

1

An introduction to gasworks sites

1.1	Introduction	1-2
1.2	Gasworks processes	1-2
1.2.1	Coal carbonisation	1-2
1.2.2	Carburetted water gas production	1-2
1.2.3	Oil-gas production	1-2
1.3	Major process units	1-3
1.3.1	Coal and coke production	1-3
1.3.2	Retort houses	1-3
1.3.3	Carburetted water gas plant	1-4
1.3.4	Oil-gas	1-4
1.3.5	Gas purification processes	1-4
1.3.5.1	Condensation and separation	1-4
1.3.5.2	Scrubbing	1-4
1.3.5.3	Oxide beds	1-4
1.3.6	Gasholders	1-4
1.3.7	Other facilities	1-5
1.4	Fate and transport of gasworks contaminants	1-5
1.4.1	Volatile aromatics	1-5
1.4.2	Phenolics	1-6
1.4.3	Polycyclic aromatic hydrocarbons	1-6
1.4.4	Inorganics	1-6
1.5	References	1-8
Appendix		
1A	Fate and transport of organic contaminants in the subsurface environment	1-9

An introduction to gasworks sites

1.1 Introduction

The gas manufacturing industry is almost two hundred years old, having initially commenced in the UK in the early 1800s and subsequently spreading to Europe and North America. In the UK and US in excess of 1000 gasworks sites manufactured gas from coke, coal and oil up until the 1960s (Turczynowicz 1993), but only approximately 54 sites existed in New Zealand. The first of these gasworks began supplying gas in Auckland in 1865, and the last gasworks closed in 1988 in Hastings.

This module covers the following:

- gasworks processes
- major process units
- fate and transport of gasworks contaminants

Additional information on the characteristics of gasworks sites and the nature of contamination can be found in Section 1 of the Users' Guide, including:

- ▲ the suggested layout of gasworks sites (Section 1.3)
- ▲ the contaminants of concern (Section 1.4)
- ▲ the waste products associated with the contaminants (Section 1.5)
- ▲ patterns of contamination (Section 1.6)

1.2 Gasworks processes

There were three principal processes used for the manufacture of gas:

- coal carbonisation
- water gas or carburetted water gasification
- oil gasification.

1.2.1 Coal carbonisation

Coal gas was produced by heating coal in a closed vessel, known as a coal-carbonisation retort, until all the volatile materials were removed. The evolved gases were collected and purified prior to use, and the remaining coke was removed from the retort.

1.2.2 Carburetted water gas production

Carburetted water gas, or 'blue gas' was produced by passing steam through a bed of incandescent carbon. The resultant gas was then further reacted with liquid hydrocarbons to produce a gas of higher calorific value.

Carburetted water gas (CWG) production was often integrated with coal gas production, using coke from the coal-carbonisation process. The CWG process was useful as it was relatively quick to start up and shut down and produced a gas useful for blending with gas from other sources to obtain a consistent calorific value.

Carburetted water gas was introduced into most of the large gasworks in New Zealand by the 1950s but their use was generally confined to meeting peak loads by augmenting the normal stream of coal gas (John Pollard pers comm).

1.2.3 Oil-gas production

Carbon and oil were used in the production of oil-gas in either a one-shell or two-shell apparatus. The steps in a one-shell apparatus were:

- blow with air to burn off carbon
- heat carbon with air and oil

- steam generation of blue gas
- oil and steam generation of a mixture of gaseous hydrocarbons
- steam purging to remove the final product.

Oil gasification came into use in New Zealand in the early 1960s. This process progressively augmented coal carbonisation as the source of gas until the production of Maui gas in the late 1970s. The feedstocks for this process included naphtha, light distillate spirit and natural gas. Approximately six sites in New Zealand are known to have used oil gasification to supplement the production of coal-gas.

