

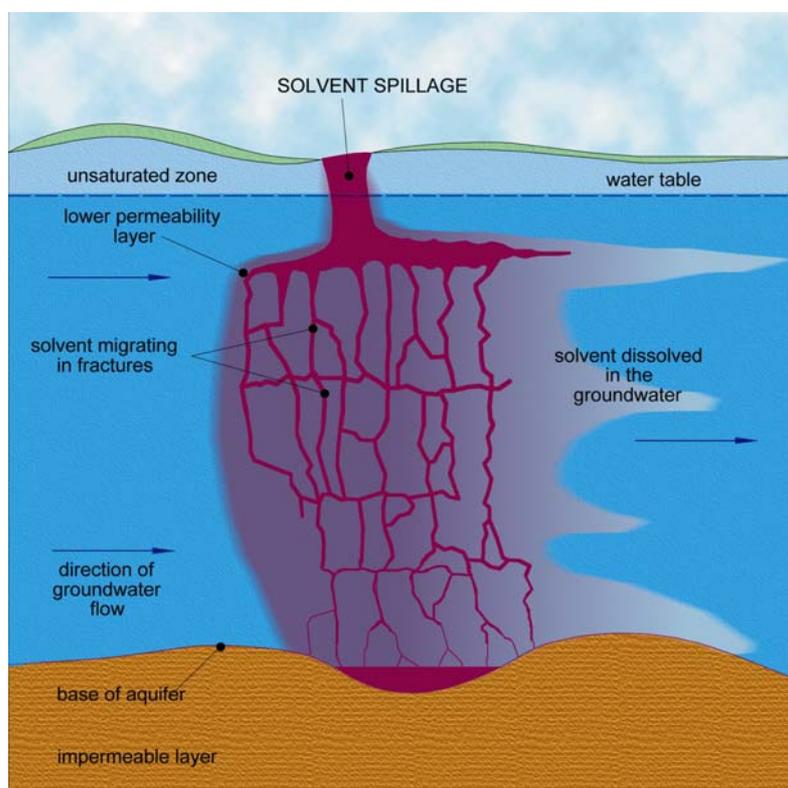
Industrial and urban pollution of groundwater

The risk from industrial chemicals

The exponential growth of the petrochemical and pharmaceutical industries in the 1950s introduced a wide range of complex organic wastes into the urban environment. A serious risk to groundwater quality has arisen from accidental spills or leaks from tanks and pipelines of petroleum products, phenols and chlorinated hydrocarbons. Some of these substances are soluble in water but many are only slightly soluble. The latter are referred to as non-aqueous phase liquids (or NAPLs) and they are divided into light and dense NAPLs according to whether they are less or more dense than water. Light NAPLs are mainly petroleum products and the dense variety include the chlorinated hydrocarbons widely used as industrial solvents. The concentration of these compounds allowed in drinking water is in the parts per billion range. Many are sufficiently soluble to make it possible to exceed these very low limits.

When a NAPL is spilled on the surface of a sandstone, it infiltrates slowly down through the saturated zone moving from pore to pore once the saturation of the hydrocarbon exceeds a threshold known as the residual saturation. The volume of the contaminant that is mobile steadily decreases because some is retained in each pore at the residual saturation. Thus with a small spill the contaminant may be retained entirely in the unsaturated zone once all the spill is at residual saturation in the rocks. With a larger or continuous spill the NAPL will eventually reach the capillary fringe. As it moves down through the unsaturated zone is also spreads laterally, because capillary forces as well as gravity control its migration. In fractured rocks progress may be much more rapid with the contaminant following the most permeable route.

When the NAPL reaches the capillary fringe, if it is a light NAPL, it will accumulate near the top and flow in the direction of the hydraulic gradient



Pollution of the Chalk by the solvent tetrachloroethylene (a dense NAPL). Migration of the pollutant below the water table is retarded by a layer of chalk of low permeability. Below this layer the pollutant is migrating in the fractures in the aquifer and collecting at the base. Pollutant dissolved in groundwater is migrating through the aquifer in the direction of groundwater flow.

once a critical thickness is attained. The contaminant continues to spread until the entire spill is at residual saturation.

