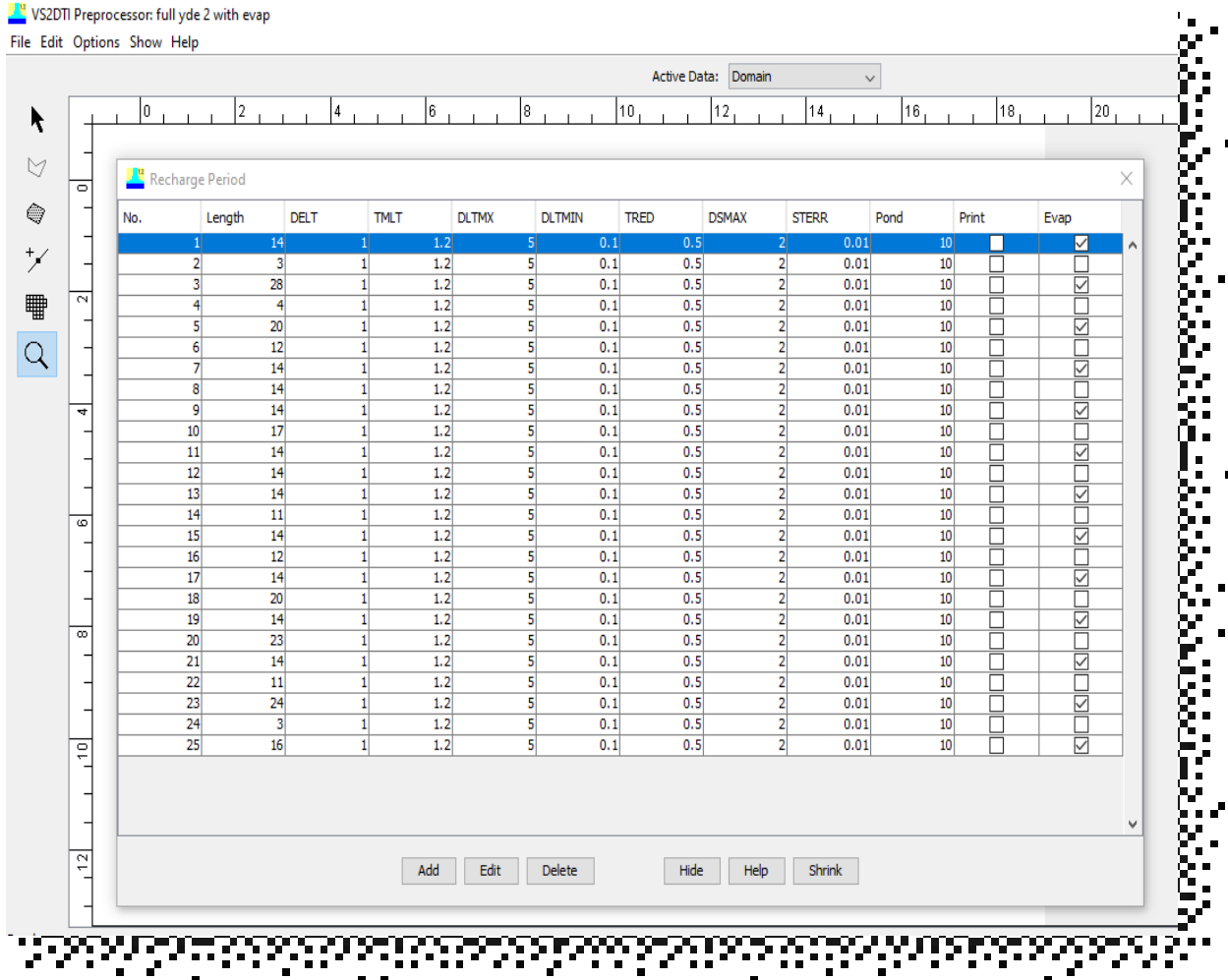drying period and the boundary conditions for the wetting periods respectively.

Figure 6: Simulation Periods Alternating Between Rainy and Dry periods
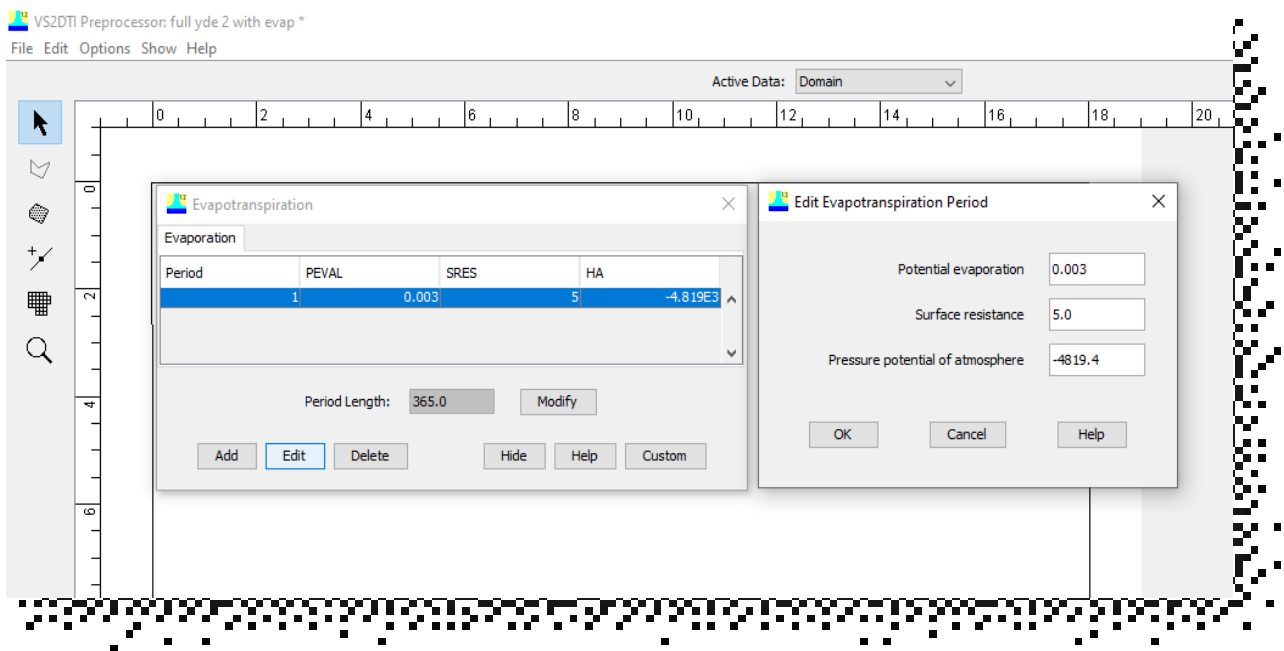
Figure 7: transpiration parameters.
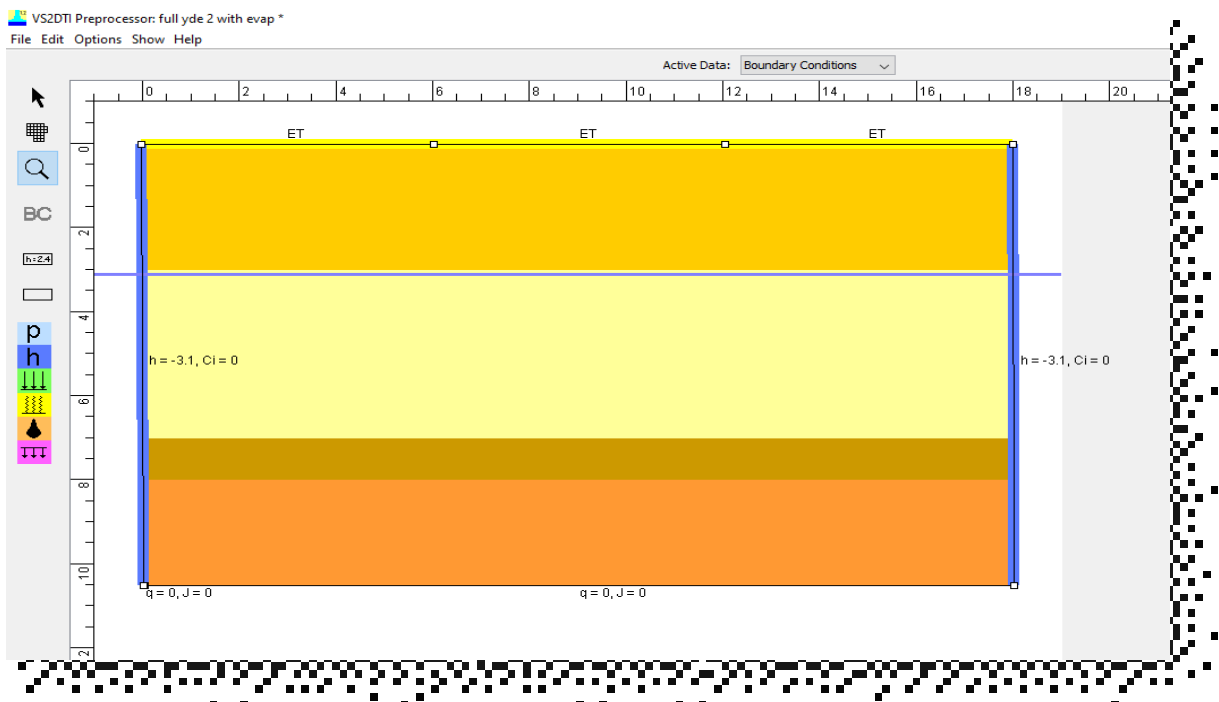
Figure 8: boundary conditions for drying period.
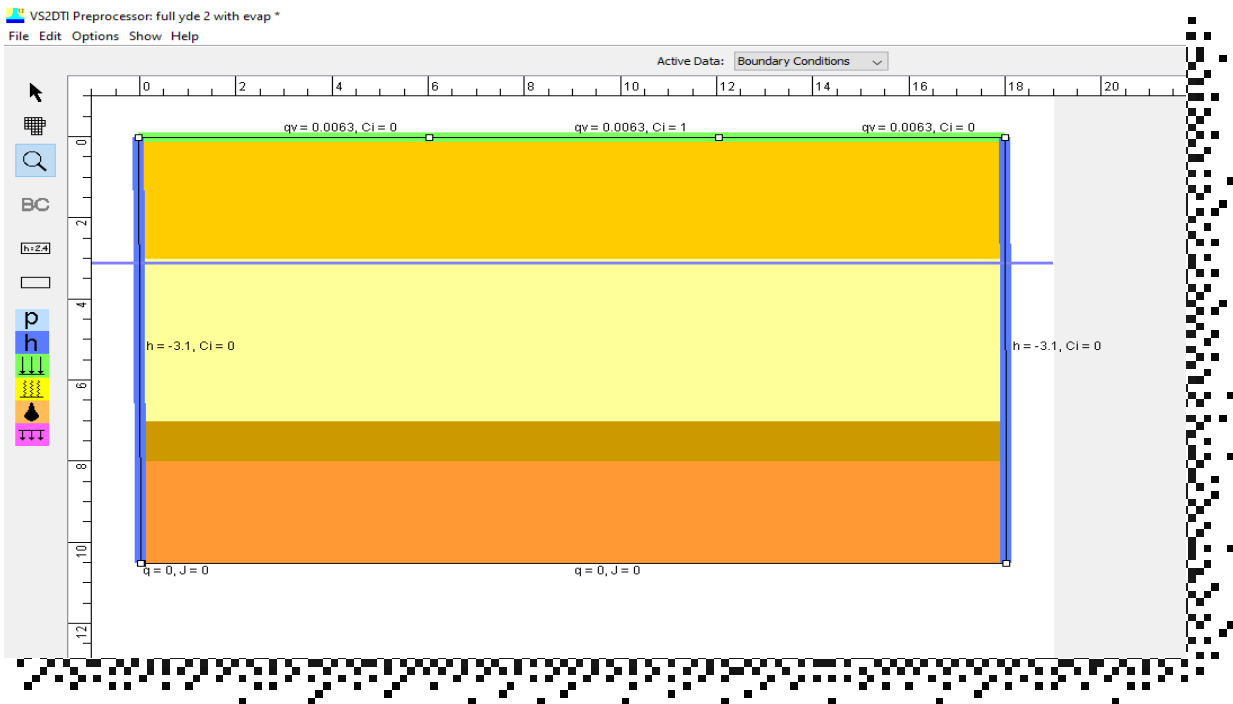
Figure 9: boundary conditions for wetting period.

