

EFFECTS OF SELECTED CONTAMINANTS ON THE PHYSICAL, CHEMICAL, AND
GEOTECHNICAL PROPERTIES OF AQUIFER SOLID

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EFFECTS OF SELECTED CONTAMINANTS ON THE
PHYSICAL, CHEMICAL, AND GEOTECHNICAL
PROPERTIES OF AQUIFER SOLID

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ABSTRACT

The primary objective of this study was to investigate the potential effects of hydrocarbons on the geotechnical properties of sand. A series of laboratory experiments were carried out to ascertain the influence of some common and widespread organic contaminants on the hydraulic conductivity of sand. Bulk sand samples from the Missouri River Valley aquifer— a major source of groundwater supply in the U.S. Midwest— were collected for this study. Sand samples, representing the aquifer and vadose zone, comprising -2.36 mm and -0.425 mm fractions respectively, prepared from the bulk samples, were used for conducting laboratory tests. Gasoline and some of its constituent chemicals—benzene, toluene, ethylbenzene, xylene (BTEX), isooctane— as well as trichloroethylene (TCE) were used to contaminate sand samples at varying saturation levels for extended periods of time to simulate changes in geotechnical properties and hydraulic conductivities of sand caused by oil tank spills and leaking petroleum pipelines. Seventy-four medium grained sand samples were contaminated with TCE and gasoline at about 25%, 50% and 100% saturation levels for 2, 4, 8, 16, and 32 weeks. In addition, five sand samples were fully saturated with BTEX and isooctane for eight weeks to compare the results of their geotechnical properties and

hydraulic conductivities with gasoline-contaminated sand. Also, 10 aquifer sand samples were exposed to aqueous solution contaminated with about 1, 2, 3, and up to 10% of TCE and gasoline for 8 weeks. Grain size parameters of the sand and its density, void ratio, porosity, and hydraulic conductivity were determined before and after the duration of exposure. All tests were performed in accordance with the American Society for Testing and Materials' standard test methods. The results showed an overall decrease in the geotechnical properties and up to 60% reduction in hydraulic conductivity of contaminated sand. Another set of experiments was carried out to determine the influence of evaporation rate of contaminating chemicals on hydraulic conductivity of sand. Results indicate that chemicals permeating sand grains have variable evaporation rates with a certain amount of chemicals left behind in sand voids. The inherent differences in the structure and nature of chemicals influenced hydraulic conductivity such that the observed decrease was greater for aliphatic than aromatic and chlorinated hydrocarbons. X-ray diffraction results show that the contaminating chemicals used in this study did not alter the mineralogy of both aquifer and upper layer sand, even after extended periods of exposure. Scanning electron microscopy of contaminated sand grains revealed highly irregular surfaces with presence of nano size grooves along with presence of prominent granules and grain fragments. This contributes to increase in surface area and decrease in porosity with attendant increase in surface tension. All of which resulted in a decrease in hydraulic conductivity of contaminated sand.

The undersigned, appointed by the Dean of the School of Graduate Studies, have examined a dissertation titled "Effects of Selected Contaminants on the Physical, Chemical, and Geotechnical Properties of Aquifer Solid," presented by Qays Jasim Saud, candidate for the Doctor of Philosophy degree, and hereby certify that in their opinion it is worthy of acceptance.

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DEDICATION

To my parents, brothers and sister

my wife, Nada,

my daughters, Mays, Mina

and my friends

who patiently waited and supported my decisions all these years

CHAPTER 1

INTRODUCTION AND PROBLEM STATEMENT

Introduction

Environmental pollution caused by careless exploitation of earth's resources and heavy reliance on fossil fuels have resulted in serious environmental problems including contamination of surface water and groundwater. According to the United States Census Bureau the current world population has increased approximately seven times: more than 7 billion now, compared to the year 1800 (U.S. Census Bureau, 2013). The rapid increase in human population along with unprecedented industrialization has placed heavy demand on mineral, energy, and water resources. In addition, globally more and more people have been migrating from rural areas to cities, and currently more than half of the humanity lives in urban areas. Large-scale industrialization combined with rapid urbanization are considered to be the main causes of environmental pollution.

Water availability is essential for human survival. Out of the 2.8% of the readily available fresh water supplies, groundwater accounts for 0.6%. Groundwater is the most important natural resource in the world. A majority of the world's population depends mainly on groundwater as an important source of water supply for industry, agricultural, and for human consumption. In the United States groundwater is a source of drinking water for about one-half of the population.

Groundwater is a valuable resource to everyone: communities that live near surface water (rivers or lakes) and communities that live far from surface water sources. Those living close to surface water source may use a part of groundwater to meet their need, but

communities located away from surface water depend entirely on groundwater to meet their daily needs. Treated water is supplied to both communities by water supply companies that own and operate municipal water treatment plants. A large number of these water treatment plants largely depend on groundwater as the source even though they may be located near surface water sources. The reason for this dependence on groundwater is due to contamination of surface water caused by pollutants that include industrial chemicals, sediment, plastics, synthetic waste, etc. Purification of polluted surface water is extremely tedious and expensive. On the other hand, groundwater is naturally purified by natural materials, e.g., sand and gravel, and the microbes. In comparison to river water, groundwater is naturally filtered thus reducing time and cost for purification. Therefore, groundwater becomes the preferred source of water intake for municipal water plants. Not only does groundwater provides drinking water but also serves as source water for industrial and agricultural uses. In the Kansas City metropolitan area, the Missouri River alluvial aquifer provides drinking water to more than 900,000 people living in 90 municipalities. This alluvial aquifer is the only aquifer that provides large volumes of pure groundwater for domestic and industrial use (Kelly, 2003).

However, many aquifers and surface water sources, at various locations all over the world, have been contaminated by inorganic and/or organic chemicals. Contamination may be caused by leaks from oil pipelines or due to leaks in underground oil or chemical storage tanks, oil tanker spills or due to poor environmental management practices. For example, the widespread oil spill that occurred in Kuwait during the 1991 Gulf War resulted in detonation and ignition of about 92% of the all producing oil wells causing major environmental and water pollution (Mukhopadhyay *et al.*, 2008). Similarly, the spill/leak, which occurred due to

explosion of the Deepwater Horizon mobile offshore drilling platform in the Gulf of Mexico on April, 2010, resulted in severe environmental and marine pollution. The attendant oil leakage had a significant impact on marine, terrestrial and aquatic biota.

Improper management of oil or hazardous industrial waste, prior to the 1980s, has left a legacy of a large number of contaminated sites containing hazardous inorganic and organic chemicals across the United States. This includes petroleum hydrocarbons and related toxic chemicals.

The United States Environmental Protection Agency (U.S. EPA) maintains a National Priority List (NPL) of highly contaminated sites, earmarked for cleanup action, and has identified 1,322 contaminated sites across the country (U.S. EPA, 2014b). United States Geological Survey (USGS) reported that chloroform, perchloroethene (PCE), methyl tert-butyl ether (MTBE), trichloroethylene (TCE) and toluene were the top five contaminants among the 15 most frequently detected volatile organic compounds (VOCs), observed in the United States aquifers (Zogorski *et al.*, 2006). The Agency for Toxic Substances and Disease Registry (ATSDR) reported that TCE is the most commonly found organic contaminant in groundwater at NPL sites (ATSDR, 1997b). According to ATSDR (1997b) and U.S. EPA (2011a), it was estimated that between 9-34% of total drinking water supply sources that were tested in the United States may contain some TCE contamination.

Benzene, toluene, ethylbenzene, xylenes (BTEX) and TCE pose the maximum threat to human health due to their known or suspected toxicity and potential for human exposure at the NPL sites (ATSDR, 2013). TCE, classified as carcinogenic to humans through all routes of exposure, is present in drinking water, indoor environments, surface water, ambient air, groundwater, and soil. It has been identified at more than 1,500 hazardous waste sites (U.S.

EPA, 2011b; 2013b; 2014a). Approximately 41 million people live within 6.5 km and approximately 3,000 people live within about 1.7 km from one or more of such sites (ATSDR, 1996a, as cited in U.S. EPA, 2001).

According to the USGS, MTBE, despite a short time of wide use, is the third most frequently detected organic contaminant in the United States shallow groundwater. TCE and toluene occupy the fourth and the fifth place among the 15 most frequently detected VOCs in the United States aquifers (Zogorski *et al.*, 2006).

In a study conducted in 1996 at Santa Monica, California, U.S. EPA discovered that two of city's drinking water well fields, Charnock and Arcadia, were contaminated with MTBE at levels of 0.61 ppm and 0.086 ppm, respectively. These two well fields represented 50% of the city's drinking water supply. Discovery of MTBE contamination in drinking water resulted in the shutdown of water supply causing the city to purchase replacement water. This was the first major MTBE-related contamination of groundwater (U.S. EPA, 2011c). Later, in July 2006, U.S. EPA also identified high levels of MTBE in groundwater at the Amorco terminal at Martinez, California, that prompted quick implementation of remediation measures. Using the pump-and-treat method about 1,815 kg of MTBE was cleaned in 5 months of operation (U.S. EPA, 2011c).

Hydrocarbon contaminants may follow a complex pathway from source to aquifers. These contaminants may move through the unsaturated zone in vapor phase (non-aqueous phase liquid (NAPL)) to travel down to the aquifer. The rate of hydrocarbon movement from the source of contamination to aquifer is controlled by several factors such as hydraulic conductivity of soil/sediment, temperature, moisture and related physical parameters.

Permeability is a time-dependent phenomenon and is a function of velocity of fluid flow, geometry of the aquifer layers, and physical and chemical interactions. Therefore, accurate quantification of the rate of contaminant permeation across the geological materials is an essential requirement for design and implementation of any remediation method. This permeability quantification may result in cost-effective method to clean up aquifers.

Environmental Problems Related to Organic Contaminants

Availability of water as well as its quality has always been a major concern in the United States and also in other countries. The world's increasing population and reliance on groundwater call for accurate information on quality and quantity of groundwater. Quantity of available groundwater depends on the amount of precipitation, the amount of recharge to the aquifers, and the quantity of water extracted from aquifers for consumption. But, the quality of water depends on the dissolved ions such as K^+ , Ca^{+2} , Na^+ or other contaminants occurring in the groundwater. One of the major sources that affect the groundwater quality and thus limits its use includes organic pollutants, such as crude oil and its derivatives. Ever-increasing dependence on oil as an energy source has led to an increase in environmental pollution across the globe (land, seas, rivers, groundwater, and air). Pollution from hydrocarbon is caused by drilling for oil extraction, oil transport, leaks in pipelines, and seepage from underground and above-ground containers.

A recent study by the U.S. Fish and Wildlife Service (2010) reported that oil leaks into the environment has the possibility to persist long after a spill, as it has been detected in sediment three decades after a spill. Moreover, oil can sink deep into a sediment on sandy beaches, and may seep into the muddy bottoms in tidal flats and salt marshes (U.S. Fish and

Wildlife Service, 2010). This long period of pollutants accumulation at contaminated sites would result in serious degradation of soil and water that may adversely impact living forms in such areas.

Several studies have addressed environmental factors associated with oil pollution and its derivatives. ATSDR (1996b; 2004), U.S. EPA (2011a; 2012a), and U.S. Fish and Wildlife Service (2010) have studied these risks and their impacts on human and wildlife. These studies focused on determination of safe levels of the contaminants in water and their remediation.

Environmental pollution due to hydrocarbons spills are well known not only from the United States, but in many other countries. An example of such a case is shown in Figure 1.1 where the recent war in Iraq, since 1980, has damaged oil pipelines and caused explosion of oil wells. This damage has led to oil release and contamination of vast areas on land and water. Another major source of hydrocarbon contamination is leakage through damaged and/or cracked pipelines that carry petroleum derivatives which could seep from underground containers (Figure 1.2); leaks also occur from chemicals stored in underground tanks at factories and industrial sites.



a.



b.

Figure 1.1. Fossil fuel spill in Al Basra, Southern Iraq. a. crude oil lake covered the soil; b. effect of crude oil spill on soil (Photos taken in 2012 courtesy, Ahmed F. Mohammed; Iraqi Geological Survey, Baghdad, Iraq (Appendix A).



a.



b.

Figure 1.2. Damaged oil pipe and underground storage tanks. a. damaged refined petroleum products pipeline (owned by Enbridge Energy); b. underground damaged tank removal at Tuba City, AZ; (Adapted from Weyler (2012) for a. and U.S. EPA (2011c) Pacific Southwest, Region 9 for b.)

Problem Statement

A large number of chemical contaminants, including hydrocarbons, are known to occur at many hazardous waste sites, of which the most common chemicals of concern are: petroleum hydrocarbons, solvents, pesticides, lead, and other heavy metals. In addition, marine pollution as a result of spills from oil tankers or oil well platforms, are not infrequent. Other sources of pollution include leaks that occur on the land leading to contamination of soil and water sources. As estimated by the ATSDR, between 9 and 34% of the drinking water supply sources in the United States may contain some TCE contamination (ATSDR, 1997a; U.S. EPA, 2011a). A study by the U.S. EPA (2013b) reported that about 2 million gallon of drinking water can be contaminated by about 1 liter of motor oil.

Most of the previous studies have focused on the impact of organic hydrocarbon pollutants on clay or similar soils. These studies did not focus on the impact of hydrocarbon contamination on the physical, chemical and geotechnical properties of the most common aquifer solids-sand. The present study attempts to fill this critical knowledge gap and to find answers for a fundamental question that is of great significance in the fields of hydrogeology and remediation science: How do common and widespread organic contaminants (hydrocarbons) upon coming in contact with sand, in the unsaturated and saturated zones, at different concentration and for varying periods of time, affect the physical, chemical, and geotechnical properties of aquifer solids?

Selection of the best remediation method for the contaminated aquifer and the overlying unsaturated (vadose) zone depends on several factors, nature of the contaminant

being one of them, its density and viscosity. Other, factors are: site geology that includes types of geologic material and hydraulic conductivity of the aquifer solid.

The time required in the transportation of contaminants from the source to aquifer is of critical importance in prompt implementation of a suitable removal or remediation method. In addition, infiltration rate and time of water passage from the land surface to aquifers through contaminated areas are significant because it will affect the velocity and quantity of infiltrating water that would enter the aquifer.

This study attempts to mimic contaminated sandy aquifers, and the unsaturated zone under laboratory condition. The study results presented here may assist in understanding the potential influence of infiltration on designing a more cost-effective remediation plan for contaminated aquifers.

CHAPTER 2

PREVIOUS STUDIES AND STUDY AREA

Introduction

Despite wide range in the amount of precipitation and temperature across the globe, even regions receiving ≤ 10 cm of annual rainfall are able to meet their water supply needs from groundwater, such as Saudi Arabia Libya, and Iraq. The same is also true for several arid to semi-arid locations in the United States. According to the United States Geological Survey's (USGS), groundwater atlas of the country, eight states (Colorado, Kansas, Nebraska, New Mexico, Oklahoma, South Dakota, Texas, and Wyoming) extract water from the Ogallala aquifer, which is a part of the High Plains Aquifer System (USGS, 2013). The principal geologic unit forming the Ogallala aquifer is the Ogallala Formation that ranges in age from Pliocene to Miocene, and mainly consists of gravel, sand, silt, and clay (USGS, 2013). This aquifer is described as a major groundwater reservoir and 30% of Ogallala groundwater is used to irrigate 20% of land in the United States Midwest agricultural fields (Peck, 2007). According to U.S. EPA (2011a) about 90% of the 155,000 public drinking water supplies in the United States are drawn from groundwater; and groundwater provides drinking-water supply to nearly 50% of the United States population. In the Kansas City metropolitan area the Missouri River alluvial aquifer supplies all or part of the drinking water to about one million people in 90 municipalities and public water-supply districts, and is the only aquifer in the area that can supply large quantities of groundwater for public and industrial use (Kelly, 2003).

Hydrocarbon contaminants pose a real threat to human life and the environment. As a result, several studies have evaluated their adverse impacts on human health and the environment (ATSDR, 1996b, 2003, 2011; U.S. EPA, 2011a).

Although, previous studies (e.g. Hueckel *et al.*, 1997; Tsao *et al.*, 1998) have focused on the effect of some oil derivatives on clay minerals, such as bentonite and others, it did not address the influence of organic contaminants on physical, chemical and geotechnical properties of sand that comprises one the most common aquifer materials.

Previous Studies

Online and physical searches on available literature revealed that no comprehensive and systematic studies have been conducted on chemical and geotechnical properties of contaminated aquifer sand. Published research focused on the effects of organic contaminants on clay minerals or top soil, and specifically dealt with adsorption and absorption phenomena. Polak and Lu (1973) studied the solubilities of hydrocarbons and water at 0 °C and 25 °C. Their results indicated that solubilities are generally lower at 0 °C than at 25 °C. This study included benzene, toluene, ethylbenzene and xylene. Their results indicated that water solubility of toluene, ethylbenzene and xylene decreased from 724 to 573 ppm, 197 to 177 ppm and 196 to 162 ppm respectively. Whereas, solubility of benzene showed an increase with increasing temperature: from 1678 ppm at 0 °C to 1755 ppm at 25 °C. Their result showed that there is an inverse relationship between solubility of some hydrocarbons and temperature.

Hueckel *et al.*, (1997) published a study on the theoretical assessment of fabric and permeability changes in clays affected by organic contaminants. Their study focused on the

changes in permeability of clay and found that interaction between liquid organic chemicals and clays were responsible for changes in permeability.

Tsao *et al.*, (1998) in their study focused on metabolism of benzene, toluene, and xylene (BTX) hydrocarbons in soil. They reported that enrichment cultures obtained from soil exposed to BTX, mineralized benzene and toluene but cometabolized only xylene isomers, forming polymeric residues.

Mohamed and Antia (1998) published a book dealing in detail with relative conductivity of soil-bentonite slurry mixtures permeated by xylene and methanol.

He *et al.*, (2006) published a study on detailed sorption isotherms of pentachlorophenol (PCP) on soils and its correlation with soil properties. They concluded that pH, soil organic carbon and organic carbon fractions, and particle size distribution are the main factors responsible for the sorption and desorption hysteresis processes. These factors worked in concert in influencing the fate of PCP sorption–desorption in soil.

Ruffino and Zanetti (2009) studied adsorption of five hydrophobic organic contaminants (HOCs) (benzene, chlorobenzene, TCE, perchloroethylene-PCE, and toluene) from an Italian unconfined aquifer material (< 2 mm) to determine the coefficient of partition K_D between soil and groundwater. They concluded that the adsorption is in the following order:

$$\text{PCE} > \text{TCE} > \text{benzene and chlorobenzene}$$

Okamoto *et al.*, (2009) studied changes in evaporation rate and vapor pressure of gasoline with progress of evaporation. Their goal was to develop a predictive model of the amount of vapor generated from gasoline spill and resulting fire and explosion hazards. Their results indicated that the vapor pressure and the evaporation rate are related to exponential

functions of the weight loss fraction. A prediction model of the amount of gasoline vapor was developed. However, their study focused on evaporation of gasoline from open pans and not from aquifer materials.

Several geological and hydrological studies have been carried out in Jackson County, Missouri; these studies are summarized below:

Beveridge (1955) in his paper “An Introduction to the Geologic History of Missouri” gives an idea about the general geologic history and the major rock types of Missouri. He divided the state of Missouri into four major geologic regions: the Ozarks; the plains to the west of Ozarks; the glaciated area of the northern half of the state; and the lowlands of southern Missouri.

Aber (2005) wrote a report on the geology of the Kansas City vicinity. This report focused on the geology, structure geology, hydrology and glacial deposits of Northwestern Missouri and northeastern Kansas. He reported that the region is situated in the stable crustal platform of the midcontinent region, and the interbedded limestone and shale layers are typical throughout the region.

Parizek (1965) described the geological formations and its lithology within the three subgroups of the Kansas City group: Bronson, Linn, and Zarah.

Hasan *et al.*, (1988) published a review paper on the geology of greater Kansas City, Missouri and Kansas. They described the geological setting of metropolitan Kansas City as well as climate, minerals, hydrology, geologic hazards, and hydrogeology. They reported that floodplain wells have been found to contain various amounts (parts per billion) of volatile organic chemicals such as vinylchloride, trichloroethylene and *trans*-1,1-dichloroethylene.

Kelly (2003) published a report on the Missouri River alluvial aquifer at Kansas City, Missouri. The goal of this work was to provide hydrogeologic data as a basis for a regional groundwater protection plan. He also described the geology of the Missouri River alluvial aquifer as well as the hydraulic properties of the water flow using MODFLOWARC and GIS software.

Location and Study Area

Missouri, one of the Midwestern states of the United States, is almost centrally located in the country and is bordered by Iowa, Illinois, Kentucky, Tennessee, Arkansas, Oklahoma, Kansas, and Nebraska. The Mississippi River forms the eastern border and the Missouri River nearly bisects the state north and south. According to the U.S. Census Bureau (2010) Missouri with a population of more than 6 million, has an area of 178,042 km², and ranks 21st among the states by size. Jackson County, situated in the northwest corner of the state, is bounded on the north by the Missouri River and touches the Kansas state line on the west. On the south is Cass County, and on the east are Lafayette and Johnson counties. The county, with 2013 estimated population of about 467,000 and an area of 1,596 km², of which, 1,567 km² is land and 30 km² or 1.88% is water (U.S. Census Bureau, 2010 and 2013), is roughly bounded by latitudes 38° 50' and 39° 10' north and longitudes 94° 10' and 94° 40' west.

Sampling Site

Bulk sand samples were collected from the exposed portion of the Missouri River aquifer that occurs as the Missouri River flood plain deposit. All sand samples were collected

from the Mid America Sand and Gravel Co. quarry located in Independence, Jackson County, Missouri (39°11'19.16"N, 94°23'42.24"W) (Figure 2.1).

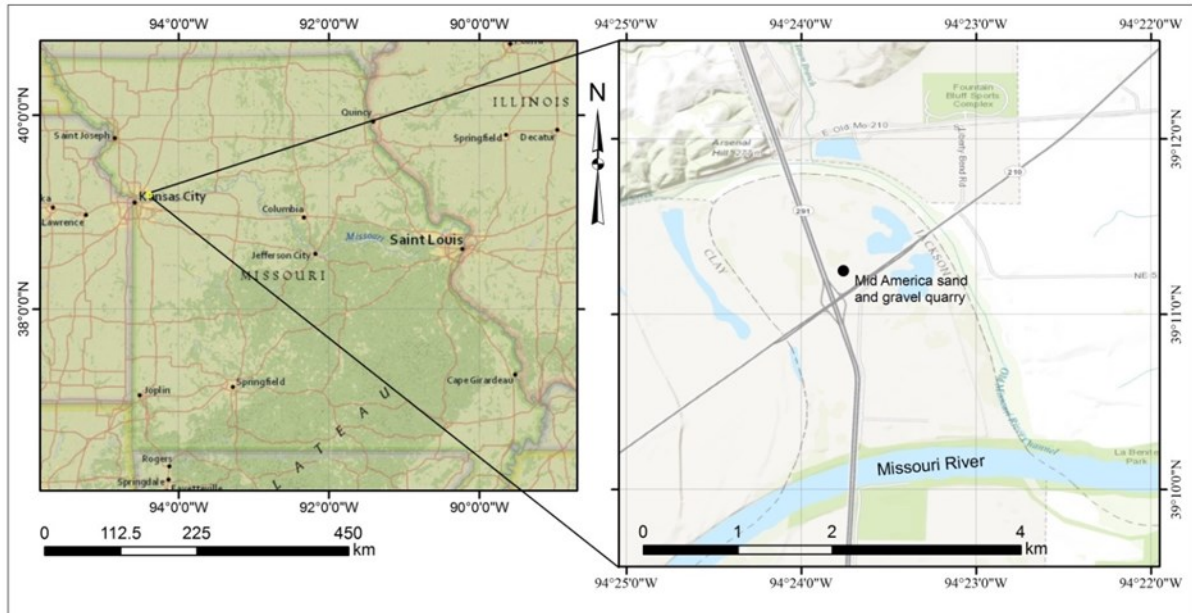


Figure 2.1. Sampling site location map; Missouri State (left), and Mid America Sand and Gravel Co. quarry (right)

Geological Setting

Geological setting of an area constitutes the basic elements of environmental and hydrogeological studies. This provides a comprehensive picture of geologic materials, processes and their geological ages, to gain a thorough understanding of the engineering properties of earth materials to determine the hydrogeological and geotechnical parameters of the aquifers in the region. Also, a study of structural geology and land movements

experienced by the region help to know the types of geological structures in the area and its possible control on the aquifer types.

Geologic formations exposed in Jackson County, Missouri, are of sedimentary origin and range in age from Pennsylvanian to Quaternary. These sedimentary rocks consist largely of interbedded limestone, shale, and sandstone. They belong to the Pennsylvanian series of the Carboniferous, Coal Measures, and are nearly everywhere overlain by unconsolidated surficial deposits of Quaternary age or by residual soil that has resulted from the weathering and decay of the rocks themselves (McCourt, 1917).

Topographically Jackson County is situated about midway between the Ozark Plateau and the Great Plains in the intervening prairie region, known as the Scarped Plains (McCourt, 1917). The rocks of this region consist of beds of unequal thickness, dipping gently away from the Ozark uplift. Erosion of these rocks has produced a series of plains and escarpments that trend in a general northeast and southwest direction; although in Jackson County the influence of the Missouri River has to some extent reversed the direction. In Jackson County the general elevation of the upland divides ranges from about 332 m above sea level (a.s.l.) along the divide in the southern part of the county, to between 274 m and 304 m along the crest of the river bluffs (McCourt, 1917); the average elevation is close to 304 m. The highest point in the county, 325.5 m a.s.l. is located southwest of Less Summit. The lowest point is in the northeastern corner of the county, about 209.7 m a.s.l. The maximum relief therefore is about 115.8 m. The flood plain of the Missouri River lies between 213 and 228 m a.s.l. (McCourt, 1917).

Structural Geology

The most thorough account of the structural geology of the study area was published by Gentile *et al.*, (1995). They stated that the regional dip of the bedrock in west-central and northwestern Missouri is about 1.89 m/km in NNW direction, and the northwesterly dip of the layers is modified by large, broad folds of county-wide extent (McCracken, 1971). These large folds are associated with smaller folds, and their structural axes are randomly oriented (McCracken, 1971).

Joints are common and three sets have been observed: the main set trends NE–SW, the secondary set trends NW–SE, and the minor set has almost N–S direction (Hinds and Greene, 1915). The joints have a steep to nearly vertical dip. Joints occur in all bedrock units and are ubiquitous throughout the metropolitan Kansas City area. The spacing between joints ranges from a few centimeters to several meters and is dependent on location, rock type and bed thickness. These joints are regularly spaced, few meters apart in most places in black fissile shale beds and thin limestone beds, whereas the spacing between major joints in thick limestone, gray shale, and sandstone beds is generally more than 6 m (Hinds and Greene, 1915).

High angle normal faults with displacement ranging from a few cm to over 30 m have been documented at several locations in the metropolitan Kansas City area. Majority of the faults strike in a northwesterly direction and run for few hundred meters. According to Gentile (1984) the faults strike in the direction of small fold axes and are related to the structural grain of midcontinent. The faults strike in the direction of the major joints and small fold axes trend in NW–SE or NE–SW.

Geology of the Missouri River Alluvial Aquifer

The floodplains of the Missouri River are underlain by alluvial deposits of clay, silt, sand, gravel, cobbles, and boulders that form the alluvial aquifer (Kelly, 2003) (Figure 2.2). Several abandoned alluvial channels are hydraulically connected to the Missouri River alluvial aquifer and exist as a result of changes in the course of the Missouri River and its tributaries during the Pleistocene glacial and interglacial periods. The aquifer thickness ranges from less than 1 m to about 70 m, the average being about 25 m (Figure 2.2). The alluvial deposits lie on top of thin units of Pennsylvanian-age shale, limestone, sandstone, siltstone, conglomerate, coal and claystone that define the bottom and walls of the alluvial aquifer (Gentile *et al.*, 1994).

Lithologically, fine grained sediment, consisting of clay, silt, and silt/sand, ranging in thickness between 15 m and 25 m, comprise the top layer. This is underlain by 8 m to 15 m thick layer of sand that constitutes the upper aquifer. This, in turn, is underlain by the lower sand and gravel aquifer between 15 m to 25 m thick (Kelly, 2003).

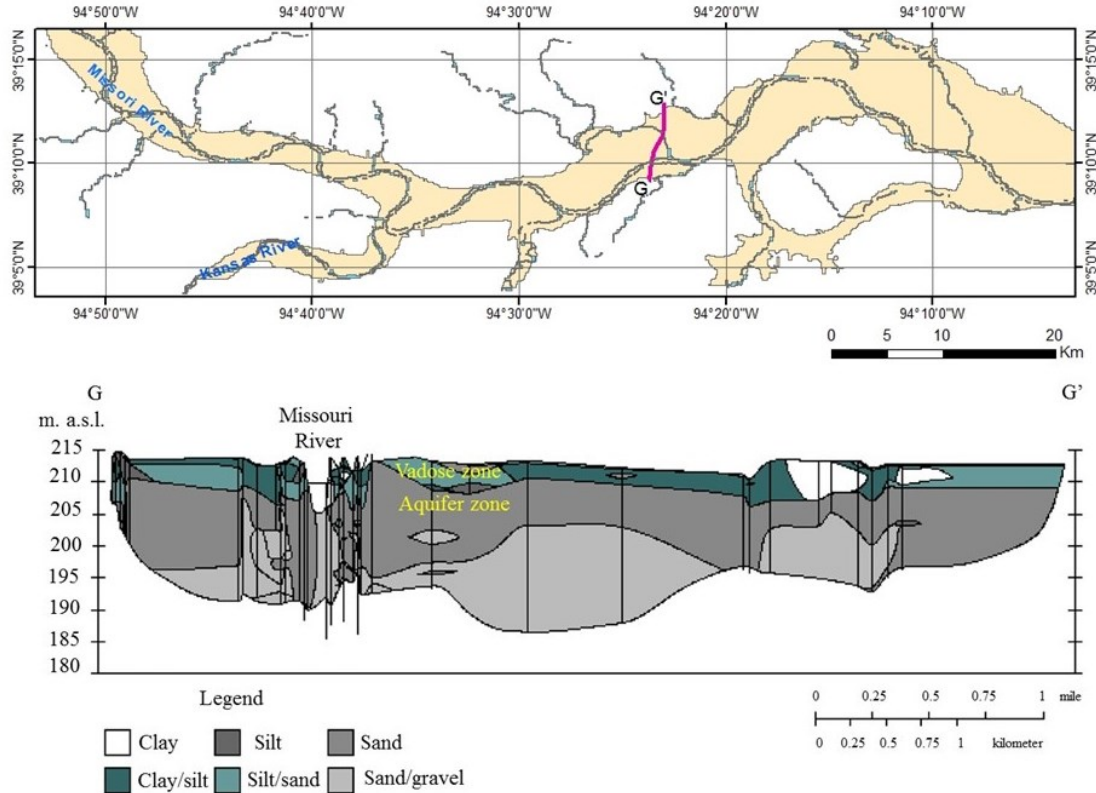


Figure 2.2. Missouri River alluvial aquifer. a. map; b. lithological section along G-G' (modified after Kelly, 2003)

Missouri's Groundwater Resources

According to the Missouri Department of Natural Resources-Water Resources Center (MDNR) groundwater is one of major natural resources in Missouri where more than 94% of the 1,191 primary public water supply systems use groundwater (MDNR, 2007). Public water supplies provide water to about 36% of Missouri residents (5 million) and about 500,000 rural residents are almost self-supplied and dependent on groundwater (MDNR, 2007).

Missouri's Groundwater Provinces and Aquifer Characteristics

Availability of groundwater in Missouri is closely tied to the geology of the regions, which is reflected in the wide variation in occurrence and distribution of groundwater in the state. The boundaries of the groundwater provinces in Missouri, drawn by the MDNR, are based on several factors including aquifer characteristics, groundwater quality changes, and geology. MDNR (2014) reported that the amount of usable groundwater is less in northern Missouri—about 12% of Missouri's drinkable groundwater. Although, the pre glacial valleys of northwest Missouri occupy only a small area, they can be an important source of water. MDNR (2014) also reported that it is generally hard to obtain drinkable groundwater in the West-Central Missouri groundwater province, water yield from it is too mineralized for domestic use.

Groundwater in the state of Missouri is divided into nine provinces, as shown in Figure 2.3 (MDNR, 2014). The largest, most extensive aquifer, is the Ozark aquifer in the Salem Plateau and Springfield Plateau groundwater provinces.

Most of Jackson County lies in the west-central Missouri groundwater province (7.3% of Missouri area) that is located in the midwest of Missouri and south of Missouri River, and includes the alluvial aquifer system. Also, it is a part of the Missouri and Mississippi River alluvial groundwater provinces, which extends as longitudinal bars around the rivers in narrow spaces. The study area is part of the west–central Missouri groundwater province.

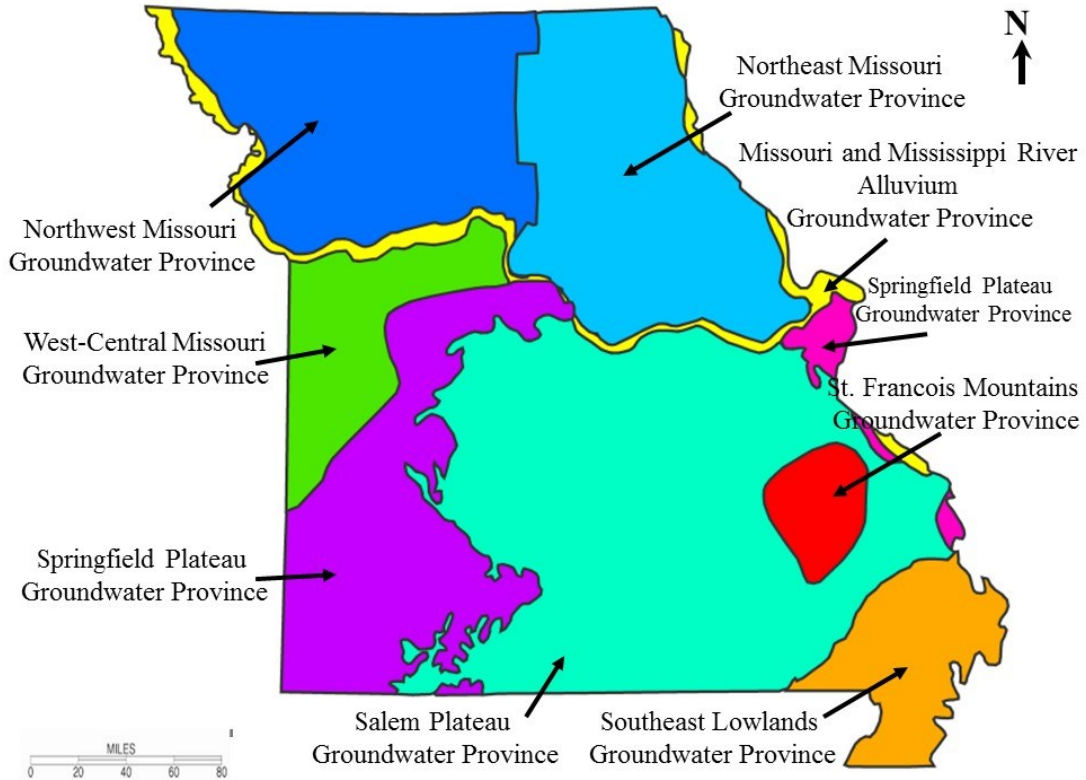


Figure 2.3. Missouri groundwater provinces (adopted from MDNR, 2014)

Hydraulic properties of the Missouri River Alluvial aquifer were studied in detail by Kelly (2003). He reported that hydraulic conductivity values of this aquifer is between 0.1 and 1400 m/day, high transmissivity values, about 7400 m²/day, and the specific yield of between 0.15 and 0.2. The alluvial aquifers yield large quantities of water to wells along the major streams of the Jackson County (Kelly, 2003).

Groundwater temperature is mostly constant in confined and deep aquifers; however, in the alluvial aquifer it fluctuates between a much narrower range than the air temperature. This fluctuation is a special feature of wells near the river where the aquifers are affected by

seasonal recharge with river water (Fishel, 1953). The average groundwater temperature from well water samples was 14.4 °C, the minimum 11.6 °C and the maximum 17.7 °C (Fishel, 1953).

Availability of groundwater in the alluvial aquifers of Missouri and Kansas Rivers valleys is dependent on the stream flow (Fishel, 1953). The available groundwater supply will be high as long as there is stream flow available to induce infiltration, and could yield 333,000 m³ per day. However, withdrawal from these groundwater sources will reduce the stream flow by the amount of the induced infiltration, but if the streams dry up, the potential supply will be greatly decreased (Fishel, 1953).

CHAPTER 3

SELECTION OF MATERIALS

Introduction

Sediment samples and the chemicals used in this study were selected after reviewing previous studies done by United States Geological Survey (USGS), United States Environmental Protection Agency (U.S. EPA) and Agency for Toxic Substances and Disease Registry (ATSDR). In addition, face-to-face meetings and discussions with experts at the USGS and Black and Veatch were conducted to determine some of the key environmental issues impacting aquifers and groundwater sources.

Selection of Samples

Sands, occurring as river floodplain deposit, comprise the most common aquifer material in the United States and worldwide. Bulk sand samples were collected from the exposed portion of the Missouri River aquifer that occurs as flood plain deposit. Sand samples used in the experiment were collected from both saturated (aquifer) and unsaturated (vadose) zones. The first set of samples was collected from exposed part of the sand and gravel layer that comprise the main aquifer, which occurs 16 m below the ground surface, and ranges in thickness from 15 m to 25 m (Figure 2.2). Groundwater level at the study area ranges between 1 m and 4.5 m below the ground surface (MDNR, 2012; 2013) (Figure 3.1).

A second set of samples, representing the upper sand layer (vadose zone) and occurring 2 m below the ground surface as the flood plain deposit, was also collected (Figure 2.2). The justification for including this geological layer is three fold: First, it is widespread

and covers large area and overlies the main aquifer layer. Second, transport of any contaminant into the aquifer will involve passage through this material. Third, understanding changes in infiltration rate following precipitation events, at hydrocarbon-contaminated sites, would help estimate the arrival time of contaminated water that would improve our ability to develop timely and effective remediation solutions before the contaminants reach the aquifer.

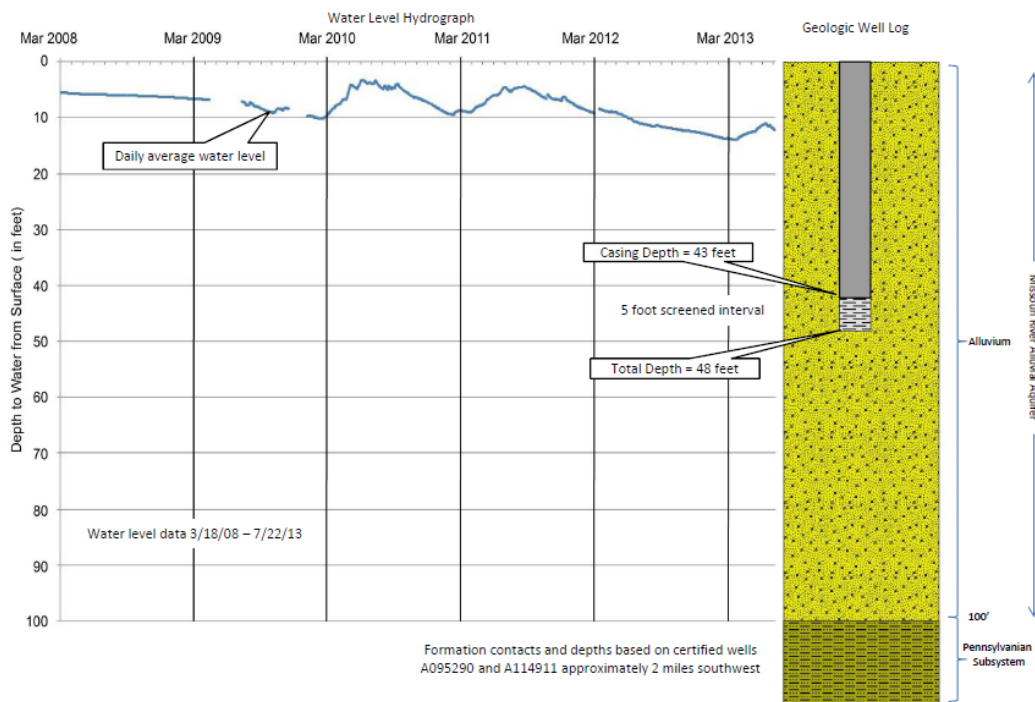


Figure 3.1. Water level hydrograph and geological well log (after MDNR, 2013)

Selection of Chemicals

The types of chemicals selected and used in this study included the most widespread chemicals found in contaminated groundwater (Zogorski *et al.*, 2006), that pose serious threats to human health and the environment (ATSDR, 2004, 2013; U.S. EPA, 2011a). ATSDR (2013) has identified 275 common chemicals found at hazardous waste sites that have been placed on the National Priorities List (NPL). Benzene, trichloroethylene (TCE), xylene, toluene and ethylbenzene, five of the most widely used industrial chemicals, were detected at about 1,300 Superfund sites (as of June 11, 2012) and have been ranked as the 6th, 16th, 64th, 74th and 130th respectively among 275 polluting chemicals prioritized by the ATSDR (ATSDR, 2013; 2014) (Table 3.1). It should be noted that the ATSDR priority list, which is revised and published every 2 years, is a prioritization of substances based on a combination of their frequency of occurrence at NPL sites, toxicity, and potential for human exposure and is not a list of most toxic substances (ATSDR, 2014).

Table 3.1. Abridged ATSDR priority list of selected hazardous substances

Substance	2013 rank (out of 275)	Priority list of hazardous substances
Benzene	6	Ranking of hazardous substances based on a combination of occurrence frequency, toxicity, and potential for human exposure at NPL sites
TCE	16	
Xylenes	64	
Toluene	74	
Ethylbenzene	130	

Source: Priority list of hazardous substances (ATSDR, 2013; 2014)

Another study conducted by the USGS pointed out that 90 of 98 aquifers in the United States contain low-level (0.0002 ppm) of VOCs (Zogorski *et al.*, 2006). These findings indicate the need to include them in groundwater monitoring programs to track the trend of these contaminants (Zogorski *et al.*, 2006). The study also reported that methyl tert-butyl ether (MTBE)—a gasoline oxygenate VOC group chemical—is the third most commonly detected class of organic contaminants in groundwater, and TCE, a common industrial solvent, is the fourth, whereas toluene is the fifth of the 15 most frequently detected VOCs in the United States aquifers. Also, a study conducted in Region 9 of the U.S. EPA, found that some drinking water well fields were contaminated with MTBE at levels of up to 0.61 ppm (U.S. EPA, 2011c). In addition, U.S. EPA on July 2006 found high levels of MTBE in groundwater at the Amorco terminal of Martinez, California. A total of about 1800 kg of MTBE was subsequently removed in the first 5 months of operation using the vapor extraction system (U.S. EPA, 2011c).

Aquifer contamination by industrial solvents, such as TCE, is also common (U.S. EPA, 2011a). Gross and Termaath (1985) detected TCE in drinking water at a concentration of 6 ppm at the Wurtsmith Air Force Base, Oscoda, Michigan, with a concentration of 10 ppm in the centerline of the plume. Also in 1981, at the Savannah River Plant, TCE was found in groundwater near an abandoned settling basin which had been used for storage of process waters. TCE at this site, with 0.1 ppm total concentration, occupied an area of about 1.46 km² (360 acres) (Boone *et al.*, 1986).

Based on such widespread occurrences, a set of chemicals were selected for this study due to their high frequency of occurrence in aquifers that pose a potentially high risk to human health and the environment. These chemicals are: TCE, isooctane (2,2,4-

trimethylpentane), MTBE, benzene, toluene, ethylbenzene, and xylenes (BTEX). These organic chemicals, present in aquifers at NPL sites in many states, are determined to constitute the most serious threat to human health and adversely impact the environment due to their known toxicity.

Gasoline was also included among the chemicals for the experiments because MTBE and BTEX are the main constituents of gasoline. However, to assure that substituting gasoline for BTEX would provide reliable result, another series of tests were designed using BTEX and isooctane; the latter being one of several isomers of octane (C_8H_{18}). All chemicals used in this study were purchased from ACROS ORGANICS except gasoline, which was purchased locally from the Quick Trip (QT) gas station.

Trichloroethylene

TCE (C_2HCl_3)—a volatile organic chemical (VOC)— is a stable, nonflammable, colorless liquid with a chloroform-like odor, denser than water with a density of 1.46 g/cm^3 at $20\text{ }^\circ\text{C}$ (Hawley and Lewis, 2001). TCE is widely used in consumer products and has been produced commercially since the 1920s in many countries by chlorination of ethylene or acetylene (U.S. EPA, 2011a; 2014). TCE is mainly used in industrial cleaning as a solvent to remove grease from metal parts. According to the U.S. EPA (2011a), 80–90% of the worldwide production of TCE is used for degreasing metals.

Despite TCE's low solubility, it can remain in groundwater for a long time, much longer than in surface water (Monosson, 2008). Leakage of sufficient volume of TCE can cause it to move downward until it reaches a lower permeability medium that would impede its movement. Because TCE is denser than water and does not break down easily in the soil,

it can settle down to the bottom of the aquifer (ATSDR, 1997a, 2003; Monosson, 2008).

Widespread use, along with improper waste management practices of the past, have caused TCE to be a common environmental contaminant that is present in drinking water, indoor environments, surface water, ambient air, groundwater, and soil (U.S. EPA, 2014a). In addition, it is frequently found in groundwater all around the world (Cotel *et al.*, 2011). TCE is a common contaminant at Superfund sites; is present at over 760 of the NPL sites and ranks as one of the six most common contaminants in the United States aquifers (U.S. EPA, 2011b; 2011d).

TCE in the Environment

TCE is released into the environment as a result of industrial activities as well as a leakage and spills from underground storage tanks. Periodic chemical analyses of groundwater samples throughout the United States have been conducted by government agencies, and the results were summarized and published by ASTDR (1997b) and U.S. EPA (2011a; 2011b; 2011c). The results show that TCE is the most frequently occurring organic contaminant in the United States groundwater.

A major TCE leak occurred in Millsboro, Sussex County, Delaware, on October 24, 2005 where TCE was found at concentrations as high as 17 ppm in groundwater samples, that draws its water supply from an unconfined aquifer (Columbia Aquifer) and serves approximately 3,825 person in this town (U.S. EPA, 2009a; ATSDR, 2012; Delaware Geological Survey, 2014). The maximum concentration level (MCL) for TCE in drinking water is 0.005 ppm (U.S. EPA, 2012a). As a result of this high concentration of TCE—3400 times greater than the MCL—in the groundwater wells of the Millsboro, U.S. EPA (2009a)

categorized this source as carcinogenic risk. The USGS (2006) study for water supply wells found that the number of samples exceeding the MCL for TCE was eight out of 2,400 domestic wells and nine out of 1,100 in public wells.

In addition to surface and groundwater, TCE has also been found in the ambient air all over the United States with the highest air concentration in densely populated industrial areas and lowest in rural regions and in forests (ATSDR, 1997b; U.S. EPA, 2011a). The mean TCE level in the air of the United States, measured in 2006, ranged from 0.03 to 7.73 $\mu\text{g}/\text{m}^3$, with an overall average of 0.23 $\mu\text{g}/\text{m}^3$ (U.S. EPA, 2007).

Toxicology of TCE

The final report by U.S. EPA (2011b) indicated that an overexposure to TCE by ingestion and inhalation will mainly affect the central nervous system causing headache, nausea, clumsiness, dizziness and sleepiness; however, high exposures to TCE can injure the liver and kidneys. In addition, inhalation of TCE within closed space can irritate the lungs, cause shortness of breath or stop breathing leading a person to pass out and die. Heart fibrillation that can cause sudden death is an effect resulting from overexposure to very high concentrations of TCE. Yauck *et al.*, (2004) published a study on the risk of exposure to TCE during pregnancy and reported that it caused an increased risk of heart defects. TCE is also absorbed through healthy human skin slowly, but rapidly through injured or damaged skin, and after long period of contact can cause aridity, cracking, irritation, inflammation, redness, and peeling.

On September 28, 2011 U.S. EPA added the final health assessment for TCE to the database of the Integrated Risk Information System (IRIS)—a human health assessment

program that evaluates the latest science on chemicals in the environment (U.S. EPA, 2011b). This assessment characterized TCE as carcinogenic to humans. Also, the National Toxicology Program (NTP), and the U.S. Department of Health and Human Services, have listed TCE as a reasonably anticipated carcinogen (NTP, 2011).

To sum up, all studies that have been done by U.S. EPA, NTP, and ATSDR show that the increased exposure to TCE and its occurrence in the environment will result in serious consequences to public health.

Gasoline

Gasoline, widely used as an automobile fuel, consists mostly of organic compounds and is a mixture of many different chemicals— more than 150— with many of them being highly toxic. These compounds differ in degree of toxicity and risks to human health. Gasoline's density ranges from 0.71– 0.77 g/cm³. The material safety data sheet (MSDS) for unleaded gasoline shows at least 15 hazardous chemicals occurring in various proportions, including BTEX, lead (not any more in the United States) and MTBE. The process by which gasoline is manufactured controls which chemicals and how much of each would exist in the gasoline mixture. In addition, the specific chemical composition of gasoline varies depending on the source of the crude oil and time of year.

Gasoline in the Environment

The occurrence of gasoline in the environment is related to many sources. The main source is leaks that occur at gas stations, which are around us everywhere. Leaks also occur from damaged refined-products pipelines that transport petroleum products and from

underground storage tanks. In the United States as a safeguard against leakage, all old underground storage tanks have been replaced by tanks with a double liner.

Chemical Nature and Toxicology of Gasoline

VOCs, found in gasoline, are highly toxic compounds, some of them are well-known carcinogens and can produce harmful effects on the liver, kidney, spleen, stomach, and heart, as well as the nervous, circulatory, reproductive, and respiratory systems (Zogorski *et al.*, 2006). There are many chemicals in, or added to gasoline, that make it toxic because of their potential carcinogenicity; some of these compounds are commonly found in groundwater (Appendix A.2). For example, toluene (C_7H_8) may comprise up to 35% volume of gasoline (TESORO, 2003), and is a common contaminant at Superfund sites, was found to be present at more than 959 of the 1,591 NPL sites in 2000 (ATSDR, 2000). People, drinking water contaminated with toluene, can experience harmful effects to their nervous system, kidneys, memory loss and liver problems. Though toluene is not classified as human carcinogen, U.S. EPA has set an MCL of 1 ppm in drinking water (ATSDR, 2004; U.S. EPA, 2012a). Xylene is another common hazardous contaminant also found in groundwater and is present in unleaded gasoline up to 25% by volume (TESORO, 2003). Xylene has been found at 840 of the 1,684 NPL sites (ATSDR, 2007). Xylene produces negative effects on the kidney and liver, but is not classified as a human carcinogen; U.S. EPA has set 10 ppm as the MCL in drinking water (U.S. EPA, 2012a).

MTBE ($C_5H_{12}O$), which was used as an anti-knocking agent and octane enhancer to replace lead in gasoline, makes up to 18% of the volume (TESORO, 2003) of gasoline.

