



Ministry for the
Environment
Manatū Mō Te Taiao

Guidelines for Assessing and Managing Petroleum Hydrocarbon Contaminated Sites in New Zealand (Revised 2011)

MODULE 2 Hydrocarbon contamination fundamentals

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2 Hydrocarbon contamination fundamentals

The purpose of this module is to provide background and understanding of the fundamental factors important to the assessment of hydrocarbon contamination.

Information is given on:

- **Petroleum handling facilities (Section 2.1)** - describing the types of sites for which these guidelines are designed to be used.
- **Petroleum hydrocarbon characteristics (Section 2.2)** - outlining the physical and chemical nature of petroleum products.
- **The subsurface environment (Section 2.3)** - giving information on the physical and chemical nature of the receiving environment (soils, rock, and groundwater).
- **Forms of hydrocarbon contamination (Section 2.4)** - describing the characteristics of each form of contaminant and the interaction between them.
- **Subsurface hydrocarbon migration (Section 2.5)** - outlining the behaviour of the hydrocarbons in the subsurface environment as exhibited in such processes as dispersion, dilution, degradation, sorption, etc.
- **Exposure effects and toxicity (Section 2.6)** - covering health and other potential effects.
- **References and further reading (Section 2.7).**

2.1 Petroleum handling facilities

The types of petroleum handling facilities, and the sources of contamination are outlined below.

2.1.1 Types of sites

These guidelines are designed help when assessing the sites which typically might give rise to hydrocarbon contamination in New Zealand. Such sites include:

- existing and former service stations
- truck stops
- airport bulk supply depots
- refueling facilities depots which service industry, farms, aerodromes, councils etc.
- oil and bulk storage terminals.

2.1.2 Sources of contamination

The types of facilities which might give rise to contamination on a site are as follows:

- underground storage tanks
- above ground storage tanks
- pumps or dispensers
- fuel lines between tanks and pumps
- fill points and lines (normally remote from the tanks)
- air vent pipelines
- waste oil tanks
- drum storage and filling areas
- stormwater interceptors.

Contamination may arise at any of the above facilities depending on their age, type of construction and method of operation, for example, through:

- corrosion or stress of metal parts
- improper installation
- overfilling of tanks
- poor maintenance of drainage systems
- surface spillage.

Depending on the facility, the contamination may result from a slow leak over time or a fast release (spill). The spill or leak may occur at or near the surface, or at depth.

2.2 Petroleum hydrocarbon characteristics

This section discusses in detail the physical and chemical properties and characteristics of petroleum products and common petroleum hydrocarbon compounds. A knowledge of these general properties is useful when performing a site assessment, as it will lead on to an understanding of petroleum hydrocarbon compound behaviour in the environment.

Petroleum is a liquid mixture of thousands of different substances, most of them hydrocarbons, formed from the decomposition of marine plants and animals and transformation resulting from heat and pressure changes beneath the earth's surface. The chemical composition and physical properties of crude and refined petroleum vary significantly depending on the location of origin and, for the refined products, on the nature of the refining processes.

The composition and properties of individual hydrocarbon compounds and of blends, directly affect changes in phase state (solubilisation, volatilisation, photochemical and microbial oxidation), migration behaviour (dispersion, dilution, sorption, etc.), and impact on receptors (surface coating, biological toxicities) following a release. It is therefore necessary to understand the behaviour of both the individual hydrocarbon compounds and the blends.

Hydrocarbons are often described by the number of carbon atoms in their molecules, e.g. methane is C₁ because it has one carbon atom. The chemical structure of some of the more common or significant constituents of petroleum are depicted in Figure 2.1. As indicated in Figure 2.1, petroleum hydrocarbons are categorised as aliphatic or aromatic depending on the arrangement of the hydrocarbon molecules. Aliphatic hydrocarbons are arranged in a straight chain and aromatic hydrocarbons are arranged in a six-sided ring. Aromatic hydrocarbons are further categorised depending on the number of rings. Monocyclic aromatic hydrocarbons (MAHs) consist of one ring. The significant MAH constituents of petroleum include benzene, toluene, ethylbenzene and xylenes (BTEX). Dicyclic hydrocarbons are comprised of two rings and polycyclic aromatic hydrocarbons (PAHs) are comprised of more than two rings.

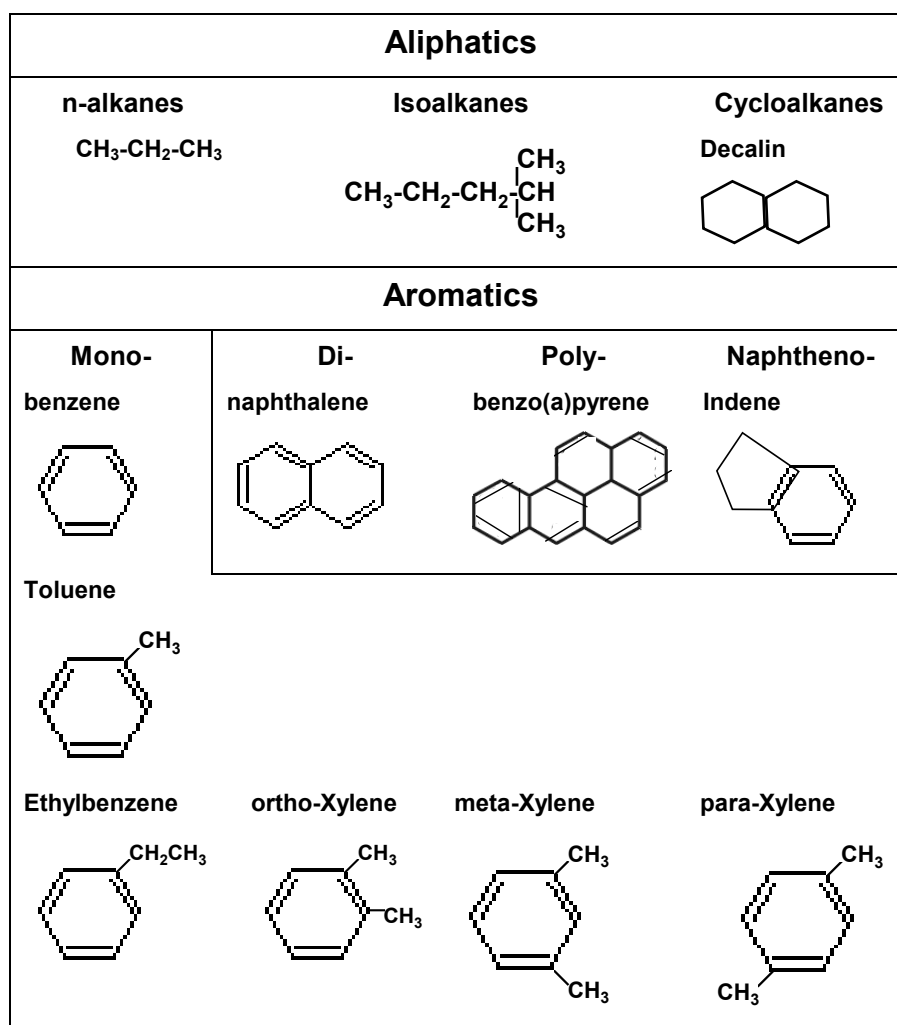


Figure 2.1 Chemical structures of selected hydrocarbons

The range of molecules in various petroleum products is summarised in Table 2.1. The petroleum products with a range of molecules that include C₆ and greater (i.e. petrol, kerosene, etc.) are comprised of both aliphatic and aromatic hydrocarbons.

Table 2.1 Characteristics of some common petroleum products

Product	Average specific gravity	Primary range of molecules	Entire range of molecules
Natural gas	(vapour)	C ₁ to C ₂	C ₁ to C ₄
Propane	(vapour)	C ₃	C ₃ to C ₄
Petrol	0.75	C ₅ to C ₁₂	C ₄ to C ₁₄
Kerosene	0.79	C ₁₀ to C ₁₆	C ₆ to C ₁₈
Jet fuels	0.80	C ₁₂ to C ₁₆	C ₆ to C ₂₀
Diesel fuel	0.85	C ₁₀ to C ₂₀	C ₆ to C ₂₅
Lubricating oil	0.90	C ₂₀ to C ₃₀	C ₁₂ to C ₃₀₊
Heavy fuel oil	0.96	C ₂₀ to C ₃₀	C ₁₅ to C ₃₀₊

Section 2.2.1 provides a description of how crude is converted to refined products such as petrol, kerosene, diesel oils, etc., and presents the physical and chemical properties of the refined products. The physical and chemical properties of individual hydrocarbon compounds are discussed in Section 2.2.2.

2.2.1 General properties of petroleum products

Crude oil is converted by physical and chemical processes into a wide range of refined products including petrol, kerosene, heating oils, diesel oils, lubricating oils, waxes and asphalts. The various physical and chemical processes used in refining fall into two broad categories: separation processes which separate the complex mixture into various fractions, and conversion processes which alter the molecular structure of the hydrocarbon components themselves. In refined products, the major hydrocarbons are alkanes, naphthenes, aromatic compounds and alkenes.

Distillation is the fundamental process involved in refining petroleum. Practically all crude oil that enters a refinery undergoes distillation where it is heated to temperatures as high as 425°C and is separated into fractions. Each fraction contains a mixture of hydrocarbons that boil within a particular range. Processing generates both petroleum products made up of blends of hundreds of compounds, and pure compounds (petrochemicals), such as butane and benzene. The following are the common names associated with several of these fractions along with their predominant uses:

1. Gases boiling below 20°C are taken off at the top of the distillation column. This fraction consists of low molecular weight hydrocarbons, mainly propane, butane, and 2-methylpropane. These three hydrocarbons can be liquefied under pressure at room temperatures. The liquefied mixture is known as liquefied petroleum gas (LPG).
2. Naphthas are mixtures of C₄ to C₁₀ alkanes and cycloalkanes which have boiling points between 20°C and 220°C. The naphthas also contain some aromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylenes. The light fraction, with boiling points of 20°C to 150°C, is the source of straight-run petrol and on average makes up about 25% of crude petroleum.
3. Kerosene is a mixture of C₉ to C₁₅ hydrocarbons with boiling points of 140 - 300°C.
4. Gas oil has a boiling point range of 190 - 400°C and is a mixture of C₁₅ to C₂₅ hydrocarbons. Diesel is obtained from this fraction.
5. Lubricating oil and heavy fuel oil distill at temperatures over 320°C and are primarily a mixture of C₉ to C₃₀ hydrocarbons.