When a dense NAPL reaches the capillary fringe, downward flow continues as before once the residual saturation of each pore is exceeded. This continues until it reaches the base of the aquifer, again until the entire spill is at residual saturation. The direction of flow in this case may not coincide with the hydraulic gradient.

Pollution of an aquifer by NAPLs can increase by slow dissolution in groundwater. The resulting contaminant plume can be much larger than the spread of the spill itself and, because of the slow rate of dissolution, can persist as a source of pollution for decades.

Light NAPLs are more easily controlled as they float on the water table and occur at relatively shallow depths. Dense NAPLs move under the influence of their density and can penetrate to considerable depths. Once an aquifer is contaminated it is likely to remain so as remedial measures tend to be ineffective.

A single spill has the potential to contaminate a very large volume of water to levels in excess of the low concentration acceptable in drinking water. The wide distribution of petrol stations and extensive networks of pipelines carrying petroleum products illustrates the potential risk to groundwater quality.

A spill of the solvent tetrachloroethylene, a dense NAPL, at a leather-processing factory in Cambridgeshire, polluted the Chalk to a depth of 50 m and extended for at least 2 km in the direction of groundwater flow. A major public water supply pumping station became contaminated. Because of the scale of the spill and the gradual dissolution of the contaminant in the groundwater, the contamination is likely to persist for many years.

At present the water industry must combat the threat by treating polluted water or replacing the source — both are very expensive options to overcome a problem largely caused by carelessness.

Prevention is cheaper than cure

The Groundwater Protection Policy of the environment agencies sets out a framework of guidance within which everyone can ensure groundwater resources are safeguarded for the future. One advantage is that developments which pose a risk to the quality of groundwater can be assessed at the planning stage and if necessary modified or even rejected.

An example that poses a particular risk is a petrol filling station on an aquifer such as the Chalk,

particularly if it is close to a public supply borehole.

The very fractured nature of the chalk, and its resulting high permeability, provides a ready passage for the flow of pollutants from the ground surface to the water table. In this situation a petrol station on the Chalk undoubtedly poses a considerable risk to groundwater quality. It is unacceptable in Zone I of the Source Protection Zone (see 'Vulnerable aquifers need protecting') and should be discouraged in Zones II and III around a public supply borehole.

Modern petrol stations should incorporate a multi-layered system to contain any leakage from their storage tanks or the forecourt. These include double-skinned tanks in a concrete vault lined with synthetic polymer membranes, and compacted clay. In the short-term these precautions do afford an adequate safeguard, but components deteriorate, concrete cracks, synthetic membrane may be breached, and, as the integrity of such a system cannot be monitored in a practical manner, it does not provide a reliable effective long-term barrier against leakage.

What may be immediately at risk from a petrol station is a source of public supply providing perhaps 5 million litres of water per day for some 30 000 people. The Drinking Water Standard for dissolved or emulsified hydrocarbons is only 10 micrograms per litre (that is 1 part per 100 million parts of water). Once a fine-grained aquifer such as the Chalk is contaminated it is well nigh impossible to clean it up to drinking water standards. The cost of a replacement water supply could be at least £5 million. The careful assessment of planning applications for the storage of chemicals in a Groundwater Protection Zone is, therefore, a wise precaution.

The disposal of radioactive waste

Much concern has been expressed about the safe disposal of radioactive waste. For the general public it has become an emotive subject as the waste remains radioactive for many years and unless proper safety precautions are taken radiation can be a risk to health.

Small amounts of very low-level radioactive waste have been disposed of in landfills, but most low-level waste is deposited in concrete vaults and trenches in glacial deposits at Drigg, near Sellafield in Cumbria.

A favoured preference for the disposal of intermediate-level waste, and also longer-lived low-level waste, which cannot be disposal of at Drigg, was deep disposal in an underground repository, constructed at a depth of about 1 km in very impermeable rocks.

Classification of radioactive waste

- Low-level waste, mainly discarded clothing and wrapping materials. It comprises about 90% of the total volume of radioactive waste and represents only a small risk.
- Intermediate-level waste comprising metal fuel cladding, reactor components and chemical sledges. It forms 10% of the total waste volume and has a long lifespan of radioactive decay. This waste must be shielded from the environment and an option is disposal in a deep repository.
- High-level waste arising from reprocessing of nuclear fuel. It comprises only 0.1% of the total but contains 95% of the radioactivity. The current policy is to store this waste at the surface in a vitrified form, until its temperature has dropped sufficiently to allow safe disposal.