Hydrodynamic parameters for hydrocarbon pollutants such as the coefficient of molecular diffusion in the porous medium (CMD), and longitudinal-transverse dispersivity (LD and TD, respectively) were defined. Following the model grid distribution, the longitudinal dispersion was set to 0.5m and the transverse dispersion to 0.05m.

These values were kept constant irrespective of the soil textural class since the model simulates the intrinsic vulnerability of the system

CHAPTER 3: RESULTS AND DISCUSSION.

Introduction

In this chapter, we will present the results obtained from the research carried out. The results will be discussed and interpreted and these interpretations will help us gauge the danger that garage malpractices pose to human and environmental health as well as propose appropriate solutions to mitigate the damage caused and prevent further environmental degradation.

3.1 RESULTS OF QUALITATIVE ANALYSIS

The well water samples were collected from 5 wells located in the areas of Chapel Obili and Biscuiterie in Biyem-assi. These wells were chosen for their proximity to garages. For each well, two samples were collected and prepared for GC-MS analysis following the procedures described in chapter 2. One set of samples was used to test for alkanes and the other set of samples was used to test for metabolites of BTEX. The mass spectrometry detected substances at different retention times and after comparing the results with the National Institute of Standards and Technology (NIST) database, the software drew up the most probable substances.

The first set of samples, analysed primarily for alkanes gave the results shown in tables 7 to 11. The highlighted substances are not considered to be contaminants from the water but from the solvent used during sample preparation.

Table 7: GC-MS Results of Well 1, Sample 1.

Retention time /mins	Well 1, Sample 1
1.756	n-Hexane
2.197	**Hexane, 2,2-dimethyl-**
3.153	Heptane
3.187	1-Hexene, 2-methyl-
3.238	**Pentane, 2,2,3-trimethyl-**

Table 8: GC-MS Results of Well 2, Sample 1.

Retention time /mins	Well 2, Sample 1
2.203	**Hexane, 2,2-dimethyl-**
3.198	**Hexane, 2,2-dimethyl-**
3.158	Heptane

Table 9: GC-MS Results of Well 1, Sample 1.

Retention time /mins	Well 3, Sample 1
2.203	**Hexane, 2,2-dimethyl-**
3.164	**Pentane, 2,2,3-trimethyl-**
3.204	1-Hexene, 2-methyl-

Table 10: GC-MS Results of Well 1, Sample 1.

Retention time /mins	Well 4, Sample 1
2.208	**Hexane, 2,2-dimethyl-**
3.164	Heptane
3.198	**Hexane, 2,2-dimethyl-**

Table 11: GC-MS Results of Well 1, Sample 1.

Retention time /mins	Well 5, Sample 1
2.208	**Hexane, 2,2-dimethyl-**
3.164	Heptane
3.204	Cyclohexanamine

The results obtained from GC-MS analysis of water samples can be summarized as shown in table 12.

Table 12: Contaminants found in Wells Following First Analyses.

Well	Contaminant
Well 1	n-Hexane; Heptane; 1-Hexene,2-methyl
Well 2	Heptane
Well 3	1-Hexene,2-methyl
Well 4	Heptane
Well 5	Heptane; Cyclohexanamine

Heptane

Uses

n-Heptane is an aliphatic alkane with the molecular formula C7H16. Naturally occurring n-heptane is isolated from natural gas, crude oil, or pine extracts. It has historically been used as a test fuel component in antiknock test engines as it causes knocking and is therefore an undesirable component of gasoline. Many different isomers of n-heptane are used in organic syntheses and are ingredients of gasoline, as petroleum mixtures used as fuels or solvents and mixed isomers for use as thinners in paints and coatings (Clough, 2014a).

Environmental Fate and Behaviour

Heptane is a seven-carbon aliphatic compound that is a natural constituent in the major paraffin fraction of crude oil and also found in natural gas. Pure n-heptane is a colourless liquid that is highly flammable and lighter than water. It has a gasoline-like odour with an olfactory threshold around 200mgm^{-3} (low) and 1280mgm^{-3} (high). Heptane has a molecular weight of 100.2 g mol^{-1}. At 20 °C, n-heptane has a solubility in water of 3.4 mgl^{-1}, an estimated vapor pressure of 46 mmHg, and a Henry's law constant of 2.0 atm-m^3 mol^{-1}. The log octanol/water partition coefficient is 4.66. If released into water, n-heptane is expected to adsorb to suspended solids and sediment based upon an estimated Koc of 8200. Based on 100% degradation within 25 days during aerobic biodegradation screening tests, n-heptane is expected to biodegrade in natural water. Volatilization from water surfaces is expected to be an important fate process based on the preceding estimated Henry's law constant. This however may be attenuated by adsorption to suspended solids and sediment in the water column. If released to dry

soil, n-heptane may volatilize thanks to its high vapor pressure. Adsorption to moist soil is expected to attenuate volatilization. n-Heptane is expected to biodegrade in soil based on 100% degradation after 4 and 25 days in screening tests using gasoline contaminated soil (Clough, 2014a).

Exposure and Monitoring

Because n-heptane can exist as a liquid or vapor at normal temperature and pressure, the most probable route of exposure, as seen in most occupational settings, occurs by either dermal contact or inhalation. Oral exposure most likely is either incidental or accidental. Monitoring data also indicate that the general population may be exposed to n-heptane via ingestion of food and drinking water, although these pathways are considered minor when compared with inhalation (Clough, 2014a).

Hexane

Uses

n-Hexane is a component of many products associated with the petroleum and gasoline industries (one study found 1.5% of vapours encountered during gasoline handling were attributed to n- hexane). It is sometimes used as a denaturant for alcohol, and as a cleaning agent in the textile, furniture, and leather industries, although it has largely been replaced with other less toxic 'green' solvents. The aforementioned uses, however, are declining due to its known neurotoxicity (Clough, 2014b).

Environmental Fate and Behaviour

Hexane is a six-carbon aliphatic compound that is a natural constituent in the paraffin fraction of crude oil and is also found in natural gas. Pure hexane is a colourless volatile liquid that is highly flammable and lighter than water. It has a gasoline-like odour with an olfactory threshold of about 465 mg m?3 (130 ppm). Hexane has a molecular weight of 86.17 g mol^{-1}. At 20 °C, n-hexane has water solubility of 9.5 mg/l, an estimated vapor pressure of 120 mm Hg, and a Henry's Law constant of 1.8 atm m^{-3} mol^{-1}. The log octanol/water partition coefficient is 3.90 (Clough, 2014b).

Exposure and Monitoring

Because n-hexane can exist as a liquid or vapor at normal temperature and pressure, the most probable route of exposure, as seen in most occupational settings, would occur by either dermal contact or inhalation. Minor exposures may occur from fugitive vapours that occur when refuelling automobiles at gasoline stations. Ingestion or dermal contact would be a less common exposure route, with the former expected to occur either inadvertently or during an accidental poisoning and the latter occurring from a spill (Clough, 2014b).

Cyclohexanamine.

Description and Use

Cyclohexanamine is a clear, colourless to yellow liquid organic compound, belonging to the aliphatic amine class and has the formula, $C_6H_{13}N$. It is basically cyclohexane carrying an amino substituent. It is soluble in water and can be miscible with common organic solvents such as ethanol, ethyl acetate, heptane, benzene and the like. Cyclohexanamine has a molecular weight of 99.18, a melting point of -18°C, boiling point 134.5°C and a density of 0.867 g/mL at 25 °C Vapour pressure at 20 °C is 11mmHg and it is highly basic with a pH value of 11.5(100g/l).