6. Bitumen (asphalt in the US) is the black tarry residue that remains after the removal of the other fractions.

Petrols, middle distillates, heavy fuel and lube oils, and bitumen are discussed in more detail below.

2.2.1.1 Petrols

Petrols and finishing oils are blends of petroleum hydrocarbons and additives that improve fuel performance, engine life and product identification. The automotive petrols (unleaded and leaded super, unleaded regular) and aviation petrols are part of this group. These fuels can contain more than 250 different compounds. The composition varies due to the crude oil source, refining processes, reformulation, seasonal variations, mixing during transport, and the types of additives used. The main hydrocarbon components in petrols are C₄ to C₁₀ aliphatics (e.g. pentane, hexane, and octane), short-branched chain alkanes, cycloalkanes, and aromatics (e.g. BTEX). In general, petrol is a mixture of chemicals with boiling points lower than 215°C. Table 2.2 lists some of the main constituents on a percent by volume basis for New Zealand petrols. The BTEX constituents present in a New Zealand petrol are shown in Table 2.3.

Table 2.2 Main constituents of New Zealand petrols

Constituent	96 Octane (% w/v)	91 Octane (% w/v)
Mono aromatics	42.5	39.1
Polyaromatics	0.2	0.15
Alkanes	43.8	48.7
Olefins	3.4	3.8
Cyclic aliphatics	10.2	11.3

% w/v = percent weight by volume

Table 2.3 BTEX constituents in a New Zealand petrol

Constituent	96 Octane (% w/v)	91 Octane (% w/v)
Benzene	3.3	2.3
Toluene	12.2	9.9
Ethylbenzene	2.1	1.4
Xylenes	12.2	10.2

% w/v = percent weight by volume

Several additives have been used to improve the performance of petrols. Until recently, lead alkyl compounds were added to petrol to produce anti-knock properties as measured by the octane rating of the petrol. However, lead left deposits in engines, so lead scavengers were then added to petrols to flush out the lead. Lead occurs naturally in the subsurface and it should be used cautiously as an indicator.

The organic lead added to petrol in New Zealand contains tetramethyl lead. Petrol imported in an already refined ready-to-use state may contain both tetramethyl lead (TML) and tetraethyl lead (TEL). Both TML and TEL are fat-soluble compounds, which cause intoxication not only by inhalation but also by absorption through the skin. These alkyl compounds are highly toxic. When exposed to sunlight or allowed to evaporate they decompose to trimethyl or triethyl lead salts, which are also poisonous compounds, and ultimately, within a few hours, to inorganic lead oxides.

2.2.1.2 Middle distillates

The middle range distillate group includes diesel, kerosene, jet fuel and lighter fuel oils. These products may contain more than 500 different compounds; however, these compounds tend to be more dense, less volatile, less water soluble, and less mobile than the compounds in the petrol boiling range. The middle distillates also contain less of the lighter-end aromatics such as BTEX. Benzene is present at concentrations in the order of 0.5% by weight.

Kerosene is a mixture of C₉ to C₁₅ hydrocarbons. Diesel is obtained from the gas oil fraction and is a mixture of primarily C₉ to C₂₅ hydrocarbons. Diesel is composed mainly of straight chain alkanes with a flash point between 43 - 88 °C. Diesel fuel contaminated soils are not expected to contain high concentrations of aromatics such as BTEX. Typically, with older releases, BTEX constituents will have degraded or dispersed to leave very low, or possibly undetectable concentrations.

2.2.1.3 Heavy fuel and lube oils

The heavier fuel oils and lubricants are similar to the middle distillates in their types of hydrocarbon structure. They distill at temperatures over 320°C, are relatively viscous, relatively insoluble in groundwater, and have low mobility in the subsurface.

2.2.1.4 Bitumen

Bitumen is the black tarry residue that remains after the removal of the other fractions from the distillation process. It contains long chain and polycyclic hydrocarbon structures of predominantly C₂₅ or higher and with molecular weights generally around 500 - 600. Bitumen is quite stable and immobile and has been used overseas to encapsulate hazardous wastes. Bitumen does contain polynuclear aromatic hydrocarbons (PAHs), but these are generally bound up by the polycyclic and long chain aliphatics and hence are generally not available (i.e. readily released to the environment).

2.2.1.6 Chromatograms

A chromatogram is the end product of an analytical process in which the components of a mixture are separated from one another and are then sequentially detected over a period of time. In the case of TPH analysis, the order in which the components are detected is directly reflected in the order of their boiling points. The chromatogram ideally displays the presence of each component as an isolated peak, starting with the lowest boiling component on the left immediately after the large solvent peak (solvent is used in the extraction process prior to analyses). In reality, most semi-refined petroleum products contain such a large number of hydrocarbon components that full separation is not practicable. Thus, the chromatogram essentially features a series of peaks and/or mounds with progression along a horizontal axis. These peaks may be fully separated (resolved), or partially overlapping (merged), or when a very large number of components is present a mound is the dominant feature (unresolved). Although the horizontal axis will be displayed in units of decreasing time with progression to the right, it is better considered as indicating increasing boiling point.

For reference, four typical chromatograms are included in Figure 2.2. These plots are of fresh petrol, kerosene, diesel and lubricating oil products. Product aging will change chromatograms to a point where they are unrecognisable as the original product plot (Figure 2.3). The lighter end hydrocarbon molecules in the C₆ to C₉ range will have dispersed or degraded, transforming the appearance of the plot. Hence great care must be taken when trying to identify a product from its chromatogram, particularly when the product is aged or product mixtures may be present. The aging rate varies greatly with site-specific conditions.

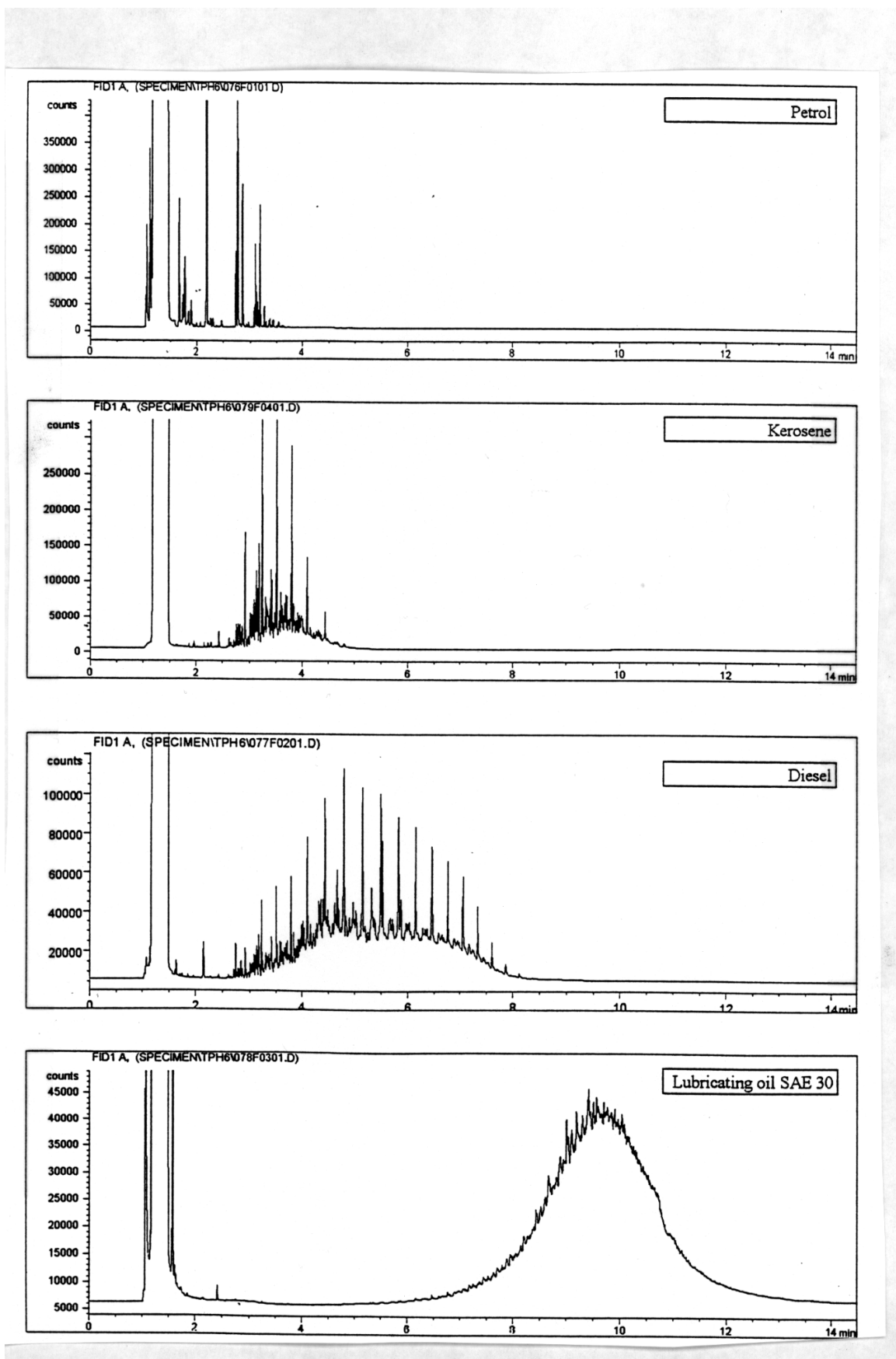


Figure 2.2 Specimen chromatograms
(courtesy of Allan Aspell and Associates)