However, the plans to develop this facility beneath Sellafield were not approved by the local council.

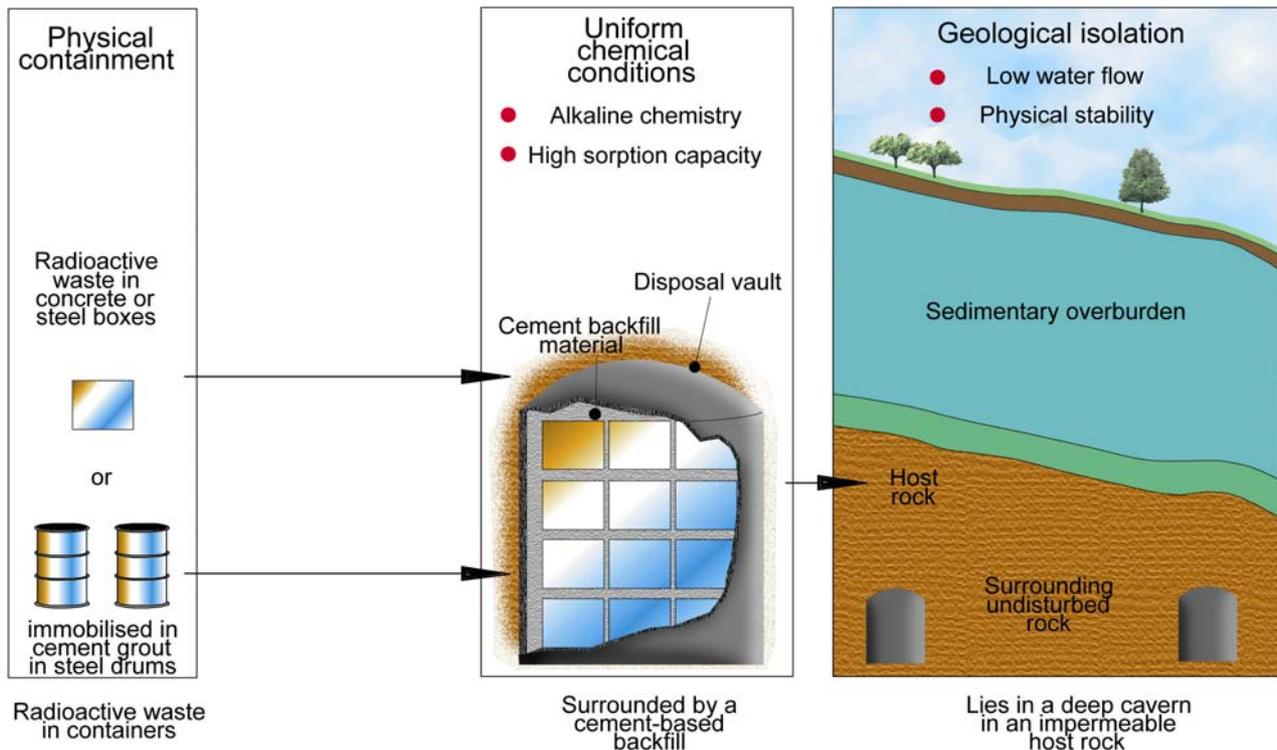
The objective was to take advantage of the fact that water in such rocks is extremely old, very

saline and is moving exceedingly slowly. To guard against the risk of contaminating the biosphere, the concept behind such deep burial was to provide a containment facility with several barriers to prevent the migration of the radio nuclides. This is referred to as the multi-barrier containment concept.