Because of MTBE toxicity, it has been phased out from gasoline in the United States since the late 1990s and has been replaced with ethanol, which is nontoxic.

MTBE has high water solubility and thus large quantities can dissolve when gasoline oxygenated with MTBE comes into contact with water bodies. According to a study by Squillace *et al.*, (1997), MTBE has water solubility of 5 g/L at 25 °C, whereas the total hydrocarbon solubility of a non-oxygenated gasoline is only about 0.12 g/L. Due to MTBE's small molecular size and high solubility in water, it moves rapidly through groundwater, faster than other constituents of gasoline (U.S. EPA, 1997a). MTBE is also a common groundwater contaminant and it is the third most commonly detected VOC in urban water wells. According to the USGS, nearly 40% of the United States population lives in areas where MTBE occurs in groundwater (USGS, 1996). U.S. EPA has not set MCL for MTBE in drinking water (U.S. EPA, 2013c) because it found that at concentrations between 0.02 and 0.04 ppm or lower there is little likelihood that MTBE in drinking water will cause adverse health effects. At high doses, however, MTBE is a potential human carcinogen (U.S. EPA, 1997a).

Another hazardous chemicals occurring in unleaded gasoline is trimethylbenzene (C_9H_{12}), which comprises about 7% volume of gasoline (TESORO, 2003). Exposure to trimethylbenzene can cause headache, fatigue, and drowsiness (U.S. EPA, 1994). U.S. EPA has not set MCL for trimethylbenzene in drinking water, and it is not classified as human carcinogen (U.S. EPA, 2014a).

Benzene (C_6H_6) is released into the environment by both natural and industrial sources and represents up to 5% by volume of gasoline (TESORO, 2003). U.S. EPA (2003) and ATSDR (2007) reported that benzene is widely used in consumer products and is present

in drinking water, indoor environments, surface water, ambient air, groundwater, and soil. Benzene is a common contaminant at Superfund sites. It is present at more than 1,000 of the 1,684 NPL sites (ATSDR, 2007). Benzene can cause harmful effects to blood-cell producing tissues, especially bone marrow (ATSDR, 2004; 2007), and is known to be a human carcinogen. Long-term exposure may cause leukemia and anemia according to the U.S. Department of Health and Human Services (2011) (U.S. EPA, 2012a, 2014a; NTP, 2014). Limited exposure for 5–10 min to benzene in air at very high levels–20,000 ppm– can lead to death (ATSDR, 2007). U.S. EPA (2012a) has set the MCL for benzene in drinking water at 0.005 ppm.

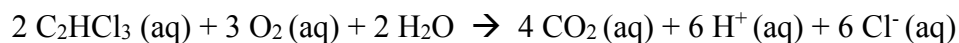
Ethylbenzene (C_8H_{10}) represents up to 5% by volume of gasoline (TESORO, 2003), and is also a common contaminant at Superfund sites. It has been found at more than 829 of 1,699 NPL sites as of 2010 (ATSDR, 2010). It is mainly used in fuels and industrial solvents and is found in natural and manufactured products such as coal, tar, petroleum, inks, insecticides, and paints. In the United States it occurs in about 3% of the surface water samples analyzed (ATSDR, 2010). U.S. EPA (2012a) has set a MCL in drinking water at 0.7 ppm. Exposure to high levels of ethylbenzene in the air can cause eye and throat irritation.

Naphthalene ($C_{10}H_8$) represents up to 1% by volume of gasoline (TESORO, 2003). High exposure to naphthalene will damage or destroy red blood cells and lead to hemolytic anemia. U.S. EPA has not set MCL for naphthalene in drinking water and has not classified it as a human carcinogen (U.S. EPA, 2012a). According to ATSDR (2005), naphthalene can easily pass through sandy soils to reach groundwater because it binds weakly to grains of sandy soils.

Hydrocarbon Density and Water Solubility

Density and water solubility are important properties that affect the availability, movement and concentration of chemicals in water. Density is a substance's mass per unit volume. Russell *et al.*, (1992) defined water solubility as the maximum concentration of a solute which can be carried in water under equilibrium conditions, and is generally reported in ppm (parts per million) or mg/L (milligrams per liter). Hydrocarbons solubilities have been studied by many investigators at varying temperatures. For instance, mutual solubilities (two or more chemicals, when brought together, have the ability to mix and form one phase) of paraffinic and aromatic hydrocarbons— benzene, toluene, ethylbenzene and xylene—and water have been determined experimentally at 0 °C and 25 °C by Polak and Lu (1973). Their results indicate that solubilities are generally lower at 0 °C than at 25 °C except for paraffin which is greater at 0 °C than at 25 °C. Their results show that solubility of toluene, ethylbenzene and xylene decrease from 724 to 573 ppm, 197 to 177 ppm and 196 to 162 ppm respectively with increasing temperature of 0 °C to 25 °C. The solubility of benzene, however, increased with increasing temperature—from 1678 ppm at 0 °C to 1755 ppm at 25 °C.

Several measurements have been made of the aqueous solubility of some chlorinated hydrocarbons, TCE and tetrachloroethylene (PCE), at ambient temperature (25 °C), and results clearly indicate significant dependence of aqueous solubility to temperature (Knauss *et al.*, 2000). Most organic water contaminants can be destroyed at higher temperatures by pyrolysis and aqueous oxidation. The following reaction for the aqueous oxidation of TCE is presented by Knauss *et al.*, (1999):



Even though this reaction is thermodynamically spontaneous ($\Delta G_r < 0$), the reaction rate is so low at usual groundwater temperatures that the process becomes insignificant. Knauss *et al.*, (1999) reported that the rate constant increases by a factor of about 2500 from 25 °C to 90 °C.

Pontolillo and Eganhouse (2001) defined octanol-water partition coefficient (K_{ow}) as, “the ratio of the concentration of a chemical in n-octanol and water at equilibrium at a specified temperature. It is assumed that the molecular speciation of the solute is the same in both solvents and that the solutions are sufficiently dilute.” The physiochemical properties of TCE, BTEX, and MTBE compounds (Table 3.2) indicate that these chemicals tend to be slightly soluble in water, or volatilize into pores of soil because of the relatively solubility and their low K_{ow} values. On the other hand, MTBE, which is part of gasoline, has one of the highest solubilities in water among the chemicals used in this study (Table 3.2). Water solubility of hydrocarbons enhances the potential to migrate through the soil into groundwater (U.S. EPA, 2011a). Table 3.2 summarizes the most important properties of the chemicals used in this study.

Table 3.2. Physiochemical properties of chemicals used in the study

Compound	Molecular weight (g/mol)	Water solubility at 20-25 °C (mg/L)	Vapor pressure at 25 °C (mm Hg)	Density at 20 °C (g/cm ³)	Dynamic viscosity at 20 °C (cP)	Log K _{ow}	Diffusion coefficient in water (cm ² /s)
TCE (C ₂ HCl ₃)	131.39	1280	58	1.46	0.58	2.71	9.1x10 ⁻⁶
Gasoline	-	-	5-15	0.72	0.6	-	-
MTBE (CH ₃ OC(CH ₃) ₃)	88.15	51000	27	0.74	0.36	1.2	-
Benzene (C ₆ H ₆)	78.12	1780	76	0.88	0.65	2.13	9.8x10 ⁻⁶
Toluene (C ₇ H ₈ or C ₆ H ₅ CH ₃)	92.15	515	22	0.86	0.58	2.69	8.6x10 ⁻⁶
Ethylbenzene (C ₆ H ₅ CH ₂ CH ₃ or C ₈ H ₁₀)	106.17	169	7	0.87	0.67	3.15	7.8x10 ⁻⁶
M-Xylene (C ₈ H ₁₀)	106.17	160	9	0.86	0.61	3.2	7.8x10 ⁻⁶
Isooctane (2,2,4-Trimethylpentane) (C ₈ H ₁₈)	114.23	Insoluble in water	41 at 21 °C	0.69	0.51 at 22 °C	4.08	9.1x10 ⁻⁶

Sources: ATSDR (1996b); Zogorski *et al.*, (1997); U.S. EPA (2011a); GSI Environmental (2013); Haynes (2013); TESORO (2003); Newell *et al.*, (1995)

CHAPTER 4

METHODOLOGY

It is hypothesized that when soil matrices that include aquifer solids come in contact with contaminating fluids, a complex set of biochemical, physical and chemical reactions sets in between the contaminants and the aquifer mineral grains that lead to new equilibrium conditions, altering many of the physical and chemical properties, including porosity and hydraulic conductivity of soils. This study is designed as a series of laboratory experiments to investigate the effects of some commonly occurring and widespread chemical contaminants on the physical, chemical, and geotechnical properties of sand with particular emphasis on the hydraulic conductivity of sand.

Bulk sand samples from the Missouri valley aquifer—that constitutes a major source of groundwater supply in the U.S. Midwest—were employed for the experimental tests. The experiment was designed to expose (contaminate) sand samples with TCE and gasoline for 2, 4, 6, 8, 16, and 32 weeks at approximately 25%, 50% and 100% saturation by volume of voids (v/v) to simulate condition in arid and semiarid regions, such as Iraq, Saudi Arabia and the southwestern United States. Because benzene, toluene, ethylbenzene, xylene, and isooctane, the main constituent chemicals of gasoline, occur very frequently at contaminated sites, including sites placed on the EPA's National Priority List, it was decided to run additional tests on five sand samples fully saturated with these chemicals to investigate their individual control on sand geotechnical properties. Moreover, 10 sand samples from the aquifer layer were exposed to aqueous solution contaminated with 1 to 10% of gasoline for 8

weeks, as well as with TCE at 100% saturation level, to simulate humid climatic environments, such as the United States Midwest.

All test samples were exposed to contaminants for specified periods of time and the same properties were measured for all samples before and after exposure to the contaminants. The objective was to see if there are any changes in their physical, chemical, and geotechnical properties, and specifically to use this information to evaluate any changes in hydraulic conductivity of the aquifer sand. The study comprised of:

- 1) Field work

Bulk sand samples were collected from the exposed part of the Missouri valley aquifer, occurring as river flood plain deposits. Samples were collected from the Mid America Sand and Gravel quarry, located in Independence, Missouri (Figure 2.1).

- 2) Laboratory studies

This phase of the study included: sample preparation, test samples contamination, measurement of geotechnical properties before and after each test; characterization of mineralogy of aquifer and vadose zones solids, and evaporation rate test for contaminating chemicals. The laboratory work involved several steps. First, bulk samples of sand were dried thoroughly by exposing it to air at room temperature following the American Society for Testing and Material (ASTM) standards (ASTM, 2013a), this was followed by homogenizing, coning-and-quartering. All sub-samples were saved in air-tight sealed plastic bags and stored for subsequent tests. Next about 550 g of sand sample were placed in Pyrex[®] bottles, with screw-on lid. Then the chemical contaminants, TCE, gasoline, BETX and isooctane, were poured into separate bottles at pre-determined quantities and immediately covered with a tight screw-on lid and sealed with Teflon tape (Figure 4.1). No free headspace

was left in the Pyrex[®] bottle and it was ensured that sand sample in each bottle was in contact only with plastic screw cap and glass in the bottle. Next, all contaminated samples, in Pyrex[®] bottles, were placed in a dark place at room temperature of about 23 – 25 °C and 1 atm pressure. After the end of each specific time period of contamination the sand samples were air dried (Figure 4.2). Finally, the physical, chemical and geotechnical properties were measured for both the uncontaminated and contaminated sand samples which included:

- a) Grain size analysis.
- b) Porosity, void ratio, dry, and saturated unit weights.
- c) Hydraulic conductivity.
- d) Mineral composition by X-ray diffraction (XRD) for sand and clay fractions.
- e) Evaporation rate of chemicals from the aquifer (saturated zone) and upper layer (vadose zone) sand samples.
- f) Mineral composition, size, shape, etching corrosion and grain fragmentation by scanning electron microscope (SEM).

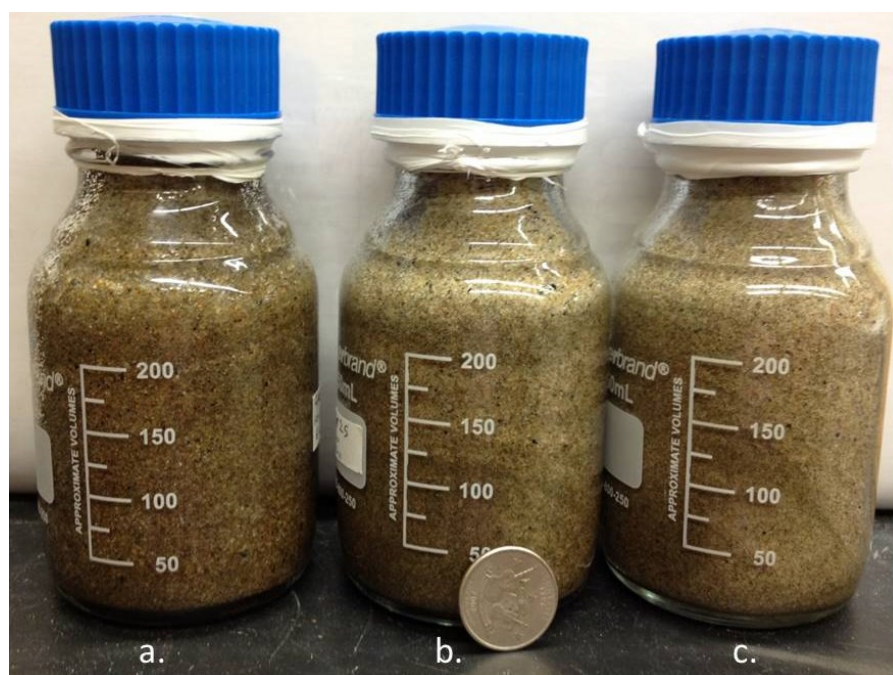


Figure 4.1. Photographs showing sand samples contaminated with gasoline: a. fully saturated; b. about 50% (v/v); c. about 25% (v/v)



Figure 4.2. Photographs of fully saturated, air dried sand samples contaminated with: a. benzene: b. isooctane: c. TCE

CHAPTER 5

LABORATORY TEST METHODS

A series of laboratory experiments were conducted on sand samples in order to evaluate the changes in physical, geotechnical and chemical attributes of uncontaminated and contaminated sand samples. Physical and geotechnical tests included several tests as shown in Table 5.1.

Table 5.1. Tests conducted for geotechnical properties

Test	Property measured	Test equipment	Test standard
Grain size analysis	Particle size classification	Ro-Tap; standard sieves	ASTM, D422–63
Porosity and void ratio	Pore volume	–	ASTM, F1815–11
Unit weight, dry (γ_d) and saturated (γ_{sat})	–	–	ASTM, F1815–11
Hydraulic conductivity	Water movement through pores	Constant head permeameter	ASTM, D2434–68

Additional tests used in this study included:

- Evaporation rate of VOCs in sand to simulate the behavior of VOC as it moves downwards through the aquifer solids after a spill or leaks, and how much of the VOC escapes as vapor and what fraction remains in the soil.
- XRD test to determine mineral composition of aquifer and upper layer sand as well as clays from the upper layer.

- Scanning electron microscope (SEM-MAG-763) to determine mineral composition, grain topography, shape, etching and corrosion of selected aquifer sand samples. In addition, sand mineral composition was determined by using Backscattered electron (BSE), and the energy dispersive spectroscopy (EDS).

Grain Size Analysis

One of the most fundamental physical properties of soil from permeability stand point is its grain size and shape. Information on grain size is used by civil engineers, petroleum geologist, hydrologists, and engineering geologist to estimate important physical properties. Information on sediment grain size can be used to study trends in surface processes related to the dynamic conditions of transportation and deposition; engineers use grain size for engineering classification of soil, and estimating its permeability, compressibility and strength; geochemists use grain size to study kinetic reactions and the affinities of fine-grained particles and contaminants; and hydrologists use it to study the movement of subsurface fluids (Blatt *et al.*, 1972; McCave and Syvitski, 1991). The objective of grain size analysis in this study was to understand its control on the movement of contaminants through the aquifer.

Sample Preparation

Bulk samples of sand that were collected from representative saturated and the unsaturated (vadose) zones were air dried to a constant weight and adequate quantities, sub-samples, of sand was prepared prior to performing grain size analysis by using the standard

procedure of the American Society for Testing and Materials (ASTM), D421–85 (ASTM, 2013a).

Particle-Size Analysis

ASTM standard test method for particle-size analysis of soils, D 422–63 (ASTM, (2011a), was used for quantitative determination of the distribution of particle sizes by using the Ro-Tap machine. The sieve mesh opening are in units of millimeter (mm) and the sieves are identified by a numbering system that corresponds to certain mesh sizes. Sieves with smaller numbers have larger mesh openings and vice versa.

Table 5.2 shows the mesh size corresponding to sieve number. Sieves number 8, 10, 16, 20, 30, 60, 100, 170, and 200 were used for grain size analysis of aquifer sand samples, and sieves number 40, 50, 60, 70, 100, 140, 170, 200, 230, and 325 were used for the upper layer sand samples analysis.

Table 5.2. Sieves number and mesh opening

Sieve number	Mesh opening (mm)	Sieve number	Mesh opening (mm)
8	2.36	70	0.212
10	2.00	100	0.15
16	1.18	140	0.106
20	0.85	170	0.09
30	0.6	200	0.075
40	0.425	230	0.0625
50	0.355	235	0.044
60	0.25		

After the test sieves were selected for grain analysis, each was thoroughly cleaned before test and each empty sieve and the pan was weighed. The sieves were stacked, one on top of the other, with the largest opening on top of the stack. A bottom pan was placed under the smallest-opening sieve to collect fine material passing through the last sieve. A cover was placed on top of the sieves stack before shaking. Next, approximately 500 g of air dried sand sample was added to the top sieve, and the entire sieves stack was placed on the Ro-Tap shaker (Figure 5.1) that was operated for 15 min. After completion of shaking, a series of weighings were done and calculations made to determine the percentage of sand finer than a particular grain size.

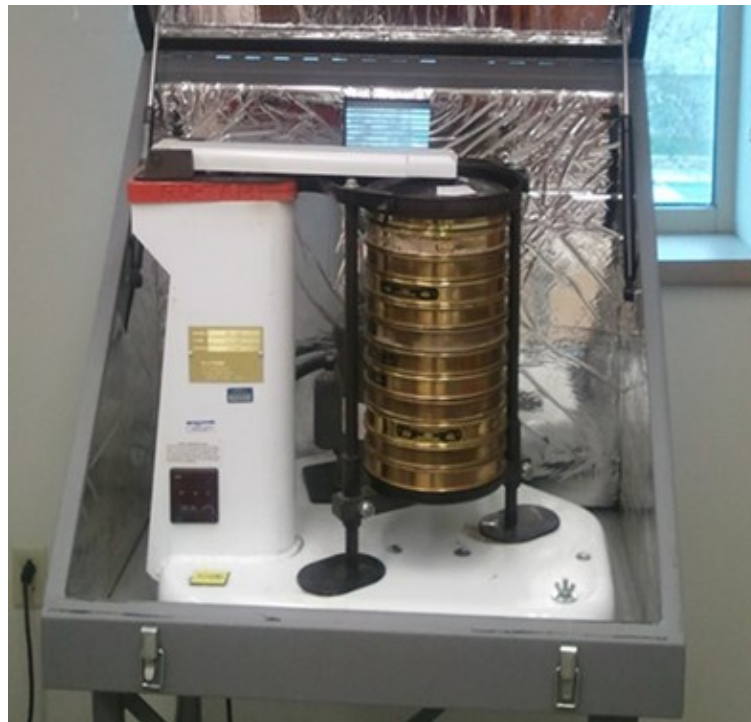


Figure 5.1. Sieves stacked in the Ro-Tap shaker

The quantity of sand passing a certain sieve-the percent finer-was used to plot the particle size distribution curve, on a semi-logarithmic graph with the grain size on the logarithmic scale on the x-axis and percent finer on the arithmetic scale on the y-axis. The resulting particle size distribution curve was used to determine the following parameters:

- a) Effective size (D_{10}) which represents the particle diameter equivalent to 10% finer.

For a granular soil this parameter is a good measure to estimate the hydraulic conductivity of sandy soil using Hazen's formula (Hazen, 1911) and is applicable to sand where D_{10} is between 0.1 to 3.0 mm, and uniform coefficient < 5 , and is expressed as:

$$K = C(D_{10})^2$$

where, K = the hydraulic conductivity

C = a constant that depends on the soil type, for sand it varies from 40 (fine sand-poorly sorted) to 150 (coarse sand-well sorted), and 1.0 (ranging from 0.4 to 1.2) for uniformly graded sand

- b) Uniformity coefficient of sediment (C_u) is a measure of the degree of sorting of the soil. It is the ratio of the grain diameter, finer than 60% (D_{60}) to the grain diameter finer than 10% (D_{10}) (Fetter, 2001), and is expressed as:

$$C_u = \frac{D_{60}}{D_{10}}$$

Large value of C_u , more than 6, indicates that the soil is well-graded, and C_u of 1 indicates a poorly-graded soil, essentially one grain size.

- c) Coefficient of gradation (C_z) is calculated by using the equation:

$$C_z = \frac{(D_{30})^2}{D_{60} \times D_{10}}$$

The soil can be classified by using the value of C_u and C_z , for instance, for a sand to be classified as well-graded, the following criteria must be met: C_u greater than 6, and C_z between 1 and 3.

Soil gradation is also an indicator of other engineering properties such as hydraulic conductivity, compressibility and shear strength.

d) Sorting coefficient (S_0) is a measure of uniformity and expressed as:

$$S_0 = \sqrt{\frac{D_{75}}{D_{25}}}$$

The sorting coefficient is mostly used by geologists and not by geotechnical engineers. The larger S_0 the more well-graded the soil is.

Evaporation Rate of VOCs in Aquifer and Upper Layer Sand Samples

VOCs basically have two phases: liquid phase and gaseous phase. Subsurface movement of the liquid phase contaminants is mostly responsible for aquifer contamination, while transport of gaseous phase through the unsaturated zone can lead to indoor vapor intrusion into buildings at or near such sites where it can produce a harmful effect to the residents (U.S. EPA, 2011e). While volatilization of VOCs is a significant natural decontamination process in the vadose zone, in the aquifer most of the VOCs due to their high vapor pressure result in impeding the passage of water through contaminated soils, affecting its hydraulic conductivity.

Rate of volatilization of gasoline and other VOCs has been studied in considerable detail by researchers in the fire science field (Mackay and Matsugu, 1973; Stiver and Mackay, 1984; Okamoto *et al.*, 2009). A study by Okamoto *et al.*, (2009) showed that free evaporation of gasoline from an open pan, under ambient laboratory conditions, resulted in only partial loss with a residual quantity left behind in the pan after 10 h of exposure. Based on this finding and to investigate the evaporation loss of gasoline from fully-saturated sand, an evaporation test on aquifer sand samples, at various levels of chemical saturation, was carried out to assess the transport of gasoline and other VOCs through sand to simulate hydrocarbon leaks and spills.

Pyrex[®] bottles, with a volume of 310 mL, neck diameter of 3 cm, surface area of about 7.07 cm² and depth of 13.5 cm, were filled with aquifer sand, weighed on laboratory electronic balance (Denver Instrument Company, Model TR-2102) with an accuracy of 0.01 g, at a room temperature between about 23–25 °C and 1 atm pressure (Figure 5.2). A calculated amount of gasoline, TCE, BTEX and isooctane was added to the sand to reach full and partial saturation with gasoline and TCE (about 50% and 25% levels) and the weights recorded. Next the bottle was placed on the electronic balance and a stop watch was used to measure evaporation loss every minute for the first 10 hours, and at longer intervals of 1 h, 5 h, 10 h, 12 h; and 24 h—the final duration of evaporation as shown in Table 5.3.

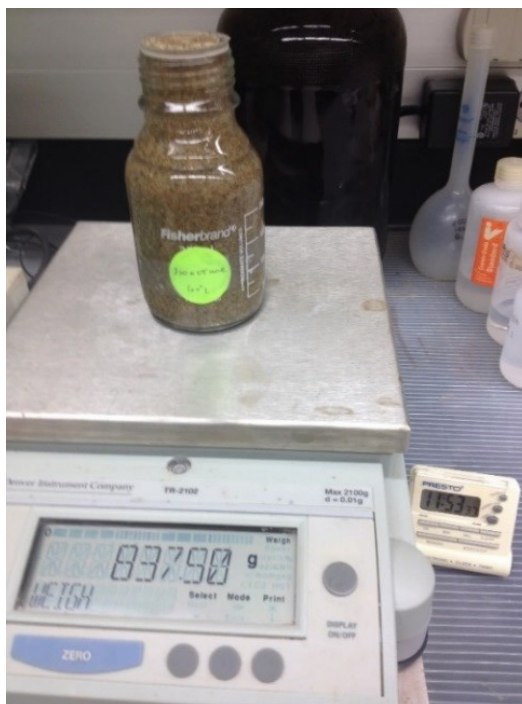


Figure 5.2. Evaporation rate measurement set up

Table 5.3. Time interval used for evaporation rate tests

Time since start of evaporation (hour)	Measurement interval
0 – 10	1 minute
10 – 15	1 hour
15 – 80	5 hours
80 – 130	10 hours
130 – 190	12 hours
190 –	24 hours

Void Ratio, Porosity, Dry Unit Weight, Saturated Unit Weight

Soil in general is composed of solids, liquids and gases, which comprise its three phases. These phases influence the physical properties of soil—for example, a fully saturated soil represents a two-phase system: solid (mineral grains) and water. On the other hand a dry soil has air and solids. A third case is a partially saturated soil where all three-phases are present: solid, water and air.

Void ratio (e) is defined as the ratio of the volume of void space (V_v) to the volume of solids (V_s), expressed as a decimal quantity, as follows:

$$e = \frac{V_v}{V_s}$$

Porosity (n), is the ratio of the volume of voids (V_v) to the total soil volume (V_t) as follows:

$$n = \frac{V_v}{V_t} \times 100$$

Porosity, usually expressed as a percentage, is an important parameter in hydrogeological studies as well as in remediation of contaminated soil and aquifers.

Unit weight, also known as the specific weight(γ), of a soil is the weight per unit volume, and is widely used in geotechnical engineering. Unit weight can be expressed as dry unit weight(γ_d), which is the ratio of the weight of soil solids (W_s) to the total volume (V_t) and is expressed as:

$$y_d = \frac{W_s}{V_t}$$

Saturated unit weight(γ_{sat}) is the ratio of the weight of a soil when it is fully saturated (W_{sat}) to total volume (V_t) and is expressed as:

$$\gamma_{sat} = \frac{W_{sat}}{V_t}$$

Hydraulic Conductivity

Hydraulic conductivity is a key factor in the movement of fluids into and through aquifers, especially at locations of hydrocarbon spills and leaks. Therefore, proper understanding of variations in hydraulic conductivity in response to hydrocarbon contamination allows for estimating the elapsed time between an incidence of hydrocarbon spill and its subsequent transport into the aquifer. Further, knowledge of elapsed time would enable prompt mobilization of plant and equipment to the site for selection of an efficient and cost-effective remediation method.

Following a spill or leak, hydrocarbons during their transport from the ground surface to the aquifer, get partitioned into: (a) light non-aqueous phase liquids (LNAPLs) — density, <1.00 g/mL, water; and (b) dense non-aqueous phase liquids (DNAPLs) — density > 1.00 g/mL. The former are also referred to as “floaters” and the latter “sinkers.” The floaters, such as acetone, ethylbenzene, vinyl chloride (ρ : 0.79, 0.87, and 0.91 g/mL respectively), tend to stay close to the groundwater table, in the shallower part of the aquifer. The sinkers, on the other hand, such as chlorobenzene, carbon tetrachloride, phenol, trichloroethylene (ρ : 1.106, 1.595, 1.058, 1.64 g/mL respectively), travel down to the deeper part, even to the bottom of

the aquifers. Of the chemicals used in this study gasoline, benzene, toluene, ethylbenzene, isooctane, and xylene are examples of LNAPLs while TCE is a DNAPL.

As the hydrocarbon moves down through the soil, following a spill or leak, it coats the soil grains, altering the soils physical structure (reduction of pore volume, initial porosity, and permeability), and induces adhesive forces on the solids affecting its water transmission capacity.

After exposing the sand to selective contaminants for varying periods of time each sand sample was air-dried for one week and its hydraulic conductivity was measured following the ASTM test methods D2434–68 (ASTM, 2011b), using the permeameter equipment (Figure 5.3).

The constant head method is based on Darcy's law which is expressed as:

$$Q = KiA$$

where, Q = volumetric flow rate or discharge (L^3/T)

K = hydraulic conductivity (L/T)

i = hydraulic gradient

A = area that water flowing through (L^2)

In the actual test these parameters are obtained by measuring the volume of water (Q) flowing for time (t), through the sand sample of length (L), and cross sectional area (A), which is the same as cross sectional area of permeameter ($A = \frac{\pi}{4}D^2$) where, D is the inside diameter of the permeameter) and head of the water (h). Hydraulic conductivity (K) is calculated from the equation:

$$K = \frac{QL}{Ath}$$

The mode of grain packing or compaction is important in controlling voids and porosity of cohesionless soils. All sand samples were compacted approximately to the same density in the permeameter to eliminate any error due to potential density variation. Figure 5.3 shows the set up used for hydraulic conductivity determination (a) and the compacted sand sample (b).

During each test water temperature was measured and recorded to apply correction factors to the viscosity of water corresponding to 20 °C. Hydraulic conductivity was calculated using ASTM standard F1815–06 (ASTM, 2010).

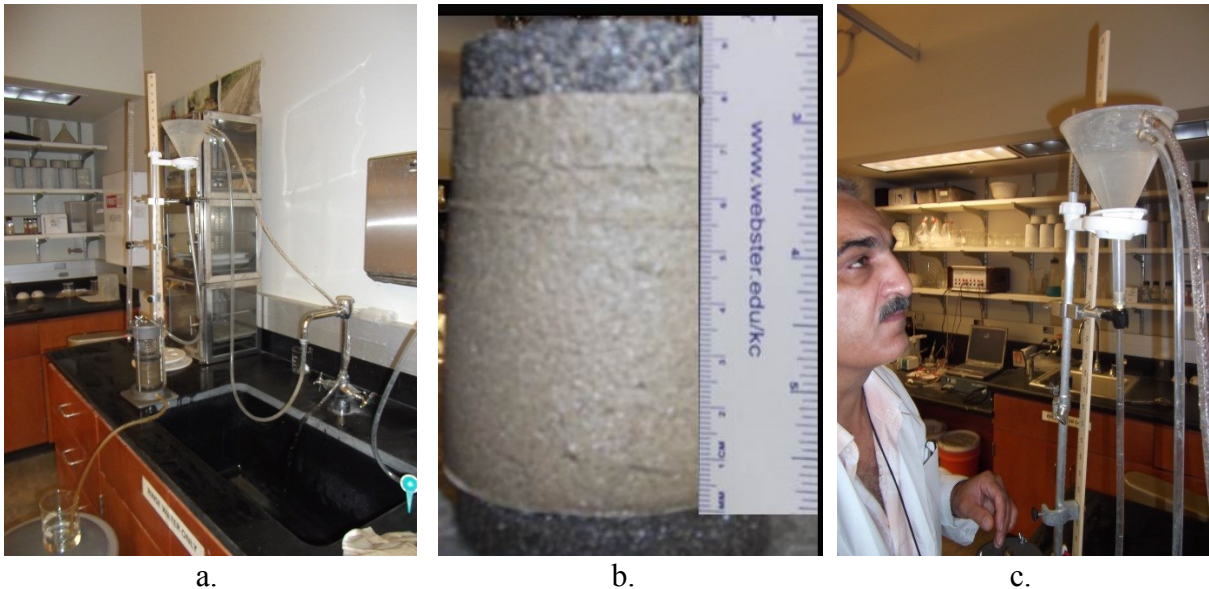


Figure 5.3. Permeameter apparatus: a. overall setup with water inlet and outlet; b. compacted sand sample in the permeameter; c. water level observation

X-Ray Powder Diffraction Analysis

The aim of using XRD analysis was to identify and compare the mineralogical composition of sand and clay samples before and after they were contaminated with selected chemicals, utilizing the procedure recommended by USGS (Poppe *et al.*, 2001). XRD is an excellent instrument to identify minerals in both soil and clay. The Rigaku MiniFlex instrument was used for this analysis (Figure 5.4) and JADE 8, X-ray diffraction software; Materials Data, Inc., Livermore, CA, was used to identify the minerals distribution of sand samples and MacDiff-4.2.5 software for clay samples. The XRD measurements were scanned at 2° per minute from 5° to 65° for all samples.

Sample Preparation for XRD Analysis

The following procedure was used to prepare powder samples for XRD analysis. A duplicate set of approximately 20 g of: (a) uncontaminated and (b) contaminated sands from the aquifer and upper layer formations were used for the XRD analysis. Each sample was air dried and ground to a fine powder using ceramic mortar and pestle to less than 10 micrometer (μm) or 200-mesh size. Next, the fine-powdered sample was packed into a circular container; smoothening the top surface of the sample uniformly by a flat spatula and a glass slide to ensure a flat upper surface. Finally, six samples were placed on the sample holder of the XRD instrument to run the analysis (Figure 5.4). Results of this analysis are presented as peak positions at 2θ and X-ray intensity in the form of an x-y plot.

For clay minerals, additional preparation was required to separate clay from the upper layer sand for XRD analysis. First, silt and clay were separated from sand using the No. 200

sieve. Next, silt and clay were separated from each other by decantation, using the USGS procedure (Poppe *et al.*, 2001). Figure 5.4 shows the XRD equipment set up.

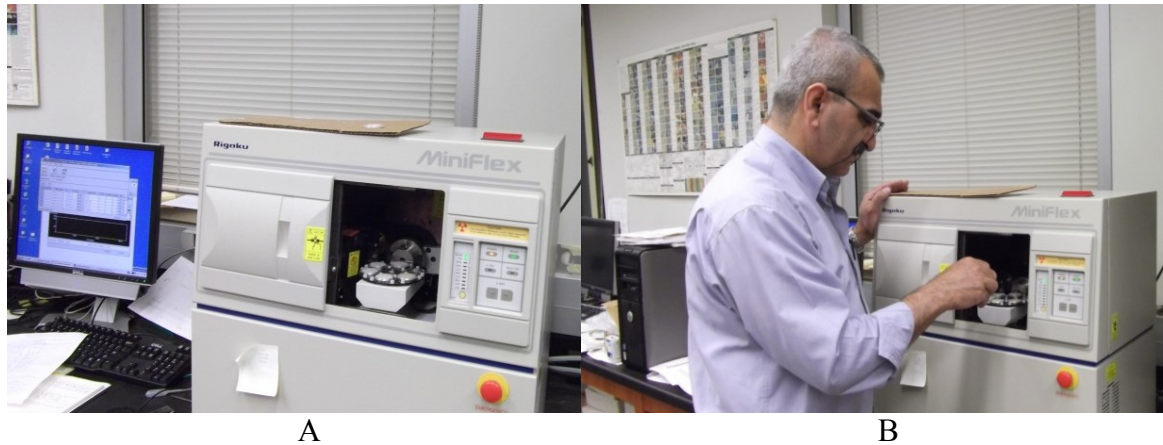


Figure 5.4. a. X-ray diffraction machine, Rigaku MiniFlex; b. Placing powder in the sample holder

Scanning Electron Microscopy

SEM is a sensitive high-resolution instrument that provides data at nanoscale about a sample's surface topography, shape, and mineral composition. It produces an image using electrons by scanning the sample with a focused beam of electrons, rather than light and lenses. Using SEM allows examination of a single grain or a number of grains, under high resolution that gives remarkably clear images and mineralogy. These advantages make the SEM one of the most useful instruments in research in many fields of sciences. SEM-MAG-763 (VEGA3 LM by TESCAN) was used in this study (Figure 5.5). Samples used for SEM analysis do not require any specific preparation other than being of right dimension to fit in the specimen chamber, called a specimen stub. SEM was used to determine aquifer and upper

layer sand mineralogy, grain shape and surface features of both the original (uncontaminated) and contaminated sand samples. To prevent any damage to the SEM device from interaction between hydrocarbon pollutant's vapor and spectrum of electrons, only selected contaminated specimens were used for testing (those exposed to chemicals for a period of 32 weeks).

A silicon lithium solid detector was used to generate the energy dispersive X-ray analysis for reason of it is a better energy resolution.

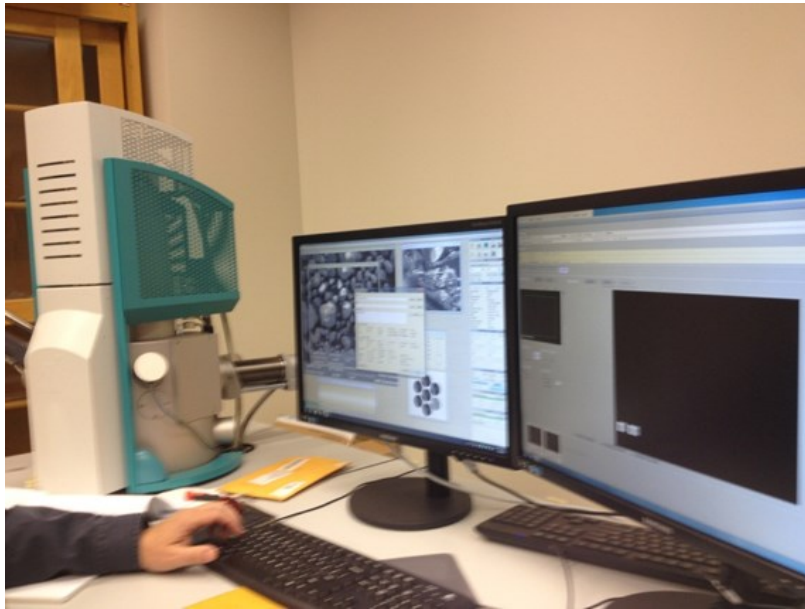


Figure 5.5. Scanning electron microscope set up

CHAPTER 6

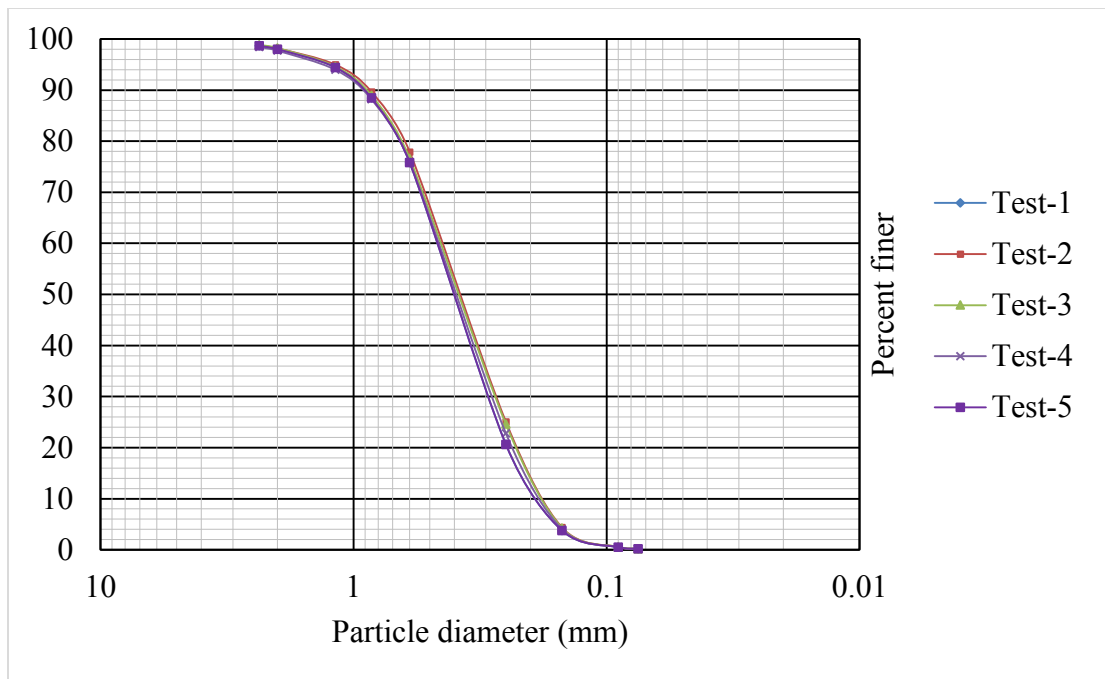
TEST RESULTS

This chapter presents results that were obtained from tests performed on aquifer and upper layer sand samples that were contaminated with selected VOCs (gasoline, TCE, BTEX — benzene, toluene, ethylbenzene, and xylenes — and isooctane) at various levels of saturation and for varying periods of time. The objective of these tests was to obtain an answer to the study question: “How do some common and widespread VOCs upon coming in contact with sand at various saturation levels and for varying periods of time, affect the physical, chemical, and geotechnical properties of sand?” Results are interpreted, in the discussion chapter, to come out with the best understanding of the impact of VOCs on the physical and geotechnical properties of sand.

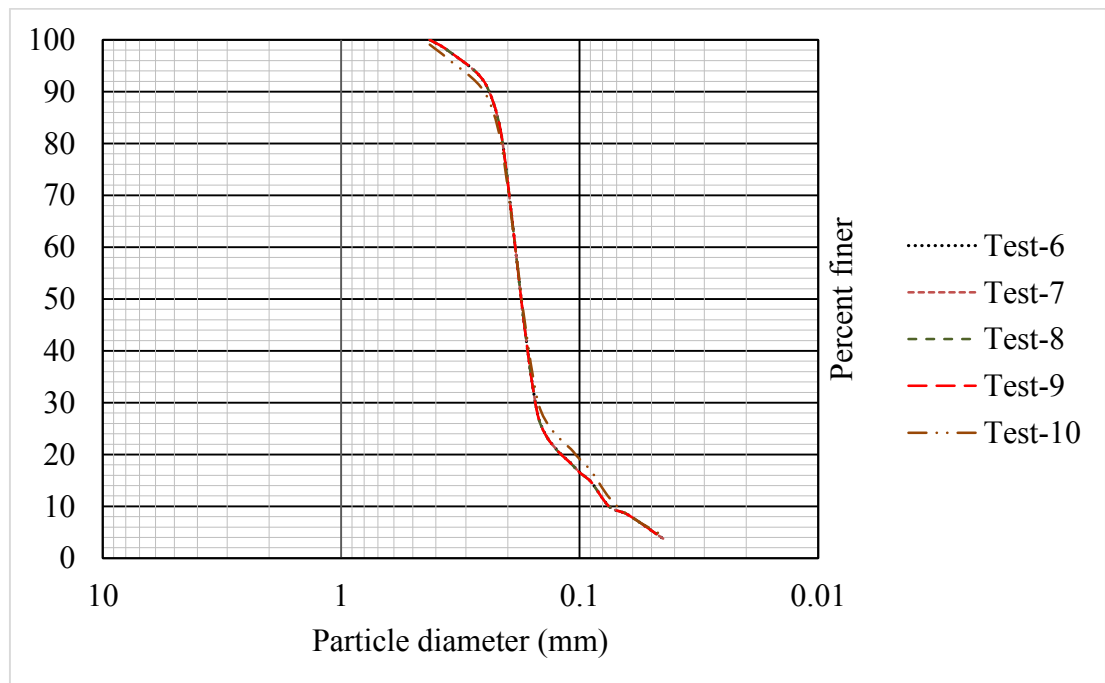
Particle Size Analyses

To ascertain that the cone-and quartered samples were truly representative of the bulk aquifer sand sample, five baseline sieve analyses of representative samples were carried out. Figure 6.1a shows particle size distribution curves, which indicate that the material comprising the –2.36 mm fraction, according to the Unified Soil Classification System, is classified as poorly graded sand—SP soil (ASTM, 2013b). Also, five sieve analyses for representative upper layer sand samples were conducted and the resulting particle size distribution curves are shown in Figure 6.1b, which indicate that this layer comprising the –0.425 mm fraction, is poorly graded sand with silt—SP-SM soil (ASTM, 2013b). The overlapping nature of the distribution curves show that all sand samples have the same shape and size range, confirming that the quartered samples are good representative of the bulk

sand samples of both the aquifer and upper layer sands. After performing the above diagnostic tests, adequate quantity of representative sands were set aside for subsequent tests. Each sample after being subjected to a particular contaminant for a specified period of time was first air-dried before performing the grain size analysis using the Ro-Tap shaker.



a.



b.

Figure 6.1. Particle size distribution curves for uncontaminated sand. a. aquifer sand samples; b. upper layer sand samples

Mechanical Analyses of Aquifer Sand Samples Contaminated with Gasoline

Sieve analyses were conducted on 21 aquifer sand samples contaminated with gasoline at about 100%, 50% and 25% saturation levels for various durations. Table 6.1 gives the sample number and duration of contamination for each sample.

Figures 6.2, 6.3 and 6.4 show the particle size distribution curve of sand samples contaminated with gasoline at about 100%, 50% and 25% saturation levels respectively; test data are presented in Appendix B.1, B.2 and B.3.

Sieve analyses results did not show any observed sand grain size changes pre- and post- contamination, indicating that gasoline does not affect the size of sand grains; in addition the parameters; D_{10} , C_u , C_z and S_0 , which were calculated from the particle size distribution curves, for all contaminated sand samples, also do not show any significant change in their values in comparison with the original aquifer sand sample. Test data included in Appendix B.4.

Table 6.1. Sample number and exposure time for aquifer sand samples contaminated with gasoline at about 100%, 50% and 25% saturation levels

Description	Time period (week)						
	1	2	4	6	8	16	32
Sample number for sand contaminated at about 100% saturation	Gas-1	Gas-2	Gas-3	Gas-10	Gas-11	Gas-12	Gas-13
Sample number for sand contaminated at about 50% saturation	Gas-20	Gas-4	Gas-5	Gas-6	Gas-14	Gas-15	Gas-16
Sample number for sand contaminated at about 25% saturation	Gas-21	Gas-7	Gas-8	Gas-9	Gas-17	Gas-18	Gas-19

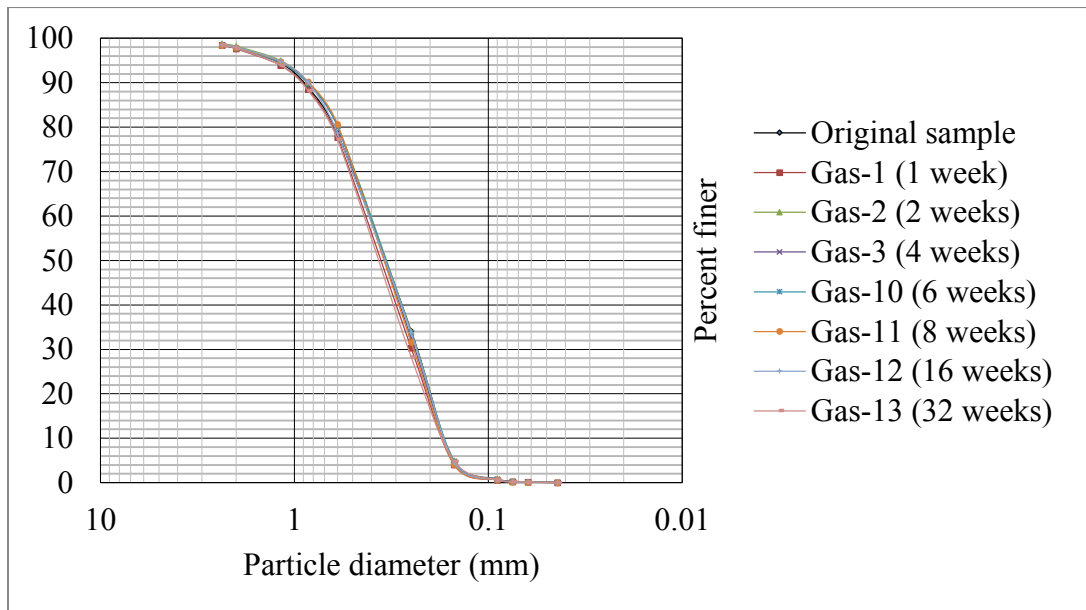


Figure 6.2. Particle size distribution curves for aquifer sand, contaminated with gasoline at about 100% saturation level

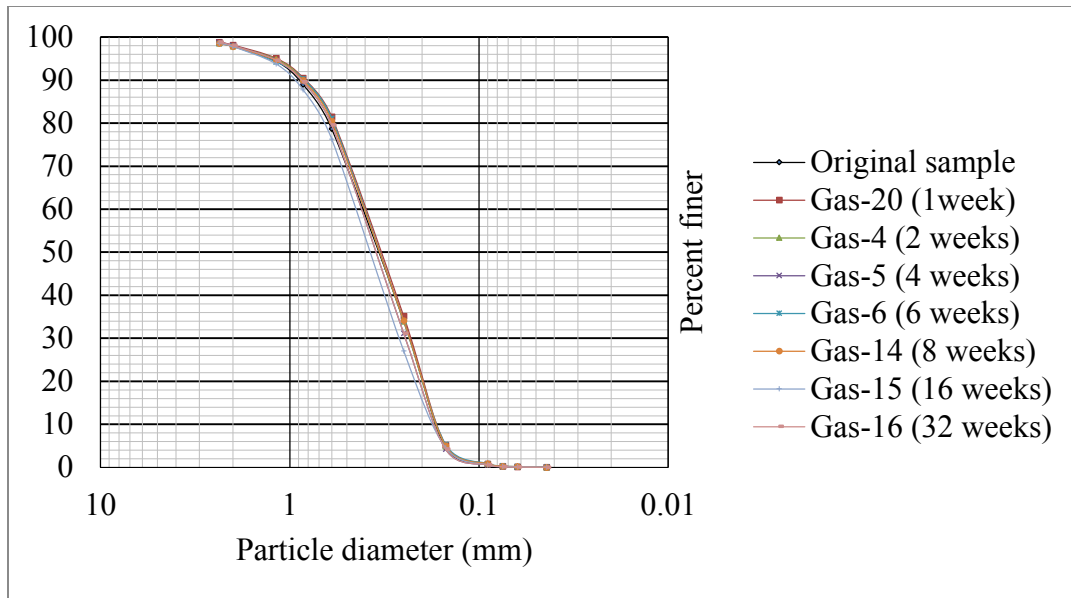


Figure 6.3. Particle size distribution curves for aquifer sand, contaminated with gasoline at about 50% saturation level

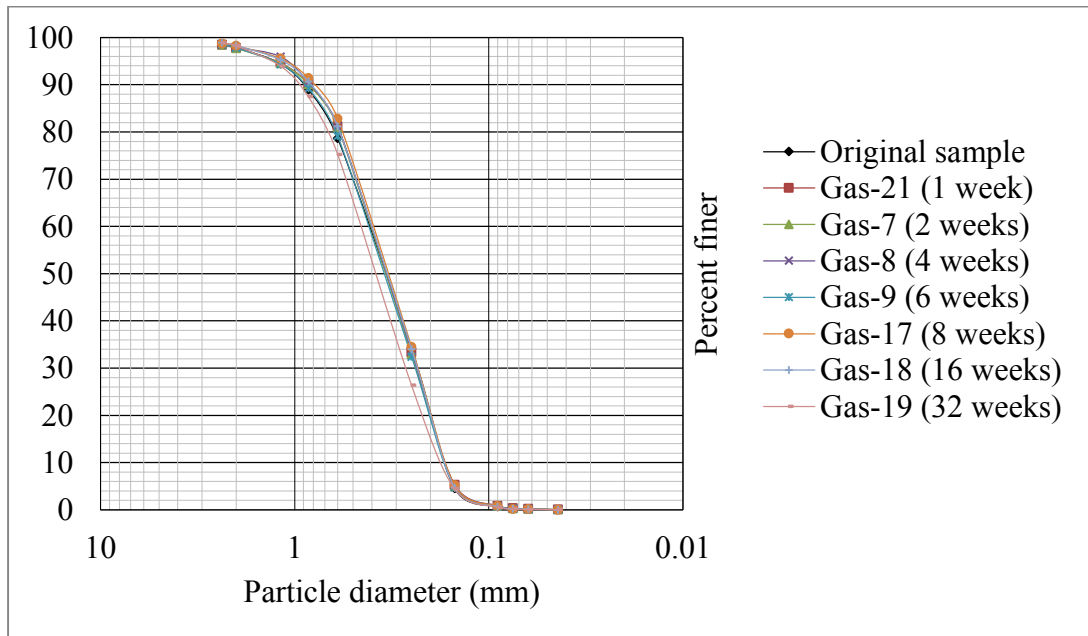


Figure 6.4. Particle size distribution curves for aquifer sand, contaminated with gasoline at about 25% saturation level

Mechanical Analyses of Aquifer Sand Samples Contaminated with TCE

Sieve analyses were carried out for 21 aquifer sand samples that were contaminated with TCE at about 100%, 50% and 25% saturation levels for various durations. Table 6.2 gives the sample number and duration of contamination for each sample.