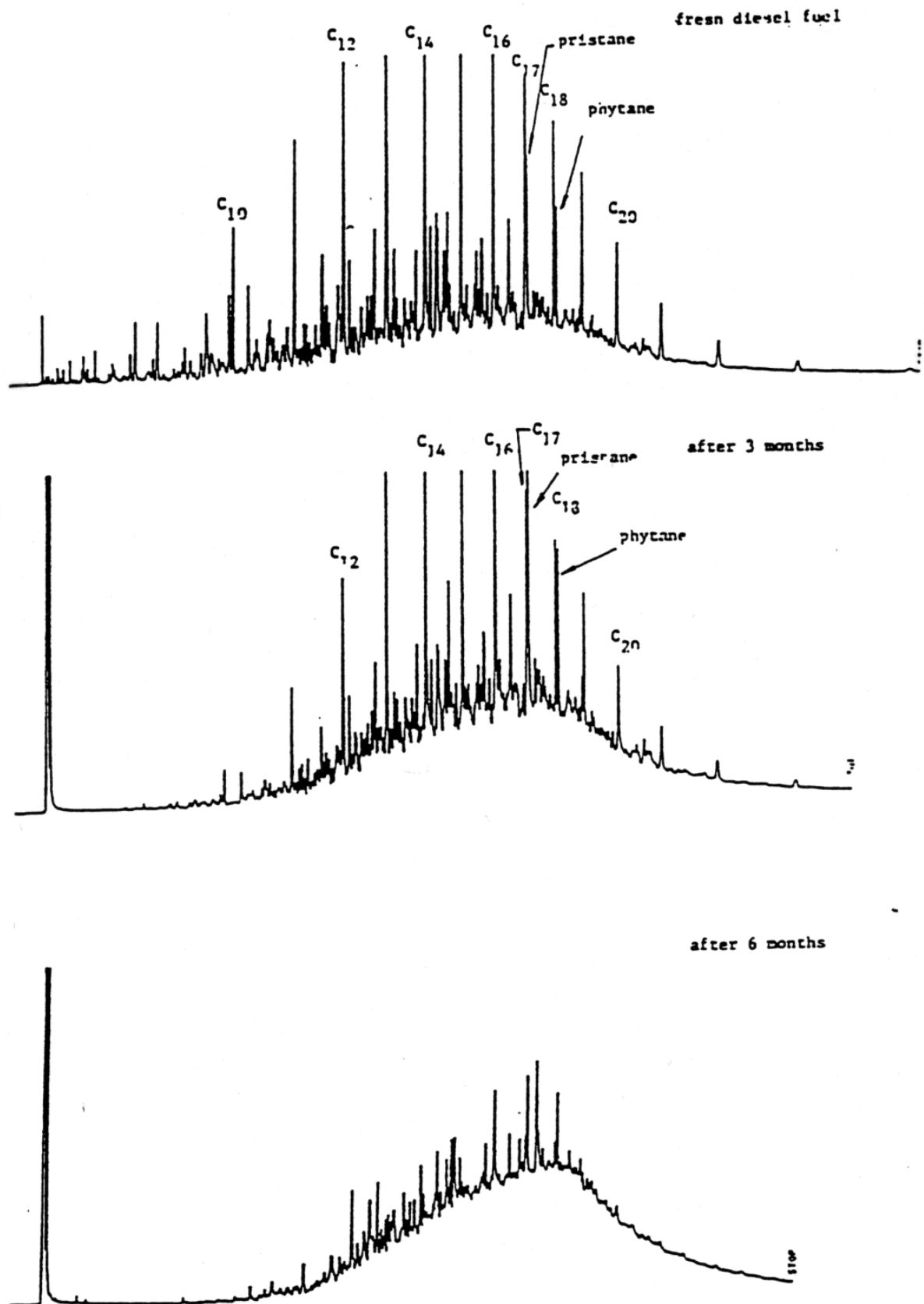


Figure 2.3 Specimen gas chromatograms of fresh and weathered diesel showing changes in n-alkane to isoprenoid ratio and emergence of the "hump".

(courtesy of Allan Aspell and Associates)

2.2.2 Physical and chemical properties of hydrocarbons

The molecular weight, density, solubility, boiling point, and vapour pressure for several of the individual hydrocarbon compounds in petrol, diesel and fuel oils are presented in Table 2.4.

Table 2.4 Physical and chemical properties of selected hydrocarbons

Constituent	Molecular weight	Density relative to water (specific gravity)	Solubility ^a in water, ppm (at °C)	Boiling point, °C	Vapour pressure, mm of Hg at 1atm and (at °C)
Pentane	72.15	0.626	360 (16)	36	430 (20)
Hexane	86.17	0.66	13 (20)	68.7	120 (20)
Decane	142.28	0.73	0.009 (20)	173	2.7 (20)
Cyclopropane	42.08	0.72	37,000	-33	760 (-33)
Cyclopentane	70.14	0.751	<1,000	-	200 (13.8)
Cyclohexane	84.16	0.779	55 (20)	81	77 (20)
Benzene	78.11	0.878	1,780 (20)	80.1	76 (20)
Toluene	92.10	0.867	515 (20)	110.8	22 (20)
ortho-Xylene	106.17	0.86	175 (20)	144.4	5 (20)
meta-Xylene	106.17	0.86	175 (20)	139	6 (20)
para-Xylene	106.17	0.86	175 (25)	138.4	6.5 (20)

Source: Nyer, 1993

a solubility in mixture is lower than pure solubility in water
ppm parts per million

Characteristic property trends within and between the main hydrocarbon compound groups associated with petroleum are listed below:

- Alkanes and aromatics are non-polar compounds and have only limited solubility in water.
- The number of carbon atoms in a compound can greatly affect its properties. Alkane chains up to 17 carbons long are liquids and have densities less than that of water at around 20°C (ambient temperatures), whereas alkane chains 18 or more carbons long are solids at room temperature.
- Alkane solubility and vapour pressures decrease and boiling points increase with an increase in the number of carbon atoms present in the compound.
- The higher the vapour pressure, the more easily the compound is volatilised.
- The cycloalkanes are similar to straight or branched chain alkanes in properties. Densities are less than that of water, solubilities and vapour pressures decrease with an increase in the carbon number and the boiling point temperatures increase.
- The simplest PAH, naphthalene, has a water solubility of 30 mg/L. Solubility decreases with increasing molecular weight of the PAH.

In general, the viscosity of a petroleum product increases as the density increases and the mobility in the subsurface decreases.

Solubility values for particular hydrocarbon compounds are given in Table 2.4. However this data can be misleading because the water solubility of a specific compound as part of a blend tends to be significantly less than the solubility of the pure compound in water. For example, benzene solubilised from petrol can be found at 5% of the pure component solubility toluene at 15% and xylenes at 10%.

2.3 The subsurface environment

This section provides an understanding of the properties and interactions between the various subterranean materials and structures which is required to assess contamination distribution and management options.

The subsurface is a dynamic environment containing various material states (solid, liquid, gaseous) and living organisms (animals, plants, micro-organisms). Structures of human origin such as tunnels, service trenches, building basements and foundations may also be present at a site.

2.3.1 Geological material characteristics

There is a great variation in soil and rock types, which can significantly affect the movement of contaminants in the ground. The various classification systems and definitions are given below.

2.3.1.1 Material types

There are a number of classification systems describing geological material types in use, including geological, engineering and soil conservation. Terms such as soil and rock have specific and sometimes different meanings in each of these systems. In this document, the engineering (geomechanical) classification system, the most widely used, is adopted (NZGS, 1988).

The geological materials that potentially can be exposed to contamination by subsurface petroleum hydrocarbon releases generally fall into two broad categories, soil and rock materials. These are defined here (following geomechanical and engineering terminology) as:

Soil

Sediments or other unconsolidated accumulations of soil particles that can usually be separated by gentle mechanical means.

Rock

A firm or consolidated naturally occurring aggregate of soil particles and/or minerals connected by strong bonds. The term implies a formation which is in situ.

Under this definition soils include:

Unconsolidated sediments

Loose materials resulting from the weathering and erosion of rock. The material may have traveled great distances to reach its current location through wind, water, ice, and gravitational forces. The individual sediment particles may vary in size from the very large (boulders, metres in diameter) to the very small (microscopic). Some volcanic deposits, such as pyroclastic materials (ash, lapilli) fall within this grouping.

Fill

Fill is any material used to backfill an excavation or low lying area, or raise the level of an area above its natural level. Fill material is deposited by human rather than natural forces. Fill can consist of boulders, gravels, sands, silts, clays, or demolition materials such as bricks, concrete and timber.

Subsoil

The subsoil is the boundary zone between soil and bedrock, and may exhibit properties of both.

The particle size ranges of the various soil types in New Zealand (geomechanical protocol) are given in Table 2.5.

Table 2.5 Soil particle size ranges

Soil Fraction	Particle Size Range (mm)
Clay	< 0.002
Silt	0.002 - 0.06
Sand fine	0.06 - 0.2
Sand medium	0.2 - 0.6
Sand coarse	0.6 - 2.0
Gravel fine	2.0 - 6.0
Gravel medium	6.0 - 20.0
Gravel coarse	20.0 - 60.0
Gravel very coarse	60.0 - 200.0
Boulders	> 200.0

Source: NZGS, 1988

Rock material includes:

- sedimentary rocks that have been hardened by natural cementation (shale, limestone, sandstone)
- igneous rocks that have crystallised from a molten state (basalt, granite)
- metamorphic rocks that have recrystallised under extreme pressures and temperatures (slate, gneiss, marble).

Information on local ground conditions can be obtained by reference to regional councils, New Zealand geological maps, soil maps, local drillers, and experienced consultants.

2.3.1.2 Liquid and vapour conducting properties

The two key physical properties of geological materials that affect the migration of liquids through them are effective porosity and hydraulic conductivity. In assessing the fate and transport of contaminants it is important to have an understanding of these concepts.

Porosity

The open spaces between particles or within the structures of geological material formations are called pores. Porosity, or total porosity, is the ratio of the volume of all the pores (or void spaces) in a material or formation (including unconnected pore spaces) to the total volume of the material or formation. Porosity is expressed as a percentage and is affected by such parameters as grain size and shape, and the way in which the various materials are put together. Figure 2.4 shows typical types of porosity associated with different rocks

Two types of porosity are defined reflecting the way in which the pores were formed:

- Pores formed during the original deposition of the materials create primary porosity (interstitial pores, Figure 2.4, a to d)
- Pores formed after the creation of the deposit or formation create secondary porosity (fractures, joints, faults, solution channels; Figure 2.4, a e and f). The porosity of bedrock is usually low, but near the surface geological processes tend to create fractures which create a secondary porosity through which fluids can flow. Dissolution of rock material by groundwater can also create secondary porosity, such as the development of cave systems in limestone.