Cyclohexanamine can be used in the preparation of the additives used in petroleum products. It is also used as a corrosion inhibitor as well as a chemical intermediate in a very wide range of industrial   fields. Cyclohexanamine is a corrosive chemical and contact can severely irritate and burn the skin and eyes with possible eye damage. Inhaling Cyclohexylamine can irritate the nose and throat. Exposure can cause headache, dizziness, light-headedness, and passing out. It may cause a skin allergy and repeated exposure may damage the liver and kidneys (Chemical Book, 2017; Forschungsgemeinschaft, 2003).

The second set of samples, analysed primarily for metabolites of BTEX gave the results shown in the tables that follow. The highlighted substances are not considered to be contaminants from the water but from the solvent and derivatizing agent used during sample preparation.

Table 13: GC-MS Results of Well 1, Sample 2.

Retention time/min	Well 1, Sample 2
1.648	**Silane, chlorotrimethyl-**
2.197	Pentane, 2,2,4-trimethyl-
3.13	**Pentane, 2,2,3-trimethyl-**
4.343	**Acetamide, 2,2,2-trifluoro-N,N-b...**
5.11	**Bis(trimethylsilyl)trifluoroacet...**
5.121	**Trisiloxane, octamethyl-**
5.253	**1-Pentamethyldisilyloxycyclopentane**
5.304	**N-(Trimethylsilyl)acetamide**
5.487	Formamide, N,N-diethyl-
5.527	Ethanimidic acid, N-(trimethylsi...
5.556	**2,3,5,6-Tetramethylphenylcyanide**
5.619	**Ethylbis(trimethylsilyl)amine**
5.682	D-Norleucine, N-methoxycarbonyl-...
6.46	**Tris(trimethylsilyl)carbamate**
6.809	**Trisiloxane, octamethyl-**
8.829	**Silanol, trimethyl-, phosphate (...**
9.138	Cyclohexasiloxane, dodecamethyl-
10.557	Cycloheptasiloxane, tetradecamet...
11.816	Phenethylamine, N-methyl-.beta.,...
12.909	Cyclononasiloxane, octadecamethyl-

Table 14: GC-MS Results of Well 2, Sample 2.

Retention time/min	Well 2, Sample 2
1.67	**Silane, chlorotrimethyl-**
2.208	**Hexane, 2,2-dimethyl-**
4.343	**Acetamide, 2,2,2-trifluoro-N,N-b..**
5.178	**Trisiloxane, octamethyl-**
5.35	**N-(Trimethylsilyl)acetamide**

5.556	**Ethanimidic acid, N-(trimethylsi..**
5.647	**Ethylbis(trimethylsilyl)amine**
5.71	2-Chloro-3-hydrazinopyrazine
6.477	**Tris(trimethylsilyl)carbamate**

Table 15: GC-MS Results of Well 3, Sample 2.

Retention time/min	Well 3, Sample 2
1.665	**Silane, chlorotrimethyl-**
2.208	**Hexane, 2,2-dimethyl-**
4.348	**Acetamide, 2,2,2-trifluoro-N,N-b...**
5.35	**N-(Trimethylsilyl)acetamide**
5.556	**Ethanimidic acid, N-(trimethylsi...**
5.647	**Ethylbis(trimethylsilyl)amine**
5.71	Trifluoromethyl isopropyl sulfide
6.477	**Tris(trimethylsilyl)carbamate**

Table 16: GC-MS Results of Well 4, Sample 2.

Retention time/min	Well 4, Sample 2
1.545	**Silane, chlorotrimethyl-**
1.636	**Silane, chlorotrimethyl-**
2.208	4,4-Dimethylazetidin-2-one
4.354	**Acetamide, 2,2,2-trifluoro-N,N-b...**
5.149	**Trisiloxane, octamethyl-**
5.327	**N-(Trimethylsilyl)acetamide**
5.544	**Ethanimidic acid, N-(trimethylsi...**
5.636	**Ethylbis(trimethylsilyl)amine**
5.699	D-Norleucine, N-methoxycarbonyl-...
6.471	**Tris(trimethylsilyl)carbamate**

Table 17: GC-MS Results of Well 5, Sample 2.

Retention time/min	Well 5, Sample 2
1.55	**Silane, chlorotrimethyl-**
1.665	**Silane, chlorotrimethyl-**
2.214	**Hexane, 2,2-dimethyl-**
4.354	**Acetamide, 2,2,2-trifluoro-N,N-b..**
5.092	**Trisiloxane, octamethyl-**
5.355	**N-(Trimethylsilyl)acetamide**
5.561	**Ethanimidic acid, N-(trimethylsi..**
5.653	**Ethylbis(trimethylsilyl)amine**
5.716	2-Chloro-3-hydrazinopyrazine
6.477	**Tris(trimethylsilyl)carbamate**

The results obtained from GC-MS analysis of water samples can be summarized as shown in table 18.

Table 18: Contaminants Found in Wells Following Second Analysis

Well	Contaminant
Well 1	Pentane,2,2,3-trimethyl,
	N,N-Diethylformamide,
	Dodecamethylcyclohexasiloxane
	Cycloheptasiloxane,tetradecamethyl
	Cyclononasiloxane,octadecamethyl
	D-Norleucine,N-methoxycarbonyl
	Phenethylamine,N-methyl-beta
Well 2	2-Chloro-3-hydrazinylpyrazine
Well 3	Trifluoromethyl isopropyl sulfide
Well 4	D-Norleucine,N-methoxycarbonyl
Well 5	D-Norleucine,N-methoxycarbonyl

N,N-Diethylformamide.

Dimethylformamide is a clear colourless to pale yellow liquid organic solvent, with formula $C_5H_{11}NO$, produced in large quantities through-out the world. It has a boiling point of 177.5 °C, melting point of -60.3°C, vapour pressure of 3.87 mm Hg at 25 °C and it is miscible in water and in organic solvents such as ethanol, ethyl ether, acetone, benzene. It is used in the chemical industry as a paint remover, graffiti removers, or general solvents N,N-Dimethylformamide's production and use as a solvent may result in its release to the environment through various waste streams. The effects of dimethylformamide on the environment have not been well studied but we do know that it has a low persistence in soil and water but is highly mobile. The exposure route is mostly related to inhalation. There is little information on effects after ingestion because of the lack of corroborating animal or human evidence. Symptoms of exposure may be delayed, however it can cause eye irritation and damage in some persons and can cause inflammation of skin on contact in some persons (MSDS, 2009; Pubchem, 2019).

Pentane,2,2,3-trimethyl.

It is an alkane whose molecular formula is C_8H_{18}. It is less dense than water, has a Boiling point of 114.9±7.0°C at 760mmHg, a melting point of -100.93°C and its vapour pressure is 23.1±0.1 mmHg at 25°C. It is hazardous to the aquatic environment and if ingested, may affect Kidney, Ureter and/or Bladder (changes in urine composition).

No uses for this substance were found, however we found it is a product of 1-butene ($CH_3CH_2CH=CH_2$) which is an organic compound, particularly an alkene which is used in the production of a wide variety of chemicals in the gasoline and rubber processing areas (Pubchem, 2019) .

Dodecamethylcyclohexasiloxane

Dodecamethylcyclohexasiloxane is a clear odourless organosiloxane with molecular formula $C_{12}H_{36}O_6Si_6$. It has a boiling point of 210°C, has a vapour pressure of 0.03 mm Hg at 25°C, has a high octanol water partition coefficient, Kow of 6.3 and is insoluble in water (0.00513 mg/l at 23°C). Dodecamethylcyclohexasiloxane is related to the maintenance and repair of automobiles, products for cleaning and caring for automobiles (auto shampoo, polish/wax, undercarriage treatment, brake grease) as well as lubricants for engines, brake fluids, oils. It is also related to all forms of cleaning/washing, including cleaning products used in the home, laundry detergents, soaps, de-greasers, spot removers. It may be harmful if ingested, Environmental precaution upon accidental release is to prevent entry to sewers and public waters and notify authorities if liquid enters sewers or public waters (Scientific, 2014).

For substances found in the water but not expatiated on, not enough information was available.