Figures 6.5, 6.6 and 6.7 show the particle size distribution curves for sand samples contaminated with TCE at 100%, 50% and 25% (v/v) saturation levels respectively. Sieve analysis data are presented in Appendix B.5, B.6, and B.7.

Results do not show any observable change, indicating that TCE-contaminated sand samples do not affect the size of aquifer sand grains, and the parameters D_{10} , C_u , C_z and S_0 for all samples were essentially unaffected. Test data indicate that there are no noticeable changes in their values in comparison with the uncontaminated sand sample. Data are presented in Appendix B.8.

Table 6.2. Sample number and exposure time for aquifer sand samples contaminated with TCE at about 100%, 50% and 25% saturation levels

Description	Time period (week)						
	1	2	4	6	8	16	32
Sample number for sand contaminated at about 100% (v/v)	TCE-01	TCE-02	TCE-03	TCE-00	TCE-010	TCE-011	TCE-012
Sample number for sand contaminated at about 50% (v/v)	TCE-019	TCE-04	TCE-05	TCE-06	TCE-013	TCE-014	TCE-015
Sample number for sand contaminated at about 25% (v/v)	TCE-020	TCE-07	TCE-08	TCE-09	TCE-016	TCE-017	TCE-018

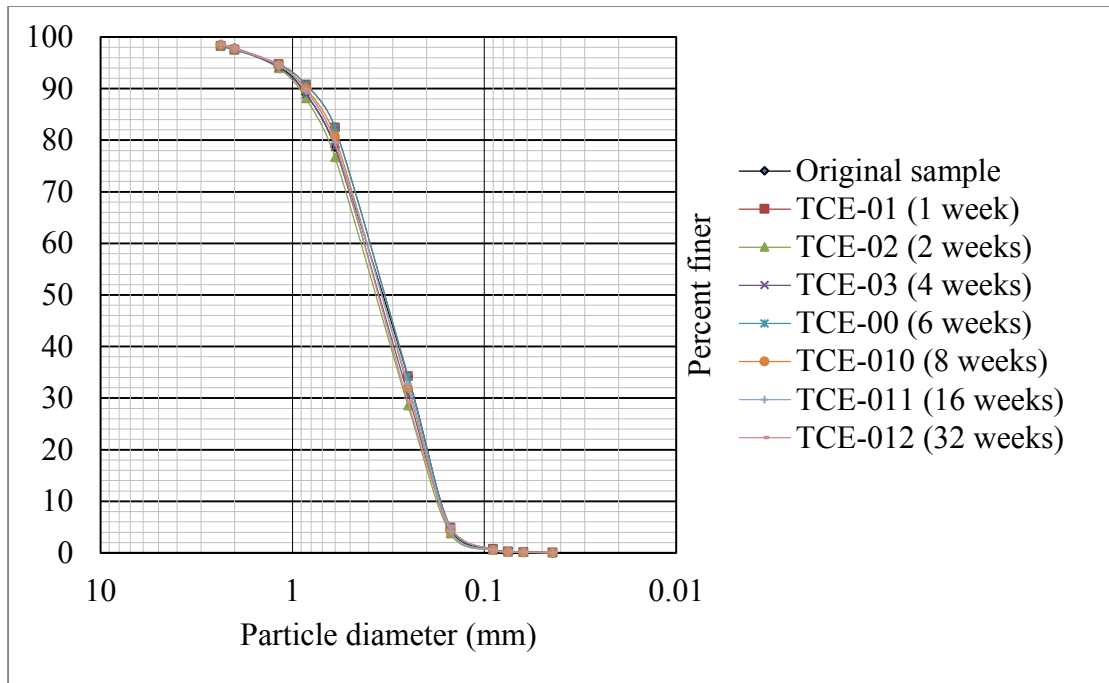


Figure 6.5. Particle size distribution curves for aquifer sand, contaminated with TCE at about 100% saturation level

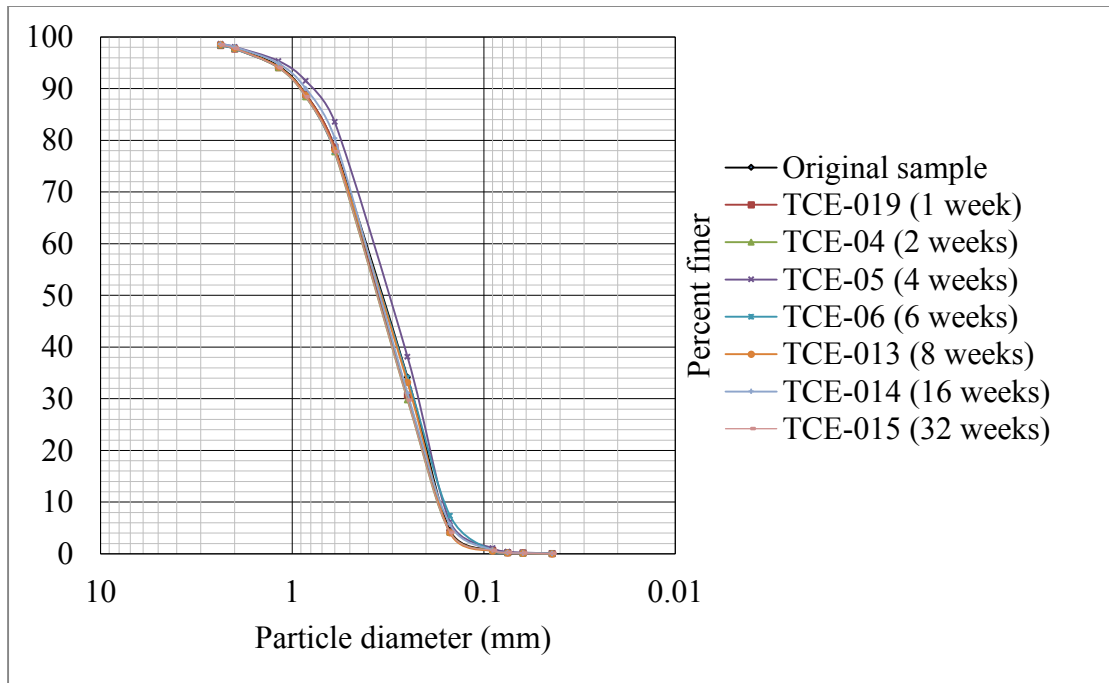


Figure 6.6. Particle size distribution curves for aquifer sand, contaminated with TCE at about 50% saturation level

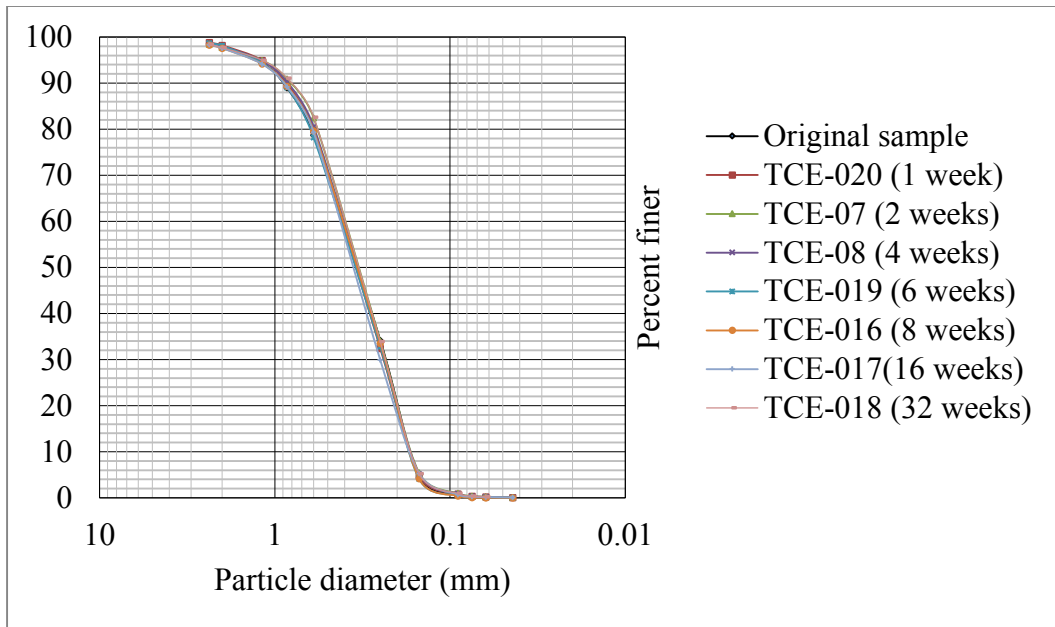


Figure 6.7. Particle size distribution curves for aquifer sand, contaminated with TCE at about 25% saturation level

Mechanical Analyses of Upper Layer Sand Samples Contaminated with Gasoline

Sieve analyses were carried out on 16 sand samples from the upper layer (vadose zone) that were contaminated with gasoline at about 100%, 50% and 25% saturation level for varying periods of time. Table 6.3 shows sample number and duration of contamination. Figures 6.8, 6.9 and 6.10 show the particle size distribution curves. Test data are included in Appendix C.1, C.2, and C.3.

Results of the sieve analysis tests for uncontaminated-and gasoline-contaminated sand samples do not show any observable change, indicating that gasoline does not affect the size of sand grains. In addition the parameters D_{10} , C_u , C_z and S_0 did not indicate any significant change in their values in comparison with the uncontaminated sand samples. Test data are included in Appendix C.4.

Table 6.3. Sample number and exposure time for upper layer sand samples contaminated with gasoline, at about 100%, 50% and 25% saturation levels

Description	Time period (week)					
	1	2	4	8	16	32
Sample number for sand contaminated at about 100%	Gas-001	Gas-002	Gas-003	Gas-010	Gas-011	Gas-012
Sample number for sand contaminated at about 50%	-	Gas-004	Gas-005	Gas-006	Gas-013	Gas-014
Sample number for sand contaminated at about 25%	-	Gas-007	Gas-008	Gas-009	Gas-015	Gas-016

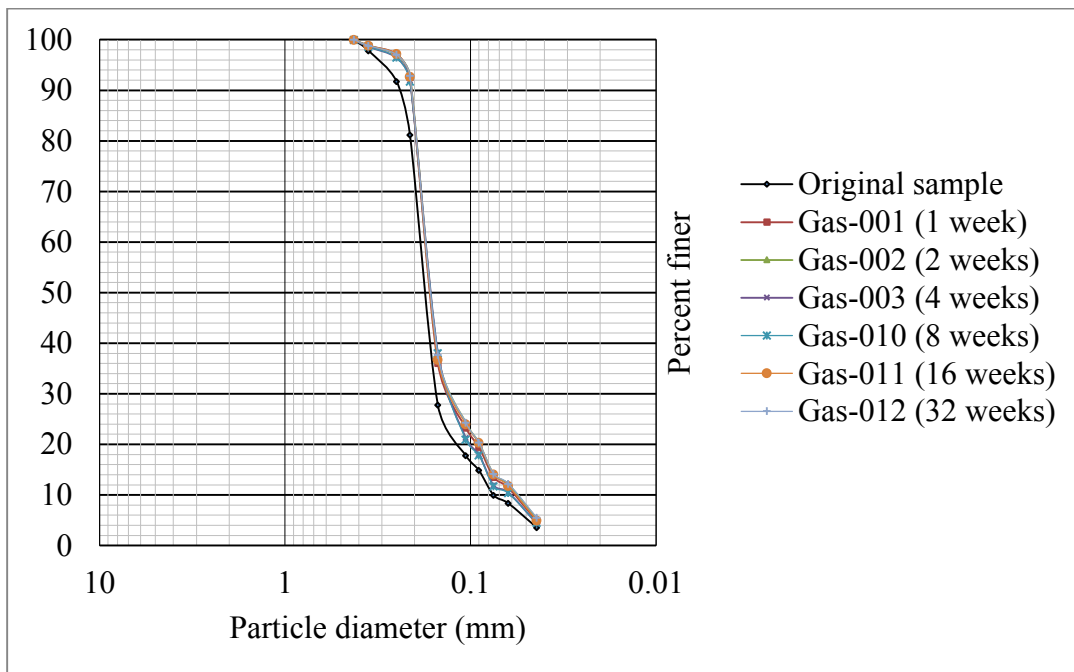


Figure 6.8. Particle size distribution curves for upper layer sand, contaminated with gasoline at about 100% saturation level

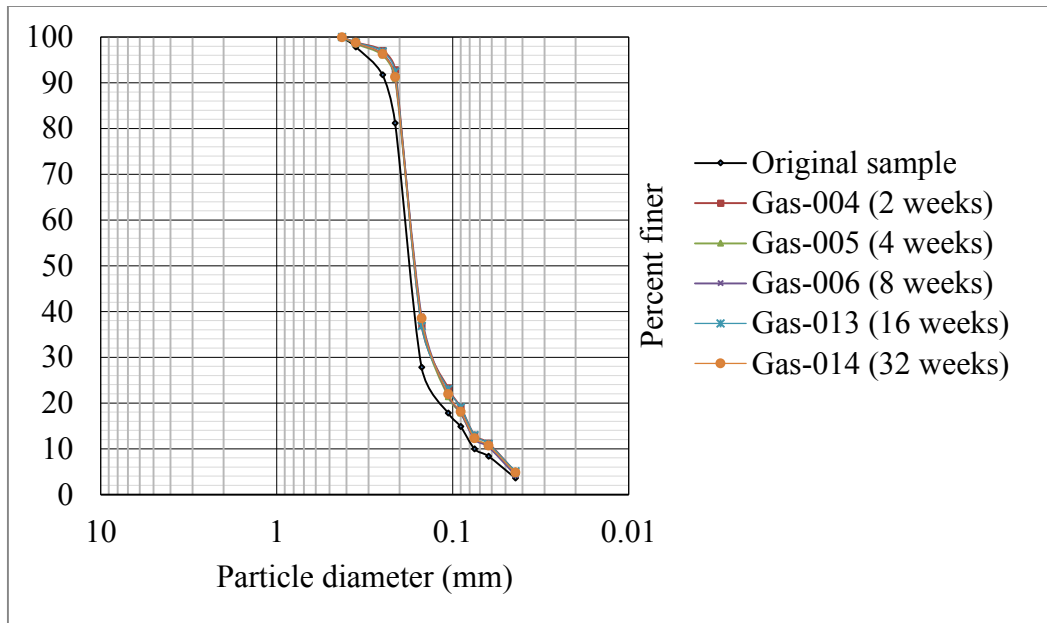


Figure 6.9. Particle size distribution curves for upper layer sand, contaminated with gasoline at about 50% saturation level

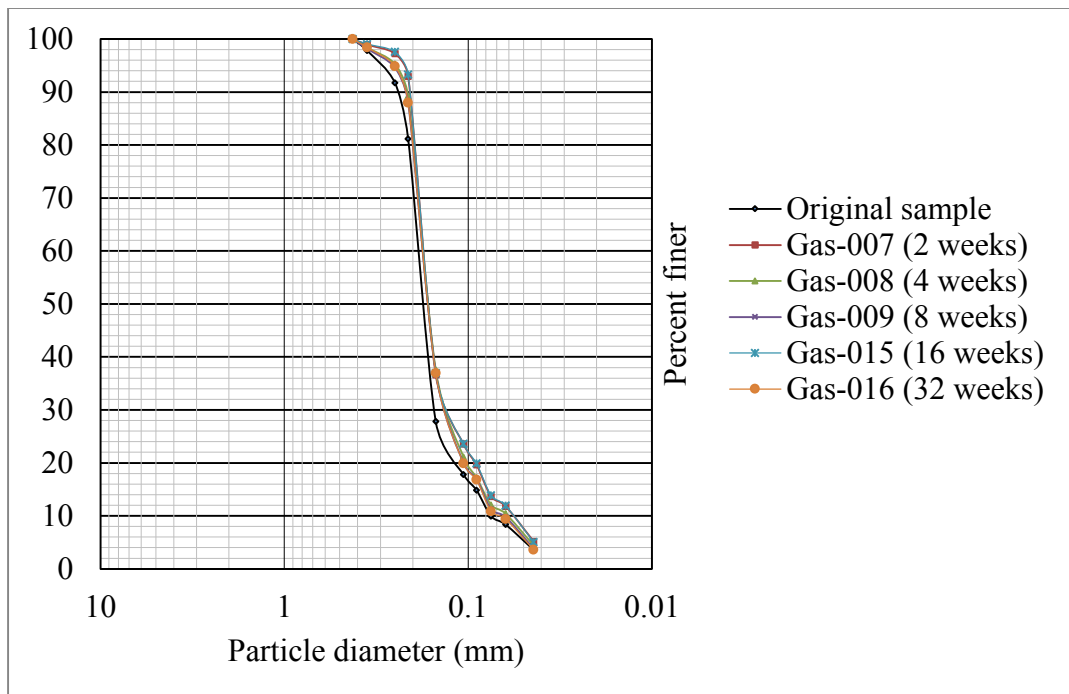


Figure 6.10. Particle size distribution curves for upper layer sand, contaminated with gasoline at about 25% saturation level

Mechanical Analyses of Upper Layer Sand Samples Contaminated with TCE

Sieve analyses were carried out on 16 sand samples from the upper layer (vadose zone) that were contaminated with TCE at about 100%, 50% and 25% saturation levels for varying periods of time. Table 6.4 shows sample number and the duration of contamination. Test data are included in Appendix C.5, C.6, and C.7.

Figures 6.11, 6.12 and 6.13 show the particle size distribution curves. Results do not show any observable change, indicating that TCE-contaminated sand samples do not impact the size of sand grains. In addition, the parameters D_{10} , C_u , C_z and S_0 did not indicate any significant changes in their values in comparison with the uncontaminated sand sample. Test data are included in Appendix C.8.

Table 6.4. Sample number and exposure time of upper layer sand samples contaminated with TCE, at about 100%, 50 and 25% saturation levels

Description	Time period (week)					
	1	2	4	8	16	32
Sample number for sand contaminated at about 100% saturation level	TCE-011	TCE-012	TCE-013	TCE-020	TCE-010	TCE-023
Sample number for sand contaminated at about 50% saturation level	-	TCE-014	TCE-015	TCE-016	TCE-021	TCE-024
Sample number for sand contaminated at about 25% saturation level	-	TCE-017	TCE-018	TCE-019	TCE-022	TCE-025

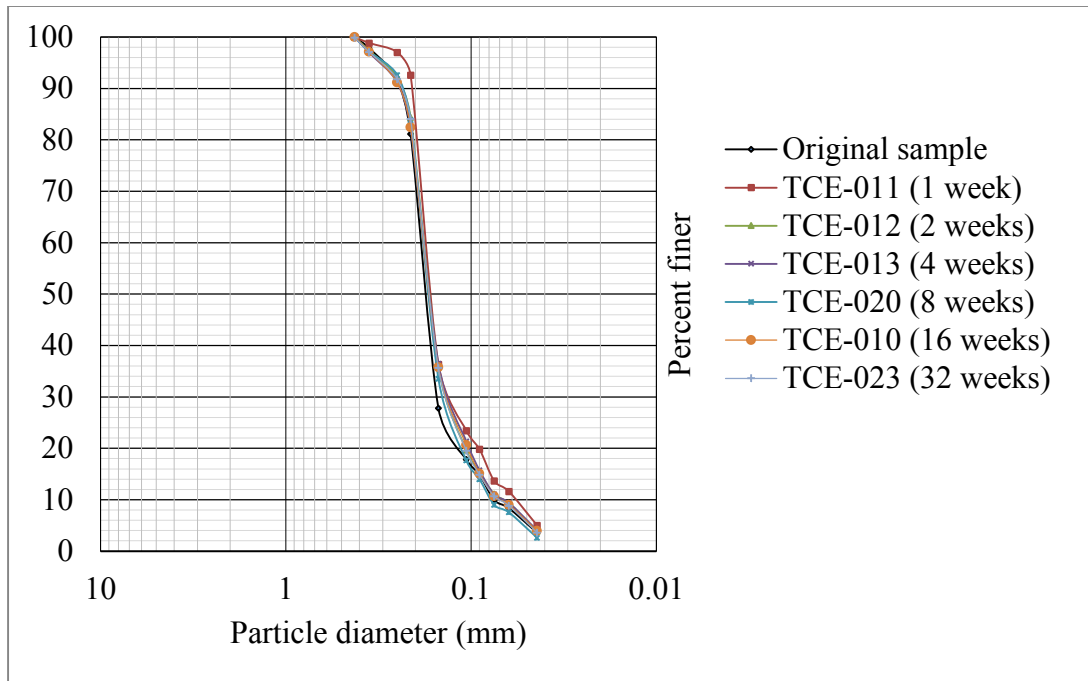


Figure 6.11. Particle size distribution curves for upper layer sand, contaminated with TCE at about 100% saturation level

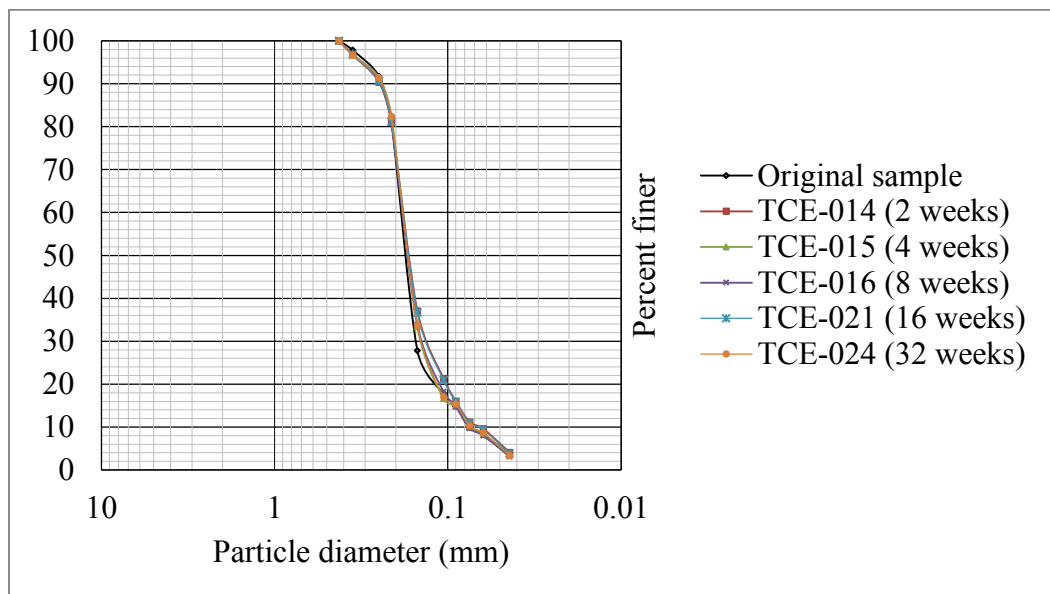


Figure 6.12. Particle size distribution curves for upper layer sand, contaminated with TCE at about 50% saturation level

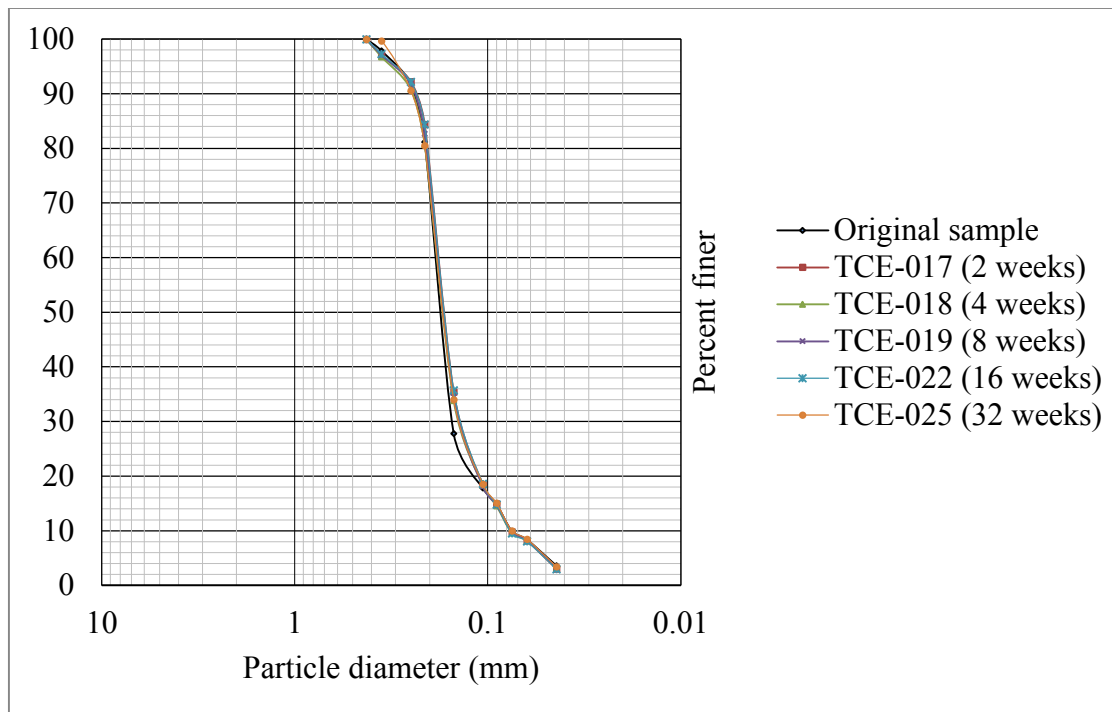


Figure 6.13. Particle size distribution curves for upper layer sand, contaminated with TCE at about 25% saturation level

Mechanical Analyses of Aquifer Sand Samples Contaminated with Benzene, Toluene, Ethylbenzene, Xylene and Isooctane

Benzene, toluene, ethylbenzene, xylene (BTEX), and isooctane, which are found in gasoline, were selected to evaluate and assure the accuracy and validity of the results obtained from the samples which had been contaminated with gasoline. Five aquifer sand samples, fully saturated, were contaminated with each of the above chemicals for 8 weeks. Figure 6.14 shows the particle size distribution curves. Test data are included in Appendix D.1.

Results of sieve analysis for uncontaminated sand samples and also for samples contaminated with BTEX and isooctane do not show any observable changes, indicating that these chemicals do not affect sand grains. In addition the parameters D_{10} , C_u , C_z and S_0 did not indicate any significant changes in their value in comparison with the uncontaminated sand. Test data are included in Appendix D.2.

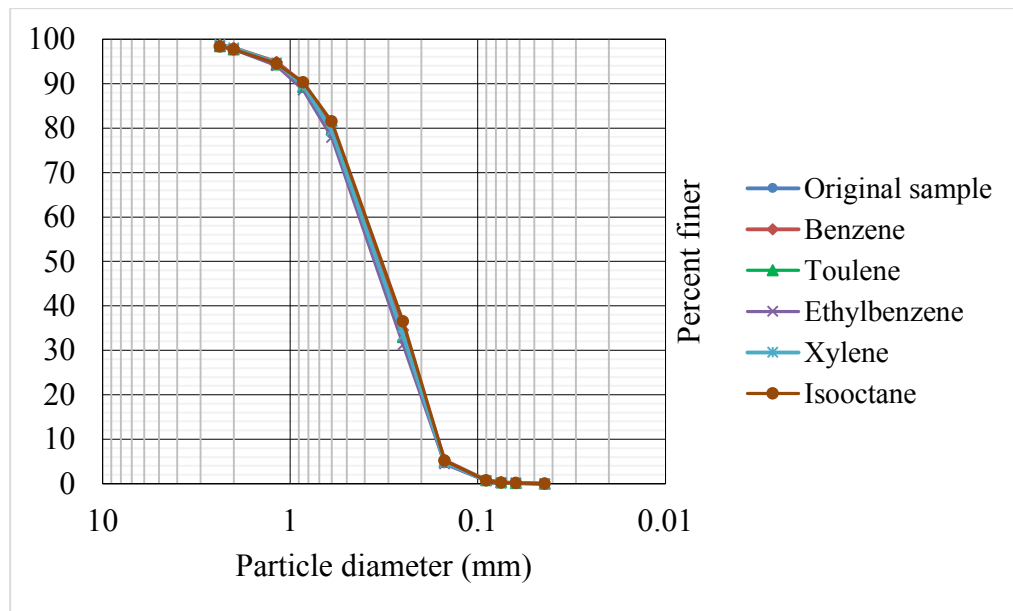


Figure 6.14. Particle size distribution curves for aquifer sand, contaminated with BTEX and isooctane at about 100% saturation level

Mechanical Analyses of Aquifer Sand Samples Contaminated with Varying Concentration of Gasoline and TCE

Sieve analyses were carried out on 20 aquifer sand samples that were exposed to aqueous solution contaminated with about 1, 2, 3....10% of gasoline, as well as with TCE.

All samples were fully saturated and allowed to remain contaminated for 8 weeks before testing. Figures 6.15 and 6.16 show particle size distribution curves. Test data are included in Appendix E.1 and E.2.

Results of the sieve analyses tests for uncontaminated-and gasoline-and TCE-contaminated sand samples do not show any observable change, indicating that aqueous solution contaminated with gasoline and TCE did not affect sand grains. In addition the parameters D_{10} , C_U , C_Z and S_0 did not indicate any significant changes in their values in comparison with the uncontaminated sand. Test data are included in Appendix E.3 and E.4.

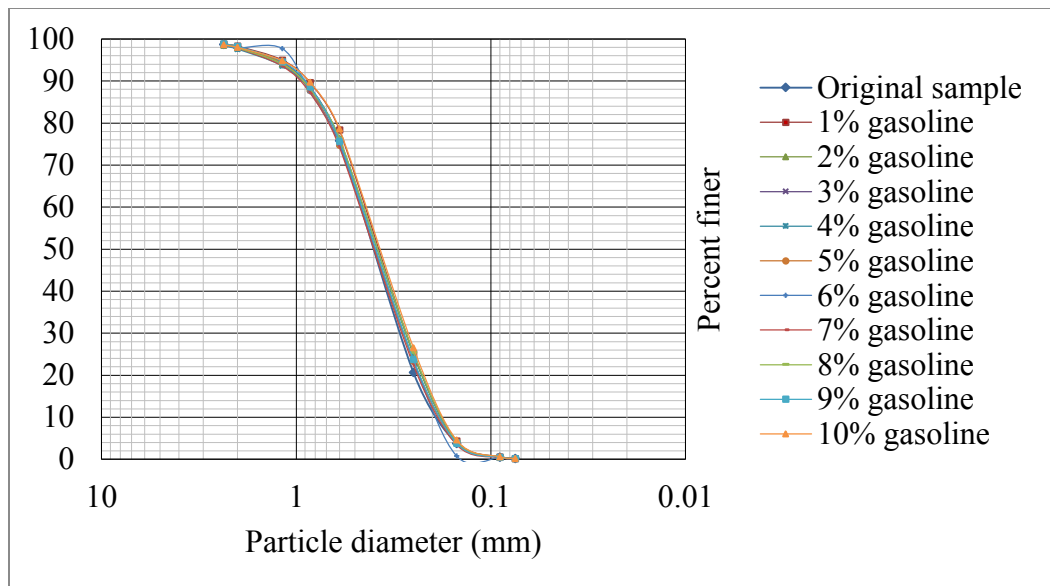


Figure 6.15. Particle size distribution curves for fully saturated aquifer sand samples contaminated with gasoline in aqueous solutions

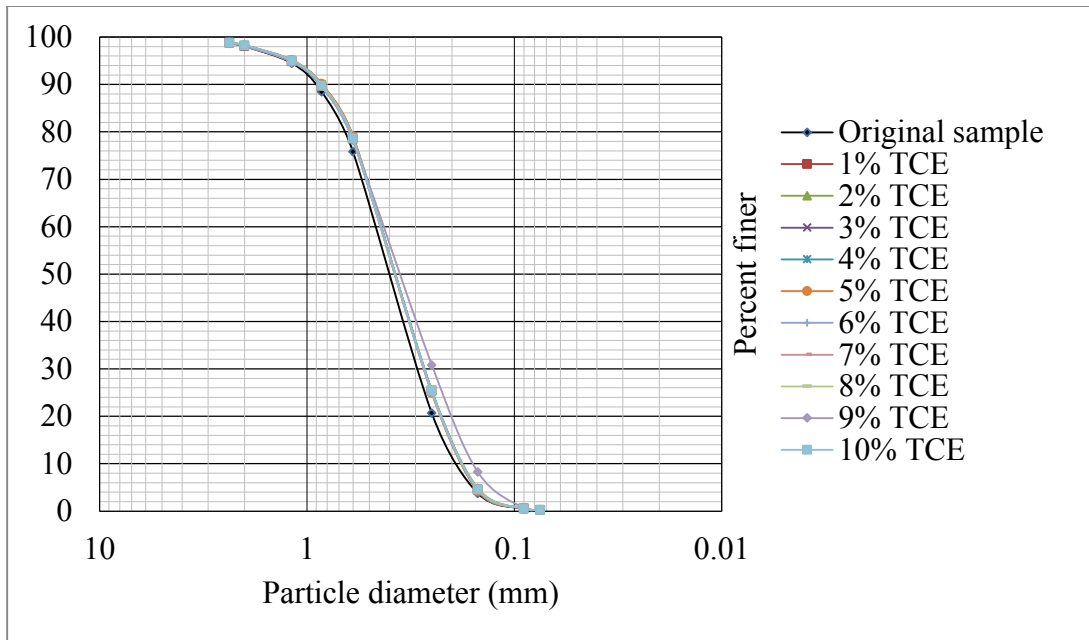


Figure 6.16. Particle size distribution curves for fully saturated aquifer sand samples contaminated with TCE in aqueous solutions

Evaporation Rate of VOCs in Aquifer and Upper Layer Sand Samples

VOCs readily evaporate at room temperature and/or when they come in direct contact with ambient air because they have a high vapor pressure, which is a function of low boiling point. Chemicals, including VOCs, vary widely in their properties such as solubility, density, viscosity, sorption, and diffusion coefficient that distinguish them from each other. The rate of evaporation of hydrocarbons is mostly dependent on these properties, especially as they seep through soil into aquifers. In addition, the ability of fluid movement through the soil depends on characteristics of both the pollutants and the soil at each polluted site (including hydraulic conductivity) that includes: degree of soil saturation, environmental conditions-temperature, wind velocity, humidity, etc.

Oil pollution can remain at a site for many decades. Oil has the potential to persist in the environment long after the spill event and has been detected in sediment three decades after a spill (U.S. Fish & Wildlife Service, 2010). Also, a study done by the Woods Hole Oceanographic Institution (WHOI) indicated that oil residues from a spill that occurred at Wild Harbor, Massachusetts, United States, has been found in the sediment after three decades and will likely remain there indefinitely (WHOI, 2007).

Rate of evaporation is a useful property as it gives an idea about the fate of a VOC as it moves downwards after a spill or leaks, and how much of the VOC escapes as vapor and what fraction remains in the soil. In order to understand the fate of a VOC spill at a site, an evaporation test was designed to gain an insight into the partitioning of the VOC into vapor and liquid phases and their influences on hydraulic conductivity of aquifer and upper layer sand.

Measurements of the rate of evaporation were conducted in the laboratory at room temperature ranging between about 23 and 25 °C and 1 atm pressure, on selected VOC-contaminated sand samples representing the aquifer and vadose zone (upper layer). The aim of this experiment was to examine the changes in evaporation rate of chemicals against time. Measurement of evaporation rate commenced 8 weeks after the sand was exposed to one of the VOCs by opening the lid of Pyrex[®] bottles, and recording the weights after set time intervals and continuing until the weigh became stable, or when the total quantity of VOCs was volatilized, as discussed in Chapter 5.

Evaporation rate test was conducted for aquifer sand samples that were: (a) fully saturated with gasoline, TCE, benzene, toluene, ethylbenzene, xylenes, and isooctane; and (b) contaminated at about 50% and 25% (v/v) saturation levels with gasoline as well as with

TCE. In addition, evaporation rate was determined for six sand samples from the upper layer, contaminated with gasoline as well as TCE, at about 100%, 50% and 25% (v/v) saturation levels. Evaporation test was carried out in duplicate for each contaminated sand sample for accuracy but no significant changes were observed.

Loss of VOCs from sand samples observed in gram (g), was converted to kilogram (kg) and a curve, mass vs time, was drawn. The slopes of straight lines represent the rate of evaporation in kg/min for each component individually. By knowing the slope and the Y-intercepts, evaporation loss can be calculated by the following straight line equation:

$$Y = mx + b$$

Where, Y = the amount of chemical vapor in kg

m = slope of the line

x = time, in minute

b = Y-intercepts

Evaporation Rate of Gasoline in Aquifer Sand Samples

The objective of evaporation rate test was to examine the changes in evaporation rate of unleaded gasoline from aquifer sand against time. Since gasoline is highly volatile, a large amount of vapor is quickly generated upon exposure to air (Okamoto *et al.*, 2009). Therefore, adequate precaution was taken during measurements of evaporation rate by observing all safety procedures and turning off any source of flame in the laboratory—a precaution used not only for gasoline, but also for other VOCs. Face masks and gloves were used as some VOCs can be harmful if inhaled or absorbed through the skin.

Evaporation rate test was conducted for three aquifer sand samples, which were contaminated by adding 64.61, 31.89 and 18.26 g of gasoline to the sand to achieve 100%, 50% and 25% saturation levels. Test results are presented in Appendix F.1.

Time-dependent variations in the amount of gasoline loss are shown in Figure 6.17 and test data are included in Table 6.5.

Analysis of evaporation rate data shows that the evaporation rate of gasoline decreases rapidly over time for all contaminated samples. The results also indicate two phases of evaporation: short duration rapid phase and long-term slow phase. The first phase phenomenon seems to be the result of quick evaporation of gasoline as it escapes from the sand voids—similar to free evaporation from pan. Whereas, the second phase of evaporation occurs after the vapor pressure overcomes surface tension and other intermolecular attractive forces caused by gasoline coatings around sand grains. Evaporation rate for all contaminated samples under varying conditions of saturation shows the same general trend: initial rapid loss for up to about 400 h; slowing down between about 400 and 1200 h; and becoming stable after about 1200 h. This pattern also indicates that although most of the VOCs are lost due to evaporation, not the entire quantity escapes the contaminated medium and a small amount stays behind as residual saturation. Figure 6.17 show the results for sand contaminated with gasoline at approximately 100%, 50% and 25% (v/v) saturation levels.

The slopes of straight lines of the evaporation rate for aquifer sand samples, contaminated with gasoline at about 100%, 50% and 25% saturation levels are: $2 \times 10^{-7}x$, $1 \times 10^{-7}x$ and $1 \times 10^{-7}x$ respectively. The test data are included in Appendix F.3.

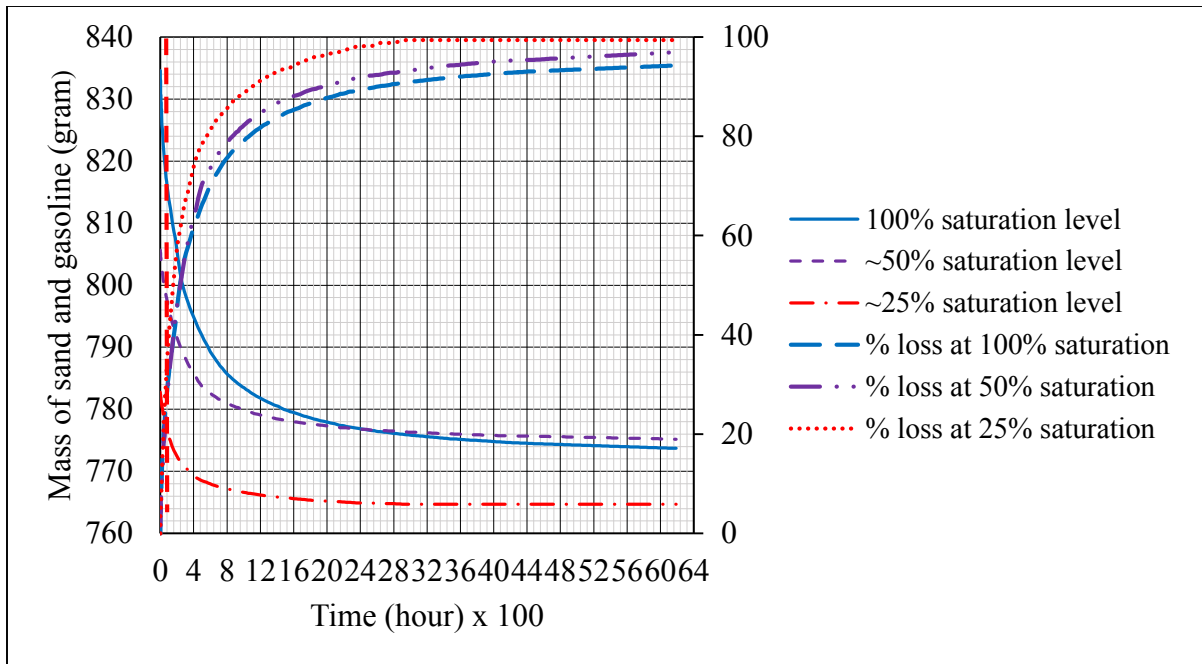


Figure 6.17. Evaporation rate of gasoline in aquifer sand sample at about 100%, 50% and 25% saturation levels

Test results show that gasoline lost 90.85, 93.26, and 99.40 % of its weight from aquifer sand samples, contaminated at about 100%, 50% and 25% saturation levels respectively after 2950 h (about 18 weeks) of air drying (Table 6.5). However, the sand sample that was contaminated at about 25% saturation level attained a constant weight after 2950 h indicating that no further loss occurred, with 0.60% remaining as residual concentration in the pores. Table 6.5 presents data on evaporation rate of gasoline at various levels of saturation for the duration of exposure. The following conclusions can be drawn from the analysis of data:

1. The rate of loss of gasoline from contaminated sand is time-dependent
2. The amount of gasoline lost by evaporation also depends on the degree of saturation but is non-uniform

3. Some residual amount of gasoline remains in the sand pores even after extended period of time—as long as 6190 h (about 36 weeks) as shown in Table 6.5

Table 6.5. Weight of aquifer sand sample and gasoline used in evaporation test and percent of loss

Saturation level of gasoline (%)	Initial weight of sand + gasoline (g)	Weight of gasoline (g) and volume (mL)	Duration and weight		Weight of gasoline lost (g)	Gasoline lost (%)	Percent of gasoline remaining in the sand
			Air drying time (h)	Weight after air drying (g)			
100	834.61	64.61	166	808.52	26.09	40.38	59.62
		89.74	2950	775.91	58.70	90.85	9.15
			6190	773.70	60.91	94.27	5.73
50	806.10	31.89	166	792.87	13.23	41.49	58.51
		44.29	2950	776.36	29.74	93.26	6.74
			6190	775.19	30.91	96.93	3.07
25	782.83	18.26	166	773.32	9.51	52.08	47.92
		25.36	2950-6190	764.68	18.26	99.40	0.60

Physical observation after air drying showed that sand grains, from both the aquifer and upper layer, appear to undergo an increase in intragranular attractive forces rendering the grains more cohesive with increase in shear strength. This phenomenon is similar to the well-known observation of temporary increase in bearing capacity of moist sand on the Daytona Beach, Florida, so much so that it supports large dynamic stresses generated by fast-moving wheels of race cars (Holtz *et al.*, 2011). Figure 6.18 (a and b) shows sand grains from aquifer and upper layer after they were air dried for 6190 h (about 37 weeks) that still retain cohesion

and stick together. This increase in cohesion between sand grains offers resistance to passage (ability to transmit) of fluids through the voids and thus leads to a decrease in permeability.

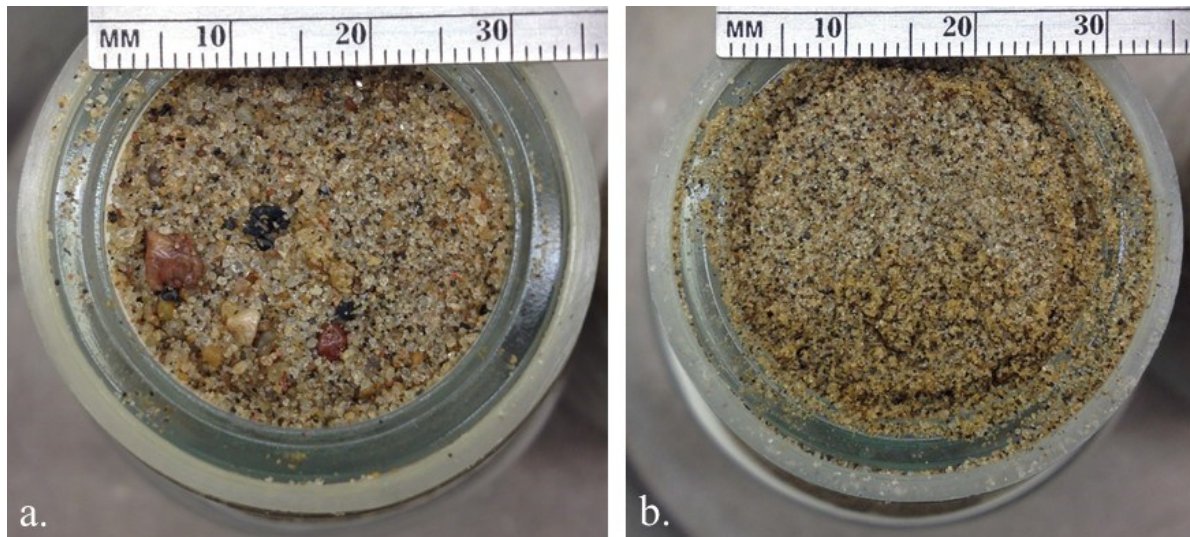


Figure 6.18. Gasoline saturated (100%) sand grains after 6190 h of air drying. a. aquifer sand sample; b. upper layer sand sample

Evaporation Rate of TCE in Aquifer Sand Samples

The experiment examined the changes in evaporation rate of TCE in three aquifer sand samples, which were contaminated by adding 124.06, 62.71 and 32.53 g of TCE to achieve 100%, 50% and 25% saturation levels and Appendix F.1 contains the data.

Time-dependent variation in the amount of TCE loss is shown in Figure 6.19 and the data are included in Table 6.6.

Analysis of the evaporation rate data shows that at 100% saturation level TCE undergoes two phases of evaporation: rapid and slow. The first phase shows: initial rapid loss for up to about 80 h, followed by a slow-down phase lasting about 1480 h, then declining

gradually and becoming stable after about 1640 h as shown in Figure 6.19. However, samples contaminated at about 50% and 25% saturation level do not show the rapid first phase. The second phase of evaporation is interpreted to occur after the vapor pressure overcomes the intramolecular attractive forces caused by TCE coatings around sand grains.

The slopes of straight lines of the evaporation rate test of aquifer sand samples, contaminated with TCE at 100%, 50% and 25% saturation levels are; $1 \times 10^{-6}x$, $1 \times 10^{-6}x$ and $8 \times 10^{-7}x$ respectively, and the data presented in Appendix F.4.

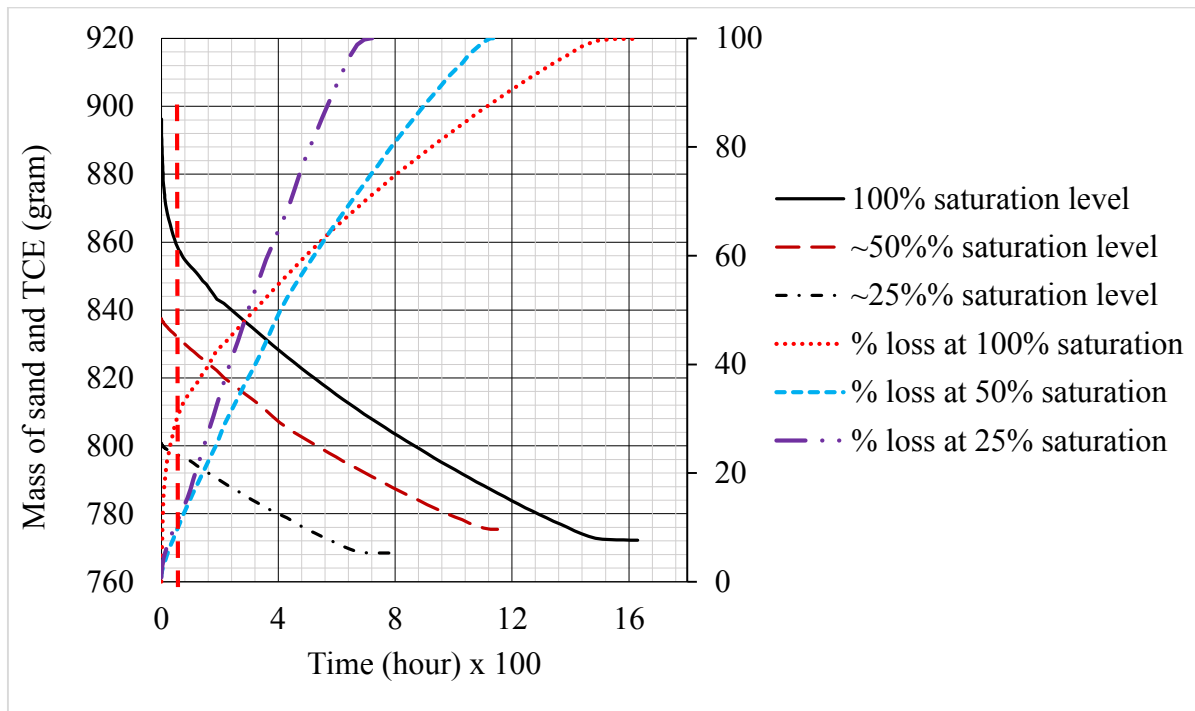


Figure 6.19. Evaporation rate of TCE in aquifer sand sample at about 100%, 50% and 25% saturation levels

Table 6.6. Weight of aquifer sand sample and TCE used in the rate of evaporation test, and percent of loss

Saturation level of TCE (%)	Initial weight of sand + TCE (g)	Weight of TCE (g) and volume (mL)	Duration and weight		TCE lost (%)	Percent of TCE remaining in the sand
			Air drying time (h)	Weight after air drying (g)		
100	896.22	124.06 84.97	80	854.80	33.39	66.61
			166	846.14	40.37	59.63
			790	804.01	74.30	25.70
			1582	772.27	99.90	0.10
50	838.11	62.71 42.95	166	823.80	22.82	77.18
			790	787.80	80.20	19.8
			1126	775.39	100.02	0.00
25	801.02	32.53 22.28	166	791.75	28.50	71.50
			790	768.48	100.03	0.00

Evaporation Rate of Benzene, Toluene, Ethylbenzene, Xylene and Isooctane in Aquifer Sand Samples

Rate of evaporation was also determined for five chemicals; benzene, toluene, ethylbenzene, xylene, and isooctane in aquifer sand samples by adding 72.40, 71.48, 70.22, 73.04 and 57.57 g of each chemical respectively to achieve 100% saturation level. The data are included in Appendix F.1.