Porosity can range from near zero to higher than 60%. The higher values are found in recently deposited sediments, whereas the lower values are encountered in dense crystalline rocks or highly compacted soft rocks such as shales.

The porosity of deposits consisting of well rounded particles of equal size will be greater than the porosity of deposits containing well rounded or angular particles of different sizes. Small grain sizes fill the gaps between the larger particles and take up more of the space between particles. Generally the wider the range of grain sizes, the lower the porosity.

The shape of grains also affects the porosity. Spherical grains flow more freely and pack together more tightly than other shapes such as plates or rods where bridging between particles can occur. Clays, for example, are composed of many different particle shapes and do not tend to pack together very well. Hence clay soils tend to have high total porosities.

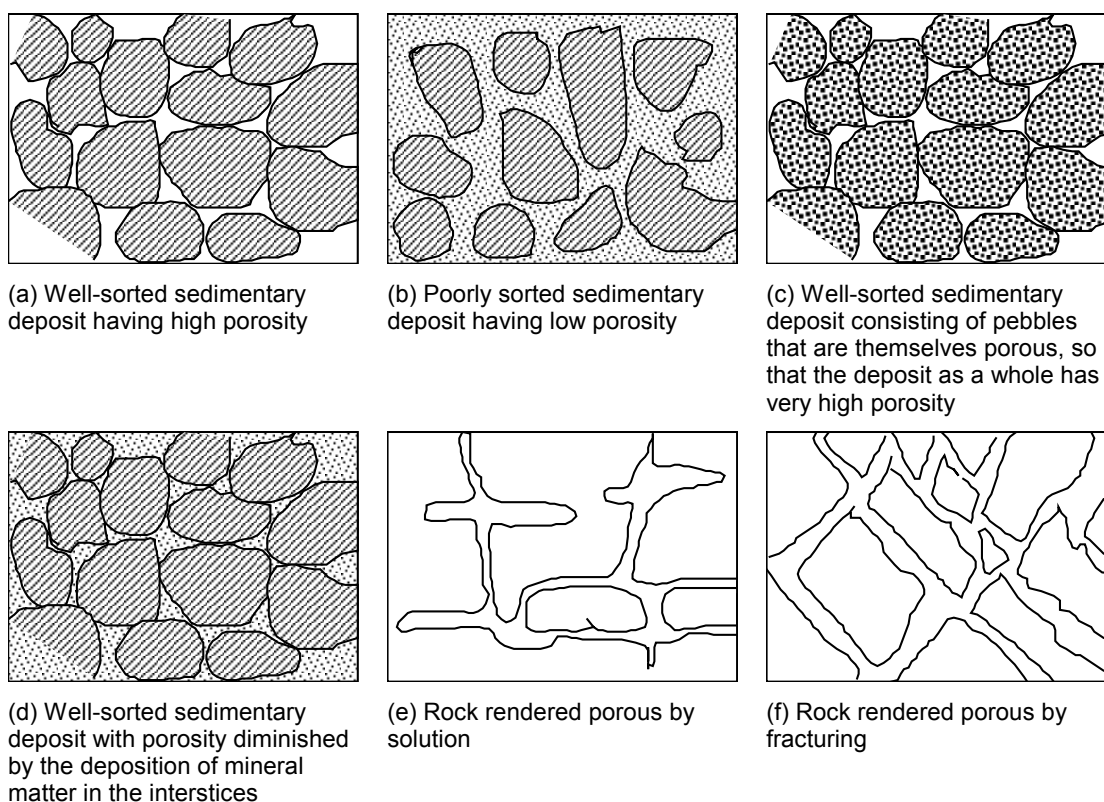


Figure 2.4 Relationship between texture and porosity

Source: Domenico and Schwartz, 1990

As a guide, general ranges of porosities for given soil types are given below in Table 2.6.

Table 2.6 Typical soil porosity values

Material	Typical Porosity Values %
SOILS	
Gravel, coarse	24 - 36
Gravel, fine	25 - 38
Sand, coarse	31 - 46
Sand, fine	26 - 53
Silt	34 - 61
Clay	34 - 60
SEDIMENTARY ROCKS	
Sandstone	5 - 30
Siltstone	21 - 41
Limestone, dolomite	0 - 20
Karst limestone	5 - 50
Shale	0 - 10
CRYSTALLINE ROCKS	
Fractured crystalline rocks	0 - 10
Dense crystalline rocks	0 - 5
Basalt	3 - 35
Weathered granite	34 - 57
Weathered gabbro	42 - 45

Source: Domenico and Schwartz, 1990

In examining the liquid conducting potential of a geological material, it is necessary to know what volume of the pore space can allow the transmission of a liquid. Effective porosity is defined as the ratio of the volume of *interconnected* pores (or void spaces) in a material or formation to the total volume of the material or formation. Although it can be difficult to measure, effective porosity is the property of greatest interest in contaminant fate and transport modeling.

Effective porosity is a measure of connectivity through the solid medium and is more closely related to hydraulic conductivity than is total porosity. Many rocks have a high total porosity, but most of this pore space is unconnected, e.g. vesicular basalt. Similarly, clays have high total porosities but have smaller intergranular voids and hence have lower effective porosities than coarser grained materials. Examples of materials with differing total and effective porosities are given below.

Table 2.7 Variation in total and effective porosity

Material	Total porosity %	Effective porosity %
Clay	34 - 60	1 - 18
Chalk	2 - 20	0.05 - 0.5
Limestone, dolomite	0 - 20	0.1 - 5
Sandstone	5 - 30	0.5 - 10
Shale	0 - 10	0.5 - 5
Granite	0.1	0.0005

Sources: Domenico and Schwartz, 1990; API 1996

Permeability and Hydraulic Conductivity

Permeability is a measure of the ability of a geologic formation to transmit any fluid. The term is used in the petroleum industry where the fluids of interest are oil, gas and water.

Hydraulic conductivity is also a measure of the ability of a geologic formation to transmit (conduct) a fluid, but is dependent on the type of fluid. For example, water has a higher hydraulic conductivity than more viscous fluids such as crude oil or diesel.

Permeability and hydraulic conductivity are frequently used interchangeably, but hydraulic conductivity is the more appropriate technical term in the context of this document.

Permeability is commonly used as a qualitative term describing the ease with which a fluid can move through a geologic formation.

As can be seen in Table 2.8, hydraulic conductivities for different materials can range over about 12 orders of magnitude, with the lowest values being in unfractured igneous and metamorphic rocks and the highest values being in gravels, karstic or reef limestones, and permeable basalts. In general, a hydraulic conductivity of approximately 1×10^{-9} m/sec or less is considered a material of low permeability. Materials included in this group are clay, chalk, till, shale, and unfractured igneous and metamorphic rock. If these rocks or sedimentary deposits are fractured, then significant secondary porosity exists, and the conductivity can rise above this defining limit by up to three orders of magnitude. Hydraulic conductivities of fractured geologic materials are typically greater than for materials having intergranular pores, but significant overlap in values is possible.

Table 2.8 Hydraulic conductivities

Material	Hydraulic Conductivity (m/sec)
SOILS	
Gravel	3×10^{-4} - 3×10^{-2}
Coarse sand	9×10^{-7} - 6×10^{-3}
Medium sand	9×10^{-7} - 5×10^{-4}
Fine sand	2×10^{-7} - 2×10^{-4}
Silt, loess	1×10^{-9} - 2×10^{-5}
Till	1×10^{-12} - 2×10^{-6}
Clay	1×10^{-11} - 4.7×10^{-9}
Unweathered marine clay	8×10^{-13} - 2×10^{-9}
SEDIMENTARY ROCKS	
Karst and reef limestone	1×10^{-6} - 2×10^{-2}
Limestone, dolomite	1×10^{-9} - 6×10^{-6}
Sandstone	3×10^{-10} - 6×10^{-6}
Siltstone	1×10^{-11} - 1.4×10^{-8}
Shale	1×10^{-13} - 2×10^{-9}
CRYSTALLINE ROCKS	
Permeable basalt	4×10^{-7} - 2×10^{-2}
Fractured igneous and metamorphic	8×10^{-9} - 3×10^{-4}
Weathered granite	3.3×10^{-6} - 5.2×10^{-5}
Weathered gabbro	5.5×10^{-7} - 3.8×10^{-6}
Basalt	2×10^{-11} - 4.2×10^{-7}
Unfractured igneous and metamorphic	3×10^{-14} - 2×10^{-10}

Source: Domenico and Schwartz, 1990

2.3.2 Subsurface water characteristics

The basic concepts which give an understanding of the types of groundwater and their behaviour are outlined in this section. In general, before the introduction of any contaminant materials such as petroleum hydrocarbons, into the subsurface environment, the pore spaces in the subsurface are filled with air, water and other minor liquid and gaseous components. (There are of course areas where

natural contamination of the pore spaces by other types of fluid will occur, such as in the case of natural petroleum hydrocarbon gas or liquid deposits and seeps, or near surface geothermal activity.)

Fluids in the subsurface are present in two forms: within pore spaces (interstitial water) and in chemical combination with rock.

The subsurface fluids in the pore spaces can be characterised according to their vertical distribution as defined below.

2.3.2.1 The vertical distribution of subsurface water and air

The vertical distribution of subsurface water and air is important in understanding liquid contaminant and vapour migration.

The vertical distribution of fluids is generally described in terms of a water profile (see Figure 2.5). The divisions in this profile are as follows:

Unsaturated zone

Unsaturated and saturated refer to the degree with which the pore spaces are saturated with water. A degree of saturation less than 100% indicates that air is present in some of the voids. The unsaturated zone is also known as the zone of aeration, and the vadose zone. In the unsaturated zone the pores are not completely filled with water (air is present), all fluids are under negative pressure, and water is held back by capillary forces. The unsaturated zone contains partially water-saturated pores, fully water-saturated pores, and air filled pores. Water moves downward due to gravity, and outwards and upwards due to capillary forces. Soil gases can move in all directions.