3.2   RESULTS OF MODELLING AND SIMULATION.

As shown in figure 9 and figure 10 respectively, the simulation started off with zero contaminant concentration in the model, indicated by the all-blue area, and ended with contaminant concentration of 1 approximately 2.9 m underground (only 0.2 m from the water table), indicated by the red area. This indicates that given regular spills and regular rainfall and evaporation conditions, within the period of one year, the aquifer will be contaminated, putting public health at risk.
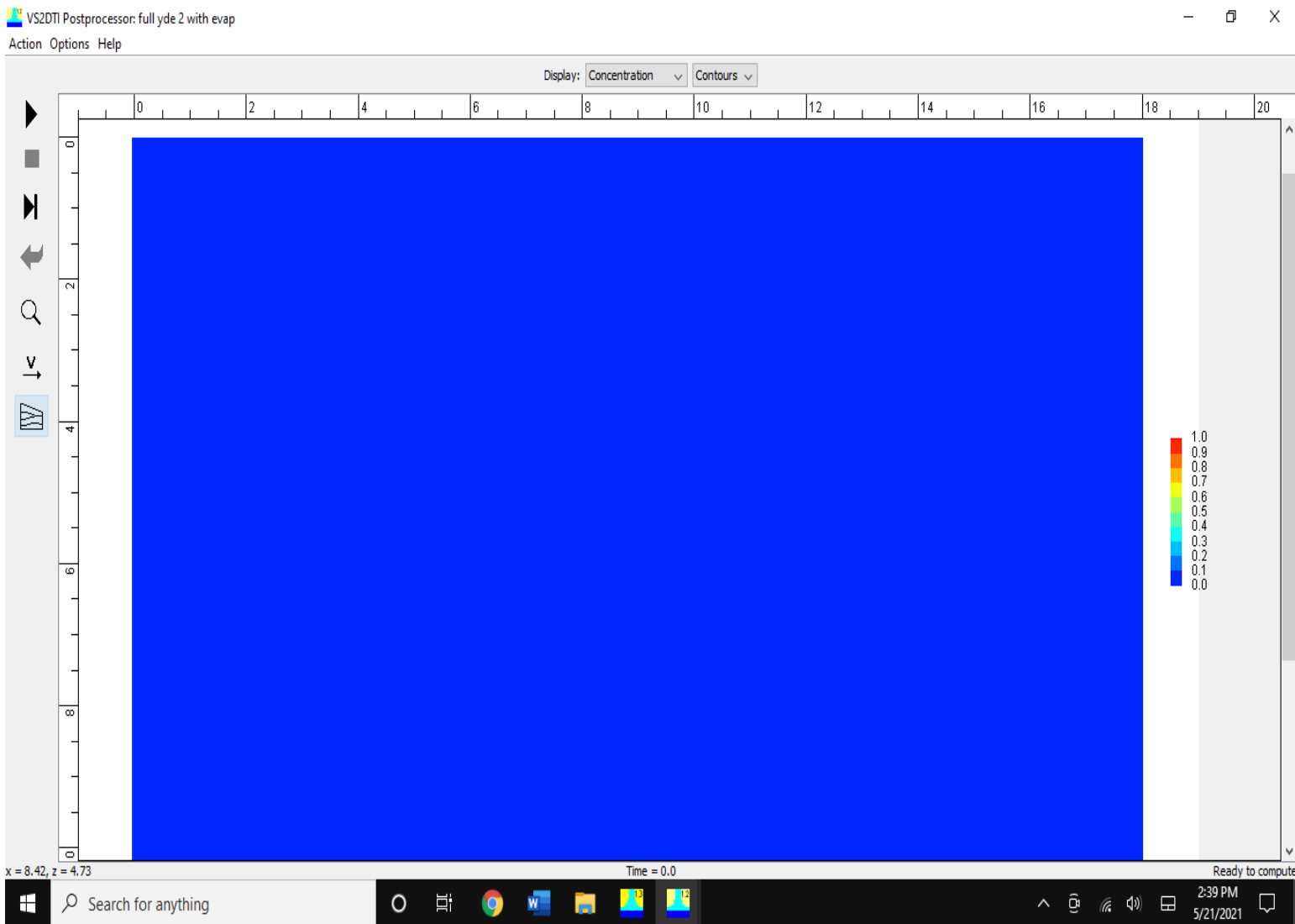

Figure 10:Contaminant Concentration Level and Distribution at Start of Simulation.
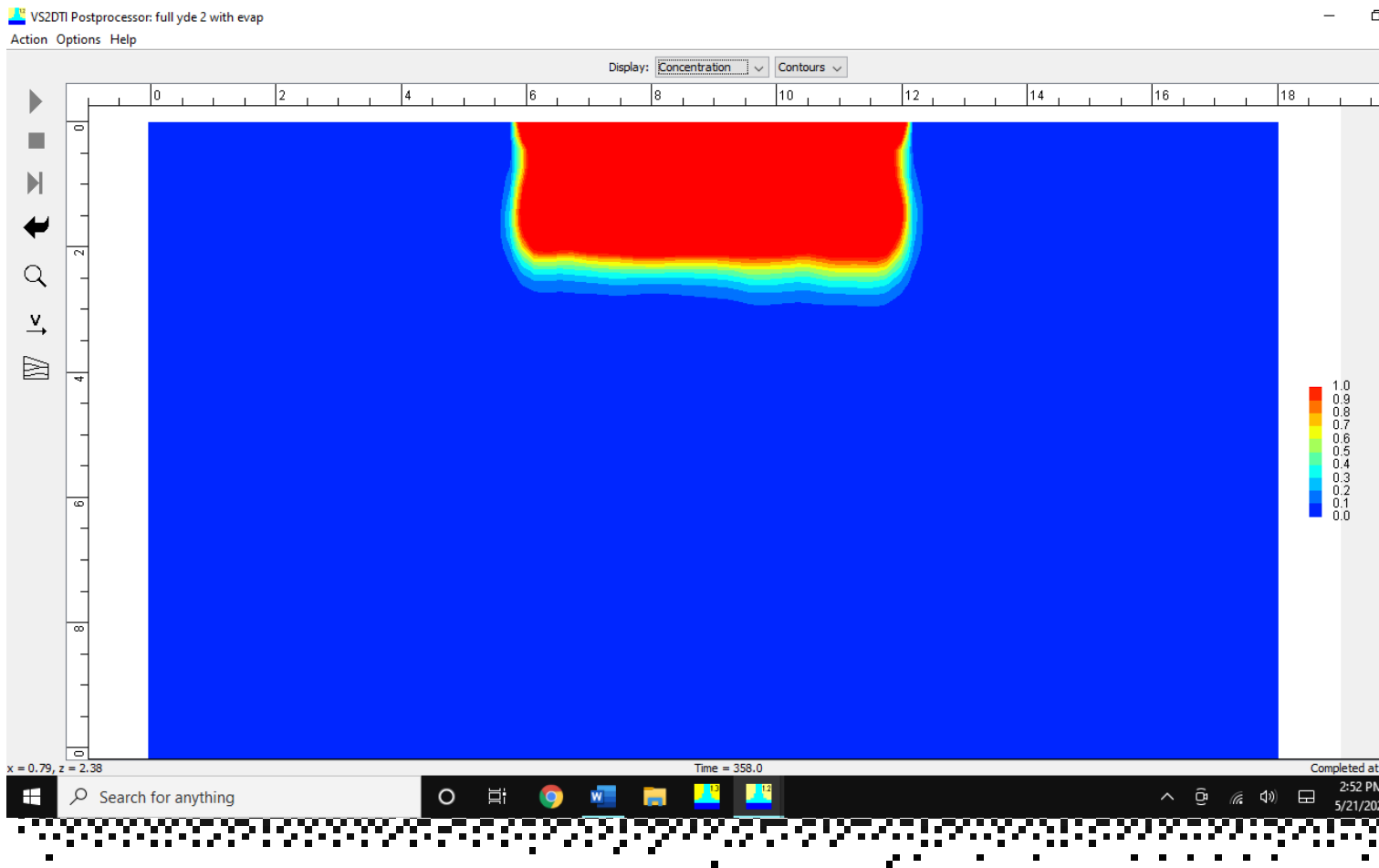
Figure 11: Contaminant Concentration Level and Distribution at End of Simulation.

Conclusion

This chapter presented the results obtained at the end of our work. Thanks to these results, we were able to realise our two objectives: we predicted the timeframe between hydrocarbon spill and groundwater contamination which was 1 year and at the end of our groundwater investigation, we discovered hydrocarbon contaminants in the well waters close to garages. These results are important to human and environmental health. As such, the next part of this work will bring out recommendations which would help prevent further cases and mitigate the already existing problem.

RECOMMENDATIONS.

- Firstly, a legal framework containing guidelines for garage design and management of garage waste. Garages ought to be enclosed spaces with sealed floors which are not only capable of taking the physical brunt of cars, dropped tools and other heavy automotive repair equipment, but also support environmental protection, by isolating hazardous materials on the flooring surface, where they can be properly cleaned up and disposed of — as opposed to allowing toxic substances such as oils, grease and other vehicle related fluids to leach through porous concrete slabs into the surrounding environment. Roofing will prevent the contribution of rainfall to the leaching of these substances into the subsoil.

- Based on the framework law, local governments should put in place management strategy for garage waste such as a plant for the offsite treatment of hydrocarbons from not only garages but any activity that generates such waste. The garages should have floor drains or sinks in service areas for fluids such as engine oil or solvents to drip or spill into during vehicle repair and maintenance. These sinks and drains would empty into disposal wells which follow regulations for leakage prevention and which would be emptied regularly to be treated at said plant. To facilitate these tasks, a department at the treatment plant could be in charge of checking these wells for leakage after the emptying to ensure that they are always in good condition.

- As for the sites that are already contaminated, the suggested modes of remediation are air sparging which is an in-situ treatment that will target the saturated zone and biopiles which is an ex-situ treatment that will target the vadose zone.

- The disposition of wells and farmland vis-à-vis should be regulated to ensure that in case of an accidental spill, the contamination does not reach these areas of interest.

GENERAL CONCLUSION

As a result of the lack of an effective intraurban public transport system in Cameroon, many Cameroonians rely on taxis and bikes as a means of transportation. That, coupled with insufficient and bad road infrastructure and policies that allow used cars of all ages into the country are factors that have led to the proliferation of garages on the territory.

The problem addressed in this research was that of these garages uncontrollably releasing their waste, specifically those of a hydrocarbon nature to the soil and eventually to the subsoil. Our primary objective of the research was to determine the extent and importance of soil and groundwater pollution by hydrocarbons generated from garages in Yaoundé. The primary objective was then divided into two secondary objectives which were firstly to; Investigate groundwater for hydrocarbon contamination and suggest remediation methods adequate for the situation. Secondly, predict the timeframe between hydrocarbon spill and groundwater pollution in order to demonstrate risk potential.

In order to attain the above-mentioned objectives, a qualitative approach was adopted. 5 wells were sampled in the Biyem-Assi area. The criteria that guided the selection of these wells was their proximity to garages. The well water samples were analysed by GC-MS for the presence of hydrocarbons at the National Laboratory for Diagnosis and Analysis of Agricultural Products and Inputs of MINADER. The results of these analyses proved the presence of some hydrocarbons which suggest contamination from the garage activities carried out in the area. In addition to qualitative analysis, we came up with a model of the Yaoundé soil profile based on the actual Yaoundé soil profile and simulated contaminant transport in the subsoil to determine the likelihood that this contamination can, in effect, attain the saturated zone and hence be a hazard to human health in the long-term. The simulation was run for a year, with continuous contamination and periodic rainfall and evaporation. The contamination did indeed reach the top of the saturated zone at the end of the simulation, implying that these garages disposing of their waste directly onto the soil does pose a problem for human and environmental health in the long run.