Table 1.1 outlines the residues resulting from the different gasmaking processes (Luthy et al 1994):

Table 1.1 Process residuals from the manufacture of gas from coal, coke, and oil

Process Residuals	Physical form and principal chemical content	Gas Manufacturing Process		
		Coal Carbonisation	Carburetted Water Gas	Oil-Gas
Ammonia liquors	Aqueous liquid: inorganics, phenolics	✓ ^a	-	-
Ash and clinker	Solid: metals (and unburned coke or coal)	✓	✓	-
Carburetted water gas	Organic liquid: PAHs, BTEX ^b	-	✓	-
Coal tar	Organic liquid: PAHs, BTEX and phenolics	✓	-	-
Coke and coke breeze	Solid: pyrolysed coal	✓	-	-
Lampblack	Sludge: elemental carbon and oil tar	-	-	✓
Light oils	Organic liquid: BTEX	✓	✓	✓
Oil tar	Organic liquid: PAHs, BTEX	-	-	✓
Spent oxide or lime, wood chips (support media)	Solid: metals, cyanide, sulphur, tar	✓	✓	-
Tar sludges	Solid liquid: PAHs, BTEX	✓	✓	✓
Tar-oil-water emulsions	Aqueous and organic liquids: PAHs, BTEX	✓	✓	✓
Wastewater treatment sludges	Solids, aqueous, and organic liquid: inorganics, phenolics, PAHs, BTEX	✓	✓	✓

a "✓" indicates that residual was produced; "-" indicates that residual was not produced in substantial amounts

b PAH = polycyclic aromatic hydrocarbons; BTEX = benzene, toluene, ethylbenzene, and xylene

1.3 Major process units

1.3.1 Coal and coke production

Coal may have been stockpiled on site for considerable lengths of time during periods of low demand. The coke from the retort was stored either for use in a carburetted water gas plant (where such a plant was installed on site) or prior to being sold. Leachate from these sources contained heavy metals, sulphides and some hydrocarbons. Surface contamination by coal and coke may also be expected.

1.3.2 Retort houses

The retorts were loaded with coal and heated for several hours to drive off all volatile material, resulting in coke which was removed from the retort. The coal was usually heated with producer gas, developed on site by heating coal or coke with air. Coal gas and coal tar

condensed from the coal gas were also used for heating if markets were not available for these by-products. Solid process residuals included ash, clinker and coke.

1.3.3 Carburetted water gas plant

Carburetted water gas was produced cyclically by first blowing air through the coke bed, burning the coke and heating the bed, then cutting the air flow and blowing steam through the bed. The steam reacted with the carbon to produce a mixture of carbon monoxide and hydrogen which was of low calorific value. Thermal cracking of liquid hydrocarbons in the mixture, using heat recovered from the air blow, produced carburetted water gas which had a higher calorific value. Process residuals included clinker and waste water.

1.3.4 Oil-gas

The process of oil-gas production varied but generally consisted of catalytic cracking and steam reforming of a particular fraction from the distillation of crude oil, e.g. light distillate spirit, naphtha, or LPG, followed by another catalytic reaction to increase the H₂/CO ratio. Blending with LPG or natural gas enriched the calorific value of the product gas. Purification was usually simpler than for coal gas, but sometimes carbon dioxide was removed by washing with potassium carbonate solution containing arsenic trioxide. Depleted nickel, uranium and vanadium catalysts were often left on sites where oil-gas production took place.

1.3.5 Gas purification processes

Purification was required to ensure that impurities did not foul the manufacturing and distribution systems. These impurities included:

- water and tars removed by condensation and separation
- naphthalene, light oils and ammonia removed by scrubbing
- hydrogen sulphide and cyanide.

1.3.5.1 *Condensation and separation*

Condensers were used to remove water and tars from the raw coal gas. Separation of the water and tar used a variety of procedures including tar extractors, electrostatic precipitators, steam distillation, centrifugation and dehydration. The tar may have been stored in a tar pit or tank prior to being further distilled into other products.

1.3.5.2 *Scrubbing*

Scrubbers removed naphthalene and light oils using other oil types for the process. Ammonia removal was usually by scrubbing with water, condensate or sulphuric acid. Phenol was recovered from the ammonia waste by washing with benzene or light oil, and then washing the benzene with sodium hydroxide resulting in a waste ammoniacal liquor. This process also recovered tar acids from the ammonia waste.