Soil gases are vapours which accumulate in the pore spaces. In this context they are the volatile fractions of the petroleum product. The movement of vapours is primarily driven by concentration gradients and diffusion.

Water in the unsaturated zone is defined by the forces influencing it. Gravitational water drains down through the zone due to the force of gravity, hygroscopic (adsorbed water) water remains adsorbed to the surface of soil particles, vadose water moves upward due to transpiration, and capillary water moves under the influence of surface tension forces.

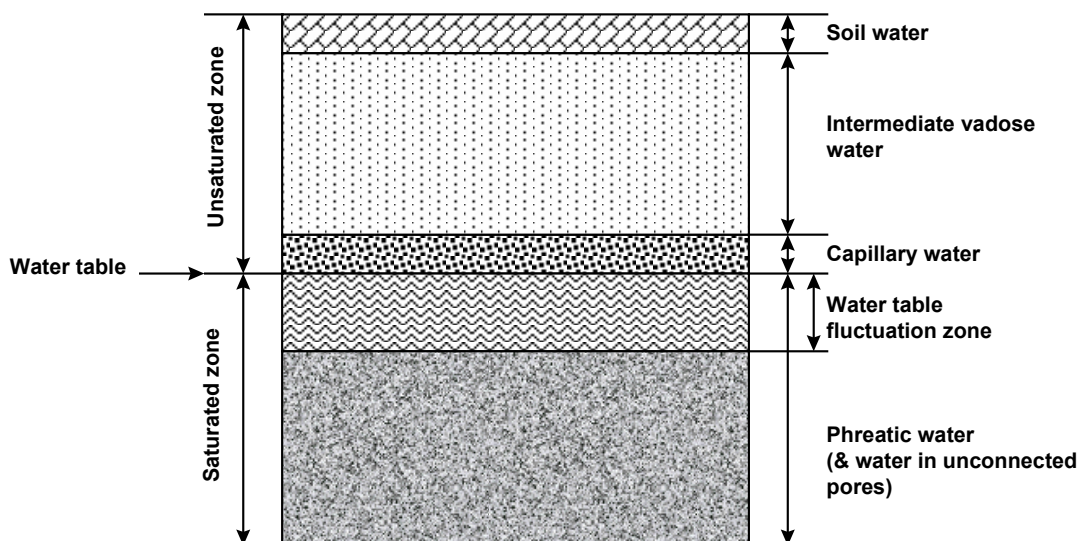


Figure 2.5 The water profile
After Domenico and Schwartz, 1990

The unsaturated zone is broken up into three sub-zones: soil water, intermediate vadose zone and the capillary zone:

The **soil water zone** varies with soil and vegetation types, extending from the ground surface down to the bottom of the major root zone. The amount of water in this zone depends on the amount of recent rainfall and infiltration. Parts of this zone can reach a near saturated state immediately following rainfall, while the intermediate vadose zone below remains unsaturated.

The **intermediate vadose zone** extends from the soil water zone down to the capillary fringe and contains water in the form of thin films adhering to pore linings. The zone can vary in thickness from being non-existent in areas of high water table and high precipitation to more than a hundred metres thick in arid regions.

The **capillary zone or fringe** extends from the water table up to the limit of capillary rise. It varies inversely with pore size and proportionally to surface tension. Capillarity comes about through the combination of the surface tension of the liquid and the ability of certain liquids to wet the surfaces they come in contact with. Capillary rise can range from 2.5 cm for a fine gravel to greater than 200 cm for silt. Just above the water table, nearly all the pores contain capillary water. The water content decreases with an increase in elevation depending on the soil type, and the air filled porosity increases as the water content decreases.

The **water table** lies at the boundary between the unsaturated and saturated zones. Water above the water table is below atmospheric pressure, whereas the water below the water table is at pressure greater than atmospheric. The water table is the water surface below ground at which the pressure is exactly equal to atmospheric pressure, and is the level to which water will rise in a well drilled into the saturated zone. The water table elevation fluctuates naturally throughout the year with changes in recharge and discharge patterns (e.g. seasonal trends, large rainfall).

Saturated zone

In the saturated zone (also known as the phreatic zone) the pores are generally full of water, although some pores may contain air that has become trapped by soil particles or beneath impermeable layers. The water is at a pressure greater than atmospheric. The saturated zone extends from the water table down to the bottom of the groundwater flow system. Here water is present as phreatic (groundwater) water, which is contained within connected pores, and hence is able to move or flow, and within unconnected pores.

2.3.2.2 Groundwater movement

Groundwater movement is the primary method by which liquid hydrocarbon contaminants migrate or are distributed outwards from the source. Groundwater is one component of the hydrologic cycle depicted in Figure 2.7. Groundwater is the water in the saturated zone which is able to flow. The velocity at which groundwater will travel through the saturated zone is dependent on the properties of geologic material such as hydraulic conductivity and porosity, and the hydraulic gradient. The main sources of groundwater in an area are from local precipitation and infiltration, or from underground flow from a recharge area. The recharge area may be an area of high precipitation or part of a river system which is itself delivering water from another remote area of precipitation.

Water from precipitation or overland flow enters the groundwater system in an area of recharge through infiltration and flows down-gradient under gravity to a discharge area such as a river, spring or abstraction well (see Figure 2.7).

The water table is a continuous surface that slopes downwards from the recharge area to the discharge area.

In general, shallow water tables will follow the fall of local surface topography. The elevation of the water table will naturally fluctuate following seasonal trends in recharge and discharge patterns as part of the hydrologic cycle under the influence of such actions as evaporation, evapotranspiration, precipitation, runoff, and underground flow. The water table fluctuation may range from near zero to many metres, depending on the area.

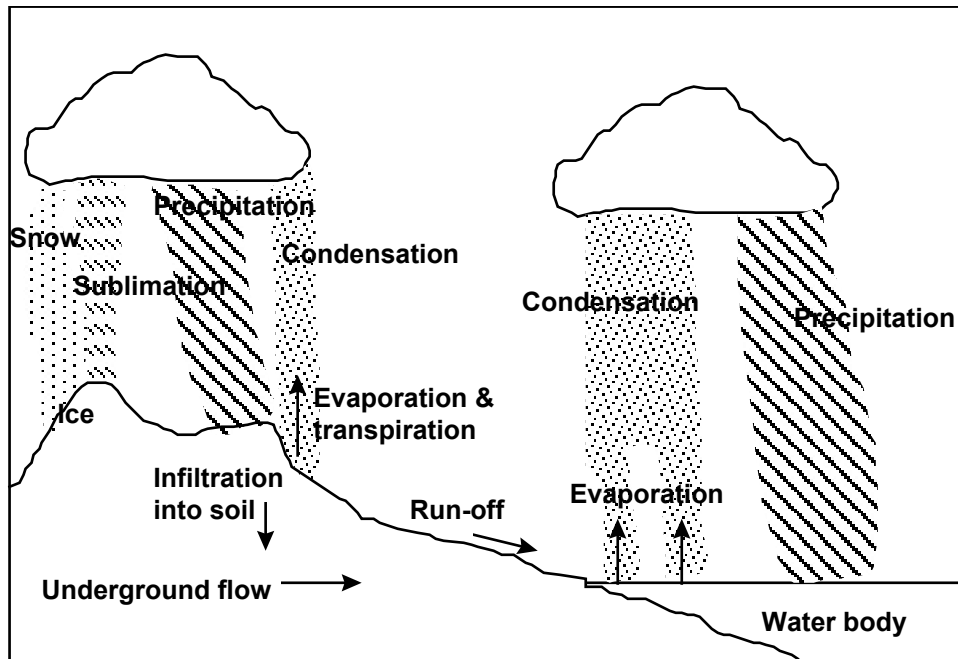


Figure 2.6 The hydrologic cycle

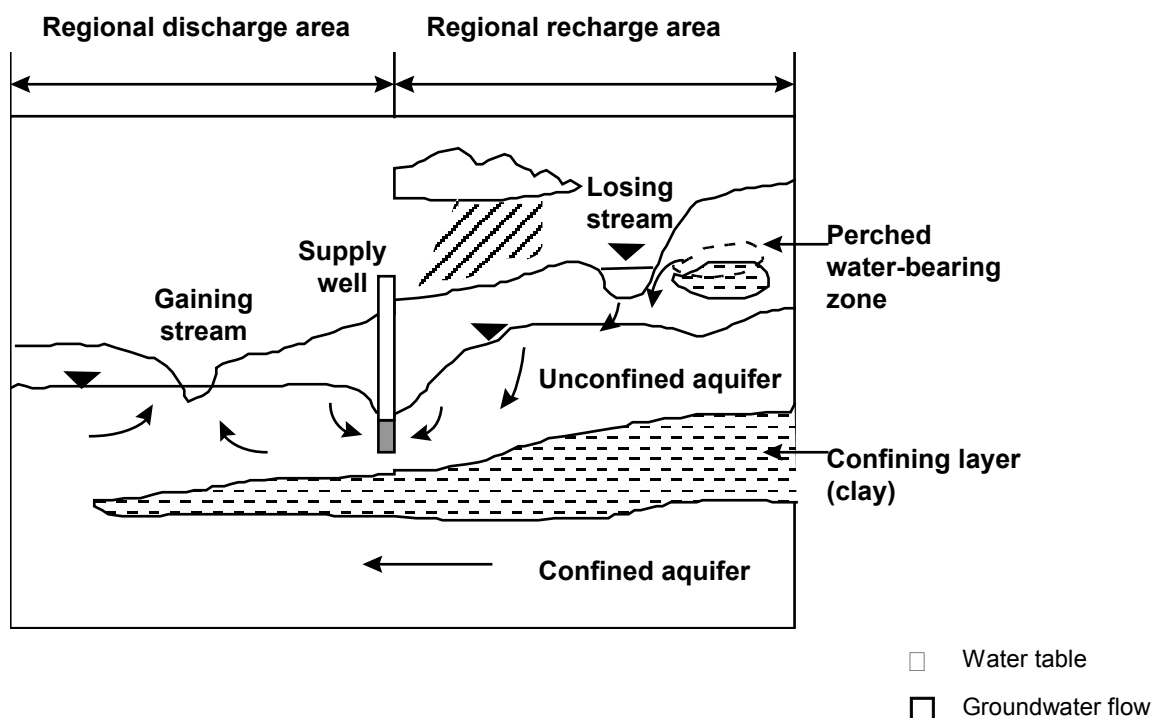


Figure 2.7 Groundwater circulation

Source: API, 1996

2.3.2.3 Groundwater aquifers

Aquifers are important in New Zealand, since in some areas a large percentage of drinking-water supplies as well as stock and irrigation water are derived from this course hence the concern with respect to potential contamination of aquifers.