Time-dependent variation in the amount of benzene, toluene, ethylbenzene, xylene, and isooctane that was lost in each evaporation experiment is shown in Figures 6.20 to 6.24 respectively. Table 6.7 show weights of sand and chemicals and percent loss at the end of evaporation periods.

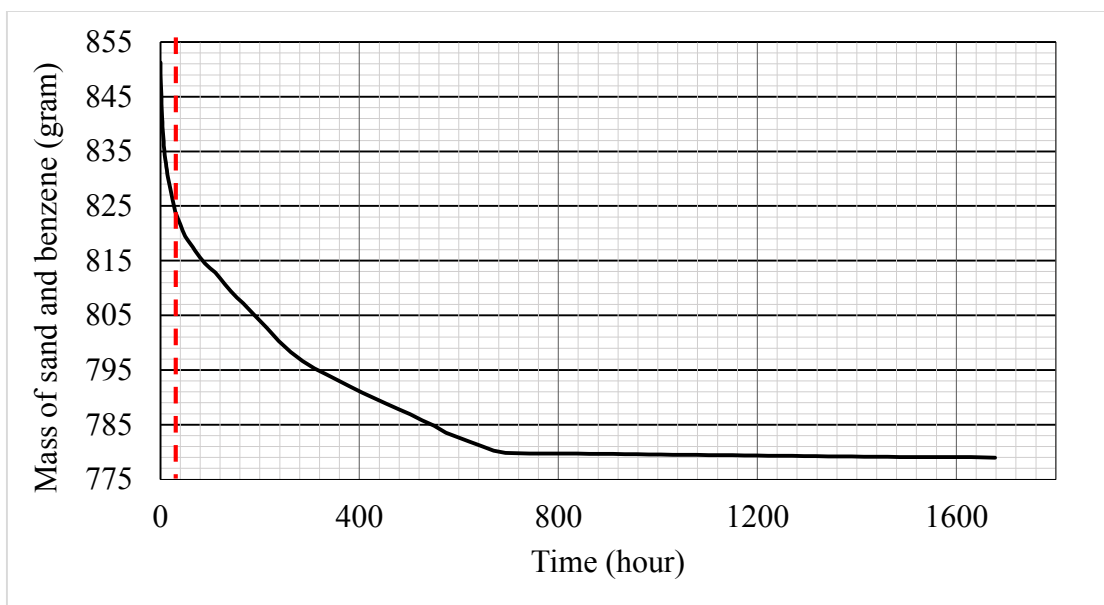


Figure 6.20. Evaporation rate of benzene in aquifer sand sample at about 100% (v/v) saturation

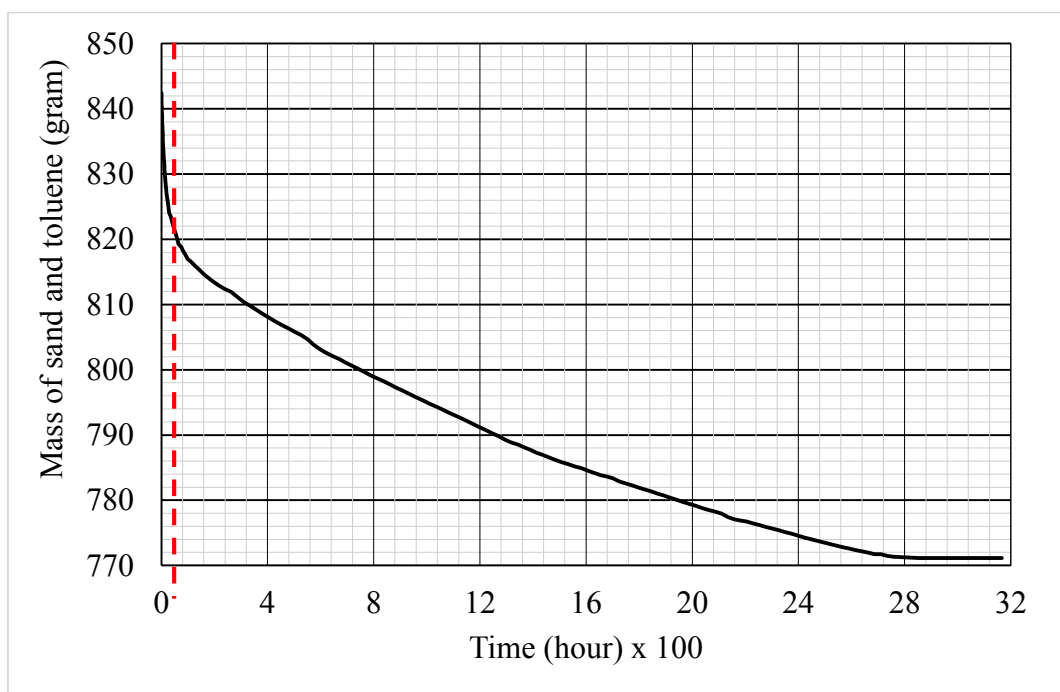


Figure 6.21. Evaporation rate of toluene in aquifer sand sample at about 100% (v/v) saturation

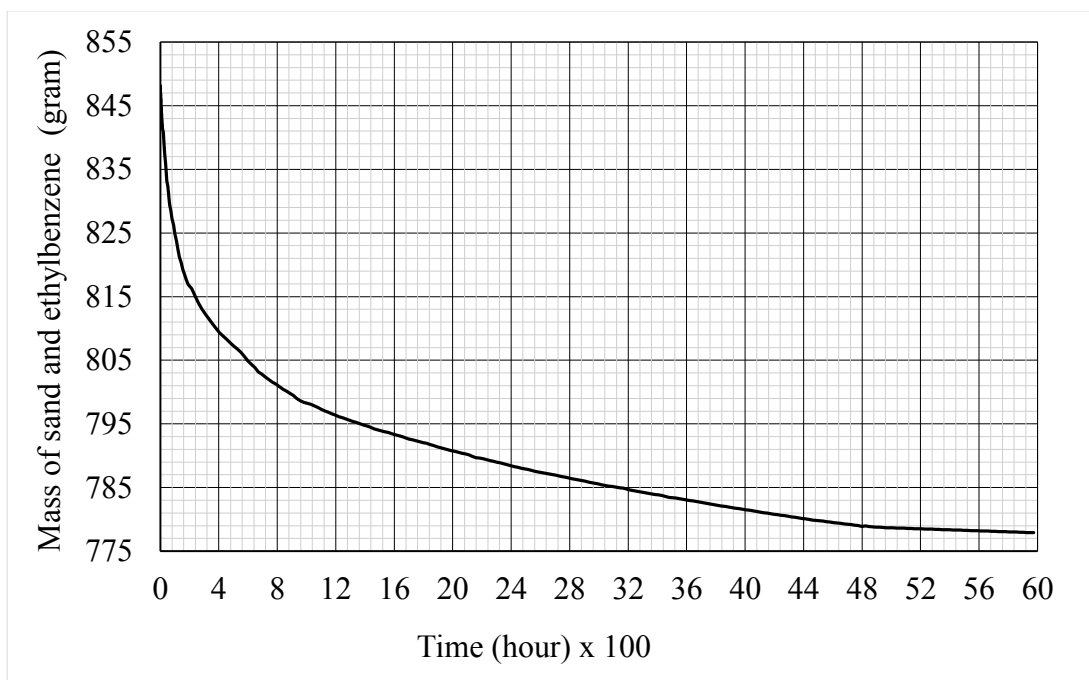


Figure 6.22. Evaporation rate of ethylbenzene in aquifer sand sample at about 100% (v/v) saturation

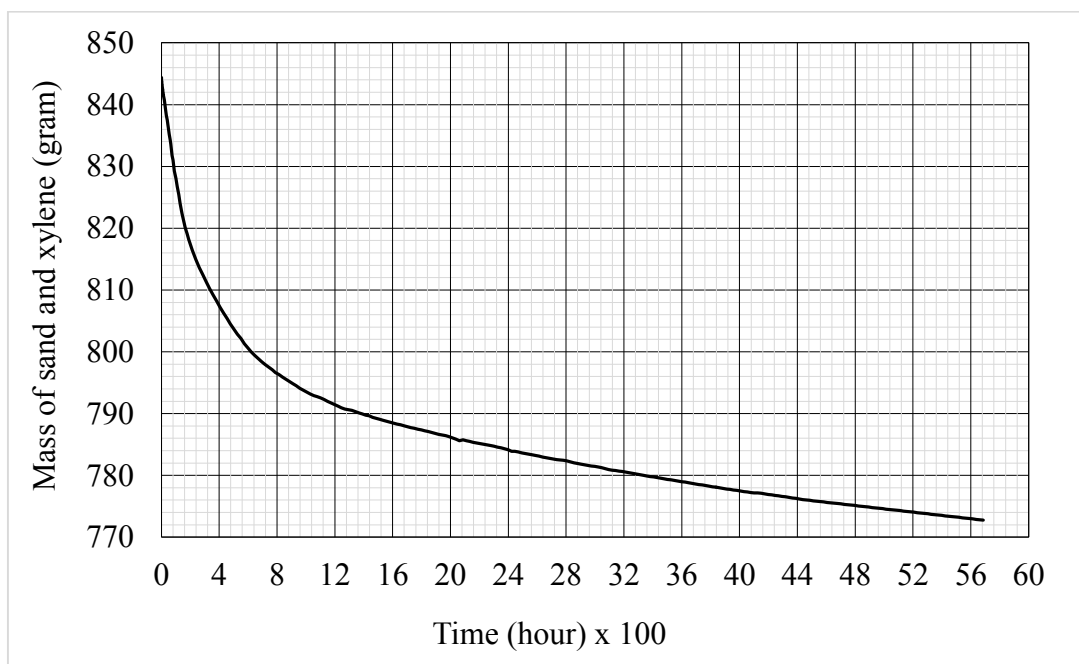


Figure 6.23. Evaporation rate of xylene in aquifer sand sample at about 100% (v/v) saturation

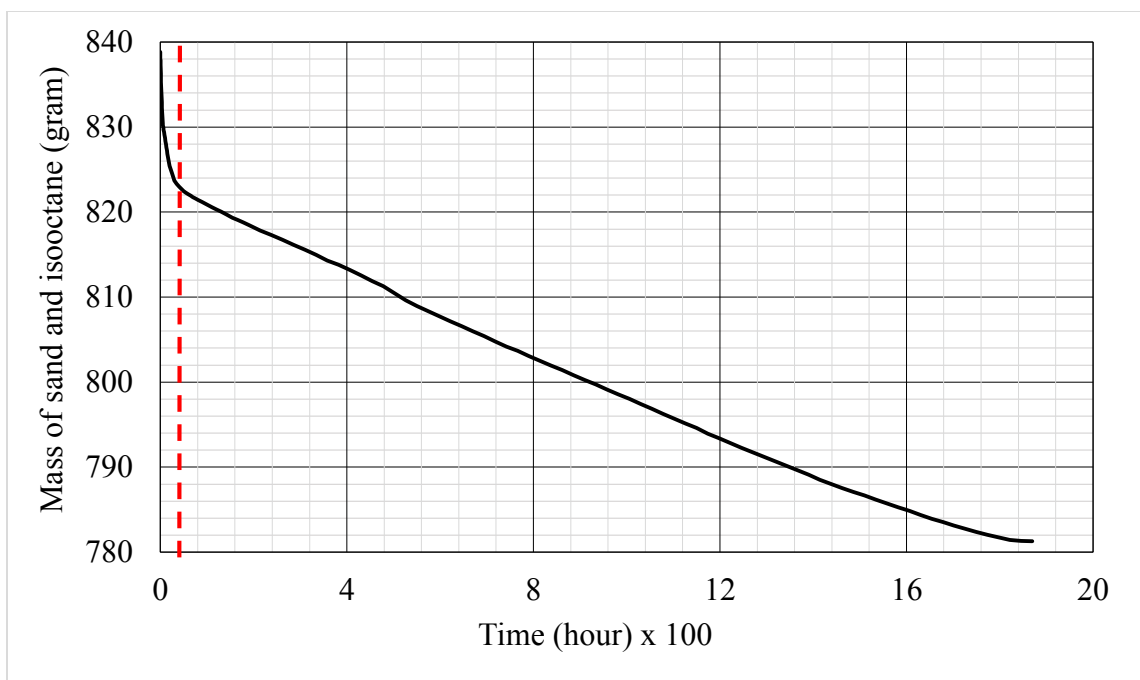


Figure 6.24. Evaporation rate of isooctane in aquifer sand sample at about 100% (v/v) saturation

Evaporation rate tests show that benzene, toluene, ethylbenzene, xylene, and isooctane lost 99.8, 82.2, 79.0, 79.0 and 96.1 % of their weights from fully saturated aquifer sand samples, respectively after 1678 h (about 10 weeks) of air drying. Results show that benzene is the only chemical that completely volatilized from the aquifer sand in about 1678 h (Table 6.7). The evaporation order for these chemicals after 1678 h is:

Benzene> isooctane> toluene> xylene and ethylbenzene

Isooctane completely evaporated after 1870 h (about 11 weeks), whereas in the same period toluene, ethylbenzene and xylene lost 84.8, 80.7 and 80.52% of their initial weight respectively (Table 6.7). Test was continued for other chemicals until they attained constant weight: for toluene it occurred at 3070 h; for ethylbenzene 5974 h (about 35 weeks), and

xylene 5686 h (about 33 weeks). The corresponding loss was 99.75%, 99.99% and 99.95% of their original weights respectively (Table 6.7). The evaporation rate data presented in Figure 6.25 show that ethylbenzene and xylene took up to three times longer to volatilize in comparison with benzene, toluene and isooctane.

Analysis of the evaporation rate data shows that the evaporation rate of benzene, toluene, ethylbenzene, and isooctane decreases rapidly over time. The results also indicate two phases of evaporation: rapid and slow. The first phase phenomenon characterizes benzene, toluene and isooctane, which seems to be the result of quick evaporation of chemical as it escapes from the sand voids—similar to free evaporation from pan, and lasted from beginning of the test to 40 h for benzene (Figure 6.20), and to 80 h for toluene and isooctane as shown in Figure 6.21 and Figure 6.24 respectively. The second phase of evaporation occurs after the vapor pressure overcomes the intermolecular attractive forces caused by chemical coatings around sand grains. Ethylbenzene and xylene show gradual loss during the slow phase and were volatilized almost at a constant rate since the beginning as shown in Figure 6.22 and Figure 6.23 respectively. Percent loss of benzene, toluene, ethylbenzene, xylene, and isooctane, with progress in evaporation, are included in Appendix F.5.

Table 6.7. Weight of aquifer sand sample, benzene, toluene, ethylbenzene, xylene, and isooctane used in the rate of evaporation test, and percent of loss

Chemical, 100% saturation level	Initial weight of sand + chemical (g)	Chemical weight (g) and volume (mL)	Duration and weight		Chemical lost (%)	Percent of chemical remaining in the sand
			Air drying time (h)	Weight after air drying (g)		
Benzene	851.25	72.40	166	807.21	60.83	39.17
		82.6	1678	778.98	99.80	0.20
Toluene	842.43	71.48	166	814.47	39.12	60.88
		81.65	1678	783.66	82.20	17.80
			1870	781.00	84.80	15.20
			3070	771.13	99.75	0.25
Ethylbenzene	848.10	70.22	166	817.61	43.42	56.58
		81.65	1678	792.62	79.00	21.00
			1870	791.42	80.70	19.30
			5974	777.89	99.99	0.01
Xylene	845.76	73.04	166	821.10	33.76	66.24
		84.54	1678	788.04	79.00	21.00
			1870	786.95	80.52	19.48
			5686	772.76	99.95	0.05
Isooctane	838.85	57.57	166	819.08	34.34	65.66
		83.43	1678	783.53	96.10	3.90
			1870	781.25	100.00	0.00

The slopes of straight lines of the evaporation rate of aquifer sand samples, contaminated with benzene, toluene, ethylbenzene, xylene, and isooctane at about 100% saturation levels are; $8 \cdot 10^{-7}x$, $3 \cdot 10^{-7}x$, $2 \cdot 10^{-7}x$, $3 \cdot 10^{-7}x$ and $5 \cdot 10^{-7}x$ respectively, as it shown in the table accompanying with Figure 6.25.

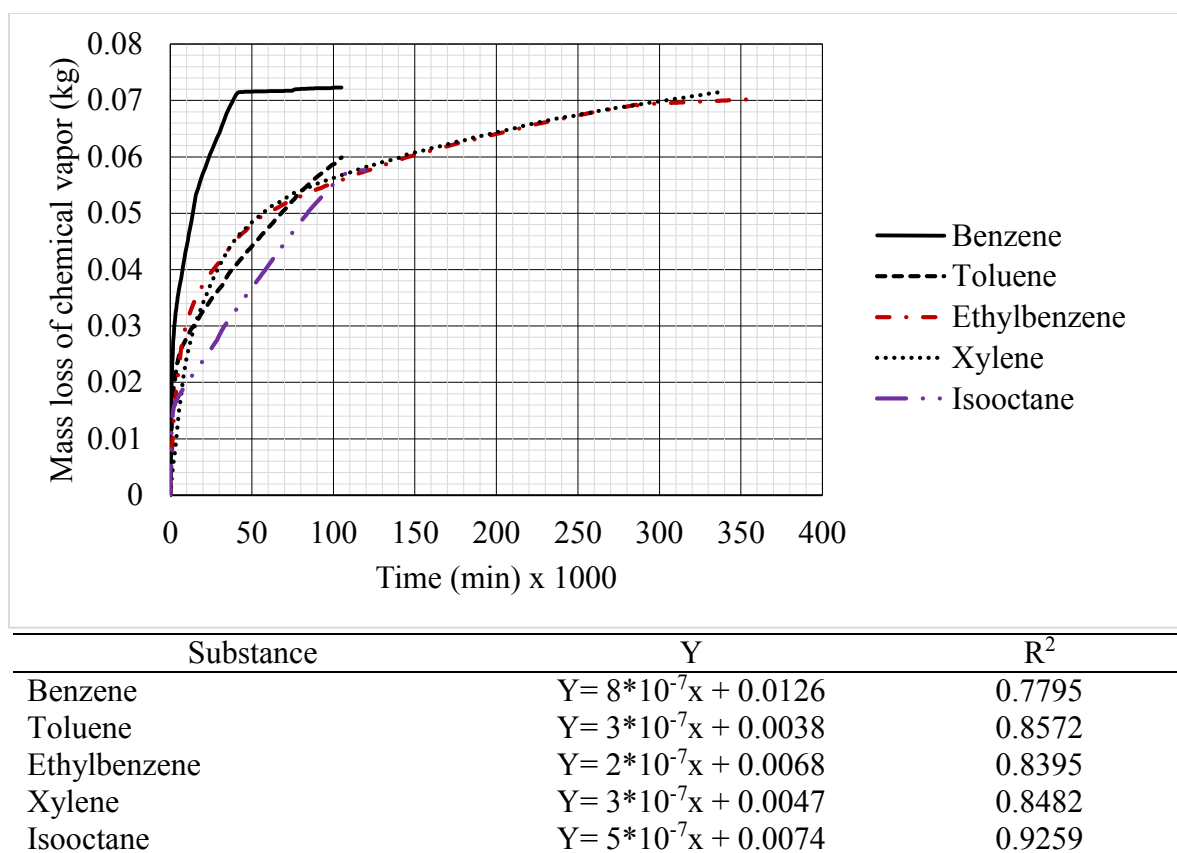


Figure 6.25. Evaporation rate of benzene, toluene, ethylbenzene, xylene, and isooctane in aquifer sand sample at about 100% saturation

Evaporation Rate of Gasoline in Upper Layer Sand Samples

Evaporation test was carried out on three upper layer sand samples which were contaminated by adding 76.63 g, 39.42 g and 19.39 g of gasoline to achieve about 100%, 50% and 25% saturation levels. Test results are presented in Appendix F.2.

Time-dependent variation in the amount of gasoline lost is shown in Figure 6.26 and the data are included in Table 6.8.

Analysis of the evaporation test data shows that evaporation rate of gasoline decreases rapidly until about 10 hours and slows down after this period for all contaminated samples (Figure 6.26). The results also indicate two phases of evaporation: rapid and slow. The first phase phenomenon seems to be the result of quick evaporation of gasoline as it escapes from the sand voids—similar to free evaporation from pan. Whereas, the second phase of evaporation occurs after the vapor pressure overcomes the intermolecular attractive forces caused by gasoline coatings around sand grains. Evaporation rate for all contaminated samples under varying conditions of saturation shows the same general trend: initial rapid loss for up to about 10 h; slowing down between about 10 and about 600 h; and becoming stable after 1600, 1200 and 400 h for about 100%, 50% and 25% saturation levels respectively. This pattern also indicates that although most of the VOCs are lost due to evaporation, not the entire quantity escapes the contaminated medium and a small amount is left behind as the residual saturation. Figure 6.26 show these results for sand contaminated with gasoline at about 100%, 50% and 25% saturation levels.

The slope of the straight lines of evaporation rate in the upper layer sand samples, contaminated with gasoline at about 100%, 50% and 25% saturation levels are; $3 \times 10^{-7}x$, $1 \times 10^{-7}x$ and $1 \times 10^{-7}x$ respectively, and the data presented in Appendix F.6.

An example for determination of the time and quantity for gasoline spill is given in Appendix F.8.

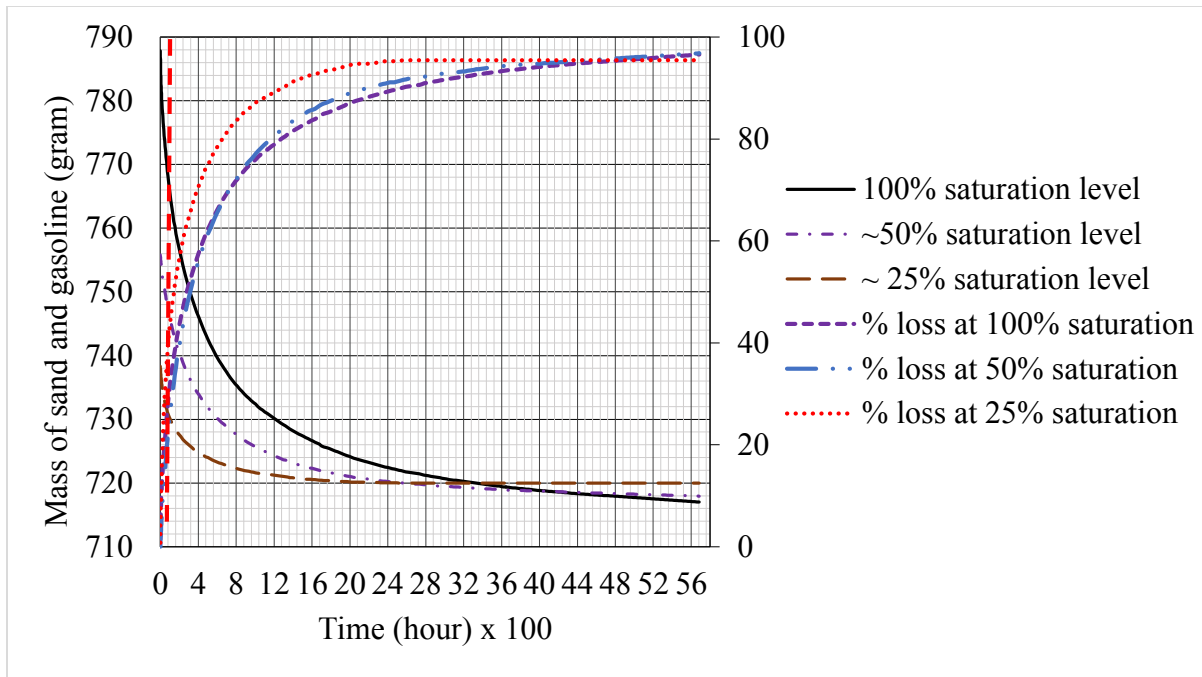


Figure 6.26. Evaporation rate of gasoline in upper layer sand sample at about 100%, 50% and 25% (v/v) saturation

Evaporation rate tests show that gasoline lost 90.4%, 91.65% and 95.46% of its original weight from upper layer sand samples contaminated at about 100%, 50%, 25% saturation levels respectively, after 2566 h (about 15 weeks) of air drying. However, sand sample that were contaminated at 25% saturation level lost about 95% of gasoline, attaining a constant weight after 2566 h (about 15 weeks) and about 5% of gasoline was left. Results show that about 3% of gasoline was left in sand samples at 100% and 50% saturation levels after 5686 h (about 33 weeks) (Table 6.8).

Test data indicate that on a long-term basis, gasoline volatilized at a slower rate from coarse-grained sand of the aquifer (Figure 6.17) than in medium-grained sand of the upper layer (Figure 6.26) because of the prevalence of small pore-size in the latter that increases capillary action; which also explains the smaller amount that remained behind (about 3% and

5% respectively). The faster evaporation rate and small amount of gasoline remaining behind in the voids implies a much reduced potential for groundwater pollution.

Table 6.8. Weight of upper layer sand sample and gasoline used in the rate of evaporation test, and percent loss

Saturation level of gasoline (%)	Initial weight of sand + gasoline (g)	Weight of gasoline (g) and volume (mL)	Duration and weight		Weight of gasoline lost (g)	Gasoline lost (%)	Percent of gasoline remaining in the sand
			Air drying time (h)	Weight after air drying (g)			
100	791.10	76.63	166	759.10	32.00	41.76	58.24
		106.43	2566	721.83	69.27	90.40	9.60
			5686	717.01	74.09	96.69	3.31
50	756.12	39.42	166	742.02	14.10	35.77	64.23
		54.75	2566	719.99	36.13	91.65	8.35
			5686	717.94	38.18	96.85	3.15
25	738.50	19.39	166	731.47	7.03	36.26	63.74
		26.93	2566-5686	719.99	18.51	95.46	4.54

Evaporation Rate of TCE in Upper Layer Sand Samples

Evaporation test was conducted for three upper layer sand samples, contaminated by adding 162.23, 82.46 and 41.04 g of TCE to achieve 100%, 50% and 25% saturation levels. The results are included in Appendix F.2.

Time-dependent variation of the amount of gasoline lost is shown in Figure 6.27 and the data are presented in Table 6.9.

Analysis of the data shows that the evaporation rate of TCE decreases rapidly until about 60 h for both samples contaminated at 100% and 50% saturation levels — slows down

between about 60 and 120 h, and declines gradually after about 120 h (Figure 6.27). The evaporation rate at about 25% saturation was gradual over the test period. The entire weight of TCE at all saturation levels was lost within about 790 h (about 5 weeks) (Figure 6.27).

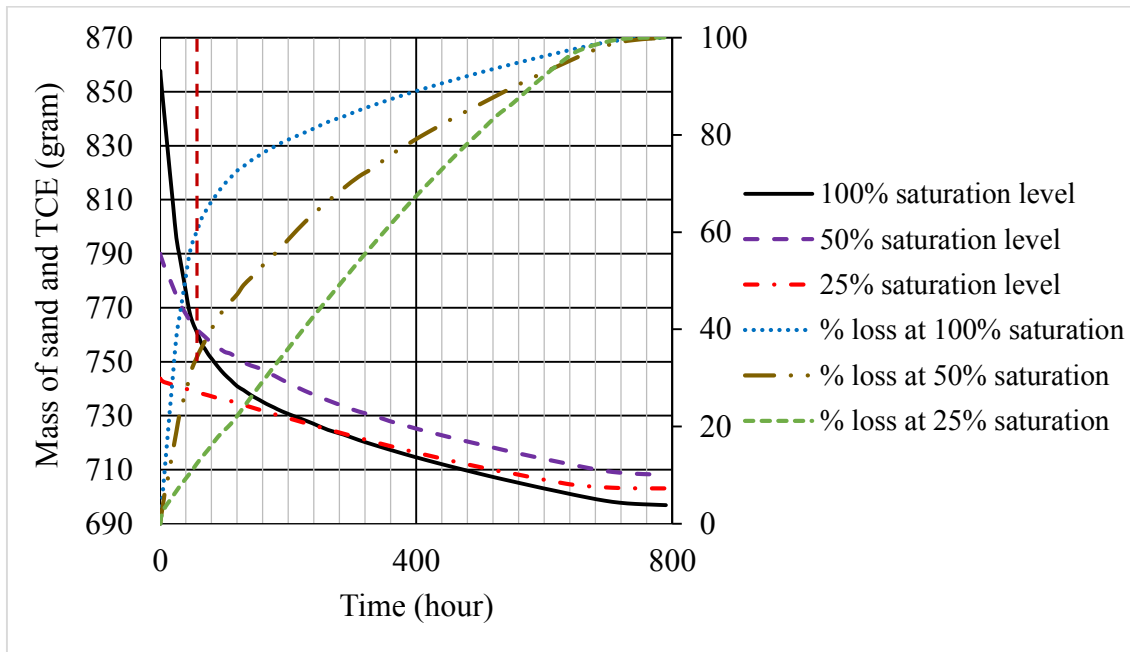


Figure 6.27. Evaporation rate of TCE in upper layer sand sample at about 100%, 50% and 25% saturation levels

The slopes of straight lines of evaporation rate of TCE in the upper layer sand samples, contaminated with TCE at about 100%, 50% and 25% saturation levels are; $4 \times 10^{-6}x$, $2 \times 10^{-6}x$ and $1 \times 10^{-6}x$ respectively (Appendix F.7). An example for determining the time and quantity for TCE spill is given in Appendix F.8.

Test data indicate that TCE in the upper layer sand volatilized faster than in the aquifer sand, and no residual saturation occurred in the sand after about 790 h and 1500 h respectively. This indicates reduced potential for groundwater pollution.

Table 6.9. Weight of upper layer sand sample and TCE used in the rate of evaporation test, and percent loss

Saturation level of TCE (%)	Initial weight of sand + TCE (g)	Weight of TCE (g) and volume (mL)	Duration and weight		TCE lost (%)	Percent of TCE remaining in the sand
			Air drying time (h)	Weight after air drying (g)		
100	859.1	162.23	166	734.36	76.89	23.11
		111.11	790	696.87	100.00	0.00
50	790.59	82.46	166	745.80	54.32	45.68
		56.48	790	708.13	100.00	0.00
25	744.16	41.04	166	731.47	30.92	69.08
		28.11	790	703.11	100.00	0.00

To sum up, all VOCs showed high mass loss via vaporization that will lead to rapid vapor transport in the vicinity of source of contamination and might pose serious hazard of vapor intrusion into nearby buildings. At the same time it can provide a natural soil/groundwater remediation pathway via the vadose zone to the atmosphere.

Porosity, Void Ratio, Dry Unit Weight, and Saturated Unit Weight

Porosity is a primary factor that controls the storage and movement of fluids in sediment and rocks. Movement of groundwater as well as its exploitation depends on porosity and permeability of the porous medium. Porosity (n) can be represented as a value between 0–1 or as a percentage between 0–100 and can be estimated from the voids ratio (e) from the following equation:

$$n = \frac{e}{1 + e}$$

Geotechnical Properties of Aquifer Sand

Geotechnical properties—porosity, void ratio, dry unit weight (γ_d) and saturated unit weight (γ_{sat})—have been measured for two sets of 22 aquifer sand samples; 21 of each were contaminated with gasoline and TCE at about 100%, 50% and 25% saturation levels, and one was uncontaminated. Results are shown in Table 6.10 and Table 6.11 respectively.

Residual amounts of gasoline and TCE contaminants, which coat sand grains, cause a decrease in void ratio and porosity, and an overall increase in dry and saturated unit weights of the sand samples (Table 6.10).

Test results showed that gasoline causes slightly more change in the porosity and void ratio than TCE. Since gasoline has a lower vapor pressure than TCE (Table 3.2), a smaller amount of gasoline will be lost by evaporation from contaminated sand, with a correspondingly larger amount remaining behind in the pores resulting in lower void ratio and porosity. At the same time, a decrease in void ratio will require a smaller volume to accommodate the same volume of contaminated sand.

Table 6.10. Value of e, n, γ_d and γ_{sat} of aquifer sand samples contaminated with gasoline, at about 100%, 50% and 25% saturation levels

Sample number	Saturation level (%)	Void ratio (e)	Percent change in e	Porosity (n)	Percent change in n	Dry unit weight, γ_d (g/cm ³)	Percent change in γ_d	Saturated unit weight, γ_{sat} (g/cm ³)	Percent change in γ_{sat}
Original sample		0.455	--	0.312	--	1.675	--	1.988	--
Gas-1	100	0.527	+15.82	0.345	+10.62	1.68	+0.30	2.02	+1.61
Gas-2	100	0.466	+2.42	0.318	+1.88	1.72	+2.69	2.038	+2.52
Gas-3	100	0.473	+3.96	0.321	+2.92	1.678	+0.18	2.00	+0.60
Gas-10	100	0.572	+25.71	0.364	+16.62	1.68	+0.30	2.00	+0.60
Gas-11	100	0.412	-9.45	0.292	-6.48	1.686	+0.66	1.977	-0.55
Gas-12	100	0.48	+5.49	0.324	+3.95	1.64	-2.09	1.968	-1.01
Gas-13	100	0.55	+20.88	0.355	+13.73	1.73	+3.28	2.06	+3.62
Average		0.497	+9.23	0.331	+6.09	1.688	0.78	2.01	+1.11
Gas-20	50	0.52	+14.29	0.342	+9.65	1.62	-3.28	1.956	-1.61
Gas-4	50	0.32	-29.67	0.242	-22.3	1.644	-1.85	1.965	-1.16
Gas-5	50	0.512	+12.53	0.339	+8.53	1.682	+0.42	2.02	+1.61
Gas-6	50	0.512	+12.53	0.339	+8.53	1.611	-3.82	1.949	-1.96
Gas-14	50	0.47	+3.30	0.32	+2.48	1.69	+0.90	2.01	+1.11
Gas-15	50	0.335	-26.37	0.251	-19.57	1.692	+1.01	2.02	+1.61
Gas-16	50	0.47	+3.30	0.32	-2.48	1.71	+2.09	2.03	+2.11
Average		0.448	-1.54	0.31	-0.6	1.66	-0.89	1.99	+0.1
Gas-21	25	0.46	+1.10	0.315	+0.98	1.63	-2.69	1.94	+2.41
Gas-7	25	0.502	+10.33	0.334	+7.12	1.628	-2.81	1.963	-1.26
Gas-8	25	0.461	+1.32	0.316	+1.13	1.656	-1.13	1.971	-0.86
Gas-9	25	0.482	+5.938	0.325	+4.24	1.641	-2.03	1.966	-1.11
Gas-17	25	0.479	+5.27	0.324	+3.8	1.703	+1.67	2.027	+1.96
Gas-18	25	0.469	+3.08	0.319	+2.33	1.684	+0.54	2.00	+0.6
Gas-19	25	0.47	+3.30	0.32	+2.48	1.70	+1.49	2.02	+1.61
Average		0.474	+4.17	0.32	+2.56	1.66	-0.89	1.98	-0.4

Table 6.11. Value of e , n , γ_d and γ_{sat} of aquifer sand samples contaminated with TCE, at about 100%, 50% and 25% saturation levels

Sample number	Saturation level (%)	Void ratio (e)	Percent change in e	Porosity (n)	Percent change in n	Dry unit weight (γ_d) (g/cm ³)	Percent change in γ_d	Saturated unit weight (γ_{sat}) (g/cm ³)	Percent change in γ_{sat}
Original sample		0.455	---	0.312	---	1.675	---	1.988	---
TCE-01	100	0.473	+3.956	0.321	+2.921	1.652	-1.373	1.973	-0.755
TCE-02	100	0.417	+8.352	0.294	-5.678	1.727	+3.104	2.02	+1.61
TCE-03	100	0.456	+0.22	0.313	+0.38	1.655	-1.194	1.968	1.006
TCE-00	100	0.43	- 5.495	0.301	-3.622	1.65	-1.493	1.973	-0.755
TCE-010	100	0.417	- 8.352	0.294	-5.678	1.717	+2.507	2.011	+1.157
TCE-011	100	0.433	- 4.835	0.302	-3.153	1.716	+2.448	2.02	+1.61
TCE-012	100	0.435	- 4.396	0.303	-2.841	1.72	+2.687	2.02	+1.61
Average		0.437	-3.96	0.304	-2.56	1.691	+0.95	1.997	+0.45
TCE-019	50	0.468	+2.857	0.319	+2.18	1.67	-0.299	1.997	+0.453
TCE-04	50	0.425	-6.593	0.298	-4.408	1.661	-0.836	1.959	-1.459
TCE-05	50	0.325	-28.57	0.245	-21.38	1.662	-0.776	1.987	-0.05
TCE-06	50	0.464	+1.978	0.317	+1.583	1.644	-1.851	1.961	-1.358
TCE-013	50	0.405	-10.99	0.288	-7.61	1.732	+3.403	2.02	+1.61
TCE-014	50	0.444	-2.418	0.307	-1.449	1.674	-0.06	1.981	-0.352
TCE-015	50	0.41	-9.89	0.291	-6.801	1.728	+3.164	2.02	+1.61
Average		0.42	-7.69	0.295	-5.45	1.681	+0.36	1.989	+0.05
TCE-020	25	0.45	-1.099	0.31	-0.531	1.69	+0.896	2.00	+0.604
TCE-07	25	0.403	-11.43	0.287	-7.935	1.687	+0.716	1.974	-0.704
TCE-08	25	0.439	-3.516	0.305	-2.22	1.691	+0.955	2.00	+0.604
TCE-09	25	0.448	-1.538	0.309	-0.836	1.674	-0.06	1.984	-0.201
TCE-016	25	0.392	-13.85	0.282	-9.741	1.699	+1.433	1.98	-0.402
TCE-017	25	0.426	-6.374	0.299	-4.251	1.704	+1.731	2.00	+0.604
TCE-018	25	0.431	-5.275	0.301	-3.465	1.71	+2.09	2.01	+1.107
Average		0.427	-6.15	0.299	-4.17	1.694	+1.13	1.99	+0.1

In order to simulate hydrocarbon spill and leaks in humid climatic conditions, laboratory tests were carried out on the aquifer sand samples using aqueous solutions of gasoline and TCE at concentrations of 1 to 10%. Table 6.12 and Table 6.13 give the results for each of them respectively.

Test results for aquifer sand samples that were exposed to aqueous solution contaminated with gasoline and TCE, show that there is a slight decrease in void ratio and porosity, but increase in dry and saturated unit weights values as shown in Table 6.12 and Table 6.13 respectively.

Table 6.12. Value of e , n , γ_d and γ_{sat} of aquifer sand samples fully saturated with aqueous solution contaminated with varying concentration of gasoline

Sample number	Void ratio (e)	Percent change in e	Porosity (n)	Percent change in n	Dry unit weight (γ_d) (g/cm ³)	Percent change in γ_d	Saturated unit weight (γ_{sat}) (g/cm ³)	Percent change in γ_{sat}
Original sample	0.455		0.312		1.675		1.988	
Gas-1%	0.386	- 5.16	0.278	- 10.74	1.73	+3.28	2.014	+1.31
Gas-2%	0.382	-16.04	0.276	- 11.41	1.75	+4.48	2.02	+1.61
Gas-3%	0.392	-13.85	0.282	- 9.74	1.742	+4.00	2.02	+1.61
Gas-4%	0.396	-12.97	0.284	-9.08	1.77	+5.67	2.05	+3.12
Gas-5%	0.41	- 9.89	0.291	-6.80	1.753	+4.66	2.04	+2.62
Gas-6%	0.38	-16.48	0.275	- 11.74	1.74	+3.88	2.02	+1.61
Gas-7%	0.375	-17.58	0.273	- 12.59	1.76	+5.07	2.03	+2.11
Gas-8%	0.386	-15.16	0.278	- 10.74	1.74	+3.88	2.02	+1.61
Gas-9%	0.383	-15.82	0.277	- 11.24	1.743	+4.06	2.02	+1.61
Gas-10%	0.396	-12.97	0.284	- 9.08	1.73	+3.28	2.01	+1.11
Average	0.389	-14.51	0.28	-10.26	1.746	+4.24	2.024	+1.81

Table 6.13. Value of e , n , γ_d and γ_{sat} of aquifer sand samples fully saturated with aqueous solution contaminated with varying concentration of TCE

Sample number	Void ratio (e)	Percent change in e	Porosity (n)	Percent change in n	Dry unit weight (γ_d) (g/cm ³)	Percent change in γ_d	Saturated unit weight (γ_{sat}) (g/cm ³)	Percent change in γ_{sat}
Original sample	0.455		0.312		1.675		1.988	
TCE- 1%	0.404	-11.21	0.288	-7.77	1.729	+3.22	2.02	+1.61
TCE- 2%	0.418	-8.13	0.295	-5.52	1.743	+4.06	2.038	+2.52
TCE- 3%	0.312	-31.43	0.238	-23.78	1.693	+1.07	2.01	+1.11
TCE- 4%	0.31	-31.87	0.237	-24.15	1.73	+3.28	2.04	+2.62
TCE- 5%	0.468	+2.86	0.319	+2.18	1.71	+2.09	2.02	+1.61
TCE- 6%	0.435	-4.40	0.303	-2.84	1.732	+3.40	2.03	+2.11
TCE- 7%	0.449	-1.32	0.31	-0.68	1.737	+3.70	2.047	+2.97
TCE- 8%	0.461	+1.32	0.316	+1.13	1.715	+2.39	2.031	+2.16
TCE- 9%	0.49	+7.69	0.329	+5.40	1.685	+0.60	2.014	+1.31
TCE- 10%	0.449	-1.32	0.31	-0.68	1.732	+3.40	2.042	+2.72
Average	0.419	-7.91	0.294	-5.77	1.721	+2.75	2.03	-2.11

Geotechnical properties (n , e , γ_d and γ_{sat}) were also determined for five aquifer sand samples, which were fully saturated with benzene, toluene, ethylbenzene, xylenes and isooctane for 8 weeks. Table 6.14 represents the results. Test results show that there is a slight decrease in void ratio and porosity, except for isooctane, but increase in dry and saturated unit weights values. However, results of n , e , γ_d and γ_{sat} show smaller changes in their value in comparison with TCE and gasoline, after period of contamination (Table 6.14).

Table 6.14. Value of e , n , γ_d and γ_{sat} of aquifer sand samples, fully saturated with benzene, toluene, ethylbenzene, xylenes and isooctane

Sample number	Void ratio (e)	Percent change in e	Porosity (n)	Percent change in n	Dry unit weight (γ_d) (g/cm ³)	Percent change in γ_d	Saturated unit weight (γ_{sat}) (g/cm ³)	Percent change in γ_{sat}
Original sample	0.455	--	0.313	--	1.675	--	1.988	--
Benzene	0.44	-3.409	0.306	-2.38	1.683	+0.478	1.99	+0.101
Toluene	0.433	-5.00	0.302	-3.46	1.71	+2.09	2.02	+1.61
Ethylbenzene	0.45	-1.136	0.31	-0.85	1.71	+2.09	2.02	+1.61
Xylene	0.44	-3.409	0.306	-2.38	1.72	+2.687	2.03	+2.113
Isooctane	0.463	+1.818	0.316	+1.11	1.696	+1.254	2.01	+1.107

Geotechnical Properties of Upper Layer Sand

Geotechnical properties (e , n , γ_d and γ_{sat}) were also determined for 32 upper layer sand samples that were contaminated with gasoline as well as TCE at about 100% 50 and 25% saturation levels for varying periods of time (Table 6.15 and 6.16).

Results of void ratio and porosity tests of upper layer sand samples, contaminated with gasoline, show a decrease as shown in Table 6.15. The values of dry and saturated unit weights, on the other hand, show an increase (Table 6.15).

Table 6.15. Value of e , n , γ_d and γ_{sat} of upper layer sand samples contaminated with gasoline, at about 100%, 50% and 25% saturation levels

Sample number	Saturation level (%)	Void ratio (e)	Percent change in e	Porosity (n)	Percent change in n	Dry unit weight (γ_d) (g/cm ³)	Percent change in γ_d	Saturated unit weight (γ_{sat}) (g/cm ³)	Percent change in γ_{sat}
Original sample		0.688	--	0.408	--	1.362	--	1.733	--
Gas-001	100	0.493	-28.34	0.33	-19.07	1.516	+11.31	1.784	+2.94
Gas-002	100	0.598	-13.08	0.374	-8.28	1.466	+7.64	1.877	+8.31
Gas-003	100	0.545	-20.78	0.353	-13.54	1.501	+10.21	1.85	+6.75
Gas-010	100	0.54	-21.51	0.351	-14.06	1.50	+10.13	1.85	+6.75
Gas-011	100	0.49	-28.78	0.329	-19.4	1.52	+11.6	1.85	+6.75
Gas-012	100	0.488	-29.07	0.32	-21.57	1.516	+11.31	1.845	+6.46
Average		0.53	-22.97	0.34	-16.67	1.5	+10.13	1.84	+6.17
Gas-004	50	0.593	-13.81	0.372	-8.76	1.54	+13.07	1.912	+10.33
Gas-005	50	0.561	-18.46	0.359	-11.92	1.569	+15.2	1.928	+11.25
Gas-006	50	0.498	-27.62	0.332	-18.52	1.41	+3.52	1.742	+0.52
Gas-013	50	0.592	-13.95	0.372	-8.86	1.54	+13.07	1.912	+10.33
Gas-014	50	0.561	-18.46	0.359	-11.92	1.558	+14.39	1.912	+10.33
Average		0.561	-18.46	0.359	-12.01	1.523	+11.82	1.88	+8.48
Gas-007	25	0.593	-13.81	0.372	-8.76	1.446	+6.17	1.819	+4.96
Gas-008	25	0.419	-39.1	0.295	-27.63	1.465	+7.56	1.791	+3.35
Gas-009	25	0.573	-16.72	0.364	-10.72	1.453	+6.68	1.817	+4.85
Gas-015	25	0.593	-13.81	0.372	-8.76	1.443	+5.95	1.816	+4.79
Gas-016	25	0.59	-14.24	0.371	-9.05	1.483	+8.88	1.855	+7.04
Average		0.554	-19.48	0.355	-12.99	1.458	+7.05	1.819	+4.96

Results obtained from tests of TCE-contaminated sand upper layer sand samples indicate a decrease in e and n ; and increase in γ_d and γ_{sat} as shown in Table 6.16.

Test results showed various changes in geotechnical properties values between gasoline and TCE-contaminated sand. Changes in the geotechnical properties are due to the residual amount of the compounds that are adsorbed on sand grains. This remaining portion of hydrocarbon plays an essential role in changing the geotechnical properties of the medium, as they change the interfacial tension and degree of wettability of the sand grain-water

mixture. According to the U.S. EPA (1996b), residual hydrocarbons in a media are usually immovable because they are tightly bound and scattered in pore spaces, which may lead to long-term contamination of groundwater. In addition, Ruffino and Zanetti (2009) indicated that the adsorption of TCE is more than that of benzene, which is part of gasoline component.

Table 6.16. Value of e, n, γ_d and γ_{sat} of upper layer sand samples contaminated with TCE, at about 100%, 50% and 25% saturation levels

Sample number	Saturation level (%)	Void ratio (e)	Percent change in e	Porosity (n)	Percent change in n	Dry unit weight (γ_d) (g/cm ³)	Percent change in γ_d	Saturated unit weight (γ_{sat}) (g/cm ³)	Percent change in γ_{sat}
Original sample		0.688	--	0.408	---	1.362		1.733	
TCE-011	100	0.551	-19.91	0.355	-14.85	1.466	+7.64	1.821	+5.08
TCE-012	100	0.537	-21.95	0.349	-16.78	1.406	+3.23	1.755	+1.27
TCE-013	100	0.53	-22.97	0.346	-17.78	1.492	+9.54	1.838	+6.06
TCE-020	100	0.558	-18.9	0.358	-13.92	1.523	+11.82	1.88	+8.48
TCE-010	100	0.53	-22.97	0.346	-17.78	1.494	+9.69	1.842	+6.29
TCE-023	100	0.534	-22.38	0.348	-17.20	1.405	+3.16	1.754	+1.21
Average		0.54	-21.51	0.35	-14.22	1.464	+7.48	1.815	+4.73
TCE-014	50	0.581	-15.55	0.367	-11.02	1.429	+4.92	1.797	+3.69
TCE-015	50	0.51	-25.87	0.338	-20.80	1.584	+16.3	1.921	+10.85
TCE-016	50	0.392	-43.02	0.282	-44.88	1.563	+14.76	1.844	+6.41
TCE-021	50	0.573	-16.72	0.364	-12.00	1.43	+4.99	1.797	+3.69
TCE-024	50	0.51	-25.87	0.338	-20.80	1.585	+16.37	1.922	+10.91
Average		0.513	-25.44	0.338	-17.16	1.518	+11.45	1.856	+7.09
TCE-017	25	0.545	-20.78	0.353	-15.66	1.53	+12.33	1.881	+8.54
TCE-018	25	0.43	-37.5	0.301	-35.68	1.52	+11.60	1.82	+5.02
TCE-019	25	0.563	-18.17	0.360	-13.27	1.48	+08.66	1.838	+6.06
TCE-022	25	0.61	-11.34	0.379	-7.69	1.52	+11.60	1.896	+9.41
TCE-025	25	0.44	-36.05	0.306	-33.53	1.55	+13.80	1.85	+6.75
Average		0.518	-24.71	0.34	-16.67	1.52	+11.6	1.86	+7.33

Geotechnical properties (n , e , γ_d and γ_{sat}) were also determined for five upper layer sand samples, which were fully saturated with benzene, toluene, ethylbenzene, xylenes and isooctane for 8 weeks. Table 6.17 represents the results. Test results show that there is a slight decrease in void ratio and porosity, but increase in dry and saturated unit weights values. However, results of n , e , γ_d and γ_{sat} show less changes in their value in comparison with TCE and gasoline, after period of contamination (Table 6.17).

Table 6.17. Value of e , n , γ_d and γ_{sat} of upper layer sand samples, fully saturated with benzene, toluene, ethylbenzene, xylenes and isooctane

Sample number	Void ratio (e)	Percent change in e	Porosity (n)	Percent change in n	Dry unit weight (γ_d) (g/cm^3)	Percent change in γ_d	Saturated unit weight (γ_{sat}) (g/cm^3)	Percent change in γ_{sat}
Original sample	0.688	--	0.408	--	1.362	--	1.733	--
Benzene	0.61	-11.34	0.379	-7.14	1.401	+2.86	1.74	+0.40
Toluene	0.592	-13.95	0.372	-8.86	1.52	+11.60	1.92	+10.79
Ethylbenzene	0.54	-21.51	0.351	-14.06	1.594	+17.03	1.931	+11.46
Xylene	0.598	-13.08	0.374	-8.28	1.445	+6.094	1.817	+4.85
Isooctane	0.622	-9.59	0.383	-6.01	1.47	+7.930	1.825	+5.31

Hydraulic Conductivity Test

Permeability is a qualitative expression of the relative ease or difficulty of fluid to move through pores in rocks or soil. Hydraulic conductivity, on the other hand, is a numerical representation of the actual rate of movement of water through the geological material.