However, this work was limited by the absence of standards that would have been used for the quantitative analysis of the well waters in order to quantify the contamination found and compare to WHO and national limits for human health. Further research is therefore required to give this piece of work its completeness by addressing these limitations.

PERSPECTIVES

i. In order to complete this work, the limitations encountered during this work, specifically inability to perform quantitative analysis of well waters, need to be overcome.

ii. It would be sensible to do a financial evaluation of what it would take to remediate contaminated sites and put in place a petroleum waste collection and treatment system.

iii. Investigations need to be carried out to find other areas round the country with garage clusters and find out the effects of these spills on the health of members of these communities.

iv. The research can be extended to assessment of soil contamination by garage wastes in relation to effects on soil fertility, adsorption by plants and destruction of subsoil ecosystems.

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ANNEXES

In these annexes are the results generated by the gas chromatography-mass spectrometry performed on the well water samples. They are graphs of substance abundance versus time. Each peak in the graph represents a retention time at which a substance (hydrocarbon was detected). Retention times are substance specific and thanks to this, we were able to determine which substances the peaks represented.

```
Data Path : C:\MSDCHEM\1\
Data File : GC TEST.D
Acq On    : 31 May 2021   2:17
Operator  :
Sample    : Well 1, Sample 1
Misc      :
ALS Vial  : 1   Sample Multiplier: 1

Search Libraries:   C:\Database\NIST11.L          Minimum Quality:   0

Unknown Spectrum:   Apex
Integration Events: RTE Integrator - lscint.p
```
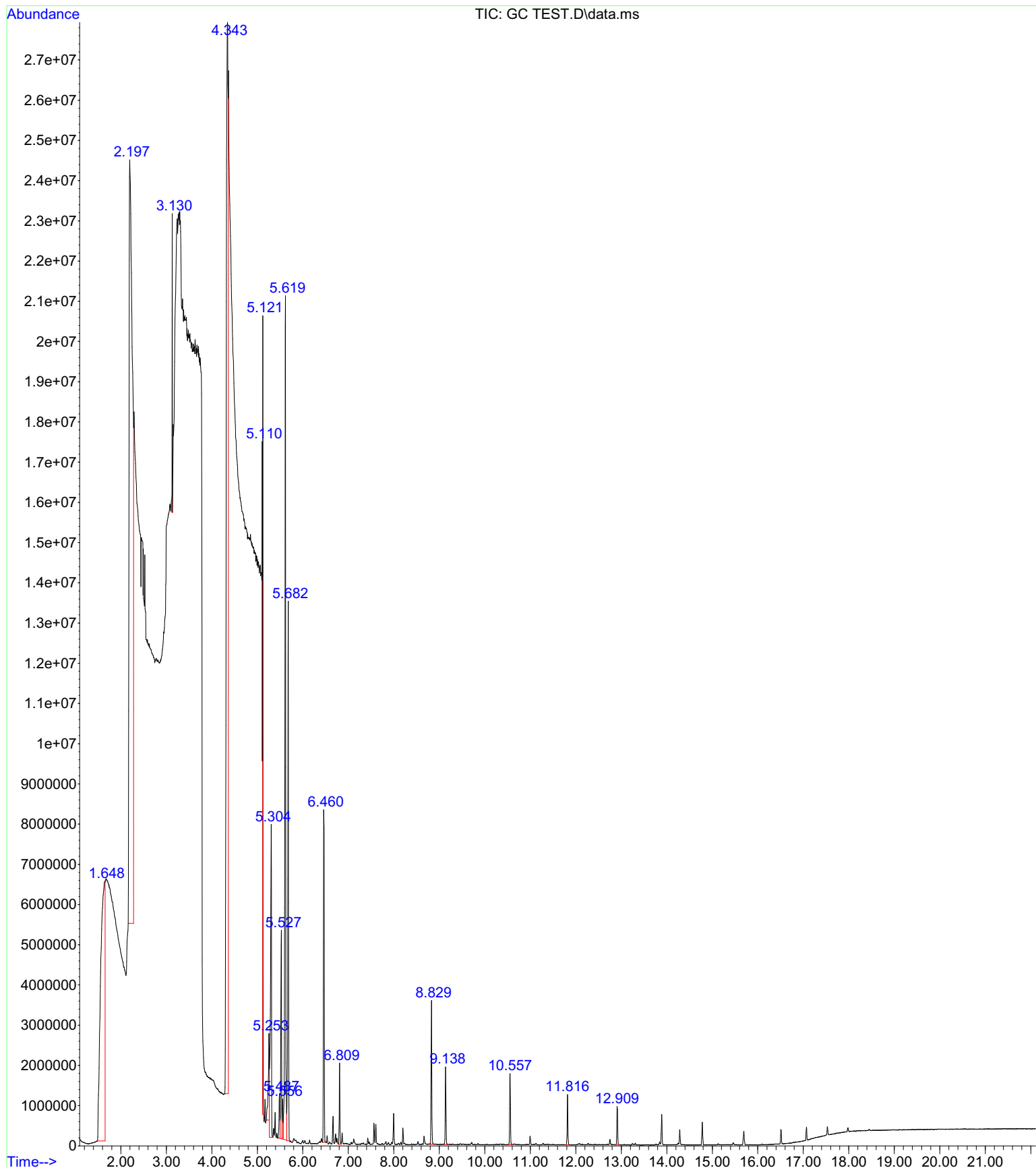

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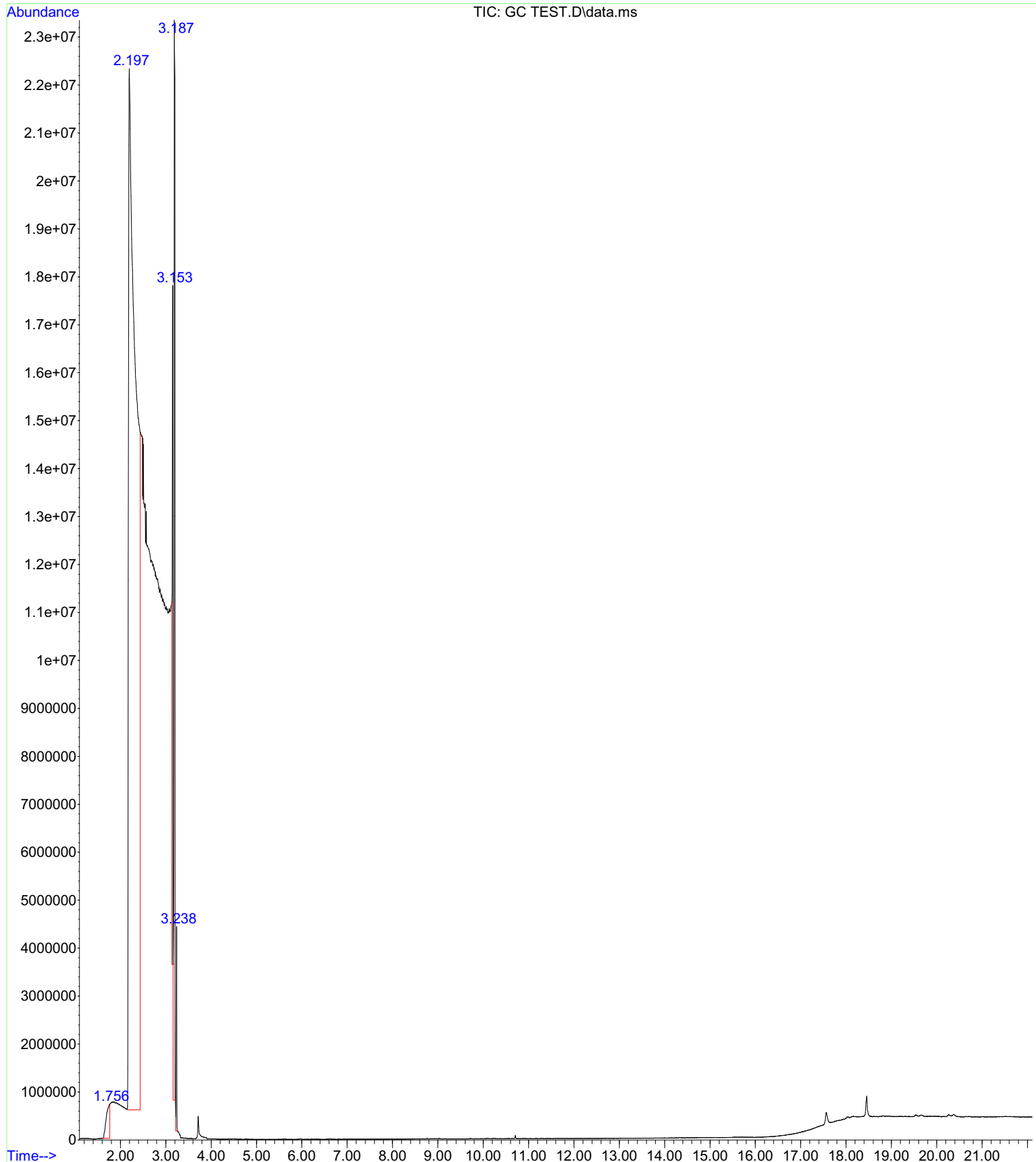
Data Path : C:\MSDCHEM\1\
Data File : GC TEST.D
Acq On   : 1 Jun 2021 11:30
Operator :
Sample   : Sample 1A
Misc   :
ALS Vial : 1   Sample Multiplier: 1