An aquifer can be defined as a water-bearing formation that contains sufficient saturated permeable material to yield significant quantities of water to wells and springs. The term significant is subjective and depends on the quantity and quality of water needed for a particular purpose.

Aquifers generally extend over wide areas and the flow of groundwater, in to and out of them, is characterised by the permeability of geologic formations that overlay or underlie them. They may contain aquicludes, a relatively impermeable confining unit, that has a very low hydraulic conductivity and prevents virtually any flow of water through the formation (for example a clay soil) and aquitards; poorly permeable formations or deposits such as a sandy clay soil that allows only very low flow of water into adjacent aquifers (that is, it retards fluid movement). Aquifers can be present in unconsolidated or consolidated materials.

Aquifers can also be characterised by the effective porosity of the aquifer geologic materials. This will indicate the water storage capacity of the aquifer. Aquifers are capable of yielding large volumes of water when composed of sands and gravels, or only small amounts from silts and clays (per unit volume of the material basis). Aquifers can be thought of as groundwater storage reservoirs that receive recharge from sources such as rainfall, and discharge by gravity or by pumping from wells.

Aquifers may be classified as unconfined or confined, depending on the location of the top of the aquifer with respect to the water table. An unconfined aquifer is one where the water table exists within the aquifer and rises and falls with changes in the volume of water stored. Unconfined aquifers are usually close to the ground surface and are more frequently affected by hydrocarbon releases than confined aquifers. Recharge of unconfined aquifers usually comes from downward seepage through the unsaturated zone, through lateral groundwater inflow and from upward flow of water from deeper confined aquifers. A perched water table is an example of an unconfined water body that is sitting on top of an impermeable layer, such as a clay lens, separated from the saturated zone.

Confined aquifers occur where groundwater is confined by a formation of relatively low hydraulic conductivity (aquiclude or aquitard) and the water in the aquifer is at a lower level of elevation than the recharge area. That is, water at the top of the aquifer is at greater than atmospheric pressure. In a well penetrating the confining layer, the water level will rise above the bottom of the confining layer. If the water level rises above the land surface, a flowing well or spring known as an artesian well or spring results. Recharge of a confined aquifer can occur through infiltration in recharge areas or by slow leakage of water down through the confining layer from an aquifer above.

A confined aquifer can conduct water from a recharge area to locations of natural or artificial discharge. The level that water rises to in a well penetrating into either an unconfined or confined aquifer is equivalent to the total hydraulic head (the hydrostatic pressure level) of water in the aquifer at that location. The total hydraulic head is usually expressed in terms of water elevation for both unconfined and confined aquifers. The sum of elevation head and pressure head equals total head. Flow within an aquifer occurs from locations of high head to locations of low head. In going from the recharge zone to the discharge zone through the aquifer, the hydrostatic pressure level forms what is known as the hydraulic grade line, or the piezometric or potentiometric surface. A confined aquifer becomes unconfined when the piezometric surface drops below the bottom of the upper confining layer.

Equipotential lines can be drawn (in plan view) through the water table levels for an unconfined aquifer or through the piezometric levels for a confined aquifer. Lines drawn perpendicular to the equipotentials indicate the direction of groundwater flow in the direction of decreasing head (down-gradient). Almost all water table (or potentiometric) surfaces are sloped indicating that groundwater is moving.

2.4 Forms of hydrocarbon contamination

Following release to the subsurface, petroleum hydrocarbons will be present in a combination of solid, liquid, dissolved, and vapour phase as described in this section.

2.4.1 Liquid phase

In the subsurface, hydrocarbons in liquid phase can occur in the following ways:

- mobile or free (free product) liquids moving down through the unsaturated zone
- immobile residual liquids in the unsaturated zone
- immobile residual liquids trapped in the saturated zone
- free product on top of water table.

The particular form taken or distribution between forms depends on the extent to which hydrocarbon saturation is possible in the pore spaces and on the wetting characteristics of the geologic materials, or in terms of processes, the degree to which adsorption or absorption affects the contaminant plume and how much of the liquid is retarded and becomes immobile.

The amount of petroleum product that can be retained by the subsurface materials is dictated by capillary interactions between the soil and petroleum product. The amount that can be retained under gravity drainage conditions is often referred to as the residual saturation, and it is dependent on the soil particle size, soil type, liquid density, and surface tension.

The degree of adsorption depends on:

- chemical equilibria
- soil organic carbon content
- product and soil chemical composition
- the existence of preferential pathways.

In the unsaturated zone the exposed surfaces of most geologic materials will be coated with a thin film of water, which acts as a wetting fluid. Liquid hydrocarbons can also act as a wetting fluid coating the water film and soil particles as it migrates through the vadose and capillary fringe zones. Residual saturation levels of hydrocarbons resulting from such wetting are generally higher in fine-grained soils than in coarse-grained soils.

Typical average values of residual hydrocarbon concentrations the unsaturated zone for some petroleum products and soil types are given in Table 2.9.

Table 2.9 Typical residual hydrocarbon concentrations in the unsaturated zone

Soil type	Petrols		Middle distillates		Fuel oils	
	L/m ³	mg/kg	L/m ³	mg/kg	L/m ³	mg/kg
Coarse gravel	2.5	950	5	2,200	10	4,800
Coarse sand	7.5	2,800	15	6,500	30	15,000
Fine sand/silt	20.0	7,500	40	17,000	80	39,000

Source: API, 1996

2.4.2 Dissolved phase

Dissolved phase hydrocarbons exist in the following areas:

- water infiltrating through the unsaturated zone
- the residual films of water covering solid surfaces or filling pore spaces
- groundwater within the saturated zone.

2.4.3 Vapour phase

Hydrocarbon vapours in the subsurface can be present in:

- pore spaces in the unsaturated zone not already occupied by liquids. This is the predominant area of distribution for vapours. In these zones, vapours are potentially highly mobile
- the free liquid hydrocarbon plume
- water in the underlying capillary fringe and saturated zone.

In the first two instances above, as small bubbles vapour becomes entrained in the liquids. The bubbles are relatively immobile, but may move slowly with liquid flow, dissolve into the groundwater or be released into the soil air.

Under certain conditions, methane, carbon dioxide and hydrogen sulphide may be present as a result of microbial degradation of hydrocarbons.

2.5 Subsurface hydrocarbon migration

The ways in which petroleum hydrocarbons migrate within the subsurface are central to assessing the fate and transport of the contaminant. This section provides basic background information on migration processes which are used in contaminant modeling and hence in developing criteria for site assessment.

As discussed in Section 2.4, a spill or leak of hydrocarbons will exist in the subsurface as free product, dissolved in groundwater and/or as a vapour. Some of the main processes affecting hydrocarbons in the hydrogeological environment include sorption (adsorption and absorption), chemical degradation, diffusion (dilution and dispersion), volatilisation, and biodegradation. These processes affect the rate at which the hydrocarbon contaminant migrates through the subsurface by dispersing or retarding the hydrocarbon compounds.

2.5.1 Physical and chemical processes

The following are definitions of chemical and physical processes which will have an impact on hydrocarbon fate and transport.

Adsorption involves surface to surface chemical bonding with organic compounds (organic carbon) and inorganic compounds (e.g. clay particles). It is affected by reaction equilibrium, the organic carbon content of the soil (f_{oc}), chemical composition, and preferential pathways. Non-adsorbed compounds move with groundwater. Adsorption effects the migration of chemicals in the subsurface. For example, the leading edge of a dissolved chemical plume moves slower than groundwater flow due to adsorption.

One way to compare the migration and adsorption potentials of various compounds is through the use of K_{oc} (organic carbon / water partition coefficient) values. A K_{oc} value is a measure of the tendency of an organic compound to be adsorbed by the soil. The higher the K_{oc} , the higher its potential to be adsorbed and the lower its potential to migrate. Table 2.10 presents K_{oc} values for some of the constituents in petrol.

The distribution coefficient, K_D , which is the ratio of the chemical concentration in the solid phase to that in solution at equilibrium, is equal to $K_{oc} \times f_{oc}$ where f_{oc} is the organic carbon content of the soil.

Table 2.10 Adsorption coefficients for selected constituents of petrol

Constituent	K_{oc} value
n-Pentane	568
n-Hexane	1097
n-Heptane	2361
Benzene	50
Toluene	339
ortho-Xylene	255
Naphthalene	1288
Benzo(a)pyrene	891,000

Source: Nyer, 1993; Karickhoff et al, 1979; and Meylan et al, 1992

Diffusion is the process whereby molecular or ionic constituents migrate in the direction of decreasing concentration. If there is a gradient, the rate of diffusion will be greater and will be from higher towards lower areas of concentration. Characteristics such as temperature or density can also drive diffusion.

Advection is the transportation of chemical constituents by groundwater movement. It is dependent on geologic material, hydraulic conductivity and groundwater flow rates.

Dispersion results from advection (i.e. there is no dispersion if there is no advection), and is generally a result of the fact that fluids must flow around soil particles. It may occur on the micro- or macro scale and is often referred to as a mechanical mixing process.

Chemical degradation through abiotic transformations due to naturally occurring chemical reactions may result in attenuation of a plume. BTEX compounds are not expected to be subject to this, but several halogenated compounds undergo hydrolysis and dehydrohalogenation reactions in groundwater.

Volatilisation is the process by which a compound passes from a liquid state into a vapour or gaseous phase. This is one process by which compounds are transported away from the soluble groundwater plume, through the capillary fringe, and into the soil gas of the vadose zone. Under hydrogeological conditions the mass of a contaminant like benzene removed through this mechanism is expected to be very low (the order of a few percent). Optimum conditions for volatilisation would be directly from the unsaturated zone, or in groundwater of shallow depth and high temperature. Volatilisation can be very significant in the removal of hydrocarbons from shallow or exposed soil sequences. Light hydrocarbons tend to be more volatile than heavier ones. Volatilisation can be significant in that it allows migration to areas of higher oxygen where biodegradation can occur.