Hydraulic conductivity was measured for uncontaminated sand samples from both the aquifer and upper layer as well as for contaminated sand samples following the ASTM test methods D2434–68 (Constant Head) using the standard permeameter equipment (ASTM, 2011b). The compacted dry density (ρ_d) and moist density (ρ_w) were also measured for all sand samples to ensure same level of compaction for all test. In addition, hydraulic conductivity was determined for some aquifer sand samples that were fully saturated—without air drying—with gasoline, TCE and isooctane for 32 weeks.

Hydraulic Conductivity of Aquifer Sand Samples Contaminated with TCE and Gasoline

Hydraulic conductivity was measured for 21 aquifer sand samples that were contaminated both with gasoline and TCE for varying periods of time. Results of the hydraulic conductivity and compacted densities are given in Appendix G.1 and G.2 respectively. Figures 6.28 and 6.29 show the variation of hydraulic conductivity of sand contaminated with gasoline and TCE respectively over time.

Data show that gasoline causes a reduction in hydraulic conductivity of sand between 24.38% and 50.56 % (Appendix G.1) and TCE causes reduction between 24.27% and 41.01% (Appendix G.2). Results show that the reduction in the hydraulic conductivity fluctuated during the first few weeks of contamination, but stabilized after 8 weeks.

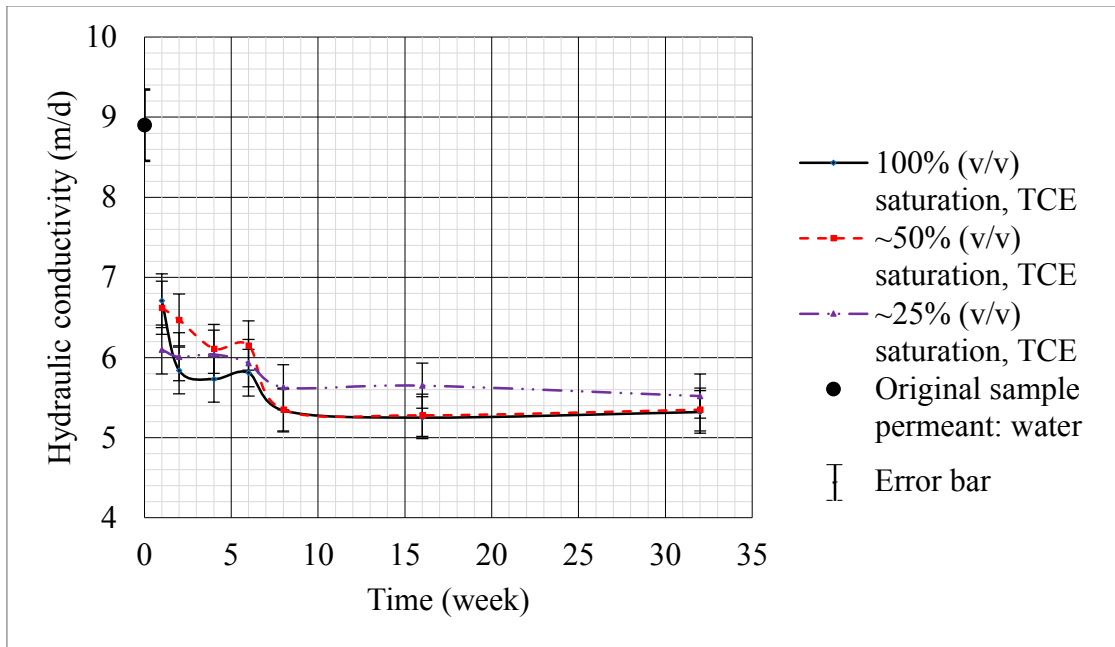


Figure 6.28. Hydraulic conductivity of aquifer sand samples contaminated with gasoline, at about 100%, 50% and 25% saturation levels

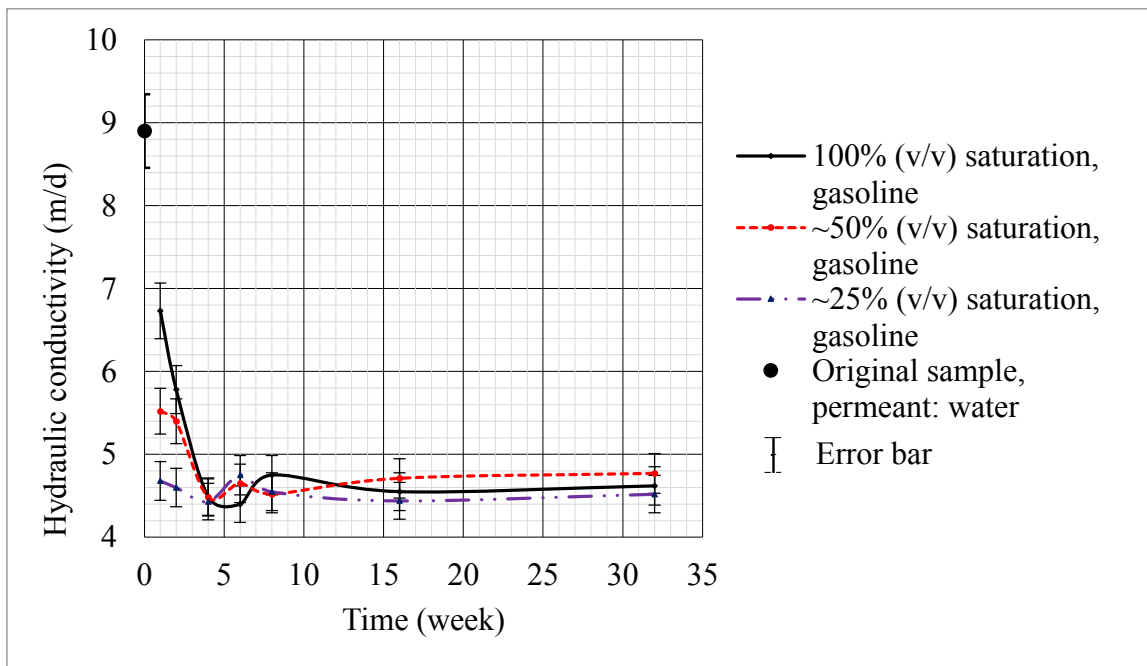


Figure 6.29. Hydraulic conductivity of aquifer sand samples contaminated with TCE, at about 100%, 50% and 25% saturation levels

Hydraulic conductivity was measured for 10 sand samples that were exposed to aqueous solutions contaminated with about 1, 2, 3 and up to 10% (1 to 10*10⁴ ppm), of TCE and gasoline for 8 weeks. This was done to determine whether or not small quantities of contaminants would influence hydraulic conductivity. Tables 6.18 and 6.19 give the results of the hydraulic conductivity and compacted densities for samples contaminated with aqueous solutions of TCE and gasoline respectively, and Figures 6.30 and 6.31 shows the hydraulic conductivity and percent of reduction. Results show a reduction in hydraulic conductivity of fully saturated sand samples contaminated with TCE and gasoline of up to 63.93% and 52.58% respectively (Tables 6.18 and Table 6.19).

Table 6.18. Compacted density and hydraulic conductivity of aquifer sand samples, fully saturated with aqueous solution contaminated with varying concentration of TCE for 8 weeks

Sample description	Dry density $\rho_d(\frac{g}{cm^3})$	Moist density $\rho_w(\frac{g}{cm^3})$	Hydraulic conductivity (m/day)	Percent reduction in hydraulic conductivity
Sand sample, permeant water	1.717	2.014	8.9	--
TCE 1%	1.677	1.906	4.12	53.71
TCE 2%	1.596	1.814	4.50	49.44
TCE 3%	1.569	1.784	4.38	50.79
TCE 4%	1.550	1.766	4.36	51.01
TCE 5%	1.577	1.789	5.14	42.25
TCE 6%	1.656	1.881	4.81	45.96
TCE 7%	1.658	1.855	3.21	63.93
TCE 8%	1.690	1.917	4.13	53.60
TCE 9%	1.660	1.840	3.66	58.88
TCE 10%	1.690	1.916	3.78	57.53

Table 6.19. Compacted density and hydraulic conductivity of aquifer sand samples, fully saturated with aqueous solution contaminated with varying concentration of gasoline for 8 weeks

Sample description	Dry density $\rho_d(\frac{g}{cm^3})$	Moist density $\rho_w(\frac{g}{cm^3})$	Hydraulic conductivity (m/day)	Percent reduction in hydraulic conductivity
Sand sample, permeant water	1.717	2.014	8.90	--
Gasoline 1%	1.669	1.880	5.44	38.88
Gasoline 2%	1.676	1.875	4.90	44.94
Gasoline 3%	1.644	1.846	5.21	41.46
Gasoline 4%	1.759	1.962	5.00	43.82
Gasoline 5%	1.681	1.883	5.82	34.61
Gasoline 6%	1.671	1.871	5.56	37.53
Gasoline 7%	1.553	1.923	5.26	42.02
Gasoline 8%	1.698	1.913	4.86	45.39
Gasoline 9%	1.718	1.937	4.22	52.58
Gasoline 10%	1.700	1.923	4.75	46.63

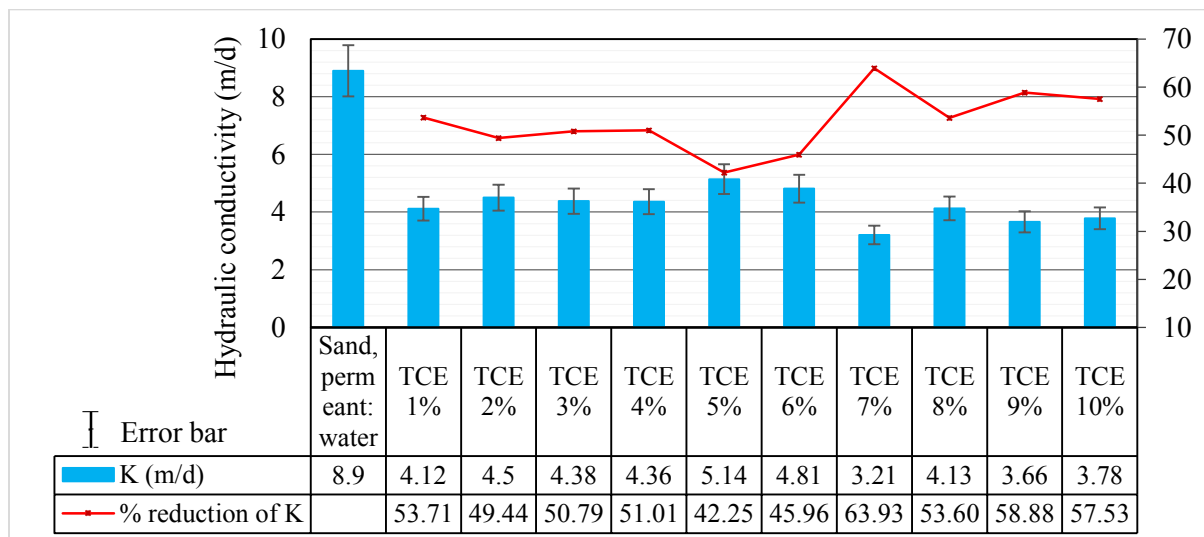


Figure 6.30. Hydraulic conductivity of aquifer sand samples, fully saturated with aqueous solution contaminated with varying concentration of TCE for 8 weeks

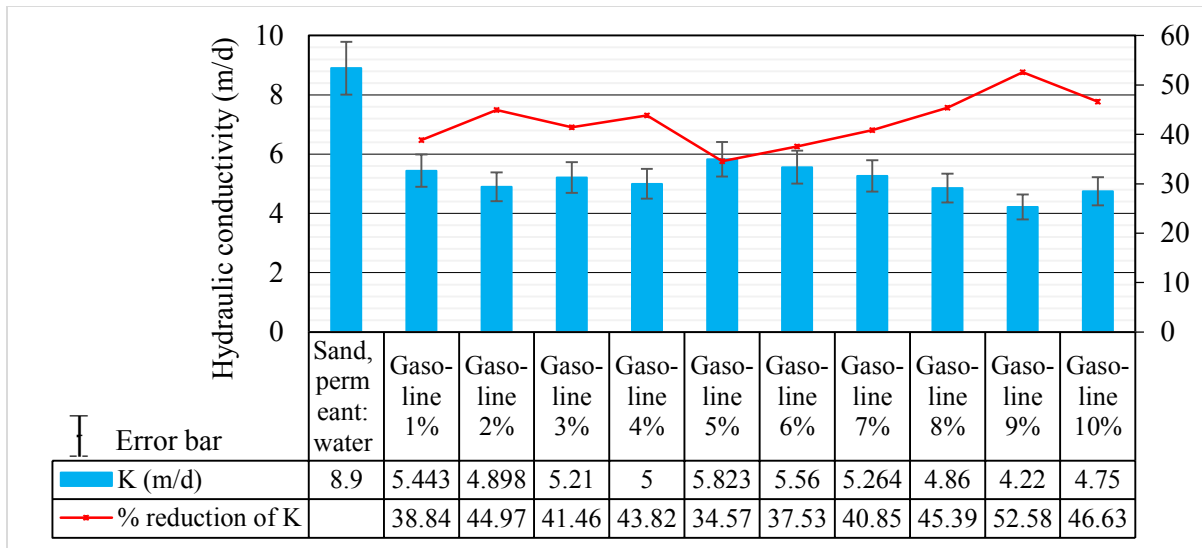


Figure 6.31. Hydraulic conductivity of aquifer sand samples, fully saturated with aqueous solution contaminated with varying concentration of gasoline for 8 weeks

Hydraulic Conductivity of Upper Layer Sand Samples Contaminated with TCE and Gasoline

Hydraulic conductivity was also measured for 18 upper layer sand samples that were contaminated with TCE and gasoline. Results of hydraulic conductivity and the compacted densities of the sand samples contaminated with TCE and gasoline are given in Appendix G.3 and G.4 and are shown in Figures 6.32 and 6.33 respectively.

Test results show that TCE causes reduction in hydraulic conductivity of the upper layer sand between 27.62% and 60.22 % (Appendix G.3), and gasoline causes a reduction between 12.71% and 48.62 % (Appendix G.4). Results show that the decrease in the hydraulic conductivity fluctuated during the first few weeks of contamination, but stabilized after 8 weeks.

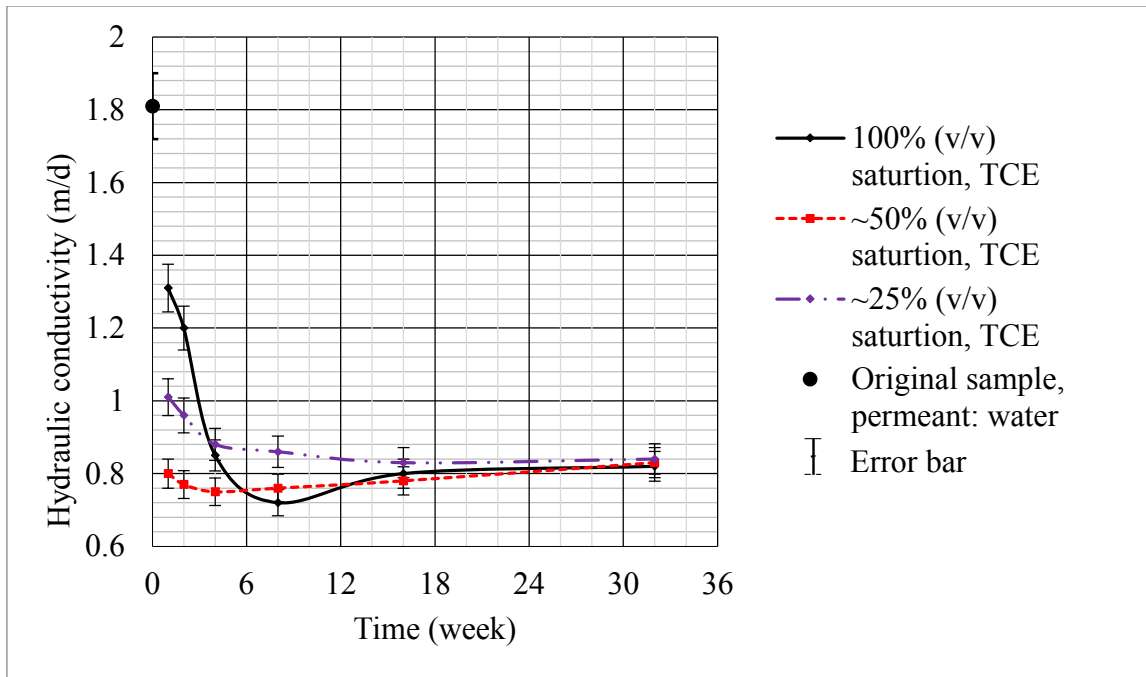


Figure 6.32. Hydraulic conductivity of upper layer sand samples contaminated with TCE, at about 100%, 50% and 25% saturation levels

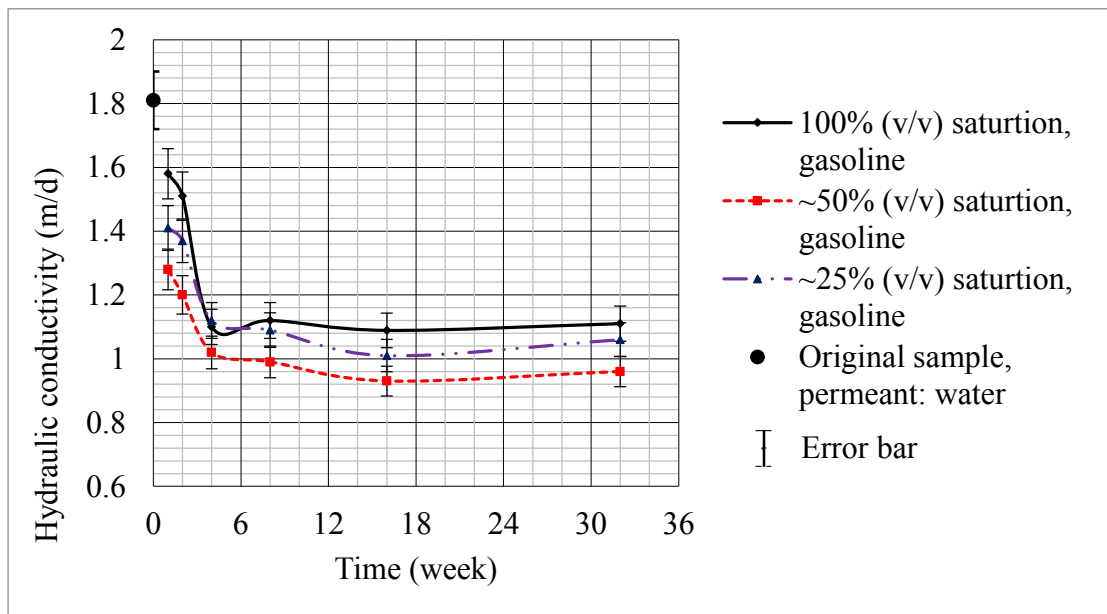


Figure 6.33. Hydraulic conductivity of upper layer sand samples contaminated with gasoline, at about 100%, 50% and 25% saturation levels

Hydraulic Conductivity of Aquifer Sand Samples Contaminated with BTEX and Isooctane

Five sand samples from aquifer layer were fully saturated for 8 weeks with individual BTEX chemicals— benzene, toluene, ethylbenzene, xylene— and isooctane to compare the results of hydraulic conductivity of them with that of aquifer sand that was contaminated with gasoline and TCE. Table 6.20 gives the results of compacted densities and hydraulic conductivity, and Figure 6.34 shows the change in hydraulic conductivity for various contaminants.

Results show a reduction in hydraulic conductivity of sand samples contaminated with BTEX and isooctane between 41.46% and 50.34% (Table 6.20). Chemical structure of the individual compound seems to influence the hydraulic conductivity, that decreases in the following order (Figure 6.34):

Aliphatic (isooctane) > aromatic (benzene and toluene) > chlorinated solvents (TCE)

The structure of aliphatic compounds could be acyclic or cyclic, whereas aromatic compounds have a cyclic structures— three carbon single and three alternating carbon double bonds— that make them more stable than normal cycloalkanes. Chlorinated solvents are mainly composed of a simple hydrocarbon chain; for instance, TCE has two carbon centers joined by a double bond, to which three chlorine atoms are covalently bonded. The hydraulic conductivity decreases in the following order with respect to polarity of chemicals:

TCE (lowest polarity) < aromatic (lower polarity) < aliphatic (nonpolar)

which is inconformity with the known polarity index— TCE 1; benzene 2.7; toluene 2.4; xylene 2.5 (Sadek, 2002).

Table 6.20. Compacted density and hydraulic conductivity of aquifer sand samples contaminated with BTEX and isooctane

Sample description	Dry density $\rho_d(\frac{g}{cm^3})$	Moist density $\rho_w(\frac{g}{cm^3})$	Hydraulic conductivity (m/day)	Percent decrease in hydraulic conductivity
Sand sample, permeant water	1.717	2.014	8.90	--
Sand saturated with benzene	1.669	1.908	5.21	41.46
Sand saturated with toluene	1.684	1.925	5.17	41.91
Sand saturated with ethyl benzene	1.693	1.936	4.95	44.38
Sand saturated with xylene	1.666	1.921	4.80	46.07
Sand saturated with isooctane	1.697	1.967	4.42	50.34

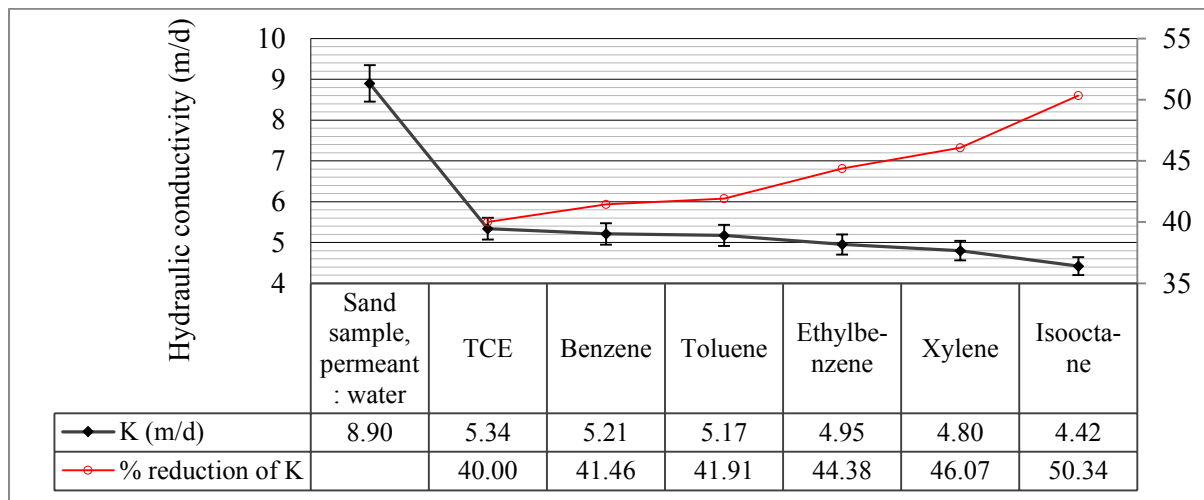


Figure 6.34. Reduction in hydraulic conductivity of aquifer sand sample, fully saturated with TCE, BTEX and isooctane, for 8 weeks

Hydraulic conductivity was also measured for three aquifer sand samples that were fully saturated for 8 weeks with TCE, gasoline, and isooctane without air drying to simulate water movement that would infiltrate into aquifer contaminated with these chemicals, and to

compare their impact on the hydraulic conductivity in contaminated sand after air drying (Table 6.21). Test results indicate that the rate of decrease of the hydraulic conductivity of sand fluctuated during the first few weeks, but generally stabilized after 8 weeks; therefore this duration was chosen for comparative tests. Based on the test results the following conclusions can be made:

- 1- Gasoline contributes to reduction in hydraulic conductivity more than the individual chemicals—BTEX and isooctane.
- 2- The aqueous solution contaminated with TCE contributed to reduction of hydraulic conductivity more than that contaminated with gasoline, at varying concentration levels.
- 3- Gasoline, TCE, and isooctane in fully-saturated aquifer sand, without air-drying, cause greater reduction in hydraulic conductivity than after air drying.

Table 6.21. Hydraulic conductivity of aquifer sand samples contaminated with gasoline, TCE, and isooctane at 100% saturation for 8 weeks (before and after air-drying)

Property	Sand sample and permeant			
	Water	Gasoline	TCE	Isooctane
Hydraulic conductivity (m/day) at 100% saturation	8.90	4.32	4.85	3.78
Percent decrease of hydraulic conductivity (m/day)		51.46	45.51	57.53
Hydraulic conductivity (m/day) after air-drying		4.75	5.34	4.42
Percent decrease of hydraulic conductivity (m/day)		46.63	40.00	50.34

Hydraulic Conductivity of Upper Layer Sand Samples Contaminated with BTEX and Isooctane

Five sand samples from upper layer were fully saturated for 8 weeks with individual BTEX chemicals— benzene, toluene, ethylbenzene, xylene— and isooctane to compare the results of hydraulic conductivity of them with that of upper layer sand that was contaminated with gasoline and TCE. Table 6.22 gives the results of compacted densities and hydraulic conductivity.

Results show a reduction in hydraulic conductivity of sand samples contaminated with BTEX and isooctane between 39.23% and 48.62% (Table 6.22). Gasoline contributes to reduction in hydraulic conductivity less than the individual chemicals—BTEX and isooctane, whereas, TCE causes greater reduction (Figure 6.35).

Table 6.22. Compacted density and hydraulic conductivity of upper layer sand samples contaminated with BTEX and isooctane

Sample description	Dry density $\rho_d(\frac{g}{cm^3})$	Moist density $\rho_w(\frac{g}{cm^3})$	Hydraulic conductivity (m/day)	Percent decrease in hydraulic conductivity
Sand sample, permeant water	1.537	1.92	1.81	--
Sand saturated with benzene	1.577	1.788	1.1	39.23
Sand saturated with toluene	1.555	1.877	1.06	41.44
Sand saturated with ethylbenzene	1.572	1.984	0.97	46.41
Sand saturated with xylene	1.61	1.949	0.96	46.96
Sand saturated with isooctane	1.595	1.991	0.93	48.62

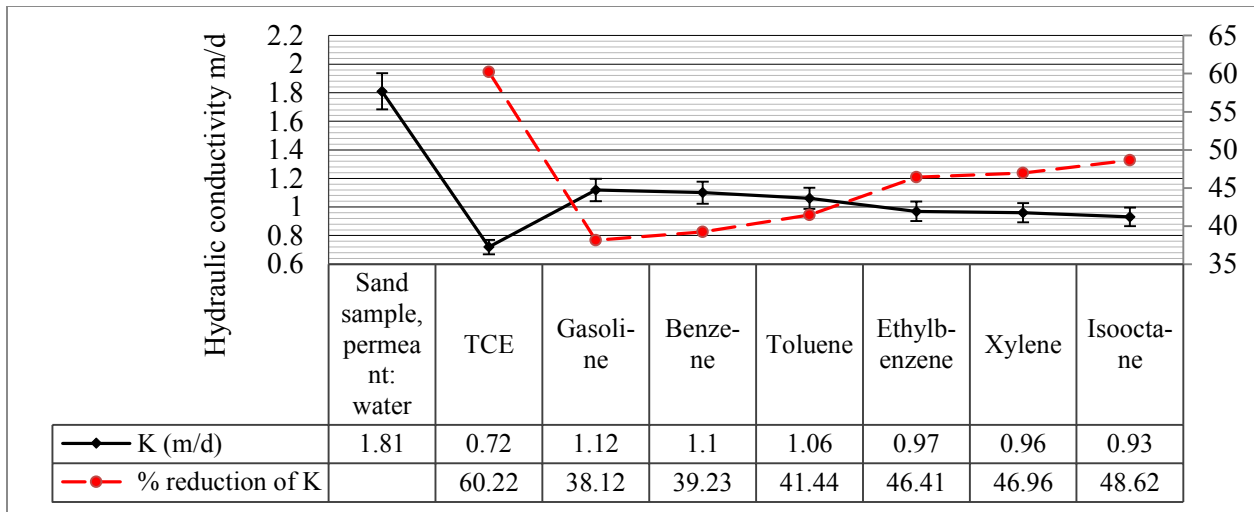


Figure 6.35. Reduction in hydraulic conductivity of upper layer sand sample, fully saturated with TCE, gasoline, BTEX, and isooctane, for 8 weeks

Mineralogy of Sand and Clay Samples Using X-Ray Diffraction

XRD was used to characterize mineralogy of aquifer and upper layer solids and to determine potential effect of contaminants on their mineral composition and how it might influence their hydraulic conductivities. The samples were scanned in the XRD device at 2θ per minute from 5° to 65° , and the JADE 8, X-ray diffraction software (Materials Data, Inc., Livermore, CA.) was utilized to identify the mineral distribution (JADE, 2010).

XRD Analysis of Aquifer Sand Samples Contaminated with Gasoline and TCE

XRD analysis was carried out on uncontaminated (original) aquifer sand sample. Results indicate that the sand is predominantly composed of quartz, albite, microcline and anorthoclase as it shown in Figure 6.36.

XRD analysis was also done on six aquifer sand samples that were fully saturated with gasoline for 1, 2, 4, 6, 8 and 16 weeks. The results are shown in Figure 6.36. In addition, XRD analysis was done for five aquifer sand samples that were partially saturated with gasoline, at about 50% and 25% saturation levels for 2, 4, 6, 8 and 16 weeks. Results indicate no change, as all of the contaminated sand was found to be predominantly composed of quartz, albite, microcline and anorthoclase as it shown in Figure 6.37 and 6.38 respectively.

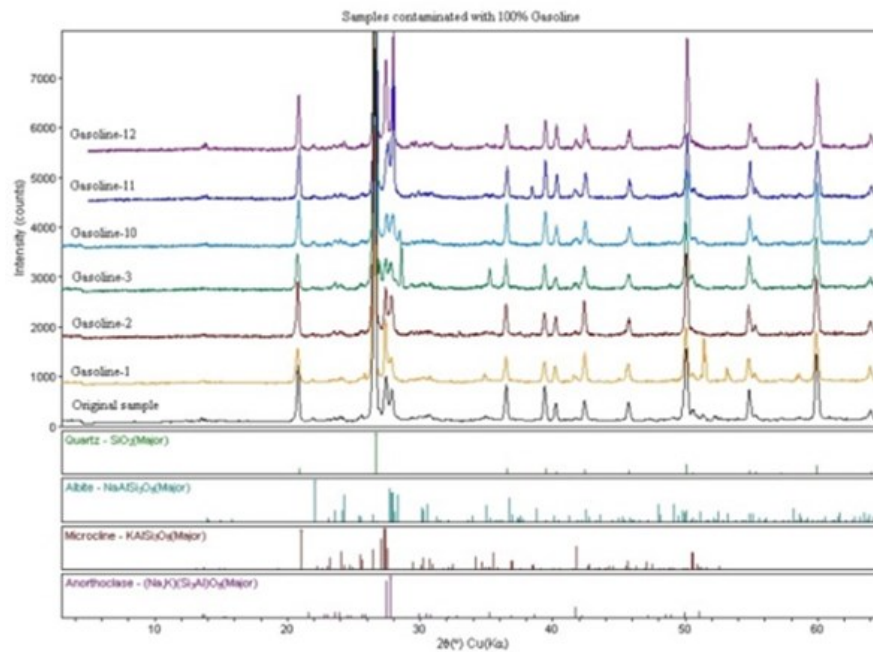


Figure 6.36. XRD result: mineralogy of aquifer sand samples contaminated with gasoline at about 100% saturation level for 1, 2, 4, 6, 8 and 16 weeks along with that of the uncontaminated (original) sample

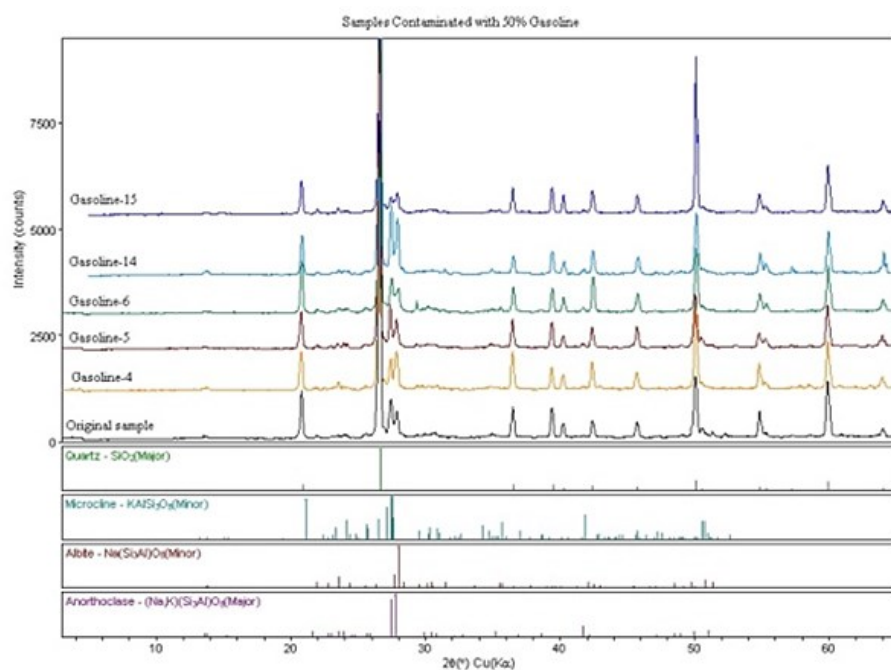


Figure 6.37. XRD result: mineralogy of aquifer sand samples contaminated with gasoline at about 50% saturation level for 2, 4, 6, 8 and 16 weeks

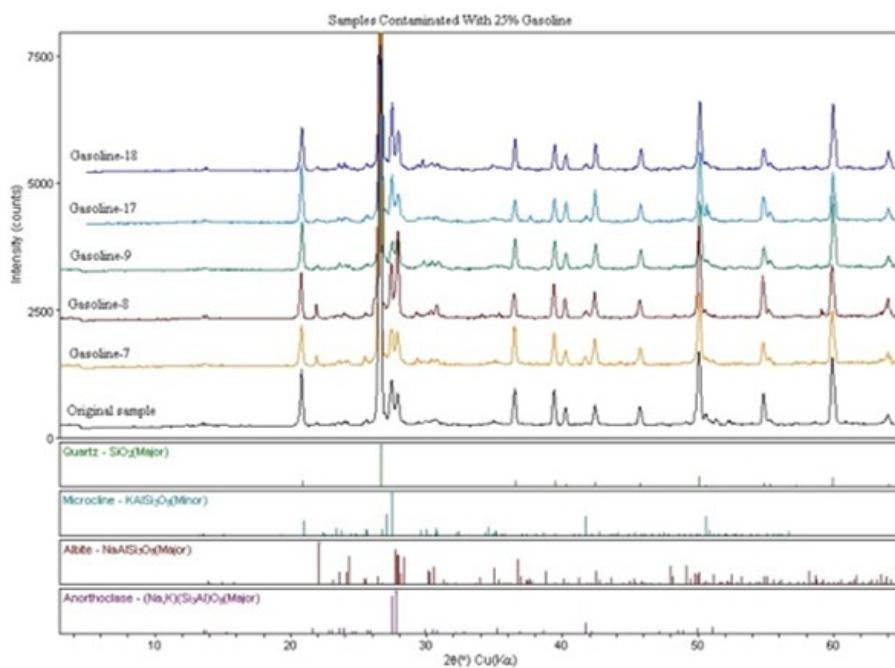


Figure 6.38. XRD result: mineralogy of aquifer sand samples contaminated with gasoline at about 25% saturation level for 2, 4, 6, 8 and 16 weeks

XRD analysis was also done on three aquifer sand samples that were fully saturated with TCE for 1, 2 and 4 weeks. The results are shown in Figure 6.39. In addition, XRD analysis was done for five aquifer sand samples that were partially saturated with TCE, at about 50% saturation level for 2, 4, 6, 8 and 16 weeks, and also for three sand samples that were contaminated at about 25% saturation level for 2, 4 and 6 weeks. Results indicate that the contaminated sand is predominantly composed of quartz, albite, microcline and anorthoclase as shown in Figure 6.40 and 6.41 respectively.

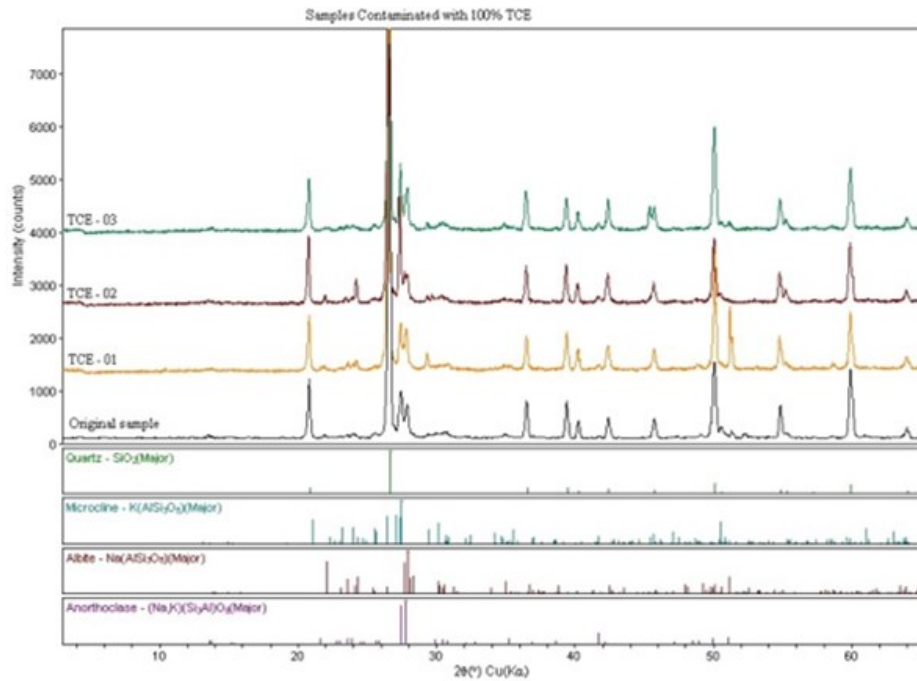


Figure 6.39. XRD result: mineralogy of aquifer sand samples contaminated with TCE at about 100% saturation level for 1, 2 and 4 weeks

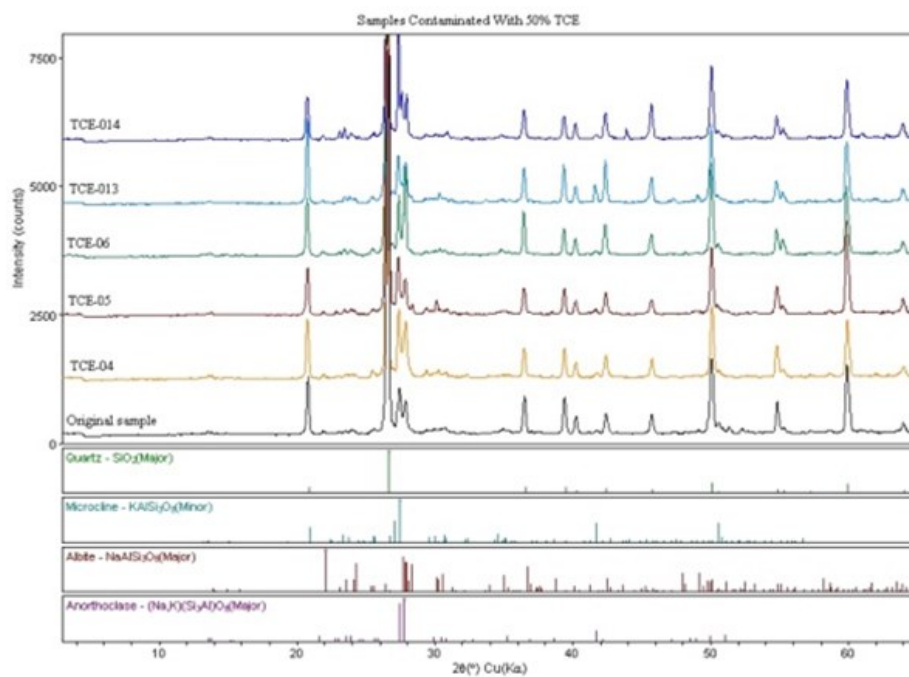


Figure 6.40. XRD result: mineralogy of aquifer sand samples contaminated with TCE at about 50% saturation level for 2, 4, 6, 8 and 16 weeks

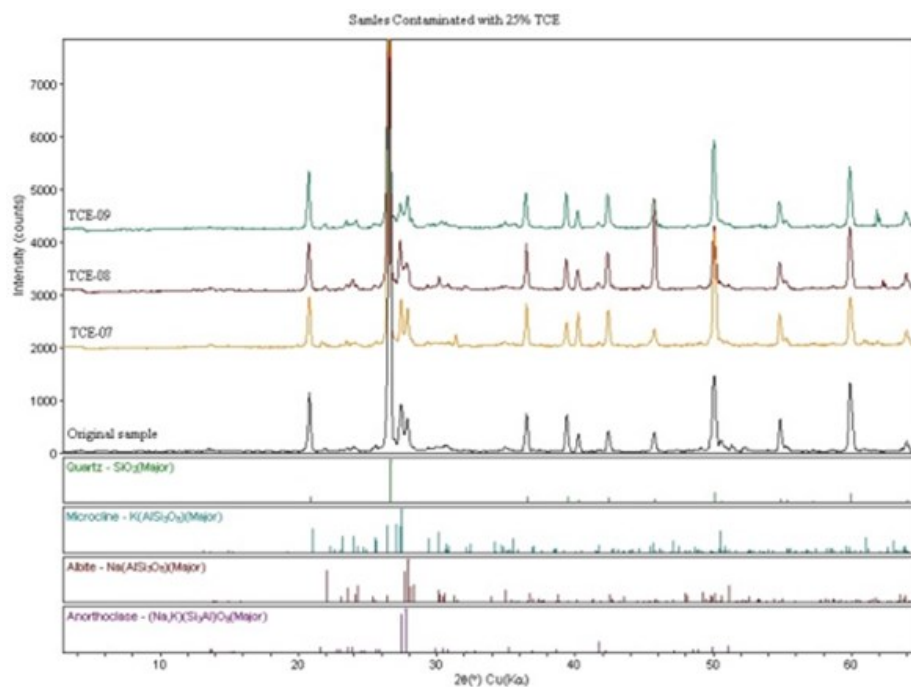


Figure 6.41. XRD result: mineralogy of aquifer sand samples contaminated with TCE, at about 25% saturation level for 2, 4 and 6 weeks

Finally, XRD analysis was also carried out on four aquifer sand samples which were fully saturated with benzene, toluene, ethyl benzene and isooctane for eight weeks. Results indicate that all contaminated sand is predominantly composed of quartz, albite, microcline and anorthoclase (Figure 6.42).

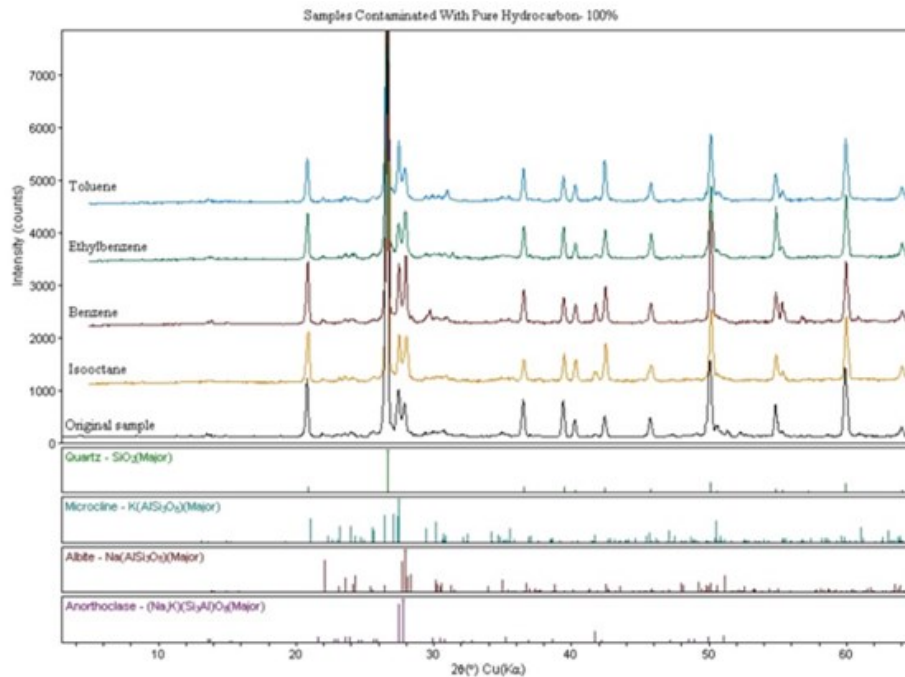


Figure 6.42. XRD result: mineralogy of aquifer sand samples contaminated with toluene, ethyl benzene, benzene and isooctane at 100% saturation level for 8 weeks

Results of XRD tests for all aquifer sand samples, contaminated with gasoline, TCE, toluene, ethylbenzene, benzene, and isooctane for varying duration of contamination, do not show any significant change in their mineralogy compared with the uncontaminated aquifer sand sample.

XRD Analysis of Upper Layer Sand Samples Contaminated with Gasoline and TCE

XRD analysis was carried out on uncontaminated sand samples from upper layer, and results indicate that the sample is predominantly composed of quartz (SiO_2), albite ($\text{NaAlSi}_3\text{O}_8$), dolomite ($\text{CaMg}(\text{CO}_3)_2$), and microcline (KAlSi_3O_8) as shown in Figure 6.43.

XRD analysis was also done for three upper layer sand samples that were contaminated with gasoline at 100% saturation level for 1, 2 and 4 weeks. The results are shown in Figure 6.43. In addition, XRD analysis was done for six upper layer sand samples that were partially saturated with gasoline, at about 50% and 25% saturation levels for 2, 4 and 8 weeks as it shown in Figures 6.44 and 6.45 respectively.

Results show no change in mineralogy as all contaminated samples were found to be predominantly composed of quartz, albite, dolomite and microcline.

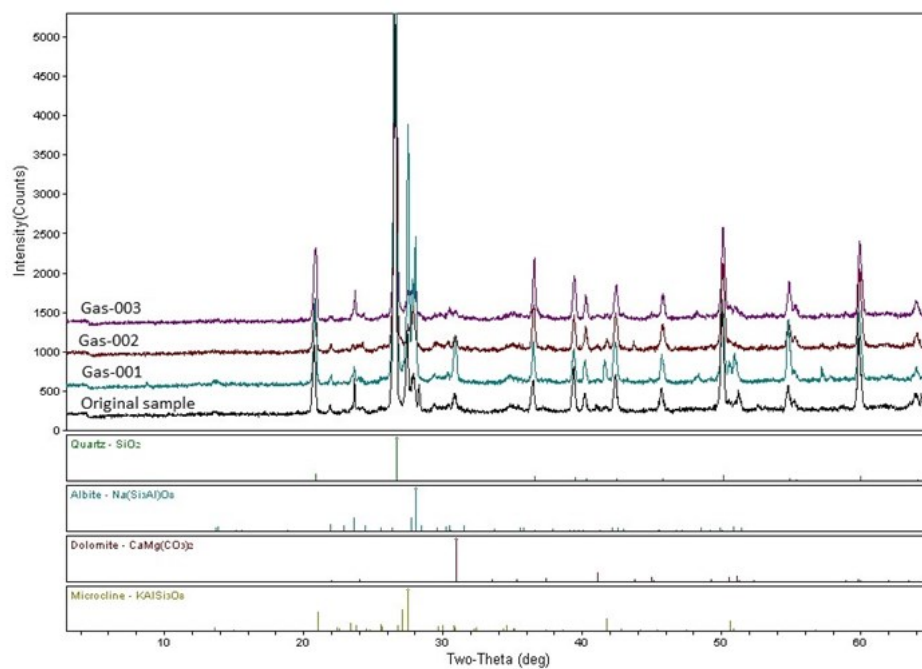


Figure 6.43. XRD result: mineralogy of upper layer sand samples contaminated with gasoline at about 100% saturation level for 1, 2 and 4 weeks

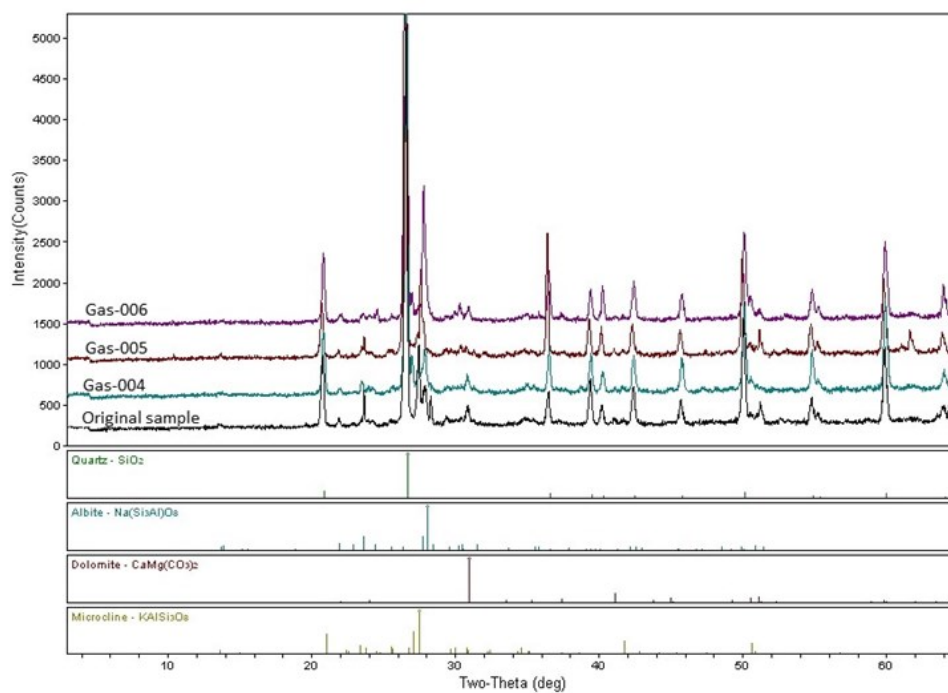


Figure 6.44. XRD result: mineralogy of upper layer sand samples contaminated with gasoline at about 50% saturation level for 2, 4 and 8 weeks

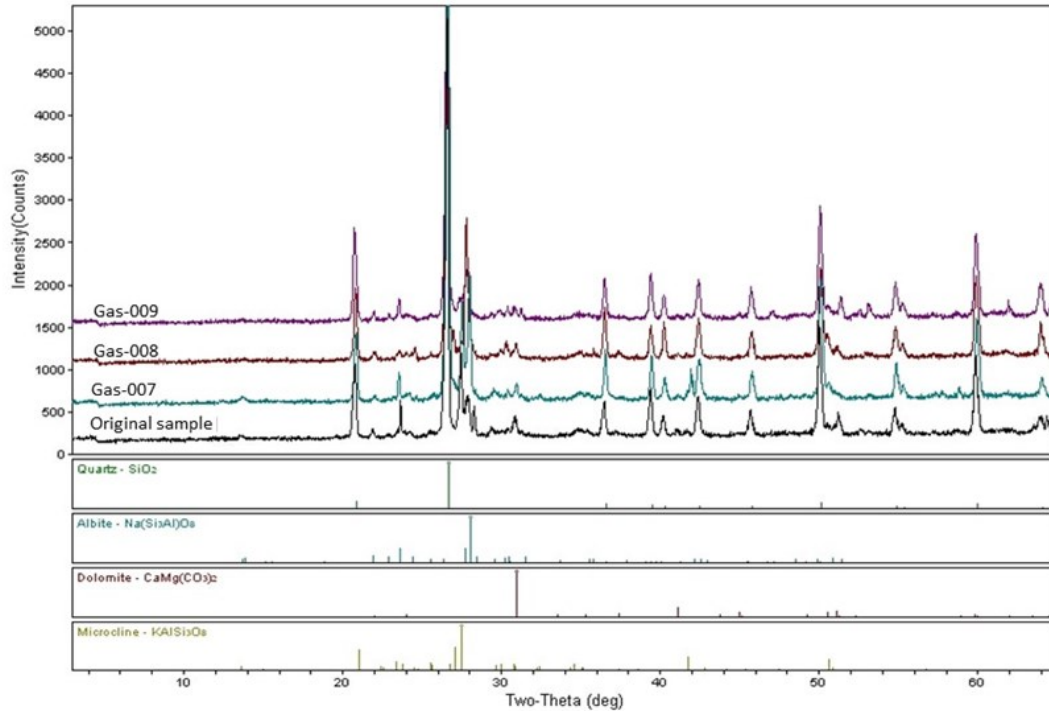


Figure 6.45. XRD result: mineralogy of upper layer sand samples contaminated with gasoline at about 25% saturation level for 2, 4 and 8 weeks

XRD analysis was also done on three upper layer sand samples that were fully saturated with TCE for 1, 2 and 4 weeks and results are shown in Figure 6.46. In addition, XRD analysis was done for six sand samples that were partially saturated with TCE, at about 50% and 25% saturation levels for 2, 4 and 8 weeks. Results are shown in Figures 6.47 and 6.48 respectively. All sand samples are predominantly composed of quartz, albite, dolomite, and microcline.