Search Libraries: C:\Database\NIST11.L   Minimum Quality: 0
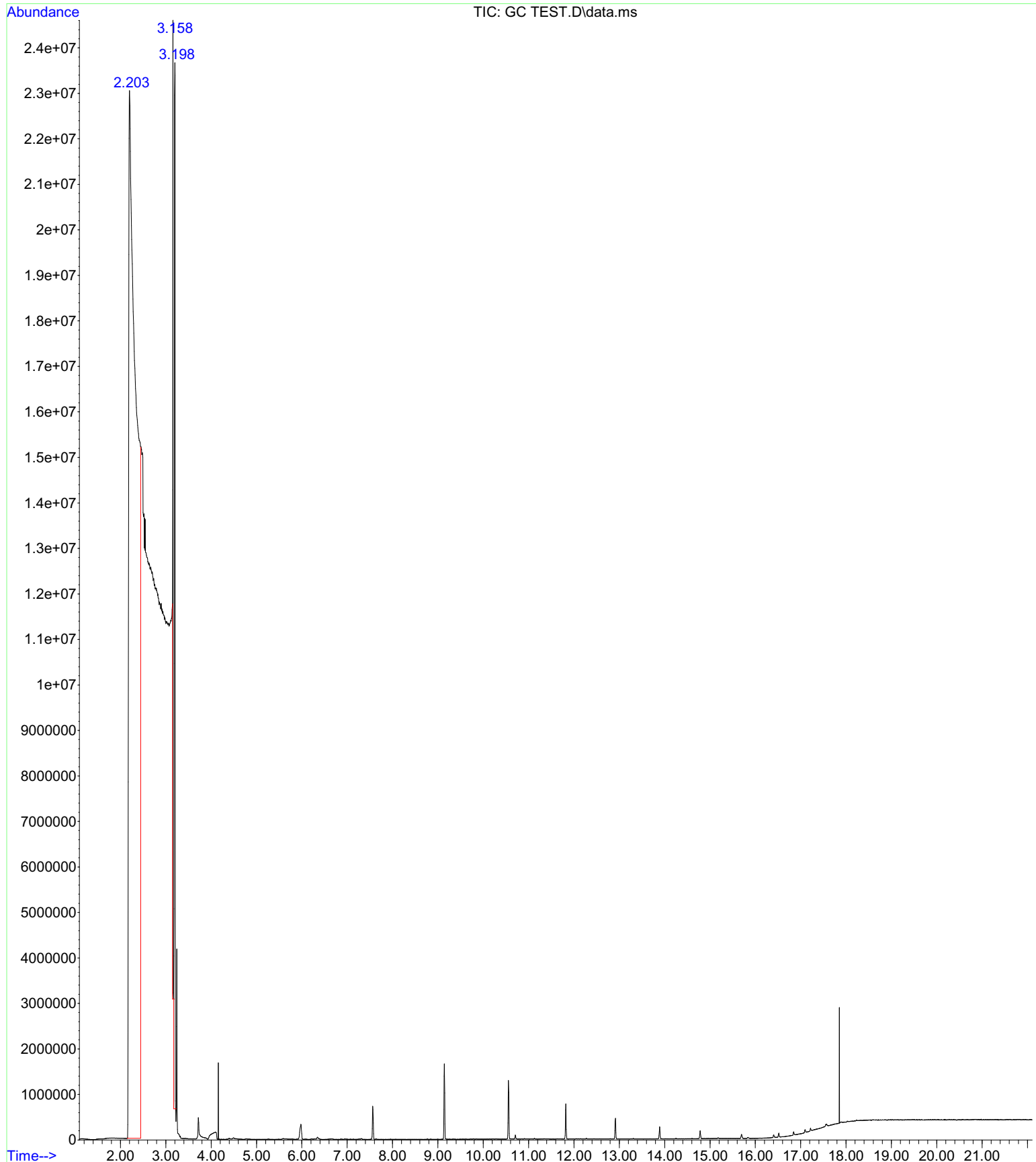
Unknown Spectrum: Apex
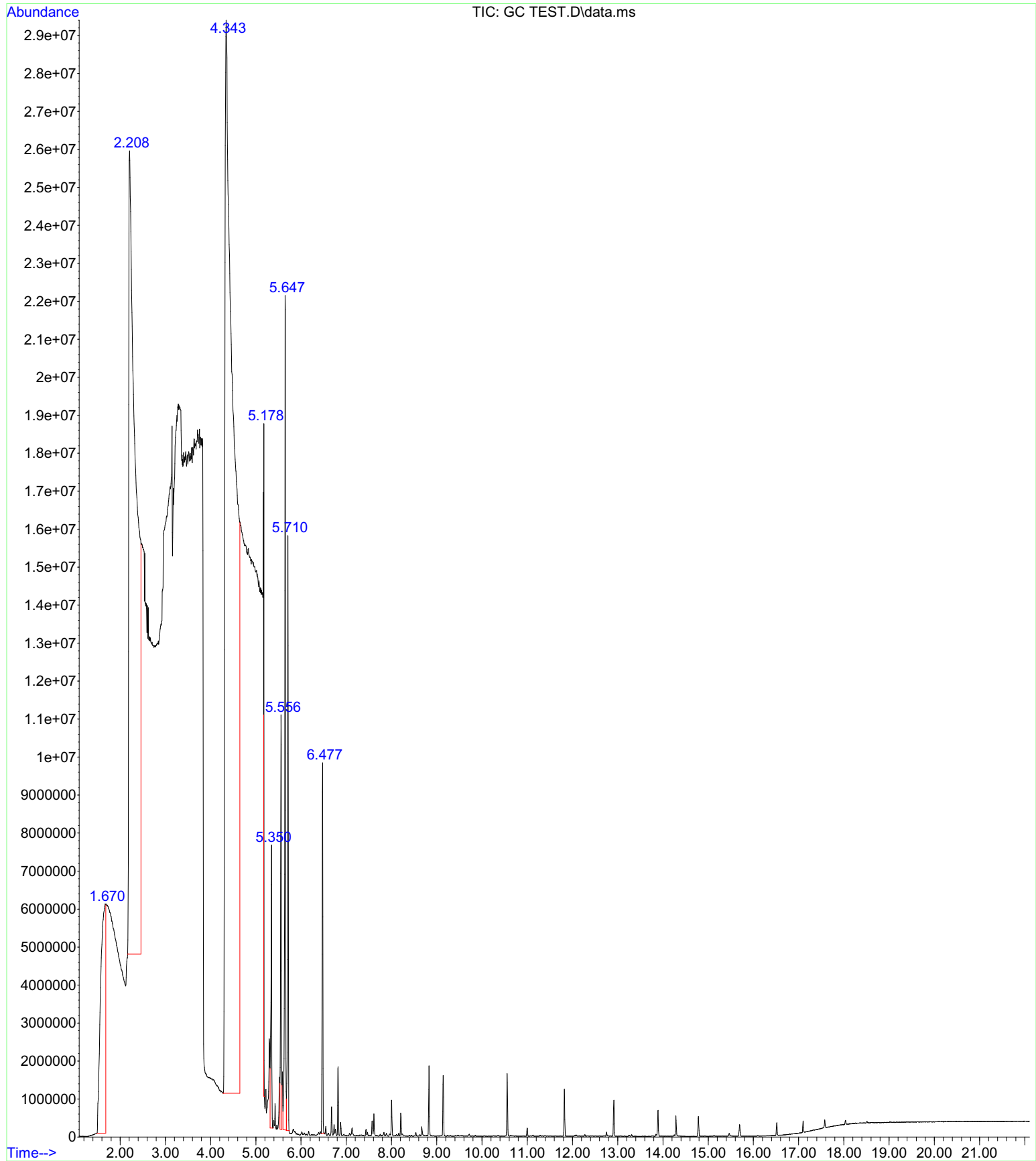Integration Events: RTE Integrator - lscint.p

TIC: GC TEST.D\data.ms

Data Path : C:\MSDCHEM\1\
Data File : GC TEST.D
Acq On   : 31 May 2021   3:26
Operator :
Sample   : Well 2,Sample 1
Misc   :
ALS Vial : 1   Sample Multiplier: 1

Search Libraries: C:\Database\NIST11.L   Minimum Quality: 0

Unknown Spectrum: Apex
Integration Events: RTE Integrator - lscint.p

TIC: GC TEST.D\data.ms

```
Data Path : C:\MSDCHEM\1\
Data File : GC TEST.D
Acq On    :  1 Jun 2021  12:21
Operator  :
Sample    : Sample 2A
Misc      :
ALS Vial  : 1   Sample Multiplier: 1

Search Libraries:   C:\Database\NIST11.L          Minimum Quality:   0

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Integration Events: RTE Integrator - lscint.p
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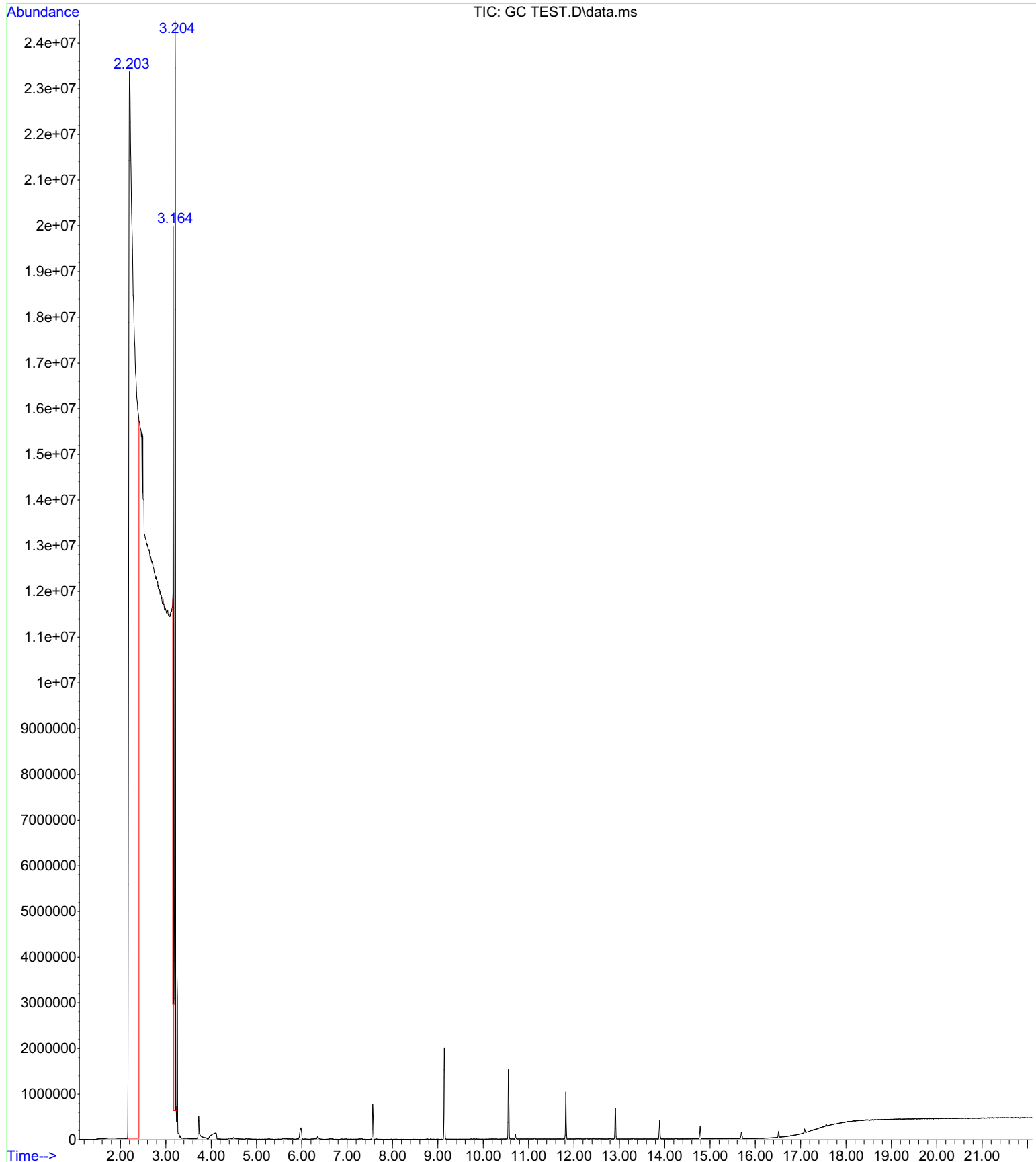

TIC: GC TEST.D\data.ms