2.5.2 Biological processes

Biological processes which result in the degradation of hydrocarbon compounds can have a significant effect on these contaminants in the ground. Therefore they can be important when considering site assessment, and management options. Subsurface micro-organisms are generally present in the form of a fixed biofilm on the surface of geologic material, and in most circumstances

these organisms can utilise carbon and energy in organic chemical pollutants as a food source. This results in the biodegradation or biotransformation of the organic chemical.

Many micro-organisms such as bacteria and fungi can metabolise either completely or partially the hydrocarbons from petroleum. Microbial oxidation is dominated by bacterial action which appears to be species dependent.

Degradation of the various fractions of petroleum hydrocarbon products varies considerably; n-alkanes, isoalkanes, BTEX, and two- and three-ring PAHs are readily degraded with eventual conversion to carbon dioxide and water. Other fractions like the cycloalkanes and more complex PAHs can degrade very slowly.

Biodegradation is dependent on the right environmental conditions being available for the micro-organisms. Some of the factors affecting biodegradation rates include:

- the composition and size of the soil microbial population
- the presence of suitable and bioavailable source of energy (carbon)
- the presence of oxygen
- conducive soil conditions: i.e. a pH between 6 and 9, warm temperatures, and high moisture content
- the presence of essential elements including: N, P, K, Ca, Mg, S, Fe, Mn, Cu, and Zn
- the toxicity of the compounds and the concentrations to which micro-organisms are exposed.

If any one of these factors is lacking, it will limit microbial activity and hence reduce biodegradation. Availability of oxygen is typically the most limiting factor to biodegradation in natural settings. At some sites, where natural attenuation has been observed, biodegradation of the BTEX constituents by indigenous, subsurface microbes appears to be the primary mechanism.

Biodegradation of aromatic compounds under aerobic conditions ($> 1 - 2$ mg/L dissolved oxygen in groundwater) is a significant mechanism for the natural attenuation of BTEX compounds. Howard et al (1991) indicate that biodegradation half-lives for benzene in groundwater can range from 10 days to 24 months for varying conditions. (The half-life is the amount of time required for the concentration of a compound to degrade to half its concentration). Half-lives are highly site-specific.

Anaerobic biodegradation rates are much slower than aerobic rates and consistent degradation of hydrocarbons under these conditions has not been demonstrated. For this reason, contamination may persist in areas where the available oxygen is depleted.

2.5.3 Liquid phase migration

In order to assess hydrocarbon contamination properly, an understanding of the transport mechanisms of the various hydrocarbon phases is required. Following a release, free liquid product (also called light non-aqueous phase liquid (LNAPL)) will move under the force of gravity down through the unsaturated zone towards the water table. A significant proportion of the free liquid (i.e. LNAPL) will become trapped as residual saturation due to capillary forces. Lateral or horizontal spreading occurs within the unsaturated zone due to the divergence of flow around grains and because of the attractive forces between liquid hydrocarbons and solid granular surfaces.

Downward and lateral migration of the free liquid hydrocarbons will occur at different rates depending on:

- the rate and volume of the release

- the density of the hydrocarbons
- soil and rock porosities
- the attractive forces between the water and the hydrocarbons.

Low hydraulic conductivity layers will slow or can stop downward migration and promote lateral dispersion of hydrocarbon liquids. Downward migrating liquids (water or hydrocarbons) can become perched above these layers. If there is sufficient volume of liquid, or if the impermeable layer is sloped downward, the liquid will migrate around laterally discontinuous perching layers, and will then continue downward migration (see Figure 2.8).

The volume of the release, the depth to the water table, and the sorptive capacities of the geologic materials will determine whether the release reaches the capillary zone. Figure 2.8(a) depicts a release where free liquid does not reach the water table. Figure 2.8(b) shows the distribution of a release where liquid has reached the water table.

When the free liquid hydrocarbons first reach the capillary fringe the petroleum product accumulates on the capillary fringe, not the water table. This compresses the capillary rise, displaces water, and creates a free liquid hydrocarbon plume with a petroleum product table. Lateral spreading of the plume near the top of the capillary fringe can occur more rapidly than the movement of groundwater below the water table. This phenomenon occurs because the initial rate of migration is controlled by the pressure head of the free liquid hydrocarbons and not by groundwater.

After reaching the capillary zone, the plume begins to migrate downgradient under the influence of gravity and groundwater flow. If the plume is small relative to the depth of the capillary zone, migration can be inhibited by the capillaries. The rate of downgradient movement varies depending on the volume of the spill, groundwater flow velocity, product lost from the plume due to phase transformation and retardation and biological degradation processes, and the hydraulic conductivity as the plume proceeds.

The size of the plume is affected by:

- release volume and rate
- porosities of soils and rocks
- hydraulic conductivity
- water table gradient
- the depth to the water table
- time of release.

Fine-grained materials have larger surface areas which tend to retain more of the liquid in a residual form and reduce the volume of free product. Coarse-grained materials and formations containing fractures and other secondary porosity features have smaller surface areas. Liquid hydrocarbons migrating through these materials are less likely to be immobilised by capillary forces (e.g. residual saturation values are smaller for these materials).

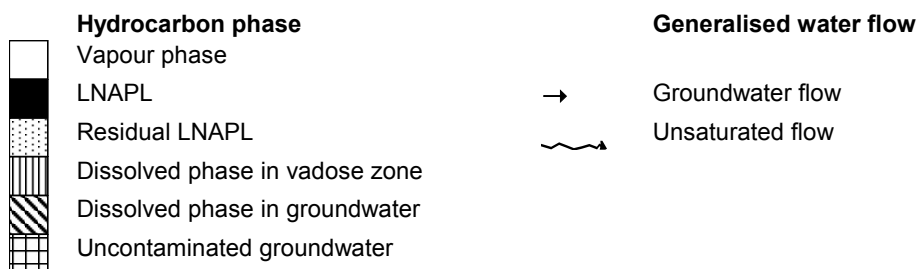
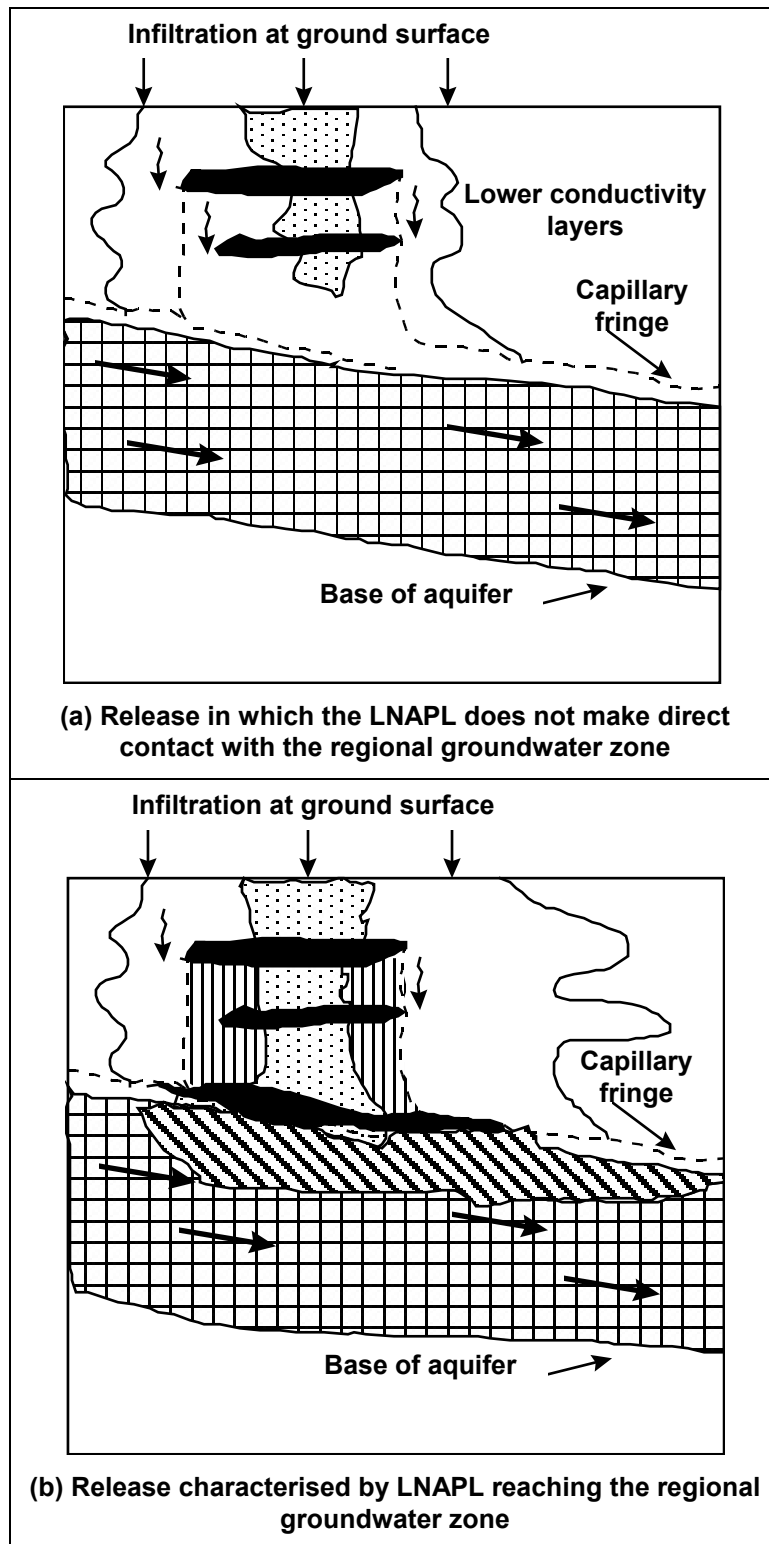


Figure 2.8 Distribution of hydrocarbons from (a) a small and (b) a large release
 Source: API, 1996

The water table gradient (and other factors affecting flow, such as permeability) also affects the shape of the plume. The steeper the gradient, the narrower the plume.