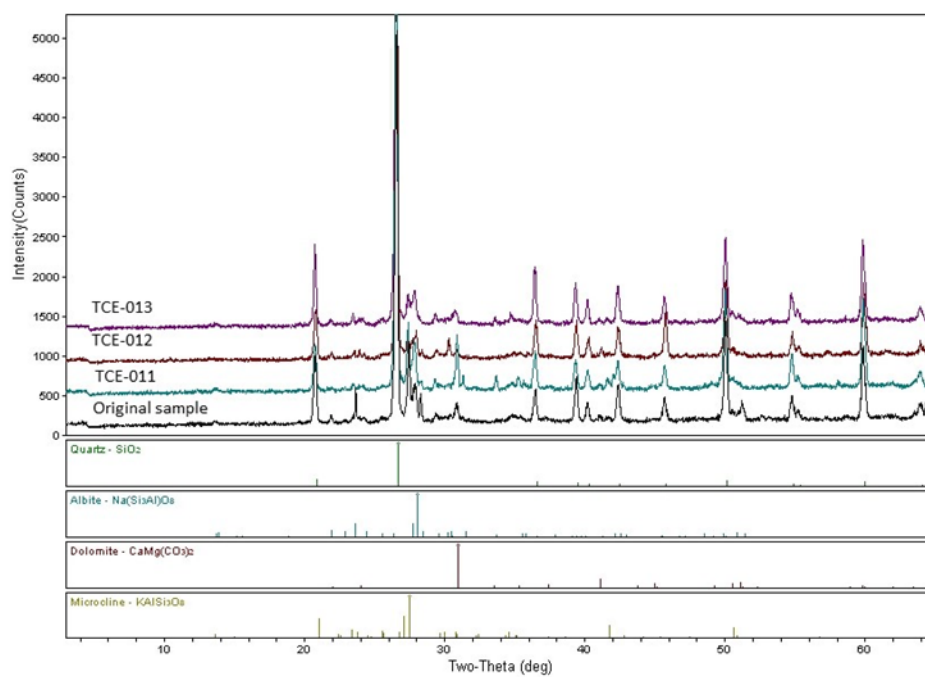


Figure 6.46. XRD result: mineralogy of upper layer sand samples contaminated with TCE at about 100% saturation level for 1, 2 and 4 weeks

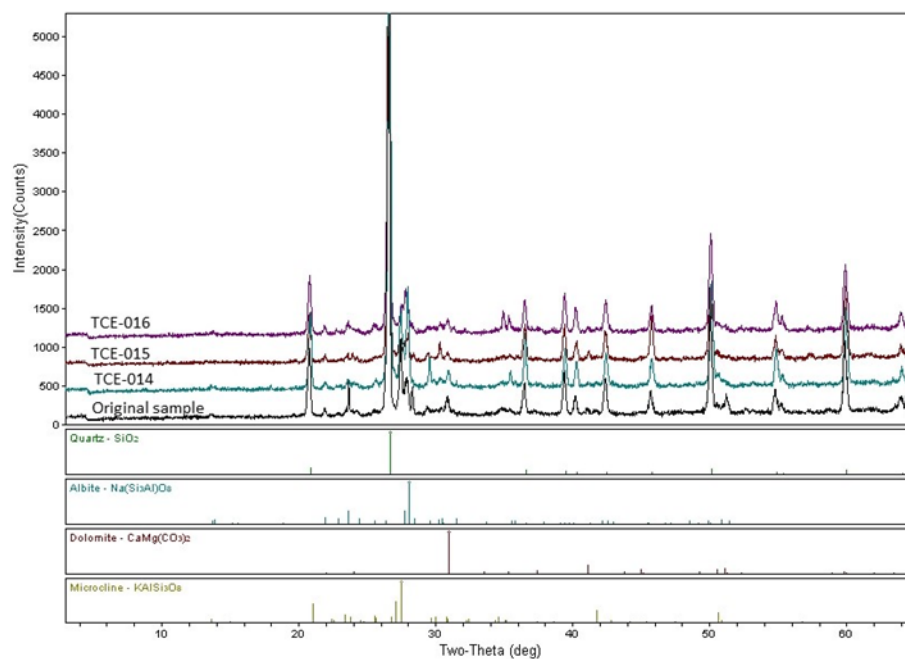


Figure 6.47. XRD result: mineralogy of upper layer sand samples contaminated with TCE at about 50% saturation level for 2, 4 and 8 weeks

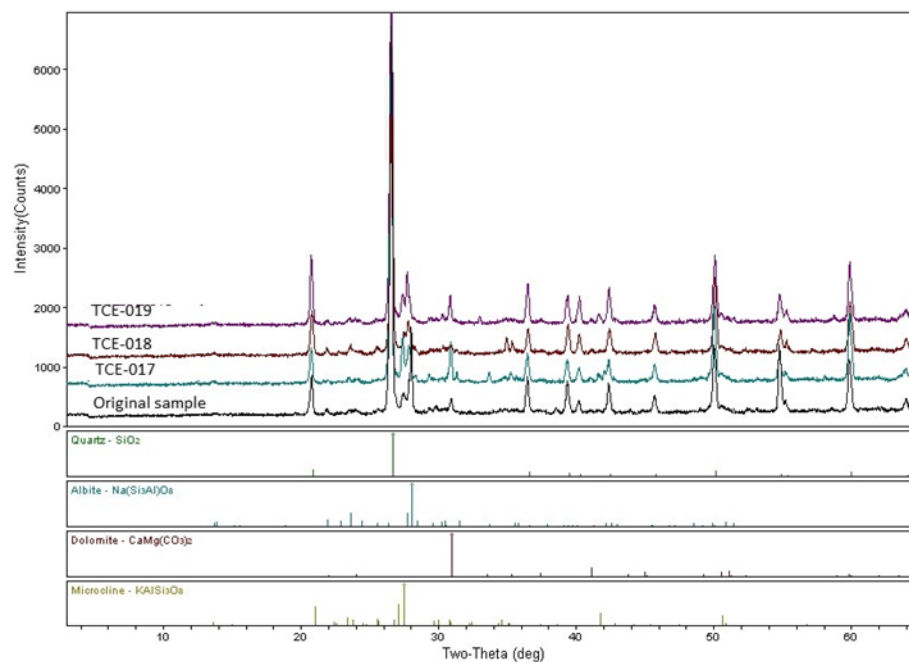


Figure 6.48. XRD result: mineralogy of upper layer sand samples contaminated with TCE at about 25% saturation level for 2, 4 and 8 weeks

Results of XRD tests for all upper layer sand samples that were contaminated with gasoline and TCE for various duration of contamination do not show any change in their mineralogy as compared to the uncontaminated sand sample.

Mineral Composition of Clays Using XRD

XRD analysis was done for uncontaminated and contaminated clay samples that were separated from the upper layer sand samples: About 0.10 g of the fine material from each sample was separated, using the USGS procedure (Poppe *et al.*, 2001). The purpose was to identify the mineralogy of clays, their relative percentages, and any change that might have resulted due to contamination. XRD was carried out on three samples contaminated with gasoline, as well as on three samples that were contaminated with TCE.

XRD analysis for uncontaminated clay sample shows that it is mainly composed of quartz and clay minerals: kaolinite, montmorillonite, and illite (Figure 6.49).

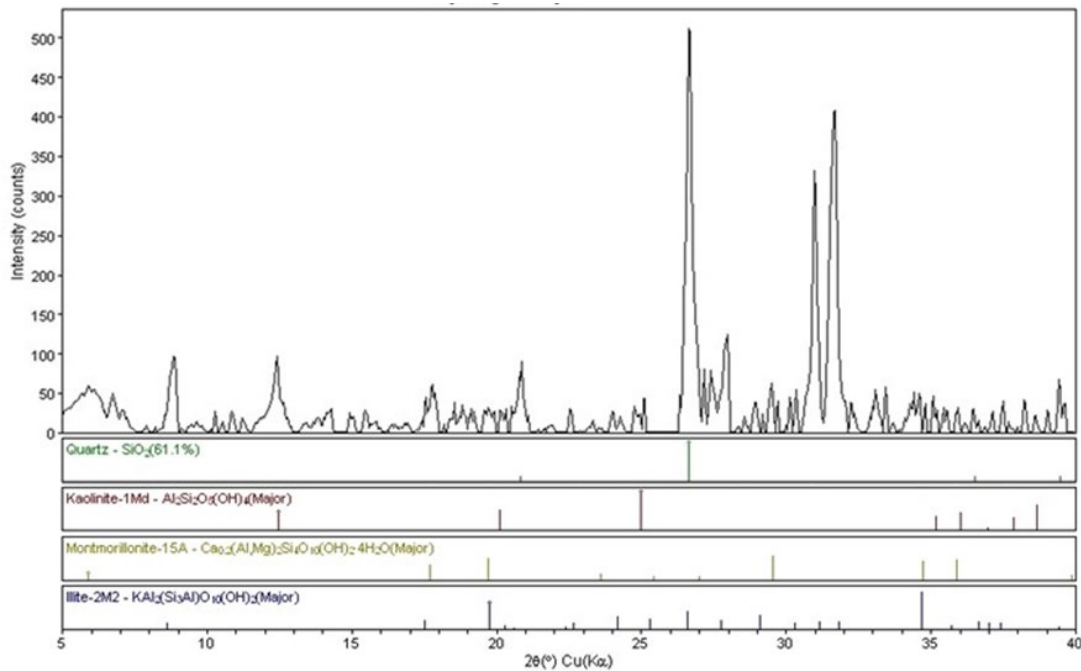


Figure 6.49. XRD result: clay minerals in uncontaminated upper layer sand sample

XRD Test Results of Clay Separates in Upper Layer Sand Samples Saturated with Gasoline

XRD analysis was done on three clay samples from the upper layer sand that were contaminated with gasoline for four weeks at different levels of saturation (v/v). The results are discussed below:

XRD analysis of the uncontaminated clay sample shows that it is composed of quartz, kaolinite, montmorillonite and illite, but clay sample contaminated with gasoline (Gas-003) at 100% saturation level showed the presence of anorthite (Figure 6.50).

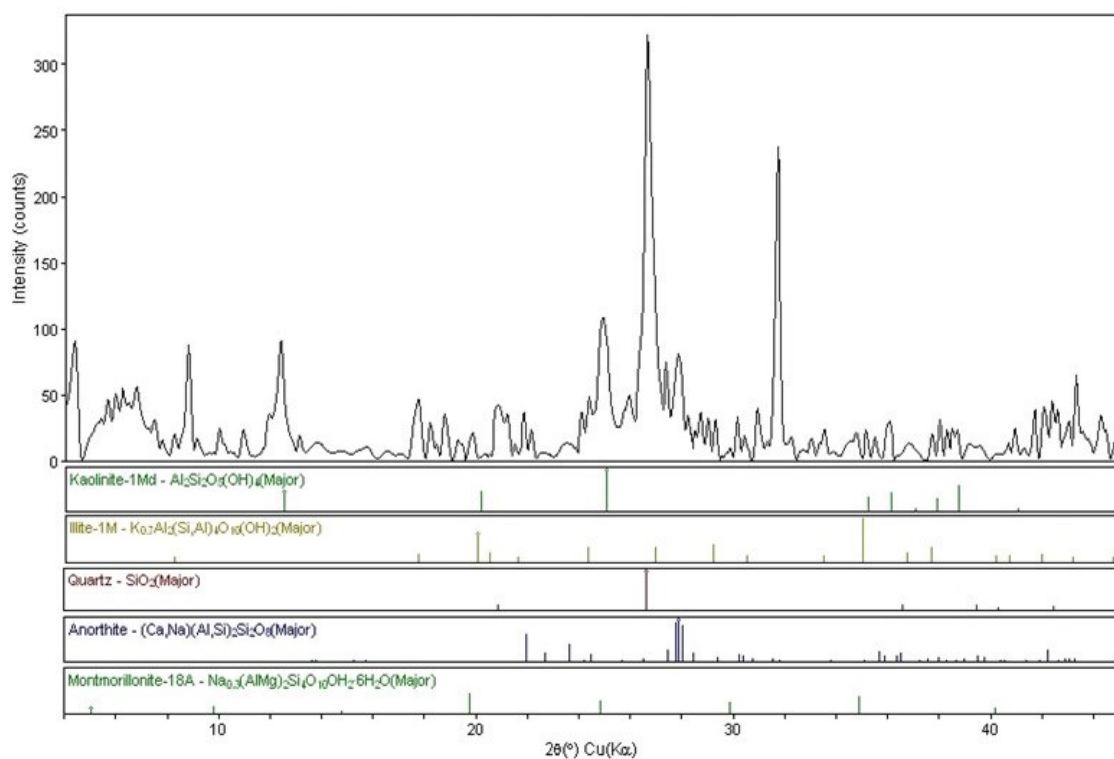


Figure 6.50. XRD result: clay minerals in sand sample Gas-003, contaminated with gasoline at about 100% saturation level for 4 weeks

A second XRD analysis was done on clay sample contaminated with gasoline (Gas-005) at about 50% saturation level for 4 weeks. Results indicate that the sample is predominantly composed of quartz, anorthite, kaolinite, and illite, but montmorillonite is missing (Figure 6.51).

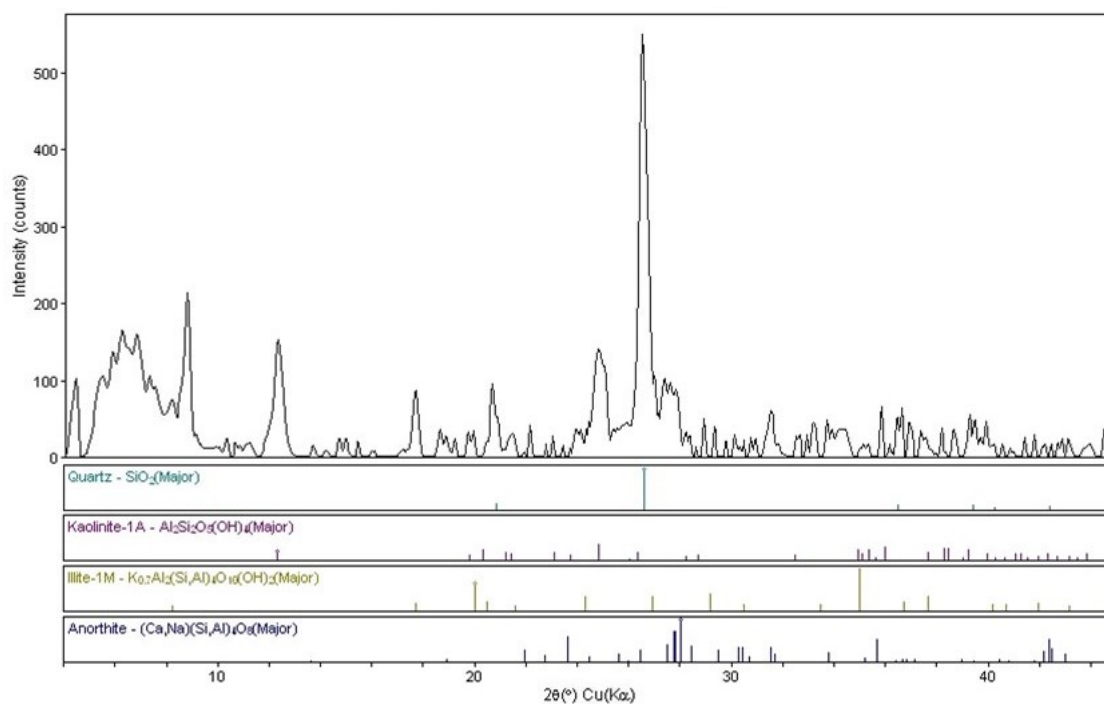


Figure 6.51. XRD result: clay minerals in sand sample Gas-005, contaminated with gasoline at about 50% saturation level for 4 weeks

A third XRD analysis was also carried out on the clay sample, saturated with gasoline (Gas-008) at about 25% saturation level for four weeks which showed that it is composed of quartz, anorthite, microcline and clay mineral kaolinite and illite (Figure 6.52).

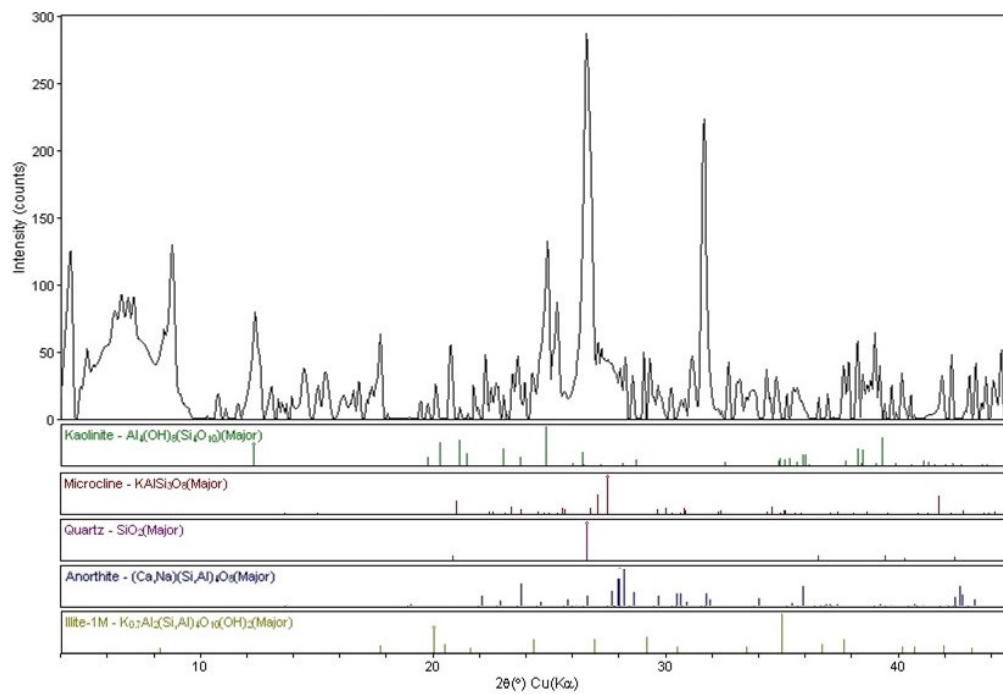


Figure 6.52. XRD result: clay minerals in sand sample Gas-008, contaminated with gasoline at about 25% saturation level for 4 weeks

XRD Test Results of Clay Separates in Upper Layer Sand Samples Saturated with TCE

XRD analysis was done on three clay samples from the upper layer sand, contaminated with TCE for 4 weeks at different levels of saturation (v/v). The results are discussed below:

XRD analysis on clay sample, contaminated with TCE (TCE-013) at 100% saturation level, indicate that the sample is predominantly composed of quartz, anorthite, kaolinite, and illite (Figure 6.53).

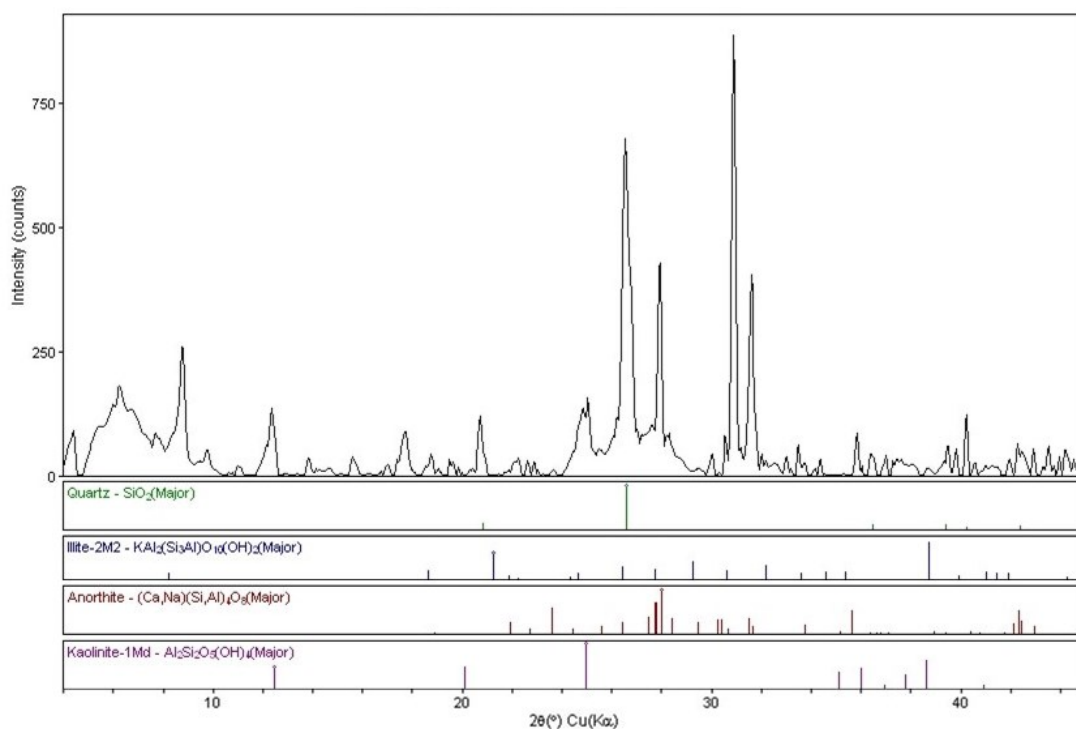


Figure 6.53. XRD result: clay minerals in sand sample TCE-013 at about 100% saturation level with TCE for 4 weeks

A second XRD analysis was done on clay sample that was contaminated with TCE (TCE-015) at about 50% saturation level for four weeks. Results indicate that the sample is mainly composed of quartz, anorthite, kaolinite, illite, and montmorillonite (Figure 6.54).

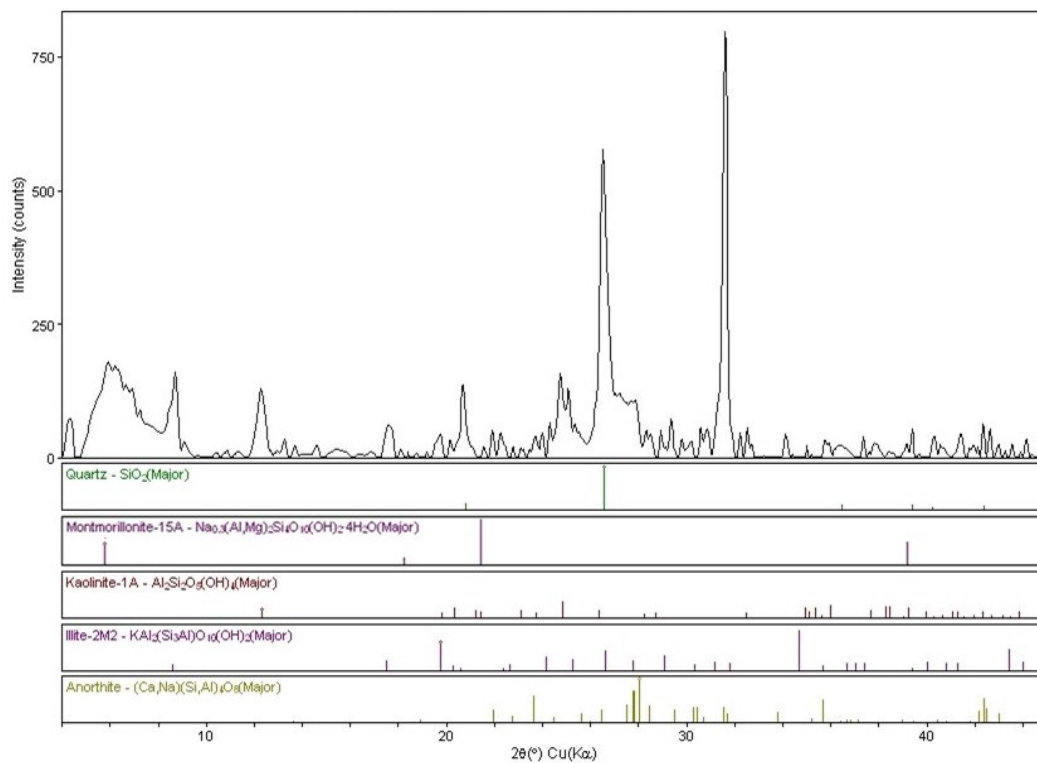


Figure 6.54. XRD result: clay minerals in sand sample TCE-015 at about 50% saturation level with TCE for 4 weeks

A third XRD analysis, carried out on the clay sample, saturated with TCE (TCE-018) at about 25% saturation level for four weeks, showed that it is composed of quartz, anorthite, kaolinite, and illite (Figure 6.55). Results of all XRD analysis are summarized in Table 6.23.

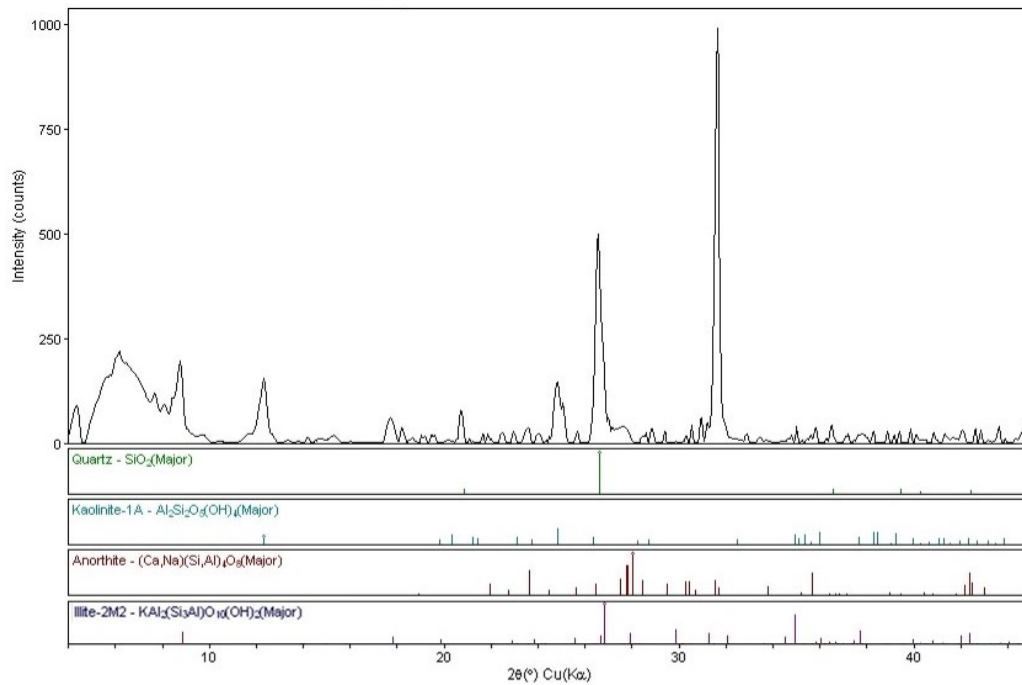


Figure 6.55. XRD result: clay minerals in sand sample TCE-018 at about 25% saturation level with TCE for 4 weeks

Table 6.23. Summary of XRD analysis of clay samples mineralogy

Uncontaminated clay sample	Sample description					
	Clay contaminated with gasoline, saturation level			Clay contaminated with TCE, saturation level		
	100%	50%	25%	100%	50%	25%
Quartz	Quartz	Quartz	Quartz	Quartz	Quartz	Quartz
Kaolinite	Kaolinite	Kaolinite	Kaolinite	Kaolinite	Kaolinite	Kaolinite
Illite	Illite	Illite	Illite	Illite	Illite	Illite
Montmorillonite	Montmorillonite	*	*	*	Montmorillonite	*
*	Anorthite	Anorthite	Anorthite	Anorthite	Anorthite	Anorthite
*	*	*	Microcline	*	*	*
* Not detected						

Mineralogy and Topography of Aquifer Sand Grains, Using Scanning Electron Microscope

Scanning electron microscope (SEM) was used in this study to determine the shape and mineralogy of uncontaminated sand sample; and of selected sand samples from aquifer and upper layer; and on clay samples after 32 weeks of contamination with selected chemicals.

Mineral Composition using Backscattered Electron Method

Backscattered electron (BSE) method was used in this study to determine mineral composition of sand samples. Images provided via SEM- BSE display compositional contrast that results from different atomic number elements in samples and their distribution; an energy dispersive spectroscopy (EDS) was used to identify what those particular elements are and their relative proportions. According to Goldstein *et al.*, (2003); BSE is a primary beam electron that may be scattered in such a way that it escapes back from the sample surface and does not go through it. BSE has a high energy level, near that of the gun voltage, because it is the original beam electrons. Images with BSE contain compositional information because heavier atoms with high atomic number scatter more strongly than lighter atoms.

A magnification (MAG) of 1987 with high voltage (HV) of 20:00 kV, and working distance of 14.1 mm were used in BSE and an EDS was used for analysis. Results are illustrated in the x-y image, where the y-axis shows the counts, number of X-rays received and processed by the detector, and the x-axis shows the energy level (keV) of those counts.

BSE images and EDS were used to analyze and identify the elemental content in the non-contaminated aquifer sand sample at two specific points. Results show that Point 1 is

composed of quartz and potassium–feldspar (KAlSi_3O_8), and Point 2 composed of quartz and potassium–sodium feldspar ($\text{KNaAlSi}_3\text{O}_8$) (Figure 6.56). Table 6.24 shows the details of the elemental content for point 1 and 2.

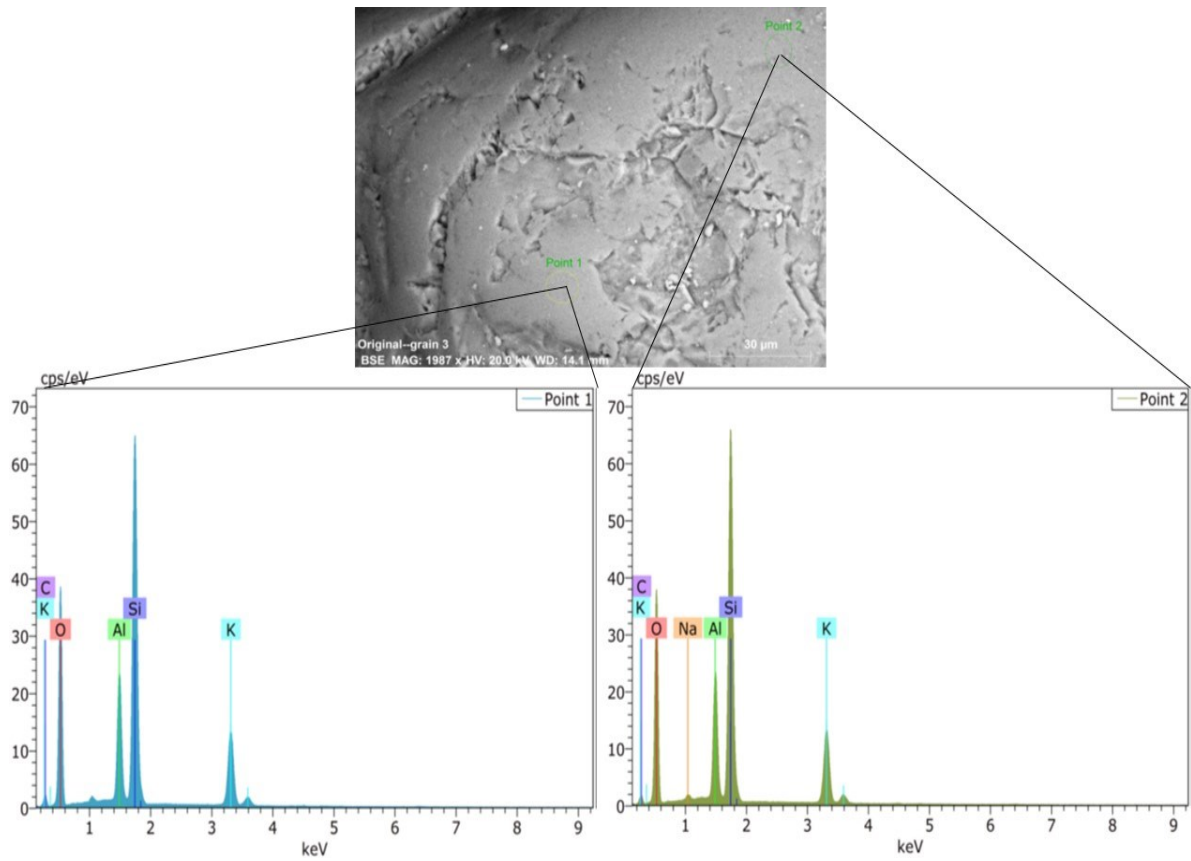


Figure 6.56. K-Na feldspar in a grain of uncontaminated aquifer sand sample

Table 6.24. Elements detected at point 1 on an uncontaminated grain from aquifer sand sample

Elements	Atomic number	Series	unn. C (wt.%)	Norm. C (wt.%)	Atom. C (at.%)	(1 sigma) (wt.%)
Elements detected at point 1						
C	6	K-series	5.56	6.31	10.10	0.88
O	8		47.15	53.48	64.28	5.23
Al	13		6.53	7.40	5.28	0.34
Si	14		19.25	21.83	14.95	0.85
K	19		9.68	10.97	5.40	0.32
	Total		88.17	100.00	100.00	
Elements detected at point 2						
C	6	K-series	4.59	4.43	7.21	0.78
O	8		54.81	52.90	64.55	6.08
Na	11		1.01	0.97	0.83	0.09
Al	13		9.49	9.16	6.63	0.48
Si	14		24.04	23.20	16.13	1.05
K	19		9.67	9.33	4.66	0.32
	Total		103.62	100.00	100.00	

BSE-EDS was also used to analyze the elemental content of aquifer sand sample that were contaminated with gasoline for 32 weeks. SEM results show that it is composed of quartz and feldspars and most grains were found to include small grains that filled tiny grooves on its surface. Three points were selected from this sample for detailed analysis as shown in Figure 6.57. Point 1, which is the whole grain, is mainly composed of quartz (Table 6.25). Point 2 analysis shows that it is composed of quartz, dolomite $\text{CaMg}(\text{CO}_3)_2$ and Ca-feldspar; its element composition is shown in Table 6.25. Point 3 analysis shows that it contains K-Na feldspar, Ca-feldspar and iron; Table 6.25 shows details of its element composition.

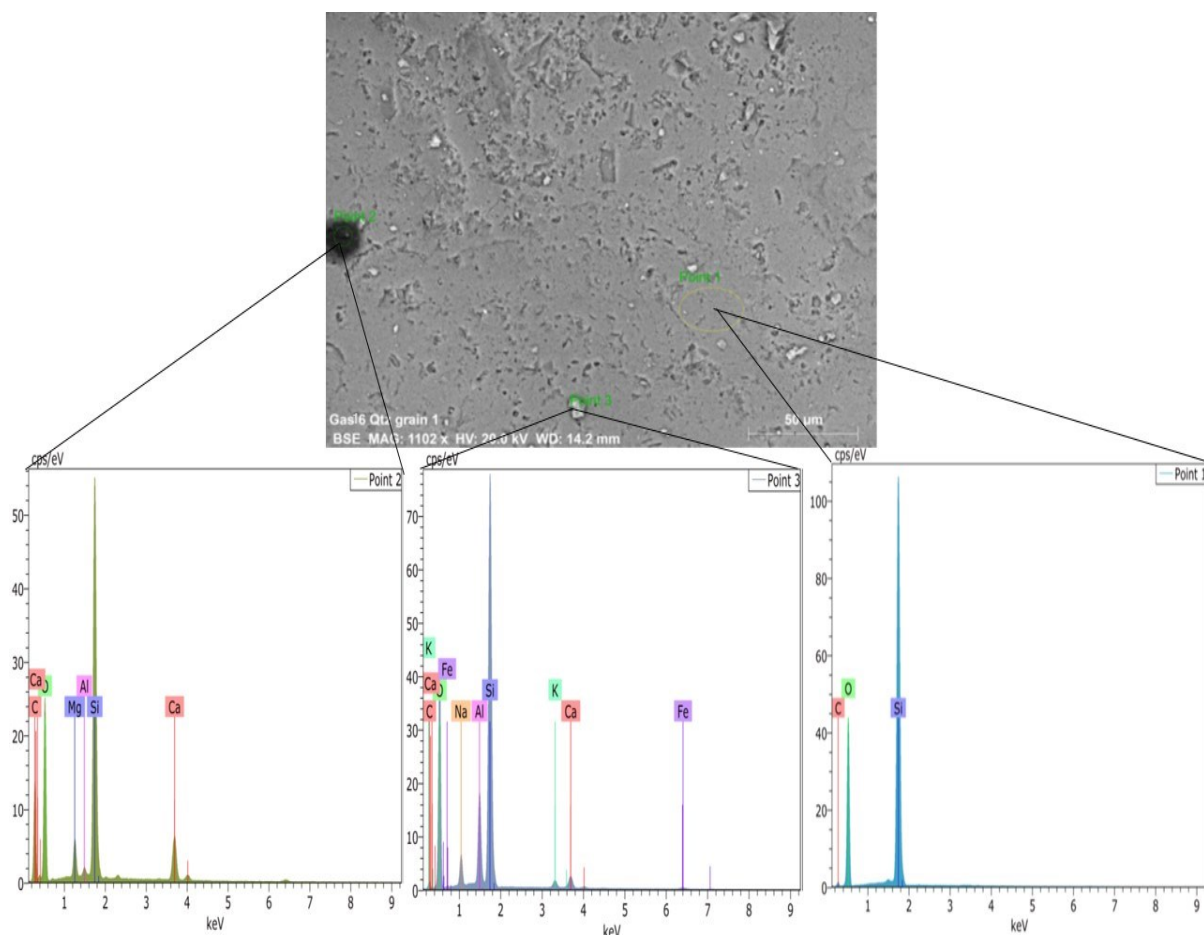


Figure 6.57. Geochemistry of quartz grain in aquifer sand sample, fully saturated with gasoline for 32 weeks

Table 6.25. Elements detected at points 1, 2 and 3 on grain from aquifer sand sample, fully saturated with gasoline after 32 weeks

Elements	Atomic number	Series	unn. C (wt.%)	Norm. C (wt.%)	Atom. C (at.%)	(1 sigma)
Elements detected at point 1						
C	6	K-series	5.38	6.27	9.79	0.89
O	8		46.93	54.71	64.15	5.18
Si	14		33.47	39.02	26.06	1.45
	Total		85.78	100.00	100.00	
Elements detected at point 2						
C	6	K-series	4.59	4.43	7.21	0.78
O	8		54.81	52.90	64.55	6.08
Na	11		1.01	0.97	0.83	0.09
Al	13		9.49	9.16	6.63	0.48
Si	14		24.04	23.20	16.13	1.05
K	19		9.67	9.33	4.66	0.32
	Total		103.62	100.00	100.0	
Elements detected at point 3						
C	6	K-series	3.62	4.29	6.93	0.64
O	8		44.23	52.46	63.58	4.89
Na	11		2.74	3.25	2.74	0.20
Al	13		5.34	6.34	4.55	0.28
Si	14		24.45	29.00	20.02	1.07
K	19		1.13	1.34	0.66	0.06
Ca	20		2.20	2.61	1.26	0.09
Fe	26		0.59	0.70	0.24	0.05
	Total		84.31	100.00	100.00	

Additionally, another analysis was done on a feldspar grain from the aquifer sand sample, Gas-16, that was contaminated with gasoline at about 100% saturation level for 32 weeks (Figure 6.58); results shows that it contains quartz and K–Na feldspar (Table 6.26).

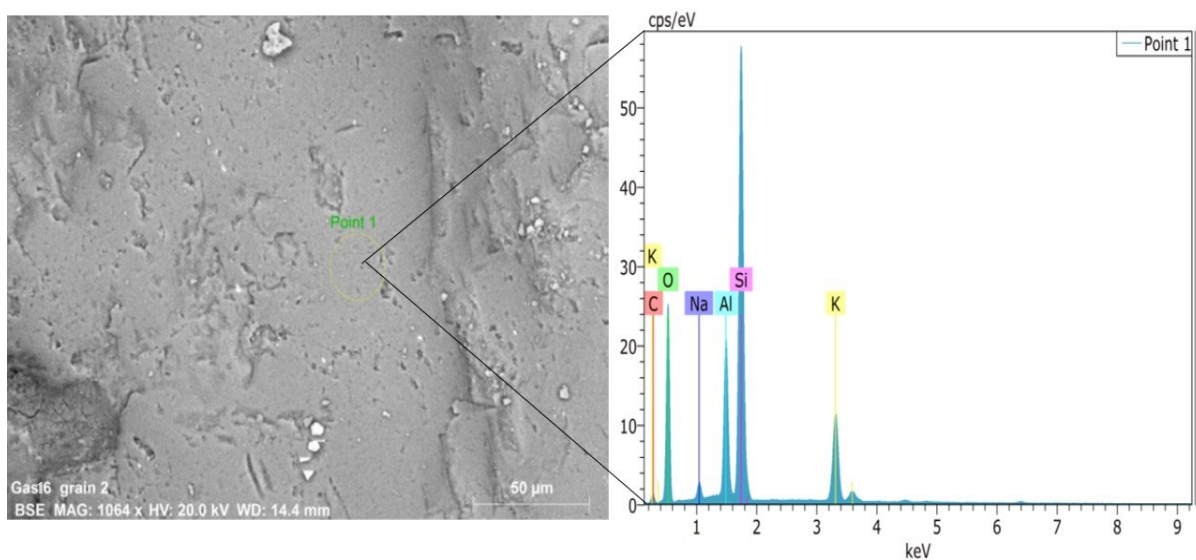


Figure 6.58. Feldspar grain in aquifer sand sample after 32 weeks of contamination with gasoline at about 100% saturation level

Table 6.26. Elements detected at point 1 in feldspar grain 2 in the aquifer sand sample after 32 weeks of contamination with gasoline at 100% saturation level

Elements	Atomic number	Series	unn. C (wt. %)	Norm. C (wt. %)	Atom. C (at. %)	(1 sigma) (wt. %)
C	6	K-series	4.36	5.28	8.76	0.76
O	8		39.38	47.71	59.46	4.47
Na	11		1.15	1.39	1.21	0.10
Al	13		7.30	8.84	6.53	0.37
Si	14		21.83	26.45	18.77	0.96
K	19		8.53	10.33	5.27	0.29
Total			82.54	100.00		

SEM as BSE-EDS analysis of aquifer sand sample, which had already been fully saturated with TCE for 32 weeks, shows several secondary crystals on its surface and between the grooves (Figure 6.59). Four points were chosen for SEM analysis for identifying

the elements. Points 5, 6 and 8 consist of quartz, gypsum and barite, with iron in points 6 and 8. Point 7 from the whole specimen is quartz (Figure 6.59). Results are given in Table 6.27 for Points 5, 6, 7 and 8.

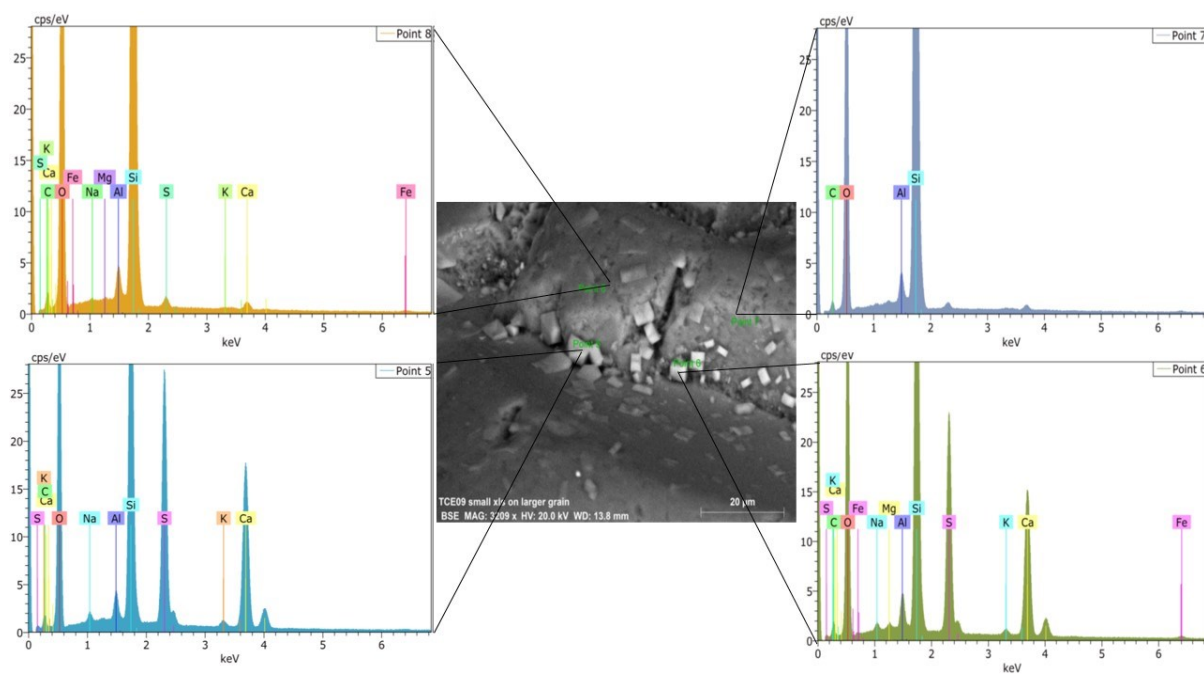


Figure 6.59. Geochemistry of aquifer sand sample fully saturated with TCE for 32 weeks

Table 6.27. Elements detected at points 5, 6, 7 and 8 from aquifer sand sample, fully saturated with TCE after 32 weeks

Elements	Atomic number	Series	unn. C (wt.%)	Norm. C (wt.%)	Atom. C (at.%)	(1 sigma)
Elements detected at point 5						
C	6	K-series	2.54	2.41	3.97	0.49
O	8		61.25	57.99	71.83	6.77
Na	11		0.91	0.86	0.74	0.09
Al	13		1.14	1.08	0.79	0.08
Si	14		13.56	12.84	9.06	0.60
S	16		11.39	10.79	6.67	0.43
Ca	20		14.83	10.04	6.94	0.46
	Total		105.62	100.00	100.00	
Elements detected at point 6						
C	6	K-series	3.22	3.16	5.19	0.59
O	8		58.02	57.02	70.25	6.43
Na	11		0.71	0.70	0.60	0.07
Al	13		1.33	1.31	0.95	0.09
Si	14		15.60	15.33	10.76	0.69
S	16		9.80	9.63	5.92	0.38
Ca	20		13.08	12.85	6.32	0.41
	Total		101.76	100.00	100.00	
Elements detected at point 7						
C	6	K-series	5.87	5.80	9.07	0.98
O	8		55.80	55.09	64.72	6.15
Al	13		1.55	1.55	1.08	0.10
Si	14		38.03	37.56	25.13	1.64
	Total		101.27	100.00	100.00	
Elements detected at point 8						
C	6	K-series	6.04	6.08	9.24	0.93
O	8		60.06	60.44	68.44	6.50
Na	11		0.56	0.57	0.57	0.06
Al	13		1.31	1.31	1.31	0.09
Si	14		30.84	31.03	31.03	1.34
Ca	20		0.58	0.58	0.26	0.04
	Total		99.38	100.00	100.00	

One uncontaminated sand sample from upper layer was selected to identify the chemical composition of grains using SEM-EDS. In addition, three clay samples were selected to analyze their mineral content, which were exposed to gasoline and TCE for varying periods of time. Magnification at 303, with high voltage (HV) of 20:00 kilovolts (kV), and working distance of 15.1 mm was used in BSE analysis. EDS was used for chemical composition analysis.

Figure 6.60 shows that uncontaminated sand sample is mostly composed of silicon (Si), sodium (Na), magnesium (Mg), aluminum (Al), potassium (K), calcium (Ca), iron (Fe) and zirconium (Zr), which are the main chemical elements of feldspar and quartz. Those elements are possibly from: quartz SiO_2 , feldspars, and clay minerals; kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, montmorillonite $(\text{Na,Ca})_{0.3} \cdot 3(\text{Al,Mg})_2 \text{Si}_4\text{O}_{10} (\text{OH})_2 \cdot n(\text{H}_2\text{O})$ and illite $(\text{K,H}_3\text{O})(\text{Al,Mg,Fe})_2(\text{Si,Al})_4\text{O}_{10} [(\text{OH})_2, (\text{H}_2\text{O})]$. Figure 6.60 also shows irregular shape and varying size of sand granules.