1.3.5.3 *Oxide beds*

Hydrogen sulphide and cyanide were removed either by the use of lime in the form of calcium hydroxide or by the use of iron oxide to produce ferric sulphide and ferric ferrocyanide complexes. Spent oxides formed a significant part of the waste stream and may have been used as fill around the site.

1.3.6 Gasholders

Gas was stored prior to distribution in gasholders or gasometers. These were set in large pits, filled with water to provide a seal, and were able to rise and fall with the change in volume of gas stored. Relief gasholders also stored raw gas from the retort house or the carburetted water gas plant prior to purification. The base of the gasholder accumulated tar and contaminated water over time. Tar was used as a lubricant for the gasholders, so it may be found spread around beyond the perimeter of the concrete bases. Gasholders were often located on the perimeter of the gas distribution system.

1.3.7 Other facilities

Tanks and pipework left on site after decommissioning may contain residual material. On site, old gas mains were sometimes used as convenient receptacles for waste holder oil and water during decommissioning. Off-site facilities such as mains, syphons and peripheral gasholders may also contain residual material. These are generally less significant sources of contamination and generally environmental assessments are confined to the actual site. However, such sources still need to be considered.

1.4 Fate and transport of gasworks contaminants

The processes affecting the fate and transport of contaminants associated with gasworks sites depend heavily on their chemical and physical properties, and the soil and groundwater characteristics of each site.

In the context of former gasworks sites, some of the important issues include:

- the potential for leaching of contaminants from soil to groundwater, which is highly dependent on soil type, depth to groundwater and the physical and chemical properties of the specific contaminant
- the presence and movement of free-phase organics (either as DNAPL or LNAPL)
- the erosion of surface contamination and its transport to adjacent surface water bodies, which is highly dependent on the nature of surface soils, proximity to surface water bodies, the nature of site drainage and the topography of the site.

Aging of contaminants will produce changes in the composition of contamination through loss of volatiles, separation of lighter and heavier fractions, biodegradation, and off-site transport of more water-soluble compounds (Turczynowicz, 1993).

The factors affecting the environmental fate and transport of gasworks contaminants are highly complex and involve a variety of both physico-chemical and biological processes. Physico-chemical processes include convective transport, dispersion, dilution and adsorption of the contaminants. Physical and chemical reactions, for example hydrolysis and oxidation/reduction, may affect the contaminant. Contaminants may be transferred between media via volatilisation, erosion, sedimentation and similar activities. Biological processes involve uptake, transformation and degradation by plants, aquatic species, microorganisms and other biota (Turczynowicz, 1993).

In soils, pH influences the chemical specification and mobility of contaminants.

Acidification of soils can often occur at gasworks sites where soil pH can drop to less than 4, which is generally considered by soil chemists to be strongly acidic. This is due to the high concentration of elemental sulphur which can be associated with former sulphur purification processes and the effect of natural microbial action resulting in the formation of sulphuric acid in the soil.

General background information on fate and transport processes affecting gasworks contaminants is presented in Appendix 1A.

1.4.1 Volatile aromatics

Benzene and other volatile aromatics are amongst the most mobile of the organic contaminants found at gasworks. The high solubility of BTEX compounds often result in significant contamination of groundwater beneath former gasworks sites. (Turczynowicz, 1993).

Volatile contaminants, such as benzene, are generally found in soil samples in areas of heavy contamination, but in relatively low concentrations compared with inorganic and PAH levels. However, groundwater samples often contain proportionally higher concentrations of BTEX relative to PAHs. Groundwater samples taken off-site may also have elevated levels of the volatile components, (often when PAHs are not detected) indicating migration of these more soluble contaminants from a source on site.

Volatile aromatics are readily lost by volatilisation and therefore are not usually found at high concentrations in surface soils. Volatilisation from heavily contaminated soil at depth can result in the accumulation of volatiles in enclosed spaces.