Fluctuations in the water table level promote vertical spreading of the plume (refer Figure 2.9). When the water table drops, free product associated with the capillary zone will descend leaving residual hydrocarbon liquid in the expanded unsaturated zone above the water table. This is known as smearing. Any subsequent rise of the water table will cause the capillary fringe and a portion of the associated product to move upwards. This may result in lateral spreading at a higher level.

The water table fluctuations can affect the amount of product detectable, and available for removal, in monitoring and recovery wells by altering the quantity of liquid hydrocarbons in a mobile state that can flow into a well. This leads to seasonal fluctuations in detectable hydrocarbon product thicknesses in wells. Smearing will also result in a continuing source of dissolved phase contamination.

Free liquid hydrocarbons can migrate into underground structures such as wells, underground service trenches and ducts, foundations, basements, and natural groundwater discharge areas like springs, creeks and rivers.

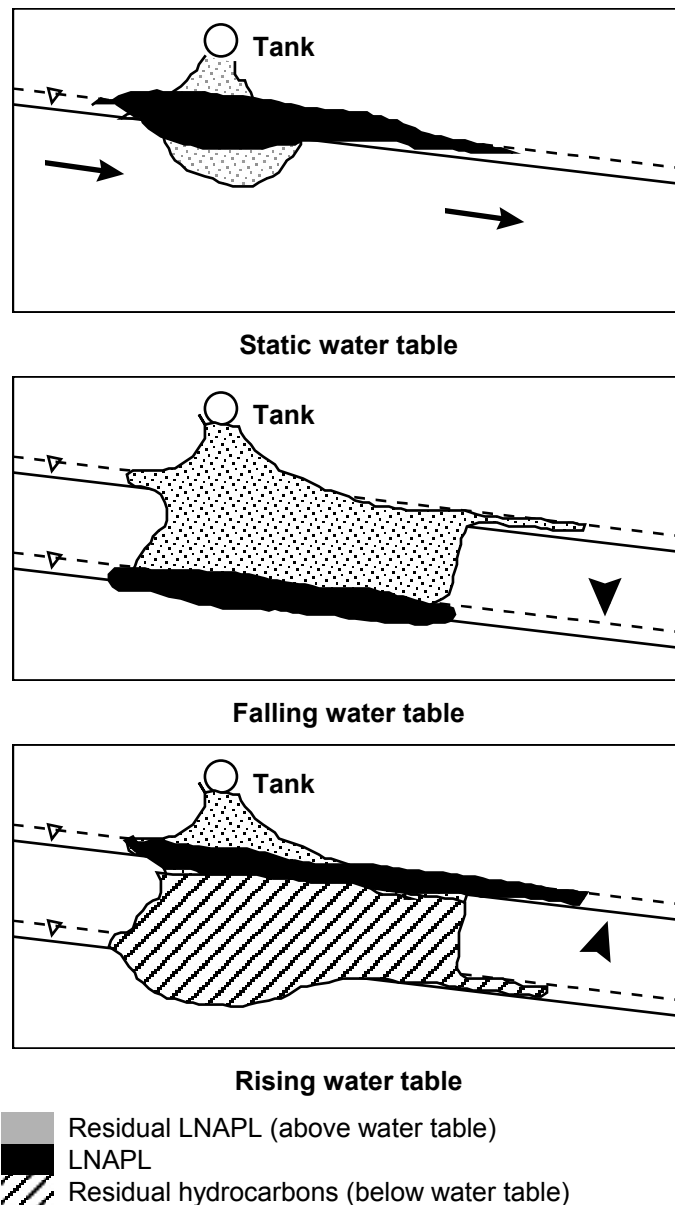


Figure 2.9 Spreading of hydrocarbons as a result of water table fluctuations
 Source: API, 1996

2.5.4 Dissolved phase migration

The transformation of liquid phase hydrocarbons into dissolved phase occurs when the liquid hydrocarbons contact subsurface water. This contact can happen when:

- water infiltrates through an unsaturated zone which contains residual adsorbed phase hydrocarbons
- groundwater flows into contact with a free hydrocarbon plume
- groundwater flows past residual liquid or adsorbed hydrocarbons in the saturated zone.

The concentration of dissolved hydrocarbon compounds in water and the rates of transfer to the groundwater system are determined by:

- the presence or absence of oxygen
- the rate of microbial degradation
- the depth to the water table
- soil and rock hydraulic conductivities
- recharge rates
- water table fluctuations
- groundwater velocity
- residual hydrocarbon concentrations
- the blend of hydrocarbon compounds in the free product liquid

The processes of advection, dispersion, and diffusion control the movement of dissolved phase hydrocarbons. The effect of dispersion and diffusion is to dilute the contaminant concentrations in the dissolved hydrocarbon plume. Mechanical mixing is the main dispersive mechanism, chemical diffusion has minimal effect except in cases of very low hydraulic conductivity or very low flow velocities.

Dispersion increases in heterogeneous material because groundwater velocities are different through differing subsurface media which results in greater mixing.

2.5.5 Vapour phase migration

Vapour phase migration is particularly important with respect to hydrocarbon accumulation in indoor air and other enclosed spaces such as utility corridors and sewers. Vapour phase hydrocarbons in the subsurface result from the volatilisation of liquid hydrocarbons. This can occur with:

- free liquid and residual liquid hydrocarbons in the unsaturated zone, and
- dissolved hydrocarbons downgradient from the release site.

The migration of vapour is controlled by many parameters including:

Chemical and physical properties of the released product:

- vapour pressure
- solubility
- concentration
- density
- viscosity

Hydrogeologic properties:

- hydraulic conductivity
- depth to groundwater
- groundwater flow direction

- water temperature
- porosity
- moisture content

Miscellaneous:

- barometric pressure
- rainfall duration and intensity
- non- natural structures.

In general, vapour tends to follow the most conductive pathways and travel from areas of greater to lesser pressure, and from higher to lower concentrations.

2.6 Exposure effects and toxicity

The importance of the potential health and environmental effects of hydrocarbons are obvious in a site assessment process. The following sections give a brief overview of these matters. More detailed information on health and environmental effects is included in Module 4.

Petroleum products vary in their toxicity according to the content of low-boiling compounds, unsaturated compounds and aromatics. The higher the concentration of these constituents, the more toxic the product. Toxicity appears to increase along the series alkanes - alkenes - aromatics.

Available data on the toxicity of cycloalkanes and cycloalkenes suggests that these compounds are more toxic than alkanes and that in some cases they are more toxic than aromatics.

2.6.1 Potential health effects

The uptake of hydrocarbons in animal or human tissue is governed by similar principles to other lipophilic substances. Adsorption occurs through respiratory surfaces, the gastrointestinal tract and external surfaces, with the hydrocarbons generally being deposited in lipid-rich tissues.

The New Zealand Drinking-water Standards (NZDWG) and the World Health Organization (WHO) Guidelines for Drinking-water Quality establish acceptable concentrations for a range of organic constituents of health significance. Guideline values are based on toxicity and/or carcinogenicity. Of these, benzene is most significant in terms of petroleum hydrocarbon contamination. Its limit is set at 10 µg/L (ppb) and is based on animal carcinogenicity test data and occupational exposure data for leukaemia. This level corresponds to a maximum additional cancer risk of 1×10^{-5} (one additional death from leukaemia per 100,000 over a lifetime (70-year) exposure).

The problems associated with ingestion of chemical constituents (i.e. via drinking water or similar) arise primarily from their ability to cause adverse health effects after prolonged exposure. Of particular concern are the contaminants that have cumulative toxic effects (i.e. heavy metals) or carcinogenic effects (WHO 1996a, b).

The World Health Organization states that Tolerable Daily Intakes (TDI) are regarded as representing intakes for a lifetime. They are not so precise that they cannot be exceeded for short periods of time. Short-term exposure levels exceeding the TDI are not cause for concern provided the individual's intake over time does not appreciably exceed the set level. The large uncertainty factors generally

involved in establishing a TDI serve to provide assurance that exposures for short periods are unlikely to have any deleterious effects on health (WHO 1996a, b)

2.6.2 Potential ecological impact

Resistance to degradation, or persistence, is an important characteristic influencing the impact of a substance in an organisation or on the environment. The persistence of some hydrocarbons in aquatic organisms have been measured in terms of half-lives as ranging from 2 - 7 days in laboratory tests and 1 - 60 days in field tests. There is still no consistent opinion on whether petroleum hydrocarbons are able to biomagnify. However it appears likely that more resistant fractions are potentially available for biomagnification.

Following a review of toxicity data, compounds have been ranked in order of increasing effect, as follows: decane, octane, heptane, hexane, pentane, cyclo-octane, naphthalene, para-xylene, cyclohexane, benzene, and cyclohexene.

As there are differences in toxicity between different hydrocarbon compounds, it is impossible to accurately predict toxic effects of contamination for which only total hydrocarbon data are available. Generally, alkanes exhibit comparatively little toxicity or other adverse physiological impacts. Such effect is usually due to the aromatic substances present. The lower molecular weight compounds are usually the more water soluble component of a product and hence attention has been focused on the water soluble fractions of petroleum and related products.

Concentrations in the environment are usually comparatively low and sublethal effects are usually more significant. As a guide, general ranges for effects on marine organisms for given concentrations of soluble aromatic hydrocarbons is shown in Table 2.11.

Table 2.11 Range of effects in marine organisms for soluble aromatic hydrocarbons

Concentration	Effect
0 - 20 ppb	Bioaccumulation may occur
10 - 200 ppb	Behavioural pattern changes
100 - 60,000 ppb	Growth and reproduction changes
1,000 + ppb	Lethal to larval and juvenile stages
100,000 + ppb	Lethal to adults

Source: Connell and Miller, 1984

2.6.3 Physical risks

Risk of fire or explosion exists on sites containing volatile hydrocarbons. The build-up of flammable vapours, particularly in low-lying and/or poorly ventilated areas, can result in atmospheres sufficiently rich in vapours for an explosion to occur, if an ignition source is introduced. The lower limit at which explosion could occur, referred to as the lower explosive limit (LEL), for many flammable compounds is approximately 1 % by volume in vapour.

2.7 References and further reading

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