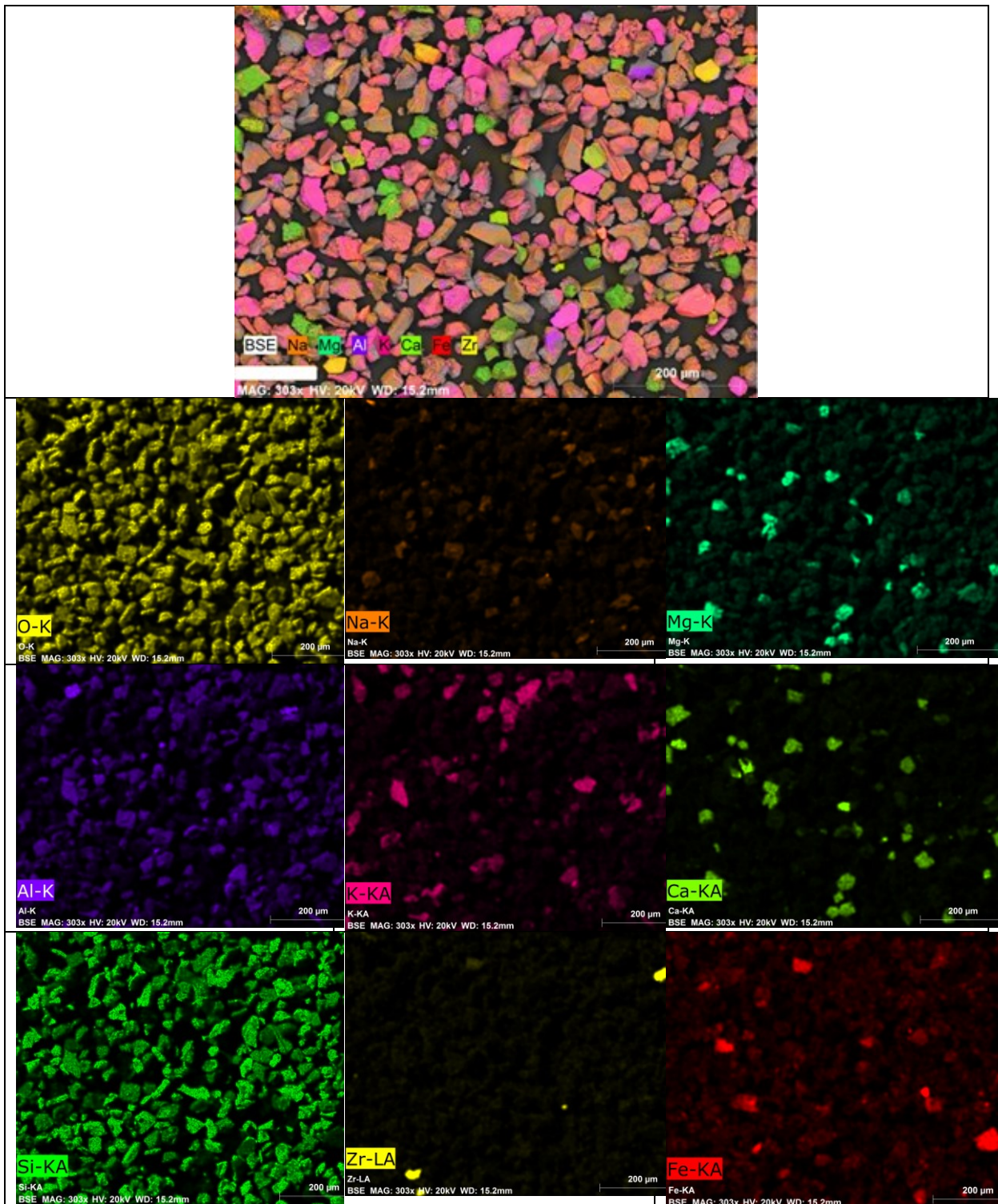


Figure 6.60. Elemental distribution and varying shape and size of uncontaminated upper layer sand

Figure 6.61 shows a distribution map of clay sample contaminated with gasoline at about 100% saturation level after four weeks. Results indicate that it contains the commonly occurring elements such as: Si, O, Na, Mg, Al, K, Ca, Ti, Fe, Zr, Mn, Nb and P in addition to rare earth elements like gadolinium (Gd) and cerium (Ce).

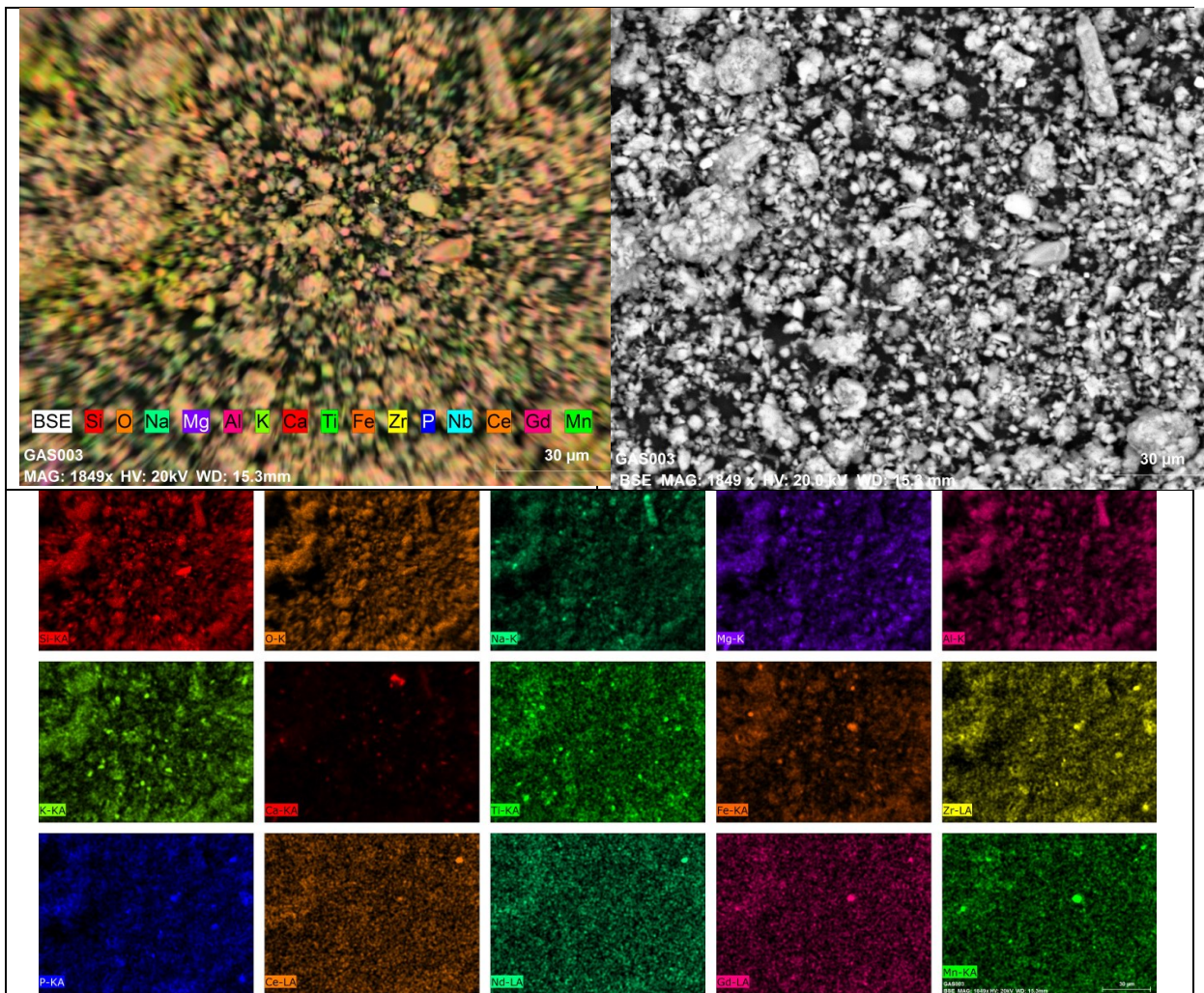


Figure 6.61. Elemental distribution and varying shape and size of clay contaminated with gasoline (Gas-003) at about 100% saturation level for 4 weeks

Clay samples, contaminated with gasoline, showed presence of a wide spectrum of chemical elements.

Distribution map of elements over the scanned area of a clay sample, contaminated with TCE (TCE-013) at about 50% saturation level for 16 weeks, is shown in Figure 6.62.

This sample mostly comprises common elements: Si, O, K, Na, Mg, K, Al, Fe, Ca and Ti.

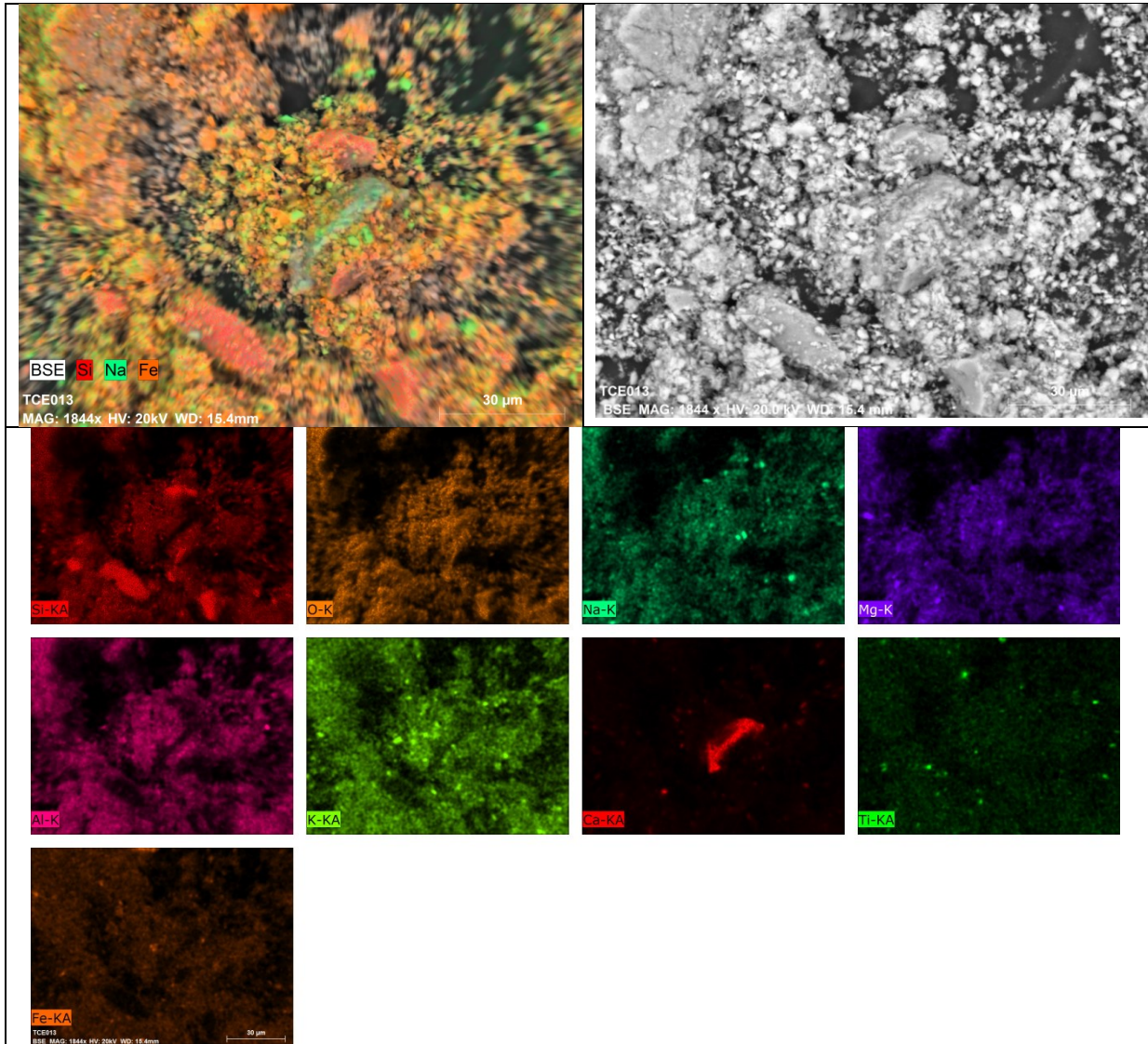


Figure 6.62. Elemental distribution and varying shape and size of clay sample contaminated with TCE (TCE-013) at about 50% saturation level for 16 weeks

Distribution map of elements over the scanned area of a clay sample, contaminated with TCE (TCE-015) at about 25% saturation level for 16 weeks, is shown in Figure 6.63.

This sample mostly comprises common elements: Si, O, K, Na, Mg, K, Ca, Al, Fe and Ti.

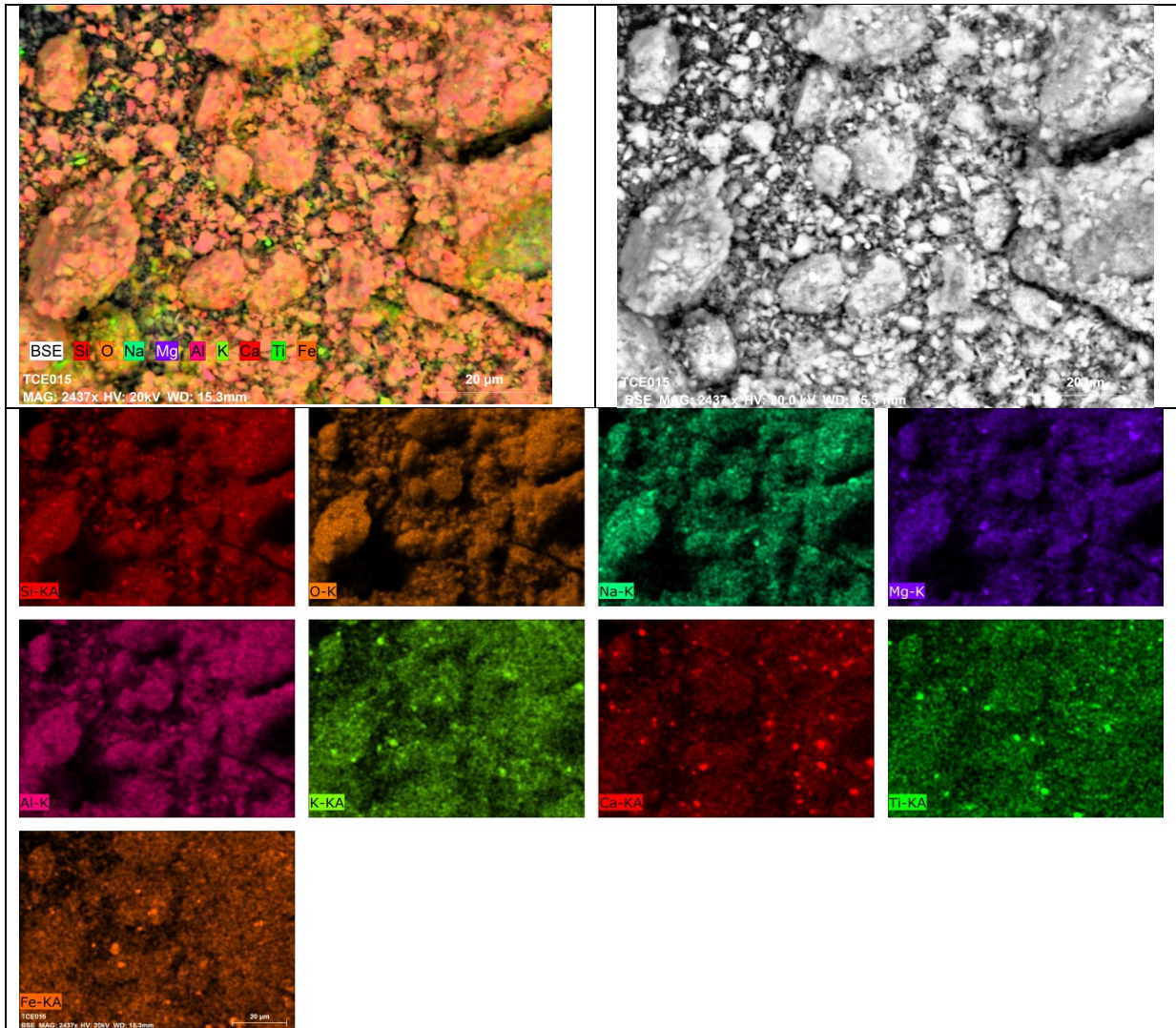


Figure 6.63. Elemental distribution and varying shape and size of clay sample contaminated with TCE (TCE-015) at about 25% saturation level for 16 weeks

Clay samples, which were contaminated with TCE, showed presence of a wide spectrum of chemical elements. Results indicate that the TCE did not produce any notable effect on clay minerals.

Topography Analyses Using Secondary Electron Method

Yet another objective of using the SEM-Secondary Electron Method (SE) was to study the effects of hydrocarbon contaminants on aquifer sand grain's shape and topography after they were exposed to selected chemicals for a certain period of time; and to detect any hydrocarbon adsorption on sand grains. SE is generated when a primary electron displaces an electron of a specimen from its surface.

A magnification that was used in the SE analysis; high voltage (HV) of 5 and 10 kilovolts (kV) and working distance up to 4 mm.

Figure 6.64 displays electron micrograph of sand particles from uncontaminated aquifer sand sample, which was tested at 5 kV with a view field of 3.11 mm, showing that the granules are irregularly shaped and vary in size. Also, images of aquifer sand grain surfaces showed grooves, and small secondary mineral fragments of gypsum and barite between the grooves as shown in Figure 6.65 a and b. The wide range in shape and grain size makes it easy to re-fill the voids between particles upon re-compaction, which is an important cause for reduction of the pore size that causes decrease in hydraulic conductivity. In practice re-compaction of aquifer solids could also occur after heavy pumping of groundwater, often resulting in ground subsidence and causing a reduction in effective stress forcing the grains to slide, roll and readjust to a denser state of compaction.

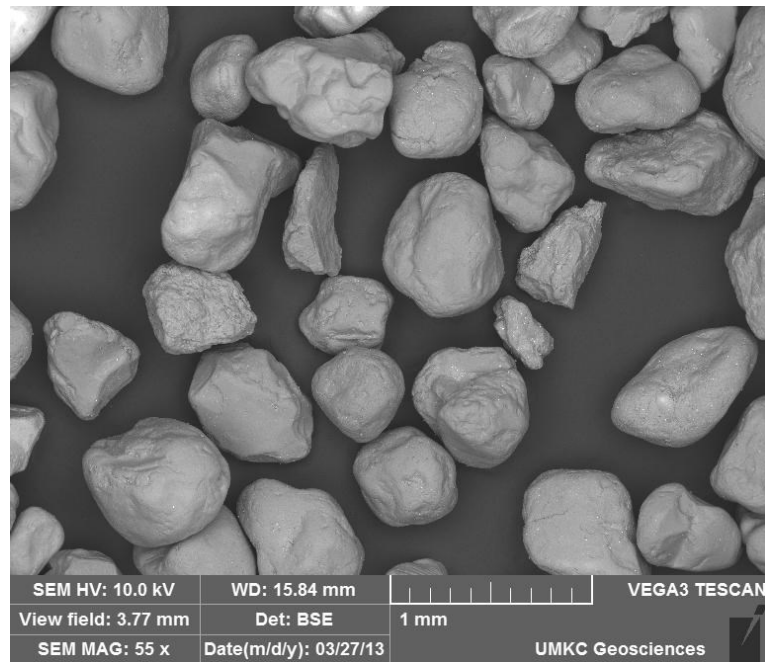
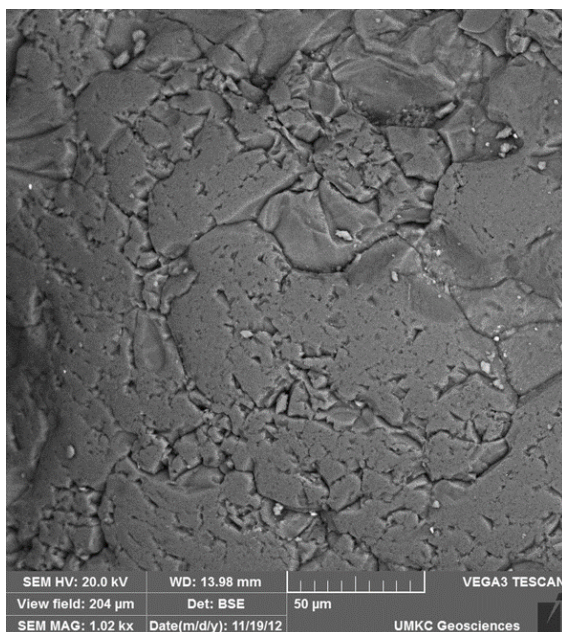
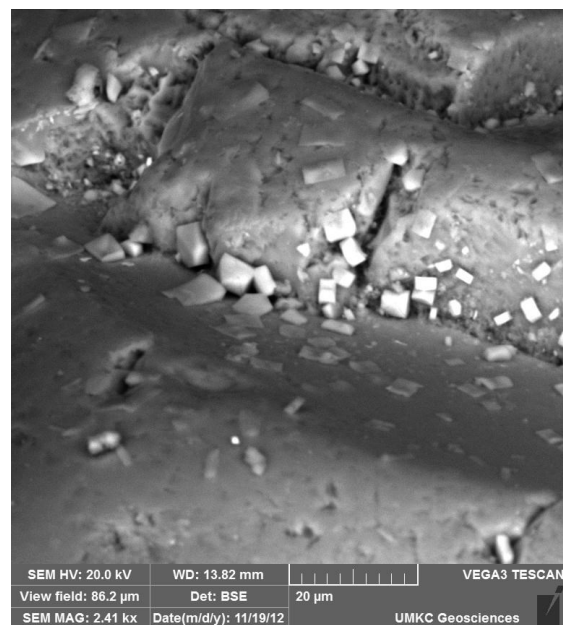


Figure 6.64. Electron micrograph of some sub-angular and sub-rounded grains in uncontaminated aquifer sand sample



a



b

Figure 6.65. Grooves on surfaces of aquifer sand sample (a); and secondary mineral fragments between the grooves (b)

One aquifer sand sample, which was fully saturated with gasoline for 32 weeks, was tested under SEM and no significant changes in grains shape compared with uncontaminated sand sample, was observed (Figure 6.66).

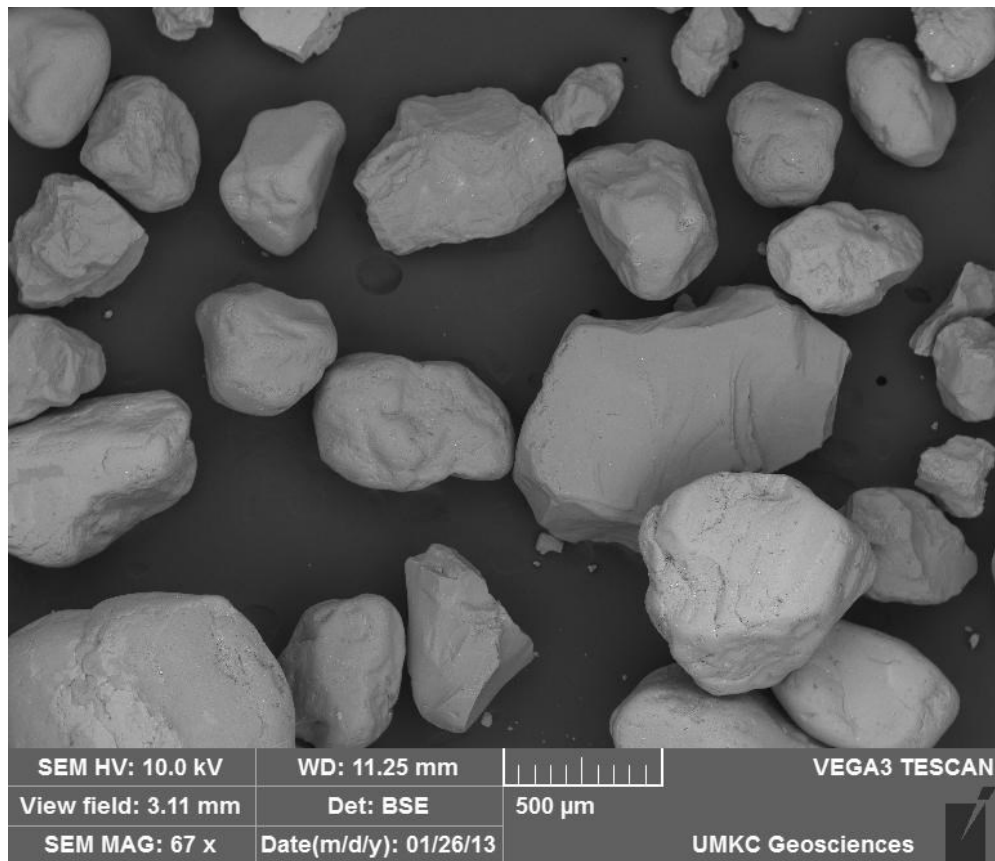


Figure 6.66. Grain shape and nanoscale fragmentation of aquifer sand sample, fully saturated with gasoline for 32 weeks

CHAPTER 7

DISCUSSION

This chapter discusses interpretations of the data that resulted from laboratory testing of the physical and geotechnical properties of aquifer and upper layer (vadose zone) sand—evaporation rate, hydraulic conductivity, XRD analyses, and scanning electron microscopy. Taken together these results provide an explanation for change in hydraulic conductivity of sand and offer an insight into contaminant transport through aquifer solids.

Cleaning up of aquifers contaminated with petroleum and petroleum products is a complex and expensive process and takes decades (Hasan, 1996; U.S. EPA, 1996a). Steffy *et al.*, (1995) reported that the LNAPL components of gasoline, despite low solubility, can be held in soil for extended periods of time. Besides geology of the aquifer layers, a number of physicochemical factors have recently been found to play important roles. For example, Parnian and Ayatollahi (2008) found that remediation of LNAPLs is extremely difficult because of high interfacial tension, existence of adhesive forces between LNAPL molecules and soil particles, and the high capillary pressure that traps LNAPL molecules in the pores. Moreover, Mukunoki and Mikami (2013) indicated that factors for trapping LNAPL in sand pore are related to the connectivity of pore structures and drastic changes in capillary pressure with bottleneck effect.

Mukunoki and Mikami (2013) used micro-focused X-ray computed tomography (MXCT) scanners and an image analysis technique to understand the mechanism of LNAPL migration in sandy soil. Figure 7.1 (a) illustrates the residual LNAPL distribution, and Figure 7.1 (b) shows the residual LNAPL, indicating that LNAPLs will form blobs, described as a

drops of a thick liquid or other viscous substance that collect in voids in the subsurface; that would occupy a significant percent of pores (Mukunoki and Mikami, 2013), resulting in reduction of effective porosity that would ultimately impede groundwater movement.

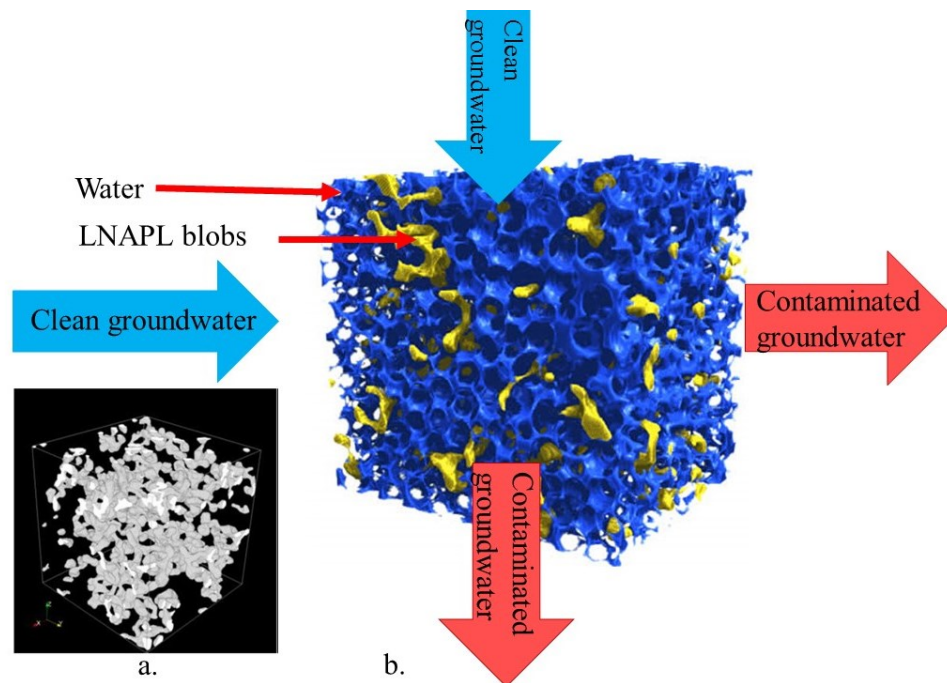


Figure 7.1. Residual LNAPL distribution (a); Three-dimensional rendition of contaminated aquifer (b) (after Mukunoki and Mikami, 2013)

Particle Size Analyses

Results of sieve analysis tests for uncontaminated-and VOCs (gasoline, TCE, benzene, toluene, ethylbenzene, isooctane and xylenes)-contaminated aquifer and upper layer sand samples do not show any change in the grain size distribution. In addition the

parameters D_{10} , C_u , C_z and S_0 did not indicate any significant change in their values in comparison with the uncontaminated sand samples.

Void Ratio, Porosity, Dry Unit Weight, and Saturated Unit Weight

To investigate the factors that might cause a decrease in the hydraulic conductivity of aquifer solids, several tests were carried out to determine geotechnical properties of the aquifer and upper layer sand samples, before and after exposure to contaminants. Results indicate that TCE, gasoline, benzene, toluene, ethylbenzene, xylene and isooctane alter the geotechnical properties of aquifer sand after it was exposed to contaminants for various periods of time. Decrease in void ratio and porosity, and increase in dry and saturated unit weights were the most common changes observed. Geotechnical properties of upper layer sand samples were affected in a similar way upon exposure to TCE and gasoline—decrease in void ratio and porosity, and increase in dry and saturated unit weights. These changes are attributed to the physical and chemical effects caused by the contaminating chemicals that include grains fissuring and granulation, difference in the amount of chemicals left behind in the pores, and adsorbed on grain surfaces, and vapor pressure of each of the contaminating VOCs. Any residual amount of VOCs in a porous medium is known to remain immovable because of strong adhesion (U.S. EPA, 1996).

Evaporation Test

Evaporation testing, performed under controlled conditions, revealed that benzene, isooctane and TCE had the fastest evaporation rate and the entire quantity was lost in about

1600 h (about 9 weeks), whereas toluene, ethylbenzene, xylene, and gasoline had a slower evaporation rate and complete volatilization did not occur even after 4400–6600 h (about 26 to 39 weeks) and a small quantity was left behind in the sand (Tables 6.5–6.9).

Figure 7.2 shows loss of benzene, toluene, ethylbenzene xylene, isooctane, gasoline, and TCE from fully saturated samples of aquifer sand. The evaporation rate results show that VOCs volatilize in the following order:

Benzene > TCE> isooctane > toluene > ethylbenzene > xylene > gasoline

On the other hand, results indicated that adsorption is greater than desorption in the opposite order:

Gasoline> xylene> ethylbenzene> toluene> isooctane> TCE> benzene

This also shows that the transport of VOCs with slower evaporation rate, through the vadose zone, will take long time, causing long-term of exposure, representing a significant exposure pathway especially for those living near contaminated sites.

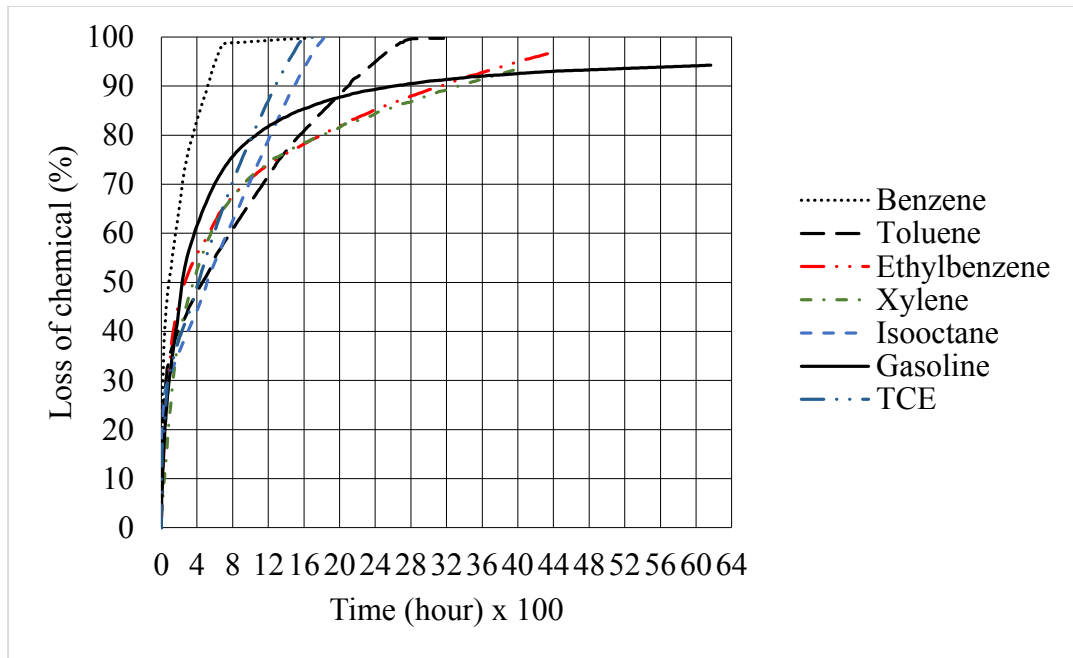


Figure 7.2. Evaporation loss curves for benzene, toluene, ethylbenzene, xylene, isooctane, gasoline and TCE, fully saturated sand samples

Since gasoline is a multicomponent mixture consisting of BTEX and isooctane, the evaporation rate of unleaded gasoline from both aquifer and upper layer sand changes significantly with the progress of evaporation, which besides other factors, is controlled by the speciation of gasoline that occurs during the process of volatilization.

In addition, rate of evaporation is influenced by air circulation in the vadose zone, which is greater near the surface and decreases with depth, becoming zero below the groundwater table.

In the field, other factors such as the quantity of hydrocarbon spill, depth, total area; ambient air temperature, humidity, and wind speed also control the rate of evaporation of volatile organic compounds (Okamoto *et al.*, 2009).

Based on the trends shown in Figure 7.2, it can be concluded that there is an inverse relationship between evaporation rate and residual saturation of chemicals.

Evaporation rate tests indicate that, for long-term of spill, both TCE and gasoline evaporate at a slower rate from coarser grained sand of the aquifer compared to the medium-grained sand of the upper layer. This is due to smaller pore-size in the latter that results in greater capillary action. Thus, the high mobility of TCE and gasoline vapor near the ground surface has a negative impact on both the environment and human health. On the other hand, it is an effective natural remediation method that significantly reduces the potential for widespread groundwater pollution.

To sum up, adsorption of VOCs affects water transport and plays an essential role in geotechnical properties of medium, as it changes the interfacial tension and degree of wettability for sand grains-water, and also groundwater pollution. A study conducted by the U.S. EPA (1996b) indicated that residual hydrocarbons in porous medium are strongly bound; therefore, they are mainly immovable, and are often an essential long-term source for groundwater contamination. Moreover, the residual VOCs will also affect the movement of groundwater and as a result will reduce hydraulic conductivity.

Applicability of Laboratory Results to Field Conditions

Laboratory experiments carried out under controlled conditions are different than field conditions. In the event of a hydrocarbon leak or spill in the field weather conditions such as, wind velocity and temperature differences within the soil layer and the amount of soil moisture will affect the amount of contaminants entering the aquifer. However, as the

contaminants move deeper, depending on contaminants density, capillary effects, air circulation, moisture content, and depth to the saturated zone, gravity will pull the hydrocarbon down until it will reach the groundwater, when some LNAPLs will dissolve in groundwater, but the remainder will displace air in the vadose zone when most of it would ultimately volatilize and escape into air. Of the quantity that would enter the aquifer, some would be held around the mineral grains, forming coatings and increasing the intramolecular attractive forces to impede water movement, thereby reducing the hydraulic conductivity.

Hydraulic Conductivity

Results of hydraulic conductivity tests indicate that gasoline, which contains BTEX and isooctane, contributes to reduction in hydraulic conductivity of aquifer sand more than the constituent chemicals, and TCE, that is controlled by several factors:

- a) As the evaporation rate data shows, certain amount of gasoline, more than other chemicals, gets trapped in sand voids, even after long time, that alters the void ratio and hence the porosity, which in turn, leads to the change in hydraulic conductivity;
- b) The high interfacial tension caused by adhesive forces between gasoline molecules and sand, contribute to decrease in hydraulic conductivity;
- c) The fact that TCE is denser than water with moderate water solubility would result in the freshly infiltrating water to become denser as it moves through TCE-contaminated sand, pushing the remaining TCE deeper until it moves past the water table. This process would cause overall increase in the density of groundwater. Josephson (1983) found that a density difference of even 1% higher or lower than that of water can

significantly influence contaminant's movement through both the saturated and unsaturated zones. Also, Russell et al., (1992) indicated that density differences may even be apparent at low solute concentrations. Therefore, with a density of 1.46 mg/L (greater than water by 46%) TCE is dense enough to cause substantial reduction in hydraulic conductivity. The results indicate that the aqueous solution contaminated with TCE contributes to reduction of hydraulic conductivity slightly more than that contaminated with gasoline, at different concentration;

- d) The differences in diffusion coefficient. TCE, BTEX and isooctane have higher diffusion coefficient than gasoline as shown in Table 3.2. Therefore, when clean water infiltrates through TCE- BTEX- isooctane-contaminated sand, it will dissolve TCE, BTEX and isooctane, trapped in the void spaces, at a faster rate than gasoline;
- e) Gasoline upon coming in contact with the environment will be subjected to oxidation and thus create blobs in the subsurface, which would impede water movement and thus cause greater reduction in hydraulic conductivity.

Two important conclusions can be made from the test results (Figure 7.3):

- 1- LNAPLs with lower solubility cause greater decrease in hydraulic conductivity and vice versa. For example: isooctane (solubility-10 mg/L) lowered hydraulic conductivity by about 50%, whereas benzene (solubility-1780 mg/L) lowered hydraulic conductivity by about 41%.
- 2- The higher the molecular weight of the chemical the greater is the reduction in hydraulic conductivity.

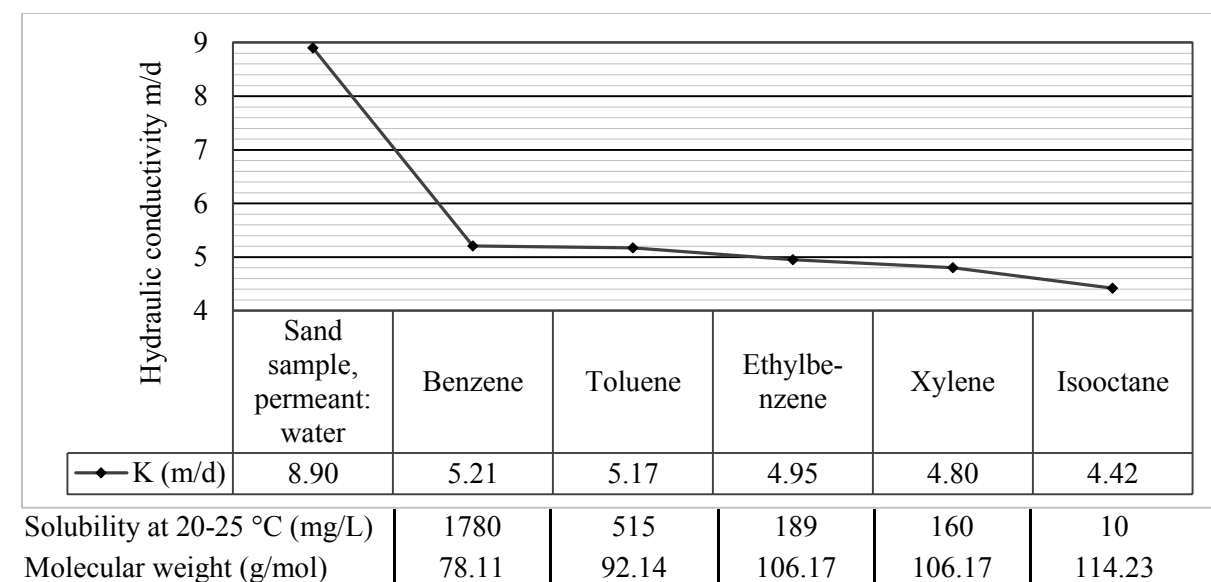


Figure 7.3. Hydraulic conductivity of benzene, toluene, ethylbenzene, xylenes and isooctane versus solubility and molecular weight. Sources: Haynes (2013); Newell *et al.*, (1995)

Reduction in hydraulic conductivity of sand is a result of the effect of various factors and represents a complex interplay of the physicochemical and geotechnical characteristics of both the chemicals and sand. In a practical sense, the reduction in hydraulic conductivity would delay the contaminants flux. Also, capillary force plays an instrumental in the movement of non-aqueous phase of contaminants in both vadose and saturated zones. For instance, Russell *et al.*, (1992) indicated that non aqueous phase of TCE will move downward into aquifer when concentration of TCE is large enough to overcome capillary forces. This knowledge of contaminant's arrival time to the affected media would lead to selection of a better and more cost-efficient remediation plan. For instance, removal of VOCs from contaminated soil in the vadose zone before reaching both capillary and saturated zone is easier by soil venting technology with aid of natural volatilization.

Precipitation is the main source of groundwater recharge via infiltration. Infiltration rate and capacity of soils are controlled by many factors such as rainfall intensity, soil texture and structure, water content of the soil, and soil temperature. However, surface runoff quantity depends on the degree of saturation of the soil and its permeability, which is related to infiltration—the quantity of runoff increases as the degree of saturation increases. Results of this study show that hydraulic conductivity of the porous medium comprising the aquifer and upper layer sand decreases when it is exposed to hydrocarbons for varying saturation levels, concentrations, and periods of time. This indicates that the runoff would increase compared to infiltration, which, in turn, means that the time required for rainwater to reach aquifers, via infiltration, will increase and water quantity will be reduced which collectively would allow more time to select and install an effective remediation system at the contaminated site.

Sand Grains Shape

Images created by SEM (SE) on the shape and surface features of sand grains revealed highly irregular surfaces with presence of micro grooves. But, it did not show any significant changes in grains shape after contamination.

X-Ray Diffraction and Scanning Electron Microscopy

XRD test results for selected sand samples from both the aquifer and upper layer, after varying duration of contamination, do not show any significant change in their mineralogy compared with the uncontaminated sand sample. However, grooving on grain

surface and nanoscale grain fragmentations were observed. Very small amount of clay-about 0.10 g from each sample, present in upper layer sand contaminated with gasoline and TCE, was examined by XRD and SEM. Results show that kaolinite and illite are the main clay minerals with some montmorillonite as well as quartz and feldspars. None of these minerals showed any change upon contamination.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

Hydrocarbons compounds, including LNAPLs and DNAPLs, have different physical properties and structures, which cause different interactions with sand grains and liquids, especially water, as it moves through the porous media. Physical properties of sand: grain size, shape, packing and porosity, along with the differences in physiochemical properties of chemicals such as density, viscosity, and chemicals structure control the rate of evaporation following spills and leaks. The following is a summary of key findings;

- Sand from the aquifer and the vadose zones showed changes in its geotechnical properties upon contamination, with a significant decrease in hydraulic conductivity which is controlled by chemical structure of contaminants along with their water solubility, vapor pressure, polarity, and molecular weight.
- Physical observation at nanoscale, indicated by grain fragmentation, cracks and grooves are believed to be minor factors in reduction of hydraulic conductivity.

Recommendations

The present laboratory study demonstrates the effects of selected hydrocarbons on the chemical and geotechnical properties of aquifer sand and its impact on hydraulic conductivity. Because the scope of this study was limited to laboratory experiments, certain follow up research should be carried out. Some of these are listed below:

1. Bench scale laboratory experiment using larger volume of sand and chemicals.

2. Field studies to validate laboratory and bench scale results.
3. Using existing production or monitoring wells, at contaminated aquifer site, both before and after contamination, to verify the differences in the hydraulic conductivity before and after spill or leak. This will provide a better understanding of the processes at field scale.
4. The results of this study could be employed in understanding the processes going on at the nanoscale, by building numerical model to simulate contaminant flow in an aquifer using the USGS-three-dimensional finite-difference groundwater model, MODFLOWARC, etc.
5. Using X-ray computed tomography (CT) technique, rather than SEM to obtain interior view of pores, grains and fluids, and to study flow rate through contaminated sand sample. Although, the SEM and X-ray CT produces images at very high resolution, but because SEM is very sensitive to potential damage from hydrocarbon vapors, SEM use may be limited for such chemicals. Imaging, using CT, would provide both qualitative and quantitative data of various pore-scale features.

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Appendix A

A. LETTER OF PERMISSION AND CHROMATOGRAM OF THE HYDROCARBONS IN UNLEADED GASOLINE

A.1. Letter of Permission

December 2013

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December 8, 2013

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The work will be used in my dissertation. The publication information is as follows: Effect of Selected Contaminants on the Physical, Chemical, And Geotechnical Properties of Aquifer Solids (dissertation) in 2014.

Please let me know if there is a fee for using this work in this manner.