Most of the volatile aromatics are readily degraded where conditions favour biological activity. For example, in aerobic aquifers benzene plumes arising from gasoline spills have been found to rarely exceed 100m in length.

1.4.2 Phenolics

Phenolics (phenol and cresols) are highly mobile in the soil environment, reflecting the relatively high solubility of these compounds compared to many other organic contaminants at gasworks sites. They are frequently detected as contaminants of concern in groundwater associated with former gasworks sites. At low to moderate concentrations phenolics are readily degraded in soils and groundwater where conditions favour biological activity.

Phenolics have a tendency to migrate through plastic pipework and have been associated with tainting potable water supplies where water passes through polyvinyl chloride (PVC) or polyethylene pipes installed in contaminated soil. Cresols, although not highly volatile, are odorous compounds and may be significant contributors to the odour encountered during excavations at former gasworks sites.

1.4.3 Polycyclic aromatic hydrocarbons

The polycyclic aromatic hydrocarbons (PAHS), with their higher molecular weight, are hydrophobic, and bind strongly to soil particles and have low solubility. These heavier PAHs are therefore generally found at higher concentrations near the source of contamination, particularly in surface soils. The lighter, more soluble PAHs, e.g. naphthalene, are frequently detected in groundwater, although volatilisation and leaching losses reduce their concentrations in surface soils (compared to the heavier PAHs).

PAH concentrations and the pattern of individual PAH compounds detected in stormwater and sediments tend to reflect the contamination in the surface soils, i.e. higher concentrations of the heavier PAHs than the lighter PAHs.

The heavier PAHs resist natural biological degradation and are consequently more persistent in the environment. Lighter PAHs such as naphthalene are readily degraded where conditions favour biological activity. The biodegradation of PAHs is heavily influenced by the extent to which they bind to the soil particles. Heavier PAHs move slowly through soils with high organic content, but the presence of surfactants or dissolved organic matter can increase their solubility and hence mobility and tendency to biodegrade (Turczynowicz, 1993).

Volatilisation can be a significant fate and transport mechanism for the lighter PAHs, accounting for considerable loss of naphthalene and methylnaphthalene (Turczynowicz, 1993).

1.4.4 Inorganics

Inorganic contamination at former gasworks sites usually occurs at or near the ground surface. The mobility of inorganic contaminants depends heavily on their solubility and factors such as pH, and the presence of other chemical species, which affect solubility and binding of contaminants to the soil.

Shallow soil contamination by inorganics can be extensive at former gasworks sites, however deeper contamination can be more variable, depending on the volume and mobility of the source and the presence of preferential migration pathways.

Cyanide, ammonia and sulphate are frequently detected in groundwater reflecting the mobility of these contaminants. Complex cyanides are not particularly mobile in the soil, however complex cyanides may break down to form free cyanide in the presence of UV light. Low-level free cyanide does not persist in the soil environment, due to chemical and biological reactions, although higher-level free cyanide can inhibit biological processes. Anaerobic conditions favour the formation of cyanide complexes.

Catalysts are inert and non-radioactive and may be buried on site.

1.5 References

1. Department of the Environment (1987). Problems Arising from the Redevelopment of Gas Works and Similar Sites (Second Edition). Prepared by Environmental Resources Limited.
2. GRI (1987) Management of Manufactured Gas Plant Sites, Vol. 1. Wastes and Chemicals of Interest. Gas Research Institute, Chicago.
3. John Pollard, former gas engineer, personal communication.
4. Luthy R G et al (1994). Remediating Tar-Contaminated Soils at Manufactured Gas Plants Sites. Environmental Science and Technology, 28(6).
5. Meade A (1934). The New Modern Gasworks Practice. Eyre and Spottiswoode, London.
6. Turczynowicz L (1993). The Assessment and Management of Gasworks Sites. Proceedings of the Second National Workshop on the Health Risk Assessment and Management of Contaminated Sites, Canberra.