```
Data Path : C:\MSDCHEM\1\
Data File : GC TEST.D
Acq On    : 31 May 2021   3:57
Operator  :
Sample    : Well 3, Sample 1
Misc      :
ALS Vial  : 1   Sample Multiplier: 1

Search Libraries:   C:\Database\NIST11.L          Minimum Quality:   0

Unknown Spectrum:   Apex
Integration Events: RTE Integrator - lscint.p
```
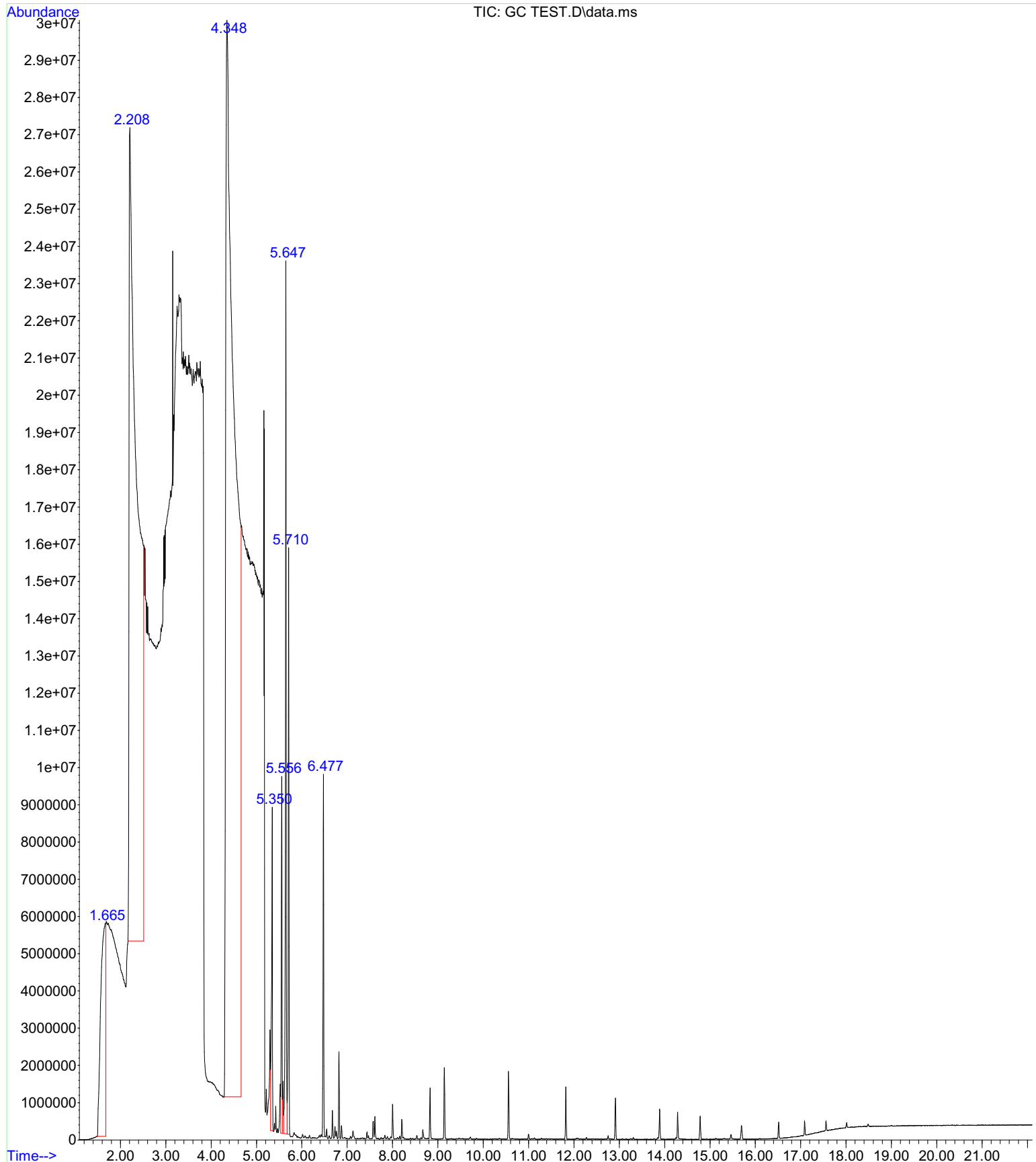

TIC: GC TEST.D\data.ms

```
Data Path : C:\MSDCHEM\1\
Data File : GC TEST.D
Acq On    :  1 Jun 2021  12:52
Operator  :
Sample    : Sample 3A
Misc      :
ALS Vial  : 1   Sample Multiplier: 1