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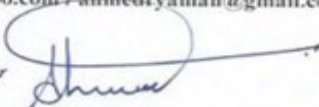
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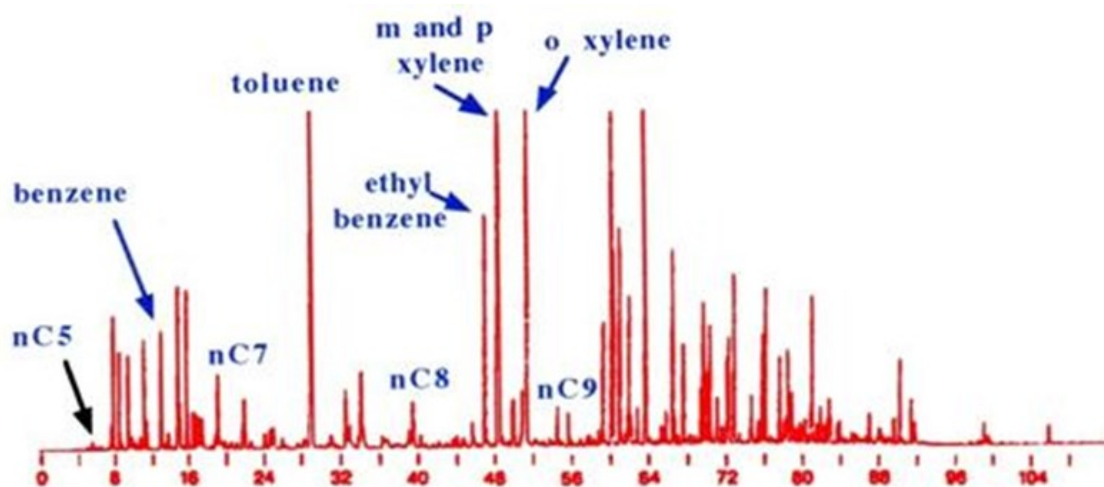
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Date: December 10, 2013



A.2. A chromatogram of the hydrocarbons in unleaded gasoline using a dispersive (Nonpolar) stationary phase (after chromatography online, 2014)

Appendix B

B. MECHANICAL ANALYSES DATA OF AQUIFER SAND SAMPLES CONTAMINATED WITH GASOLINE AND TCE

B.1. Results of sieve analyses of aquifer sand samples, contaminated with gasoline at about 100% saturation level

Sieve number	Sieve opening (mm)	Sample number						
		Gas-1	Gas-2	Gas-3	Gas-10	Gas-11	Gas-12	Gas-13
		% Finer						
8	2.36	98.45	98.78	98.52	98.44	98.47	98.61	98.55
10	2.00	97.63	98.23	97.83	97.75	97.85	98.03	97.75
16	1.18	93.91	95.00	94.62	94.5	94.77	94.83	93.9
20	0.85	88.53	90.10	89.85	89.81	90.21	90.06	88.22
30	0.60	77.73	80.40	80.14	80.29	80.66	78.69	77.26
60	0.25	30.32	34.06	32.53	33.78	31.65	33.76	28.32
100	0.15	4.02	4.95	4.84	4.84	4.04	4.49	4.81
170	0.09	0.59	0.86	0.82	0.73	0.65	0.67	0.60
200	0.075	0.21	0.33	0.30	0.23	0.17	0.20	0.20
230	0.0625	0.12	0.21	0.18	0.11	0.10	0.12	0.11
325	0.044	0.02	0.07	0.05	0.03	0.03	0.02	0.01

B.2. Results of sieve analyses of aquifer sand samples, contaminated with gasoline at about 50% saturation level

Sieve number	Sieve opening (mm)	Sample number						
		Gas-20	Gas-4	Gas-5	Gas-6	Gas-14	Gas-15	Gas-16
		% Finer						
8	2.36	98.80	98.81	98.57	98.80	98.45	98.48	98.57
10	2.00	98.04	98.15	97.88	98.04	97.84	97.78	97.79
16	1.18	94.61	95.06	94.87	94.62	94.19	94.55	93.75
20	0.85	89.57	90.52	90.18	89.57	90.31	89.93	87.73
30	0.60	79.56	81.47	80.87	79.58	81.11	80.45	76.29
60	0.25	31.15	35.15	33.87	31.14	34.01	34.12	27.08
100	0.15	4.22	5.17	4.92	4.21	5.34	5.04	4.54
170	0.09	0.60	0.80	0.78	0.59	0.90	0.85	0.58
200	0.075	0.17	0.27	0.28	0.17	0.33	0.31	0.20
230	0.0625	0.07	0.15	0.17	0.07	0.20	0.19	0.13
325	0.044	0.03	0.04	0.03	0.03	0.04	0.03	0.05

B.3. Results of sieve analyses of aquifer sand samples, contaminated with gasoline at about 25% saturation level

Sieve number	Sieve opening (mm)	Sample number						
		Gas-21	Gas-7	Gas-8	Gas-9	Gas-17	Gas-18	Gas-19
		% Finer						
8	2.36	98.44	98.42	98.45	98.56	98.70	98.87	98.86
10	2.00	97.74	97.71	97.91	97.81	98.23	98.27	98.20
16	1.18	94.58	94.51	95.91	94.32	95.50	95.23	93.92
20	0.85	90.15	90.03	90.41	89.21	91.39	90.64	87.43
30	0.60	81.24	81.01	81.27	79.10	82.81	81.14	75.22
60	0.25	33.32	32.90	33.57	32.40	34.50	34.02	26.34
100	0.15	5.29	4.93	5.22	4.72	5.19	4.69	4.39
170	0.09	0.82	0.81	0.88	0.70	0.81	0.70	0.53
200	0.075	0.31	0.30	0.33	0.23	0.13	0.22	0.17
230	0.0625	0.19	0.19	0.19	0.11	0.13	0.13	0.09
325	0.044	0.05	0.06	0.05	0.03	0.01	0.02	0.04

B.4. D_{10} , C_u , C_z and S_0 of aquifer sand samples contaminated with gasoline, at about 100%, 50% and 25% saturation levels

Sample number	D_{10}	D_{25}	D_{30}	D_{60}	D_{75}	C_u	C_z	S_0
Original sample	0.18	0.22	0.24	0.41	0.55	2.29	0.78	1.59
Gas-1	0.176	0.228	0.253	0.43	0.563	2.443	0.85	1.788
Gas-2	0.176	0.217	0.241	0.40	0.543	2.273	0.824	1.582
Gas-3	0.179	0.222	0.244	0.41	0.537	2.291	0.812	1.555
Gas-4	0.173	0.216	0.235	0.40	0.543	2.312	0.795	1.585
Gas-5	0.176	0.216	0.238	0.40	0.528	2.273	0.808	1.563
Gas-6	0.181	0.231	0.25	0.422	0.55	2.30	0.818	1.543
Gas-7	0.179	0.222	0.238	0.40	0.543	2.235	0.791	1.564
Gas-8	0.176	0.216	0.23	0.40	0.543	2.272	0.751	1.585
Gas-9	0.183	0.226	0.247	0.42	0.54	2.295	0.792	1.545
Gas-10	0.175	0.22	0.238	0.40	0.536	2.286	0.602	1.561
Gas-11	0.179	0.221	0.252	0.414	0.533	2.313	0.865	1.553
Gas-12	0.176	0.213	0.236	0.41	0.50	2.33	0.777	1.609
Gas-13	0.181	0.24	0.27	0.44	0.58	2.43	0.91	2.42
Gas-14	0.173	0.217	0.238	0.40	0.533	2.312	0.812	1.567
Gas-15	0.162	0.216	0.237	0.40	0.55	2.469	0.875	1.596
Gas-16	0.180	0.25	0.27	0.45	0.58	2.50	0.90	2.32
Gas-17	0.173	0.22	0.233	0.399	0.50	2.306	0.787	1.508
Gas-18	0.176	0.218	0.235	0.40	0.55	2.273	0.781	1.588
Gas-19	0.18	0.25	0.27	0.46	0.60	2.56	0.88	1.55
Gas-20	0.18	0.23	0.25	0.42	0.55	2.33	0.83	1.546
Gas-21	0.17	0.23	0.25	0.40	0.53	2.35	0.92	1.52

B.5. Results of sieve analyses of aquifer sand samples, saturated with TCE at about 100% saturation level

Sieve number	Sieve opening (mm)	Sample number						
		TCE-01	TCE-02	TCE-03	TCE-00	TCE-010	TCE-011	TCE-012
		Percent finer						
8	2.36	98.24	98.60	98.38	98.18	98.43	98.50	98.60
10	2.00	97.51	97.88	97.71	97.46	97.70	97.84	97.92
16	1.18	94.76	93.95	94.12	94.73	94.55	94.57	94.62
20	0.85	90.75	88.08	88.90	90.73	89.99	89.61	89.70
30	0.60	82.45	76.68	78.65	82.47	80.76	79.65	79.58
60	0.25	34.26	28.55	30.67	34.17	32.01	32.78	29.24
100	0.15	4.93	3.72	4.25	4.94	4.15	4.24	5.06
170	0.09	0.75	0.54	0.63	0.78	0.54	0.55	0.65
200	0.075	0.26	0.21	0.23	0.30	0.16	0.17	0.23
230	0.0625	0.15	0.13	0.14	0.18	0.09	0.10	0.14
325	0.044	0.04	0.05	0.03	0.07	0.02	0.01	0.07

B.6. Results of sieve analyses of aquifer sand samples, contaminated with TCE at about 50% saturation level

Sieve number	Sieve opening (mm)	Sample number						
		TCE-019	TCE-04	TCE-05	TCE-06	TCE-013	TCE-014	TCE-015
		Percent finer						
8	2.36	98.46	98.39	98.46	98.70	98.41	98.57	98.66
10	2.00	97.75	97.73	97.76	98.11	97.69	97.83	98.09
16	1.18	94.07	94.14	94.07	95.38	94.17	94.22	94.91
20	0.85	88.43	88.92	88.43	91.53	88.64	88.75	90.05
30	0.60	77.78	78.67	77.76	83.59	77.90	78.17	80.41
60	0.25	29.73	30.69	29.79	38.12	34.05	33.16	31.05
100	0.15	4.13	4.27	4.13	6.20	7.38	4.05	5.67
170	0.09	0.62	0.65	0.63	1.09	0.56	0.53	0.72
200	0.075	0.22	0.25	0.23	0.40	0.20	0.16	0.22
230	0.0625	0.13	0.16	0.14	0.24	0.12	0.09	0.12
325	0.044	0.03	0.05	0.04	0.08	0.03	0.01	0.07

B.7. Results of sieve analyses of aquifer sand samples, contaminated with TCE at about 25% saturation level

Sieve number	Sieve opening (mm)	Sample number						
		TCE-020	TCE-07	TCE-08	TCE-09	TCE-016	TCE-017	TCE-018
		Percent finer						
8	2.36	98.40	98.80	98.40	98.52	98.70	98.27	98.37
10	2.00	97.71	98.20	97.71	97.96	98.10	97.59	97.60
16	1.18	94.95	94.96	94.96	94.84	94.40	94.16	94.13
20	0.85	91.04	89.78	90.89	90.22	89.02	89.32	89.16
30	0.60	82.60	79.84	82.44	80.54	78.19	79.66	79.33
60	0.25	33.91	32.40	34.03	33.46	32.75	33.56	29.90
100	0.15	5.22	4.78	5.39	5.14	4.06	4.13	5.30
170	0.09	0.94	0.80	0.97	0.87	0.53	0.44	0.70
200	0.075	0.35	0.31	0.37	0.33	0.16	0.08	0.26
230	0.0625	0.21	0.19	0.23	0.21	0.09	0.02	0.15
325	0.044	0.06	0.06	0.06	0.06	0.01	0.01	0.08

B.8. D_{10} , C_u , C_z and S_0 of aquifer sand samples contaminated with TCE, at about 100%, 50% and 25% saturation levels

Sample number	D_{10}	D_{25}	D_{30}	D_{60}	D_{75}	C_u	C_z	S_0
Original Sample	0.18	0.22	0.24	0.413	0.554	2.294	0.78	1.587
TCE-01	0.177	0.217	0.234	0.40	0.52	2.26	0.774	1.584
TCE-02	0.181	0.20	0.236	0.44	0.575	2.431	0.867	1.695
TCE-03	0.177	0.226	0.252	0.425	0.50	2.40	0.868	1.487
TCE-04	0.181	0.232	0.253	0.43	0.562	2.376	0.821	1.556
TCE-05	0.181	0.232	0.253	0.43	0.563	2.376	0.821	1.561
TCE-06	0.172	0.209	0.238	0.380	0.50	2.209	0.865	1.547
TCE-07	0.174	0.23	0.242	0.41	0.55	2.356	0.82	1.546
TCE-08	0.174	0.218	0.237	0.40	0.50	2.298	0.804	1.514
TCE-09	0.177	2.219	0.232	0.406	0.55	2.294	0.750	1.585
TCE-010	0.18	0.228	0.25	0.40	0.55	2.222	0.868	1.55
TCE-011	0.179	0.218	0.24	0.411	0.55	2.296	0.78	1.59
TCE-012	0.181	0.24	0.26	0.425	0.55	2.35	0.88	1.51
TCE-013	0.171	0.215	0.235	0.423	0.575	2.474	0.761	1.634
TCE-014	0.180	0.22	0.24	0.418	0.57	2.362	0.784	1.609
TCE-015	0.175	0.23	0.24	0.41	0.55	2.343	0.80	1.55
TCE-016	0.18	0.229	0.24	0.42	0.578	2.333	0.754	1.589
TCE-017	0.18	0.22	0.24	0.41	0.55	2.291	0.789	1.58
TCE-018	0.18	0.24	0.26	0.42	0.55	2.40	0.919	1.48
TCE-019	0.181	0.242	0.26	0.43	0.56	2.375	0.872	1.52
TCE-020	0.176	0.217	0.242	0.40	0.50	2.272	0.832	2.304
TCE-00	0.178	0.22	0.233	0.40	0.514	2.247	0.743	1.529

Appendix C

C. MECHANICAL ANALYSES DATA OF UPPER LAYER SAND SAMPLES CONTAMINATED WITH GASOLINE AND TCE

C.1. Results of sieve analyses of sand samples saturated with gasoline at 100% saturation level

Sieve number	Sieve opening (mm)	Sample number					
		Gas-001	Gas-002	Gas-003	Gas-010	Gas-011	Gas-012
		Percent finer					
40	0.425	99.97	100	99.96	99.96	99.97	100
50	0.355	98.84	98.82	98.61	98.62	98.84	98.83
60	0.25	97.15	97.02	96.44	96.46	97.18	97.04
70	0.212	92.57	92.8	91.96	91.76	92.70	92.86
100	0.15	36.06	37.59	38.16	38.06	36.69	37.71
140	0.106	23.29	24.30	21.25	20.95	24.01	24.32
170	0.09	19.48	20.34	18.03	17.83	20.29	20.39
200	0.075	13.52	14.07	11.88	11.71	14.05	14.17
230	0.0625	11.42	12.13	10.50	10.36	11.78	12.24
325	0.044	4.87	5.35	4.38	4.49	4.96	5.52

C.2. Results of sieve analyses of upper layer sand samples contaminated with gasoline at about 50% saturation level

Sieve number	Sieve opening (mm)	Sample number				
		Gas-004	Gas-005	Gas-006	Gas-013	Gas-014
		Percent finer				
40	0.425	100	99.96	99.98	100	99.96
50	0.355	98.85	98.51	98.71	98.84	98.73
60	0.25	97.09	96.06	96.35	96.86	96.27
70	0.212	92.89	91.00	91.42	92.46	91.25
100	0.15	36.96	38.22	38.94	36.83	38.49
140	0.106	23.30	21.37	21.77	23.03	21.91
170	0.09	19.09	17.81	17.93	19.09	18.11
200	0.075	12.97	12.24	12.06	12.97	12.31
230	0.0625	11.20	10.61	10.38	11.07	10.66
325	0.044	4.94	4.59	4.25	5.10	4.78

C.3. Results of sieve analyses of upper layer sand samples contaminated with gasoline at about 25% saturation level

Sieve number	Sieve opening (mm)	Sample number				
		Gas-007	Gas-008	Gas-009	Gas-015	Gas-016
		Percent finer				
40	0.425	99.99	99.99	99.99	99.98	99.99
50	0.355	98.95	98.39	98.19	99.06	98.41
60	0.25	97.26	95.28	94.61	97.57	94.89
70	0.212	93.02	89.20	88.04	93.29	87.97
100	0.15	36.66	37.53	37.11	36.93	36.94
140	0.106	23.58	21.12	19.98	23.60	19.90
170	0.09	19.67	17.21	16.99	19.91	16.82
200	0.075	13.67	12.08	11.23	13.88	10.87
230	0.0625	11.82	10.41	9.77	11.92	9.39
325	0.044	5.19	4.43	3.82	5.05	3.63

C.4. D_{10} , C_u , C_z and S_0 of upper layer sand samples contaminated with gasoline, at about 100%, 50% and 25% saturation level

Sample number	D_{10}	D_{25}	D_{30}	D_{60}	D_{75}	C_u	C_z	S_0
Original sample	0.075	0.153	0.161	0.189	0.205	2.52	1.844	1.158
Gas-001	0.057	0.117	0.155	0.181	0.192	3.175	2.40	1.281
Gas-002	0.056	0.11	0.14	0.181	0.193	3.232	1.96	1.325
Gas-003	0.06	0.124	0.142	0.181	0.193	3.017	1.818	1.248
Gas-004	0.058	0.115	0.141	0.181	0.193	3.121	1.99	1.295
Gas-005	0.06	0.124	0.16	0.167	0.193	2.783	2.560	1.556
Gas-006	0.06	0.12	0.139	0.179	0.193	2.983	1.799	1.268
Gas-007	0.057	0.117	0.143	0.181	0.191	3.176	2.00	1.278
Gas-008	0.06	0.126	0.143	0.181	0.193	3.017	1.818	1.82
Gas-009	0.062	0.129	0.132	0.183	0.195	2.952	1.534	1.23
Gas-010	0.06	0.12	0.14	0.180	0.193	3.000	1.814	1.26
Gas-011	0.056	0.193	0.14	0.179	0.193	3.196	1.96	1.31
Gas-012	0.055	0.111	0.139	0.182	0.193	3.309	1.93	1.319
Gas-013	0.059	0.12	0.141	0.18	0.192	3.05	1.86	1.264
Gas-014	0.06	0.12	0.14	0.181	0.194	3.01	1.804	1.27
Gas-015	0.057	0.116	0.143	0.181	0.192	3.175	1.942	1.276
Gas-016	0.065	0.12	0.145	0.183	0.196	2.815	1.764	1.27

C.5. Results of sieve analyses of upper layer sand samples, saturated with TCE at 100% saturation level

Sieve number	Sieve opening (mm)	Sample number					
		TCE-011	TCE-012	TCE-013	TCE-020	TCE-010	TCE-023
		Percent finer					
40	0.425	99.98	99.94	99.98	99.96	99.99	99.86
50	0.355	98.85	97.37	96.98	97.18	97.14	97.08
60	0.25	97.04	92.14	91.16	92.62	91.15	91.80
70	0.212	92.61	84.35	82.29	83.83	82.48	84.07
100	0.15	36.33	35.76	36.43	33.52	35.74	35.61
140	0.106	23.45	19.65	21.32	17.63	20.66	19.55
170	0.09	19.83	15.3	15.71	13.99	15.12	14.86
200	0.075	13.66	11.09	11.03	9.01	10.68	10.68
230	0.0625	11.63	9.34	9.41	7.54	9.02	8.84
325	0.044	5.010	3.84	4.05	2.61	3.97	3.60

C.6. Results of sieve analyses of upper layer sand samples, contaminated with TCE at about 50% saturation level

Sieve number	Sieve opening (mm)	Sample number				
		TCE-014	TCE-015	TCE-016	TCE-021	TCE-024
		Percent finer				
40	0.425	99.99	99.98	99.97	99.99	99.98
50	0.355	96.86	96.85	96.68	96.88	96.65
60	0.25	90.39	91.49	90.72	90.60	91.35
70	0.212	80.95	82.44	80.95	81.10	82.38
100	0.15	37.09	33.32	33.87	36.66	33.64
140	0.106	21.32	16.62	18.27	20.98	17.09
170	0.09	16.03	14.90	14.74	15.87	15.38
200	0.075	11.20	9.98	9.73	11.00	10.28
230	0.0625	9.60	8.53	8.02	9.38	8.64
325	0.044	4.12	3.42	3.14	3.92	3.38

C.7. Results of sieve analyses of upper layer sand samples, contaminated with TCE at about 25% saturation level

Sieve number	Sieve opening (mm)	Sample number				
		TCE-017	TCE-018	TCE-019	TCE-022	TCE-025
		Percent finer				
40	0.425	99.97	99.96	99.97	99.97	99.96
50	0.355	97.07	96.75	97.07	97.27	99.68
60	0.25	92.23	90.78	91.76	92.18	90.60
70	0.212	84.36	80.70	82.68	84.35	80.47
100	0.15	35.41	33.81	34.54	35.69	34.02
140	0.106	18.45	18.30	18.12	18.61	18.55
170	0.09	14.89	14.55	14.69	14.81	15.08
200	0.075	9.83	9.59	9.80	9.52	10.00
230	0.0625	8.14	8.14	8.28	8.03	8.44
325	0.044	3.01	3.26	3.27	2.97	3.42

C.8. D_{10} , C_u , C_z and S_0 of upper layer sand samples contaminated with TCE, at 100%, about 50% and about 25% saturation level

Sample number	D_{10}	D_{25}	D_{30}	D_{60}	D_{75}	C_u	C_z	S_0
Original sample	0.075	0.153	0.161	0.189	0.205	2.25	1.844	1.158
TCE-011	0.056	0.117	0.144	0.180	0.193	3.214	2.10	1.035
TCE-012	0.065	0.1	0.146	0.186	0.198	2.862	1.735	1.234
TCE-013	0.065	0.125	0.143	0.184	0.200	2.831	1.666	1.265
TCE-014	0.065	0.124	0.141	0.186	0.203	2.862	1.653	1.279
TCE-015	0.075	0.141	0.152	0.187	0.200	2.493	1.641	1.189
TCE-016	0.075	0.132	0.145	0.177	0.205	2.36	1.585	1.25
TCE-017	0.075	0.135	0.146	0.183	0.198	2.44	1.556	1.211
TCE-018	0.075	0.135	0.151	0.188	0.204	2.507	1.62	1.23
TCE-019	0.075	0.136	0.15	0.186	0.20	2.48	1.607	1.213
TCE-020	0.079	0.14	0.151	0.186	0.20	2.354	1.55	1.195
TCE-010	0.065	0.125	0.147	0.184	0.20	2.83	1.83	1.265
TCE-021	0.065	0.125	0.144	0.184	0.20	2.83	1.75	1.265
TCE-022	0.075	0.134	0.184	0.186	0.20	2.48	1.58	1.222
TCE-023	0.07	0.13	0.168	0.181	0.20	2.875	2.20	1.24
TCE-024	0.07	0.136	0.152	0.188	0.20	2.69	1.643	1.282
TCE-025	0.075	0.132	0.151	0.184	0.201	2.45	1.643	1.234

Appendix D

D. MECHANICAL ANALYSES OF AQUIFER SAND SAMPLES CONTAMINATED WITH BTEX AND ISOOCTANE

D.1. Results of sieve analyses of aquifer sand samples contaminated with BTEX and isooctane, at 100% saturation level

Sieve number	Sieve opening (mm)	Contaminant in sand sample					
		Original sample	Toluene	Benzene	Ethylbenzene	Xylene	Isooctane
			Percent finer				
8	2.36	98.56	98.39	98.68	98.41	98.77	98.33
10	2.00	97.89	97.72	98.07	97.69	98.08	97.66
16	1.18	94.41	94.31	94.85	94.00	94.66	94.53
20	0.85	88.95	89.3	90.04	88.53	89.55	90.26
30	0.60	78.66	79.68	80.57	77.88	79.39	81.52
60	0.25	34.17	32.94	34.52	31.23	33.35	36.50
100	0.15	4.52	4.87	5.25	4.44	4.77	5.20
170	0.09	0.70	0.77	0.79	0.65	0.72	0.73
200	0.075	0.25	0.28	0.25	0.21	0.23	0.23
230	0.0625	0.15	0.16	0.13	0.12	0.13	0.11
325	0.044	0.03	0.03	0.00	0.01	0.03	0.01

D.2. D_{10} , C_u , C_z and S_0 of aquifer sand samples contaminated with BTEX and isooctane, at 100% saturation level

Sand sample description	D_{10}	D_{25}	D_{30}	D_{60}	D_{75}	C_u	C_z	S_0
Original sample	0.18	0.22	0.24	0.413	0.554	2.294	0.78	1.587
Benzene	0.175	0.217	0.246	0.40	0.538	2.286	0.871	1.575
Toluene	1.07	0.23	0.261	0.41	0.55	2.343	0.944	1.546
Ethylbenzene	0.177	0.228	0.27	0.43	0.562	2.43	0.961	1.57
Xylene	0.176	0.221	0.242	0.409	0.55	2.324	0.814	2.489
Isooctane	0.173	0.21	0.226	0.892	0.52	2.266	0.773	1.573

Appendix E

E. MECHANICAL ANALYSES OF AQUIFER SAND SAMPLES CONTAMINATED WITH VARYING CONCENTRATION OF GASOLINE AND TCE

E.1. Results of sieve analyses of aquifer sand samples, fully saturated with aqueous solution contaminated with varying concentration of gasoline

Sieve number	Sieve opening (mm)	Sample number - gasoline									
		1%	2%	3%	4%	5%	6%	7%	8%	9%	10%
Percent finer											
8	2.36	98.8	98.49	98.62	98.36	98.85	98.62	98.63	98.59	98.84	98.59
10	2.00	98.28	97.84	98.04	97.58	98.15	97.86	97.83	97.86	98.2	97.98
16	1.18	94.99	93.96	94.10	93.6	94.25	97.72	93.53	94.06	94.61	94.82
20	0.85	89.61	88.14	87.75	87.91	87.8	87.4	87.2	88.16	88.62	89.72
30	0.60	78.34	76.28	74.88	76.16	74.75	74.82	74.28	76.42	75.69	78.63
60	0.25	25.17	24.93	23.46	25.31	23.32	23.53	22.43	25.41	23.75	26.55
100	0.15	4.36	4.25	3.89	4.14	3.81	0.80	3.46	4.32	3.82	4.58
170	0.09	0.56	0.55	0.51	0.52	0.48	0.44	0.40	0.55	0.46	0.60
200	0.075	0.21	0.21	0.20	0.20	0.18	0.15	0.14	0.20	0.16	0.22

E.2. Results of sieve analyses of aquifer sand samples, fully saturated with aqueous solution contaminated with varying concentration of TCE

Sieve number	Sieve opening (mm)	Sample number									
		1%	2%	3%	4%	5%	6%	7%	8%	9%	10%
		TCE	TCE	TCE	TCE	TCE	TCE	TCE	TCE	TCE	TCE
Percent finer											
8	2.36	98.68	98.82	98.81	98.8	98.81	98.79	98.81	98.82	98.81	98.78
10	2.00	98.04	98.11	98.29	98.25	98.1	98.22	98.09	98.09	98.21	98.18
16	1.18	94.47	94.88	95.04	95.13	94.83	95.12	94.85	94.86	95.12	94.66
20	0.85	88.48	89.6	89.73	90.11	89.70	90.12	89.53	89.58	89.96	89.75
30	0.60	75.81	78.53	78.59	79.12	78.76	79.11	78.40	78.32	78.75	78.26
60	0.25	20.66	25.45	25.37	25.17	25.41	24.96	25.01	24.91	25.24	30.85
100	0.15	3.78	4.58	4.85	4.30	4.59	4.24	4.59	4.57	4.66	8.25
170	0.09	0.51	0.59	0.53	0.59	0.59	0.58	0.56	0.57	0.60	0.64
200	0.075	0.19	0.21	0.22	0.22	0.22	0.21	0.21	0.21	0.23	0.30

E.3. D_{10} , C_u , C_z and S_0 of aquifer sand samples contaminated, fully saturated with aqueous solution contaminated with varying concentration of Gasoline

Sample description	D_{10}	D_{25}	D_{30}	D_{60}	D_{75}	C_u	C_z	S_0
Original sample	0.075	0.153	0.161	0.189	0.205	2.25	1.844	1.158
1% gasoline	0.056	0.117	0.144	0.18	0.193	3.214	2.10	1.035
2% gasoline	0.075	0.132	0.151	0.184	0.201	2.45	1.643	1.234
3% gasoline	0.065	0.124	0.141	0.186	0.203	2.862	1.653	1.279
4% gasoline	0.075	0.136	0.15	0.186	0.20	2.48	1.607	1.213
5% gasoline	0.065	0.13	0.146	0.186	0.198	2.862	1.735	1.234
6% gasoline	0.075	0.132	0.145	0.177	0.205	2.36	1.585	1.25
7% gasoline	0.075	0.134	0.184	0.186	0.20	2.48	1.58	1.222
8% gasoline	0.07	0.136	0.152	0.188	0.20	2.69	1.643	1.282
9% gasoline	0.065	0.125	0.147	0.184	0.20	2.83	1.83	1.265
10% gasoline	0.07	0.13	0.168	0.181	0.20	2.875	2.20	1.24

E.4. D_{10} , C_u , C_z and S_0 of aquifer sand samples contaminated, fully saturated with aqueous solution contaminated with varying concentration of Gasoline

Sample description	D_{10}	D_{25}	D_{30}	D_{60}	D_{75}	C_u	C_z	S_0
Original sample	0.075	0.153	0.161	0.189	0.205	2.25	1.844	1.158
1% TCE	0.065	0.12	0.145	0.183	0.196	2.815	1.764	0.065
2% TCE	0.057	0.117	0.155	0.181	0.192	3.175	2.40	0.057
3% TCE	0.06	0.124	0.142	0.181	0.193	3.017	1.818	0.06
4% TCE	0.06	0.124	0.16	0.167	0.193	2.783	2.56	0.06
5% TCE	0.057	0.117	0.143	0.181	0.191	3.176	2.00	0.057
6% TCE	0.06	0.126	0.143	0.181	0.193	3.017	1.818	0.06
7% TCE	0.06	0.12	0.14	0.18	0.193	3.00	1.814	0.06
8% TCE	0.055	0.111	0.139	0.182	0.193	3.309	1.93	0.055
9% TCE	0.06	0.12	0.14	0.181	0.194	3.01	1.804	0.06
10% TCE	0.057	0.116	0.143	0.181	0.192	3.175	1.942	0.057

Appendix F

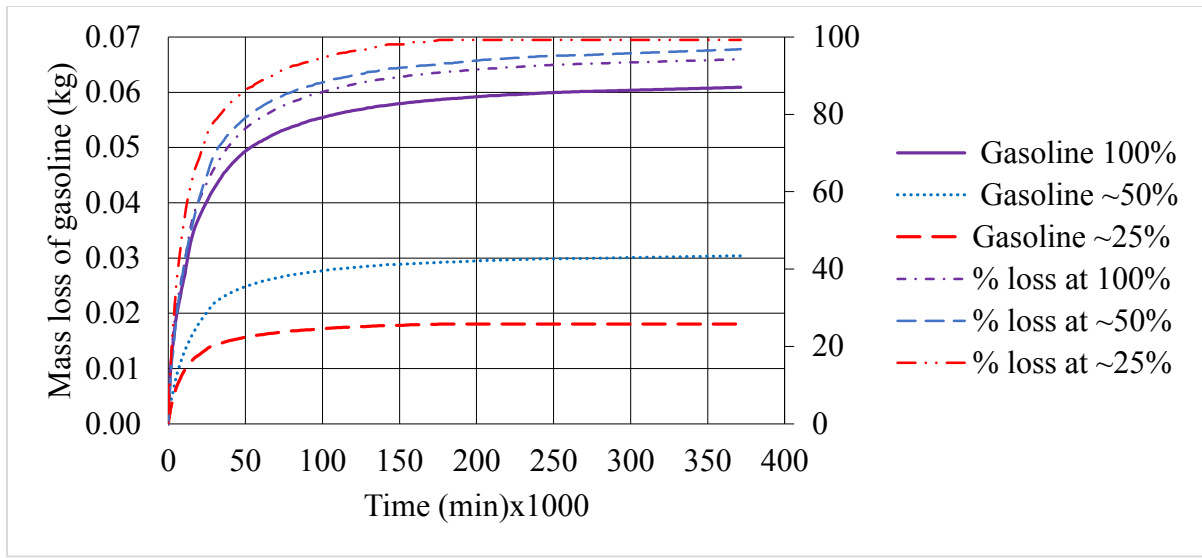
F. WEIGHT OF AQUIFER AND UPPER LAYER SAND SAMPLE AND VOLUME OF CHEMICALS USED FOR EVAPORATION RATE TEST

F.1. Weight of aquifer sand and chemicals used for evaporation rate tests

Sample description	Weight of empty container (g)	Weight of container + sand (g)	Weight of container + sand + chemicals (g)	Weight of chemical used (g) and volume (mL)
Contaminated with gasoline at 100%	228.75	770.00	834.61	64.61 89.74
Contaminated with gasoline at about 50%	229.90	774.21	806.10	31.89 44.29
Contaminated with gasoline at about 25%	229.59	764.57	782.83	18.26 25.36
Contaminated with TCE at 100%	228.55	772.16	896.22	124.06 84.97
Contaminated with TCE at about 50%	228.53	775.40	838.11	62.71 42.95
Contaminated with TCE at about 25%	229.61	768.49	801.02	32.53 22.28
Contaminated with benzene at 100%	229.51	778.85	851.25	72.40 82.60
Contaminated with toluene at 100%	228.94	770.95	842.43	71.48 83.11
Contaminated with ethylbenzene at 100%	229.56	777.88	848.1	70.22 81.65
Contaminated with xylene at 100%	228.89	772.72	845.76	73.04 84.54
Contaminated with isooctane at 100%	228.52	781.28	838.85	57.57 83.43

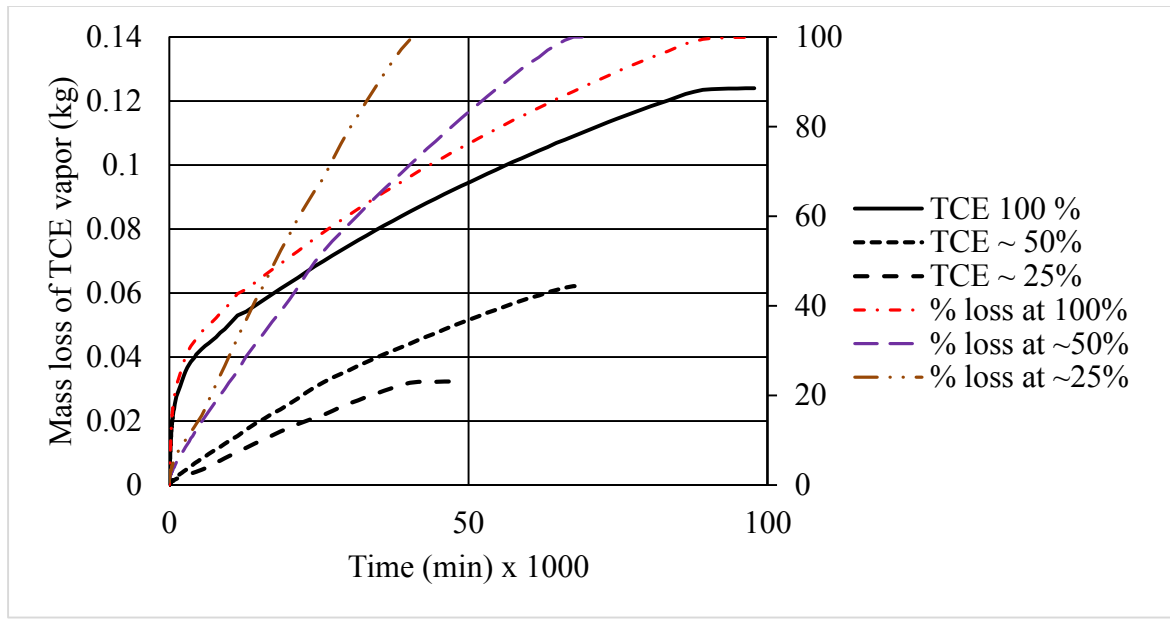
F.2. Weight of upper layer sand and chemicals used for evaporation rate tests

Sample description	Weight of empty container (g)	Weight of container + sand (g)	Weight of container + sand + chemicals (g)	Weight of chemical used (g) and volume (mL)
Contaminated with gasoline at 100%	229.46	714.47	791.1	76.63 106.43
Contaminated with gasoline at about 50%	228.8	716.70	756.12	39.42 54.75
Contaminated with gasoline at about 25%	228.47	719.11	738.50	19.39 26.93
Contaminated with TCE at 100%	228.63	696.98	859.21	162.23 111.11
Contaminated with TCE about 50%	229.17	708.13	790.59	82.46 56.48
Contaminated with TCE at about 25%	229.08	703.12	744.16	41.04 28.11



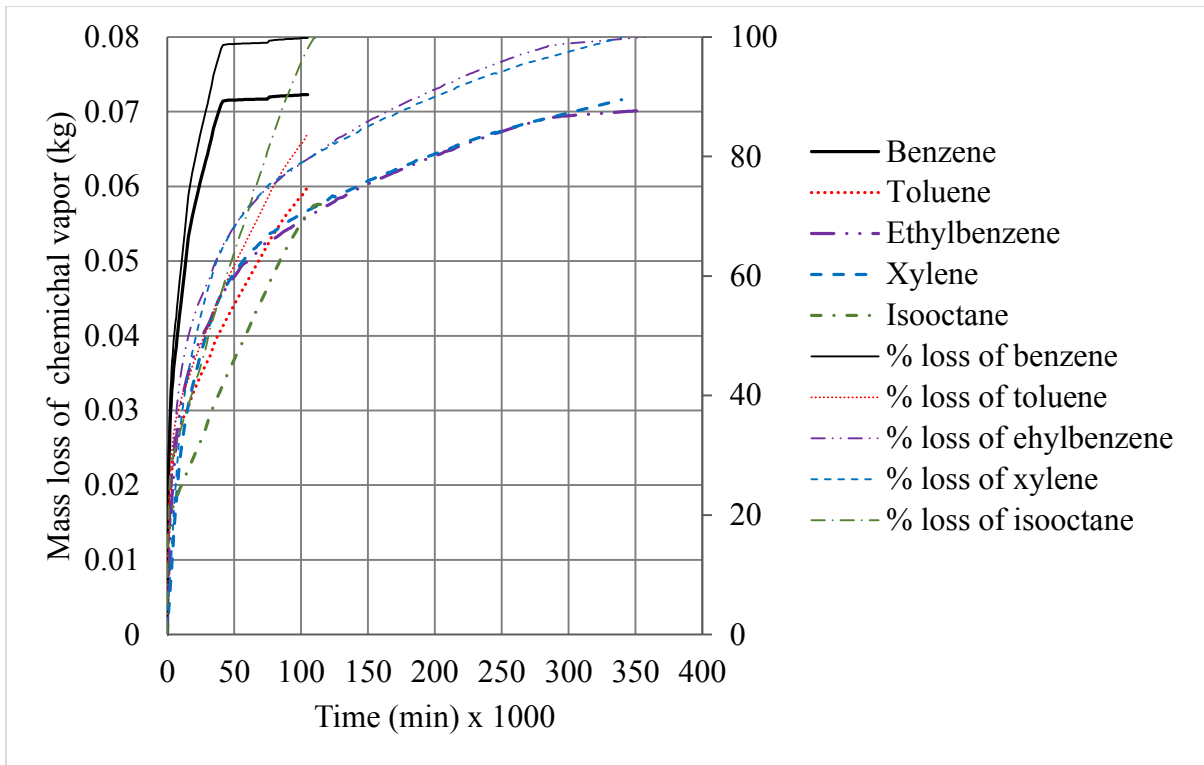
Component and saturation level (v/v)	Y	R ²
Gasoline 100%	$Y = 2 \cdot 10^{-7}x + 0.0078$	0.7849
Gasoline about 50%	$Y = 1 \cdot 10^{-7}x + 0.0033$	0.786
Gasoline about 25%	$Y = 1 \cdot 10^{-7}x + 0.0015$	0.8213

F.3. Weight loss curves during evaporation of unleaded gasoline from aquifer sand samples at about 100%, 50% and 25% saturation levels, weight of gasoline used 0.065, 0.032 and 0.018 kg respectively

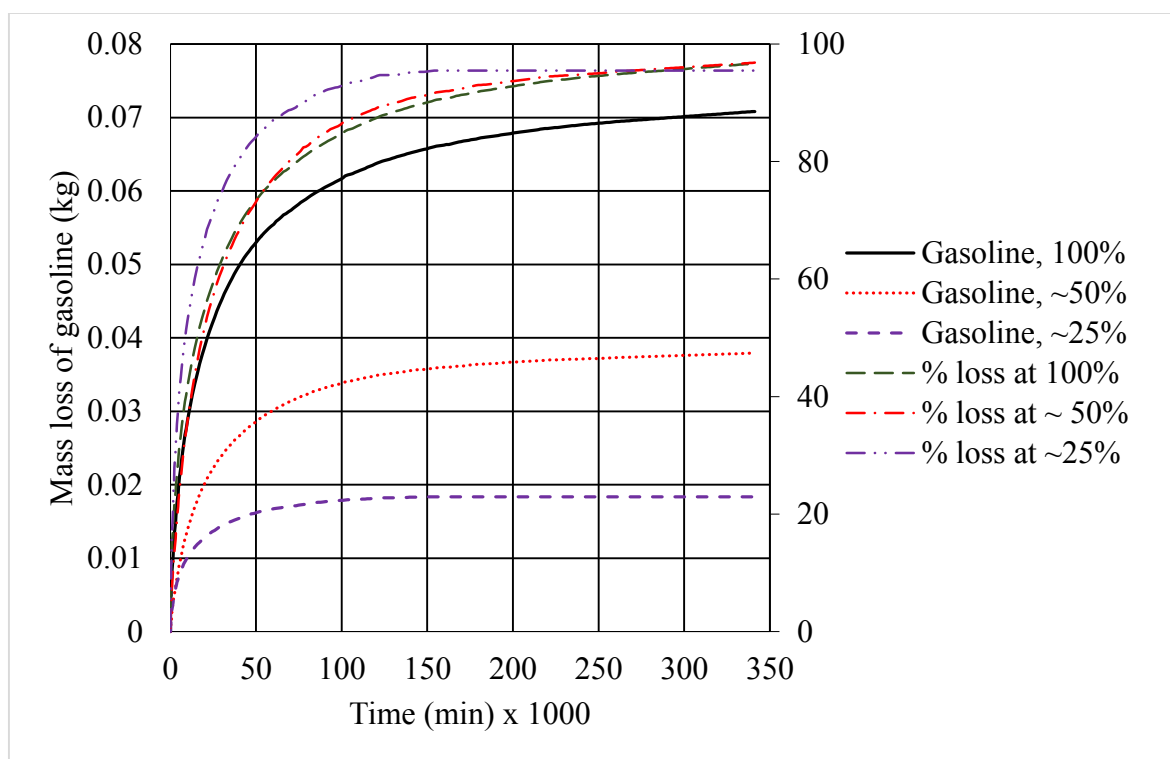


Component and saturation level (v/v)	Y	R ²
TCE 100%	$Y = 1 \cdot 10^{-6}x + 0.0146$	0.901
TCE about 50%	$Y = 1 \cdot 10^{-6}x + 0.0008$	0.99
TCE about 25%	$Y = 8 \cdot 10^{-7}x + 0.0006$	0.992

F.4. Weight loss curves during evaporation of TCE from aquifer sand samples at about 100%, 50% and 25% saturation levels, weight of TCE used 0.124, 0.063 and 0.033 kg respectively

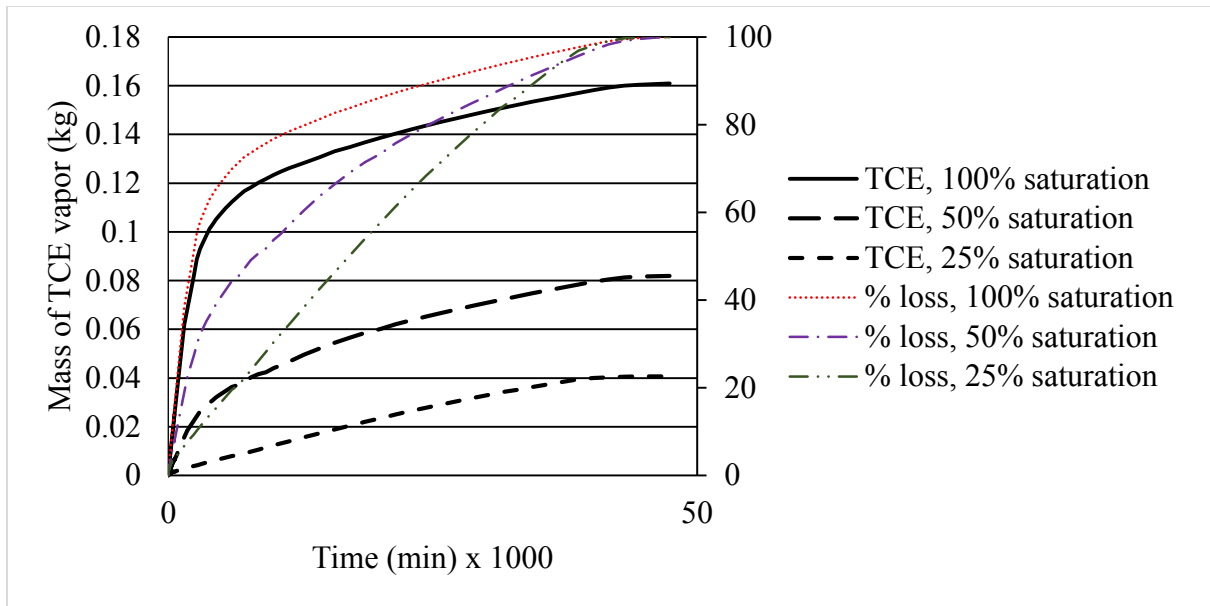


F.5. Weight loss curves during evaporation of BTEX and isooctane from aquifer sand samples at 100% saturation level, weight used is 0.072, 0.071, 0.07, 0.0734 and 0.058 kg of each one respectively



Component and saturation level (v/v)	Y	R ²
Gasoline 100%	$Y = 3 \cdot 10^{-7}x + 0.0079$	0.8168
Gasoline about 50%	$Y = 1 \cdot 10^{-7}x + 0.0032$	0.813
Gasoline about 25%	$Y = 1 \cdot 10^{-7}x + 0.0019$	0.8243

F.6. Weight loss curve during evaporation of unleaded gasoline from upper layer sand samples at about 100%, 50% and 25% saturation level, weight of gasoline used is 0.077, 0.039 and 0.019 kg respectively



Component and saturation level (v/v)	Y	R ²
TCE 100%	$Y = 4 \cdot 10^{-6}x + 0.0145$	0.7535
TCE about 50%	$Y = 2 \cdot 10^{-6}x + 0.0039$	0.9018
TCE about 25%	$Y = 1 \cdot 10^{-6}x + 0.0009$	0.9891

F.7. Weight loss curves during evaporation of TCE from upper layer sand samples at about 100%, 50% and 25% saturation levels, weight of TCE used 0.162, 0.082 and 0.041 kg respectively

F.8. Example

Determine the time and quantity in the unsaturated zone for gasoline spill of 20,000 liter in a sand layer, with hydraulic conductivity of 2 m/d; groundwater table 20 m below surface; determine the same for TCE spill.

According to the results of this study:

a) For gasoline spill

- Clean water, moving through uncontaminated layer, will reach aquifer in 10 days,

- As gasoline contaminated sand causes about 50% decrease in hydraulic conductivity that means contaminated water will reach aquifer within 20 day (about 3 weeks).
- Due to evaporation, about 41% or 8,200 liter of gasoline will be lost after one week of spill.
- Evaporation rate slows down after about 2 weeks of spill. After 36 weeks, about 95% of gasoline will be evaporated; that means 19,000 liter will be lost and 1,000 liter will remain trapped in sand grains and voids (Table F.8.1).
- Recommended remedial action is within 20 days and before wet season, because clean water infiltration through contaminated soil will carry contaminant into aquifers.

Table F.8.1 Calculated loss of gasoline in an example of sand contaminated site

Week	% loss of gasoline	Volume loss of gasoline out of 20,000 (liter)	Volume of gasoline remain in layer (liter)
1	41	8,200	11,800
2	58	11,600	8,400
3	66	13,200	6,800
4	72	14,400	5,600
5	76	15,200	4,800
6	79	15,800	4,200
7	81	16,200	3,800
36	95	19,000	1,000

b) For TCE spill

- Clean water, moving through uncontaminated layer, will reach aquifer within 10 days,

- As TCE contaminated sand causes about 60.22% decrease in hydraulic conductivity of sand that means it will be 0.79 m/d and contaminated water will reach aquifer within 25 days.
- Due to volatilization, about 40% or 8,000 liter of TCE will be lost after one week of spill. After about 10 weeks 99.92% of TCE will evaporate which means 19,984 liter will evaporate and 16 liter will be trapped in sand grains and voids (Table F.8.2).
- Although, TCE took about 2/3rd less time than gasoline to evaporate, but recommended remedial action is within 25 days and before wet season, because clean water infiltration through contaminated medium will carry TCE to aquifers.

Table F.8.2 Calculated loss of TCE in an example of sand contaminated site

Week	% loss of TCE	Volume loss of TCE out of 20,000 (liter)	Volume of TCE remain in layer (liter)
1	40	8,000	12,000
2	51	10,200	9,800
3	60	12,000	8,000
4	69	13,800	6,200
5	76	15,200	4,800
6	83	16,600	3,400
7	90	18,000	2,000
8	95.44	19,088	912
9	99.69	19,938	62
10	99.92	19,984	16

Appendix G

G. COMPACTED DENSITY AND HYDRAULIC CONDUCTIVITY

G.1. Compacted density and hydraulic conductivity of aquifer sand samples contaminated with gasoline at about 100%, 50% and 25% saturation levels

Sample number	Duration of contamination and present saturation level (v/v)	Dry density $\rho_d(\frac{g}{cm^3})$	Moist density $\rho_w(\frac{g}{cm^3})$	Hydraulic conductivity (m/day)	Percent decrease in hydraulic conductivity
Sand sample, permeant water		1.717	2.014	8.90	--
Gas-1	1 week at 100	1.716	1.982	6.73	24.38
Gas-2	2 weeks at 100	1.732	2.00	5.78	35.06
Gas-3	4 weeks at 100	1.836	2.169	4.49	49.55
Gas-10	6 weeks at 100	1.727	1.97	4.40	50.56
Gas-11	8 weeks at 100	1.725	1.924	4.75	46.63
Gas-12	16 weeks at 100	1.622	1.843	4.55	48.89
Gas-13	32 weeks at 100	1.633	1.872	4.62	48.09
Gas-20	1 week at 50	1.742	1.97	5.52	37.97
Gas-4	2 weeks at 50	1.739	1.98	5.40	39.33
Gas-5	4 weeks at 50	1.709	1.995	4.48	49.66
Gas-6	6 weeks at 50	1.652	1.929	4.65	47.75
Gas-14	8 weeks at 50	1.644	1.892	4.52	49.21
Gas-15	16 weeks at 50	1.684	1.931	4.71	47.08
Gas-16	32 weeks at 50	1.679	1.889	4.77	46.40
Gas-21	1 weeks at 25	1.695	1.958	4.68	47.42
Gas-7	2 weeks at 25	1.713	1.965	4.60	48.31
Gas-8	4 weeks at 25	1.662	1.869	4.43	50.22
Gas-9	6 weeks at 25	1.626	1.873	4.75	46.63
Gas-17	8 weeks at 25	1.613	1.83	4.55	48.88
Gas-18	16 weeks at 25	1.60	1.817	4.44	50.11
Gas-19	32 weeks at 25	1.646	1.893	4.52	49.21

G.2. Compacted density and hydraulic conductivity of aquifer sand samples contaminated with TCE at about 100%, 50% and 25% saturation levels

Sample number	Duration of contamination and present saturation level (v/v)	Dry density $\rho_d(\frac{g}{cm^3})$	Moist density $\rho_w(\frac{g}{cm^3})$	Hydraulic conductivity (m/day)	Percent decrease in hydraulic conductivity
Sand sample, permeant water		1.717	2.014	8.90	--
TCE-01	1 week at 100	1.707	1.955	6.71	24.61
TCE-02	2 weeks at 100	1.748	2.00	5.84	34.38
TCE-03	4 weeks at 100	1.746	1.996	5.73	35.62
TCE-00	6 weeks at 100	1.633	1.996	5.81	34.71
TCE-010	8 weeks at 100	1.603	1.845	5.34	40.0
TCE-011	16 weeks at 100	1.723	1.971	5.25	41.01
TCE-012	32 weeks at 100	1.725	1.952	5.32	40.22
TCE-019	1 week at 50	1.652	1.993	6.62	25.62
TCE-04	2 weeks at 50	1.719	1.966	6.47	24.27
TCE-05	4 weeks at 50	1.705	1.959	6.11	31.35
TCE-06	6 weeks at 50	1.624	1.906	6.15	30.90
TCE-013	8 weeks at 50	1.727	1.97	5.35	39.89
TCE-014	16 weeks at 50	1.702	1.943	5.28	40.67
TCE-015	32 weeks at 50	1.603	1.961	5.35	39.88
TCE-020	1 week at 25	1.692	1.963	6.10	31.46
TCE-07	2 weeks at 25	1.711	2.019	6.01	32.47
TCE-08	4 weeks at 25	1.768	2.048	6.04	32.13
TCE-09	6 weeks at 25	1.62	1.879	5.93	33.37
TCE-016	8 weeks at 25	1.652	1.87	5.63	36.74
TCE-017	16 weeks at 25	1.75	2.001	5.65	36.52
TCE-018	32 weeks at 25	1.706	1.962	5.52	37.98

G.3. Compacted density and hydraulic conductivity of upper layer sand samples contaminated with TCE, at about 100%, 50% and 25% saturation levels

Sample number	Duration of contamination and present saturation level (v/v)	Dry density $\rho_d(\frac{g}{cm^3})$	Moist density $\rho_w(\frac{g}{cm^3})$	Hydraulic conductivity (m/day)	Percent decrease in hydraulic conductivity
Sand sample, permeant water		1.537	1.9201	1.81	--
TCE-011	1 week at 100	1.575	1.912	1.31	27.62
TCE-012	2 weeks at 100	1.565	1.921	1.20	33.70
TCE-013	4 weeks at 100	1.575	1.985	0.85	53.04
TCE-020	8 weeks at 100	1.578	1.789	0.72	60.22
TCE-010	16 weeks at 100	1.566	1.918	0.80	55.80
TCE-023	32 weeks at 100	1.561	1.882	0.82	54.70
TCE-014	2 weeks at 50	1.569	1.896	0.77	57.46
TCE-015	4 weeks at 50	1.564	1.889	0.75	58.56
TCE-016	8 weeks at 50	1.556	1.877	0.76	58.01
TCE-021	16 weeks at 50	1.572	1.891	0.78	56.91
TCE-024	32 weeks at 50	1.572	1.983	0.83	54.14
TCE-017	2 weeks at 25	1.545	1.885	0.96	46.96
TCE-018	4 weeks at 25	1.574	1.904	0.88	51.38
TCE-019	8 weeks at 25	1.554	1.877	0.86	52.49
TCE-022	16 weeks at 25	1.582	1.893	0.83	54.14
TCE-025	32 weeks at 25	1.558	1.967	0.84	53.59

G.4. Compacted density and hydraulic conductivity of upper layer sand samples contaminated with gasoline, at about 100%, 50% and 25% saturation levels

Sample number	Duration of contamination and present saturation level (v/v)	Dry density $\rho_d(\frac{g}{cm^3})$	Moist density $\rho_w(\frac{g}{cm^3})$	Hydraulic conductivity (m/day)	Percent decrease in hydraulic conductivity
Sand sample, permeant water		1.537	1.92	1.81	--
Gas-001	1 week at 100	1.60	1.97	1.58	12.71
Gas-002	2 weeks at 100	1.669	2.07	1.51	16.57
Gas-003	4 weeks at 100	1.553	1.899	1.10	39.23
Gas-010	8 weeks at 100	1.632	1.894	1.12	38.12
Gas-011	16 weeks at 100	1.592	1.923	1.09	39.78
Gas-012	32 weeks at 100	1.622	1.995	1.11	38.67
Gas-004	2 weeks at 50	1.627	1.996	1.20	33.70
Gas-005	4 weeks at 50	1.57	1.896	1.02	43.65
Gas-006	8 weeks at 50	1.590	1.889	0.99	45.30
Gas-013	16 weeks at 50	1.604	1.945	0.93	48.62
Gas-014	32 weeks at 50	1.586	1.901	0.96	46.96
Gas-007	2 weeks at 25	1.612	1.987	1.37	24.31
Gas-008	4 weeks at 25	1.608	1.929	1.12	38.12
Gas-009	8 weeks at 25	1.792	2.039	1.09	39.78
Gas-015	16 weeks at 25	1.596	1.993	1.01	44.20
Gas-016	32 weeks at 25	1.565	1.876	1.06	41.44

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VITA

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Mr. Saud began his professional career in 1979 at the Iraqi Geological Survey as a geologist and worked on various hydrogeological investigation projects. He also worked as lecturer in structural geology, from 2002-2006, at the University of Baghdad, College of Engineering.

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