Appendix 1A

Fate and transport of organic contaminants in the subsurface environment

Forms of hydrocarbon contamination

Liquid phase

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

- mobile or free (free product) liquids moving down through the unsaturated zone or migrating near the top of the capillary fringe
- immobile residual liquids in the unsaturated zone
- immobile residual liquids trapped in the saturated zone
- free product on top of the water table (LNAPLs)
- free product below the surface of the water table (DNAPLs).

The particular form taken or the distribution between forms is dependent on the extent to which saturation of the pore spaces by hydrocarbons is possible and on the wetting characteristics of the geologic materials. Further, the degree of adsorption or absorption affects the contaminant plume and the extent to which the liquid is retarded and becomes immobile.

The amount of hydrocarbon product that can be sorbed is dependent on the residual saturation of the geologic formation, that is the amount of liquid the soil can hold. The residual saturation is dependent on:

- aquifer materials
- product viscosity
- the degree of water saturation
- the spill history
- rate and timing of the spill
- temporal and spatial extent of spill.

The degree of adsorption is dependent 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 water film and soil particles as they migrate through the soil-water, intermediate vadose, and capillary fringe zones occur.

Dissolved phase

Dissolved phase hydrocarbons exist in the following areas:

- in water infiltrating through the saturated zone

- in the residual films of water covering solid surfaces or filling pore spaces (water subject to sorption) in the soil water, intermediate vadose, and capillary fringe zones
- in groundwater within the saturated zone.

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 and in these zones they are potentially highly mobile
- the free liquid hydrocarbon plume
- water in the underlying capillary fringe and saturated zone.

Vapour may become entrained in the liquids (either groundwater or free organics) as small bubbles. The bubbles are relatively immobile, but may move slowly with liquid flow, dissolve into the groundwater, or be released into the soil air.

Subsurface hydrocarbon migration

The mechanisms for migration of hydrocarbon contaminants (including tars and PAHs) within the subsurface is central to assessing the fate and transport of the contaminant. This section provides information on migration processes that should be considered in the assessment of gasworks sites.

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, absorption), chemical degradation, diffusion (dilution, dispersion), solvation, volatilisation, and biodegradation. These processes affect the rate at which the hydrocarbon contamination migrates through the subsurface by dispersing or retarding the hydrocarbon compounds.

Physical and chemical processes

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

Absorption is the physical filling of pore space by a fluid.

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, chemical composition, and preferential pathways. Non-adsorbed compounds move with groundwater. A plume of adsorptive compounds will move more slowly than the groundwater.

The migration and adsorption potentials of various compounds can be compared 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.

Diffusion is the process in which molecular or ionic constituents move under their kinetic activity with or without a concentration gradient. 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 and is dependent on geologic material hydraulic conductivity, and groundwater flow rates.

Dispersion is the spread of chemical constituents in directions other than those that would be expected from advection, such as sideways spreading due to flow divergence around particles

or formations, i.e. it occurs due to mechanical mixing during advection, and attractive forces between fluids and soil particles. Diffusion is a dispersive process.

Chemical degradation through abiotic transformations due to naturally occurring chemical reactions may result in degradation of a chemical. BTEX compounds seldom chemically degrade, but several halogenated compounds undergo hydrolysis and dehydrohalogenation reactions in groundwater.

Volatilisation is the change of a compound 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 (of the order of a few percent). Optimum conditions for volatilisation would be in shallow groundwater and at high temperature. Volatilisation can be very significant in the removal of hydrocarbons from shallow or exposed soils. Light hydrocarbons tend to be more volatile than heavier ones.

Biological processes

Biological processes which result in the degradation of hydrocarbon compounds can have a significant effect on these contaminants in the ground. They can therefore be an important consideration when assessing sites and remediation options.

Subsurface microorganisms are generally present in the form of a fixed biofilm on the surface of geologic material, and in some circumstances these organisms can use carbon and energy in organic chemical pollutants as a food source. This results in the biodegradation or biotransformation of the organic chemical.

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

Degradation of gasworks contaminants varies considerably. The lighter contaminants (including MAHs and lighter PAHs) are readily degraded and eventually converted to carbon dioxide and water. PAHs are degraded more slowly.