Search Libraries:   C:\Database\NIST11.L          Minimum Quality:   0

Unknown Spectrum:   Apex
Integration Events: RTE Integrator - lscint.p
```


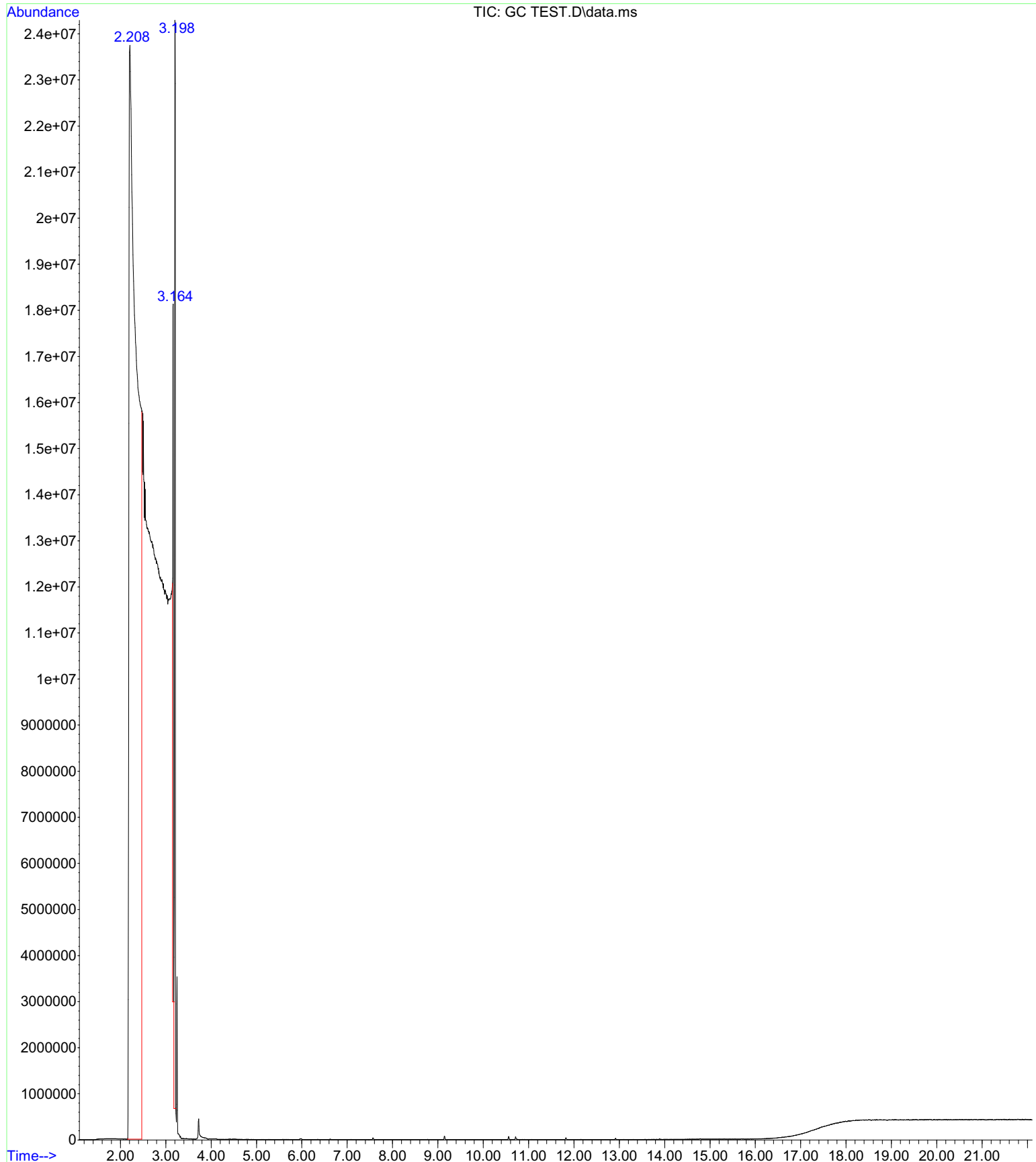TIC: GC TEST.D\data.ms

Library Search Report

Data Path : C:\MSDCHEM\1\
Data File : GC TEST.D
Acq On   : 31 May 2021   5:10
Operator :
Sample   : Well 4, Sample 1
Misc   :
ALS Vial : 1   Sample Multiplier: 1

Search Libraries: C:\Database\NIST11.L   Minimum Quality: 0

Unknown Spectrum: Apex
Integration Events: RTE Integrator - lscint.p

TIC: GC TEST.D\data.ms
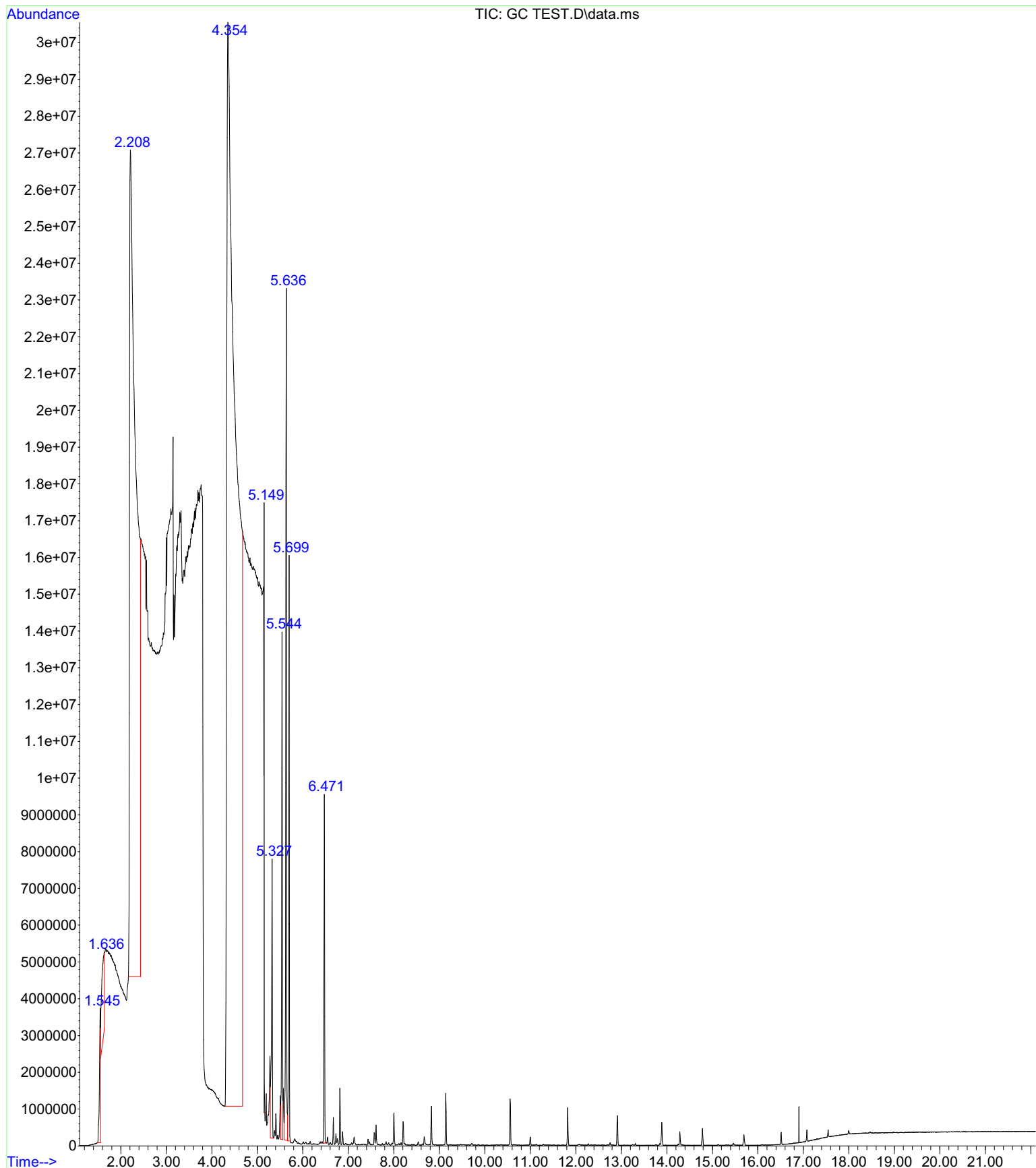
```
Data Path : C:\MSDCHEM\1\
Data File : GC TEST.D
Acq On    :  1 Jun 2021  13:21
Operator  :
Sample    : Sample 4A
Misc      :
ALS Vial  : 1   Sample Multiplier: 1

Search Libraries:   C:\Database\NIST11.L          Minimum Quality:   0

Unknown Spectrum:   Apex
Integration Events: RTE Integrator - lscint.p
```
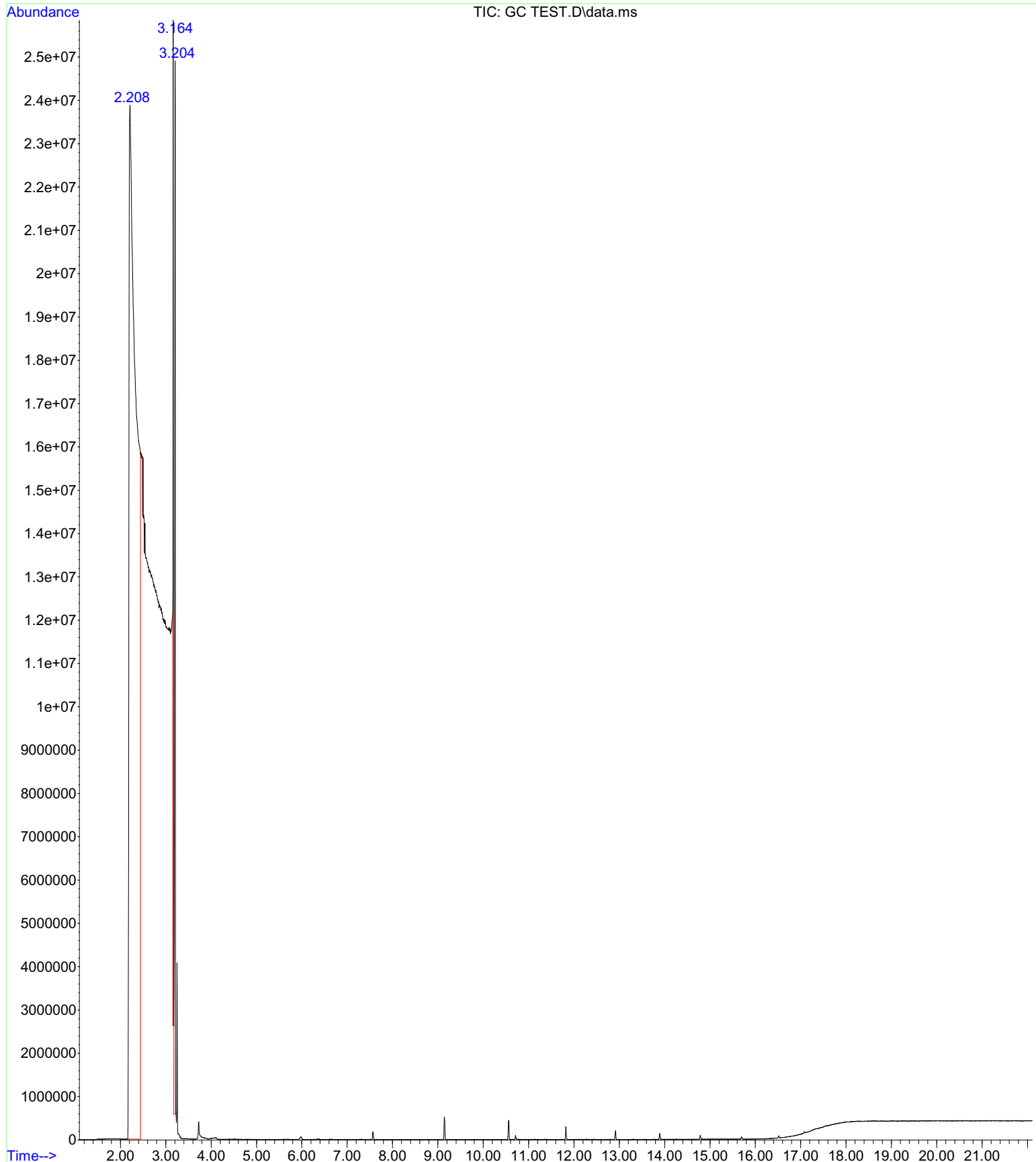

TIC: GC TEST.D\data.ms

```
Data Path : C:\MSDCHEM\1\
Data File : GC TEST.D
Acq On    : 31 May 2021   5:40
Operator  :
Sample    : Well 5, Sample 1
Misc      :
ALS Vial  : 1    Sample Multiplier: 1

Search Libraries:   C:\Database\NIST11.L              Minimum Quality:   0

Unknown Spectrum:    Apex
Integration Events: RTE Integrator - lscint.p
```


TIC: GC TEST.D\data.ms

```
Data Path : C:\MSDCHEM\1\
Data File : GC TEST.D
Acq On    :  1 Jun 2021  13:51
Operator  :
Sample    : Sample 5A
Misc      :
ALS Vial  : 1    Sample Multiplier: 1

Search Libraries:   C:\Database\NIST11.L          Minimum Quality:   0

Unknown Spectrum:   Apex
Integration Events: RTE Integrator - lscint.p
```


TIC: GC TEST.D\data.ms