Biodegradation is dependent on the correct conditions being available for the growth of microorganisms. Some of the factors affecting biodegradation rates include:

- the composition and size of the soil microbial population
- the presence of a suitable and bioavailable source of energy (carbon)
- the presence of oxygen
- the presence of heavy metals and complex cyanides
- 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.

If any of these factors is missing or deficient it will limit microbial activity and significant biodegradation will not proceed.

At some sites, biodegradation of the BTEX constituents by indigenous microorganisms appears to be the primary mechanism of natural attenuation.

Biodegradation of aromatic compounds under aerobic conditions (> 1 to 2 mg/l dissolved oxygen) is a significant mechanism for the natural attenuation of BTEX compounds. Biodegradation half-lives for benzene can range from 15 to 160 days or more for varying conditions when modelled as a first order process.

Anaerobic biodegradation rates are much slower than aerobic rates and hydrocarbons may be degraded under anaerobic conditions. For this reason contamination may occur in areas where the available oxygen is depleted.

Liquid phase migration

To assess hydrocarbon contamination, an understanding of the transport mechanisms of the various hydrocarbon phases is required. Following a release, free liquid product will move, under the force of gravity, down through the unsaturated zone towards the water table. A significant proportion of the free liquid will be absorbed into, or become adsorbed to, geologic particles as the vertical (and lateral) migration continues. 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 soil particles and hydrocarbons
- the attractive forces between the water and the hydrocarbons.

Layers with low hydraulic conductivity will slow or stop downwards migration and promote lateral dispersion of hydrocarbon liquids. Water or hydrocarbons moving downwards can become perched above these layers. If there is sufficient volume of liquid, or the impermeable layer is tilted, the liquid will migrate around laterally discontinuous impervious layers, and continue downwards migration.

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.

When the free organic liquids that are less dense than water first reach the capillary fringe the organic liquid piles up on the capillary fringe, not the water table. This compresses the capillary rise, displaces water, and creates a free organic liquid plume. 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. That is, the hydrocarbons spread more quickly than the rate of groundwater flow. This happens because the initial rate of migration is controlled by the pressure head of the free liquid and not by groundwater.

After reaching the capillary zone, the plume begins to migrate down gradient 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 plume is the lateral extension of the original subsurface hydrocarbon release. 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 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

Fine grained materials have larger surface areas which tend to retain more of the liquid, reducing the volume of free product. Coarse grained materials and formations containing

fractures and other secondary porosity features have smaller surface areas. Free organic liquids migrating through these materials are less likely to be immobilised by sorptive forces.

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. When the water table drops, free product associated with the capillary zone will descend leaving hydrocarbon liquid in the expanded unsaturated zone above the water table. This is known as smearing. Subsequent rises of the water table will cause the capillary fringe and associated product to move upwards. This may result in lateral spreading at a different 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 that are mobile and can flow into a well. This leads to seasonal fluctuations in detectable organic liquid thicknesses in wells. Smearing will also result in a continuing source of dissolved phase contamination.

Free organic liquids 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.

Dissolved phase migration

Free organic liquids are transformed into the dissolved phase when the liquid hydrocarbons contact subsurface water. This contact can happen when:

- water infiltrates through an unsaturated zone which contains residual adsorbed organics
- groundwater contacts a free organic's plume.

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

- the depth to the water table
- soil and rock hydraulic conductivities
- recharge rates
- water table fluctuations
- groundwater velocity
- water temperature
- 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 due to changing groundwater velocities which result in greater mixing.

Vapour phase migration

Vapour phase migration is particularly important with respect to accumulation of organics in indoor air. Vapour phase organics in the subsurface result from the volatilisation of organics from:

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

The migration of vapour is controlled by many parameters including:

- Chemical and physical properties of the organic 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
 - Man-made structures

In general, vapour tends to follow the most conductive pathways and travel from areas of greater to lesser pressure. Because organic vapours are generally more dense than air, they can accumulate in low areas such as buildings, sewers, underground service trenches and ducts, and other structures open to the atmosphere.