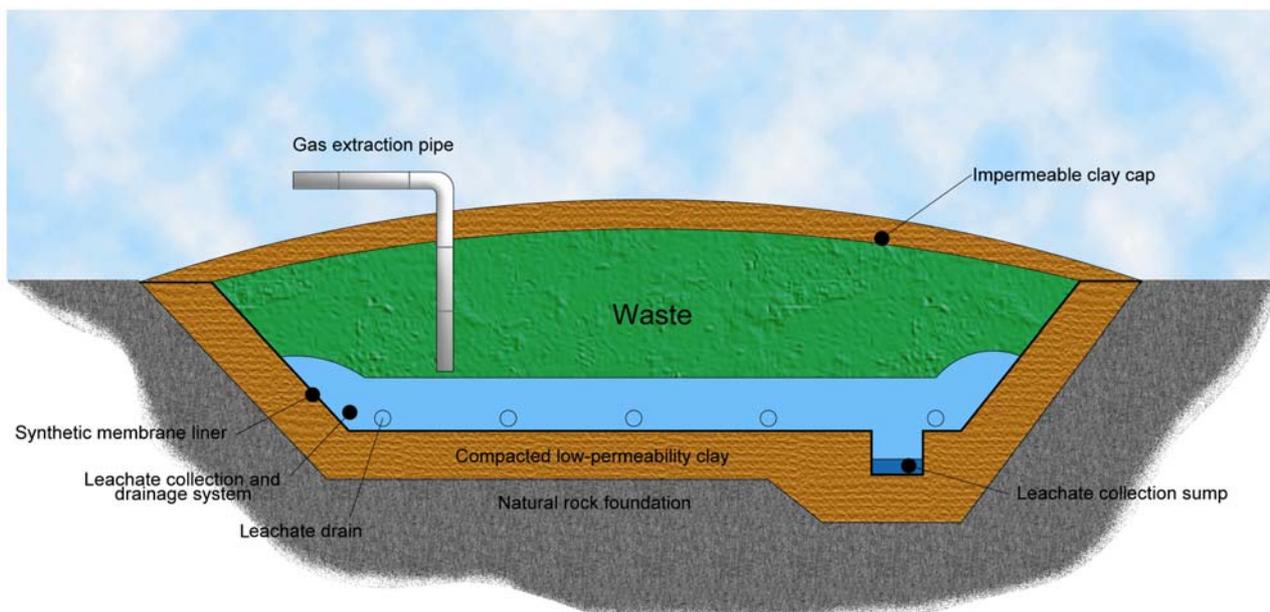
The wastes, in steel or concrete containers were to be placed in excavated chambers in the rock which were then to be backfilled with a cement-based material. The backfill would have had a high surface area to absorb radio nuclides, and it would have maintained alkaline conditions in the pore waters and thereby suppressed the solubility of important radio nuclides. The host rock itself would have provided a final barrier with a long pathway and time of travel in slowly moving groundwater to the biosphere. Any radio nuclides that entered the groundwater, slowly flowing through the rocks, would have been retarded by adsorption and diffusion into the rock matrix. The concept makes use of engineering, chemical and natural barriers to achieve long-term containment.

Leachates from landfills

Each year over 150 million tonnes of solid waste from domestic, commercial and industrial sources are disposed of in landfills. The waste ranges from inert waste with a low polluting potential to hazardous chemical wastes. Landfilling is often the cheapest disposal option.



Multi-barrier containment concept for the disposal of low-level and intermediate-level radioactive wastes.



Cross-section of a modern landfill. The design incorporates a synthetic membrane liner (about 2.5 millimetres thick) on a layer of low-permeability clay (about 1 metre thick). The leachate is drained to a sump by a network of pipes in a permeable drainage layer. Any gas generated is collected by means of a system of pipes. (Not drawn to scale).

Solid wastes pose a threat to groundwater quality through the formation of polluting liquids known as leachates.

These form as water percolates through the waste, dissolving soluble compounds and the degradation products of chemical and biochemical reactions that take place in the waste. Domestic solid waste gives rise to a very polluting leachate. It decomposes under anaerobic conditions after a brief aerobic stage of a few months; a final stage leads to the production of methane, by which time the polluting strength of the leachate is reduced. The entire decomposition process can take decades, the rate being very much a function of the amount of water that can gain access to the waste.

There are thousands of landfills in the UK. Many are old or disused and now classified as 'contaminated land'. Modern landfills are carefully constructed so that the liquid waste products are contained. In the past it was considered acceptable to allow leachates to seep from the base of the waste into underlying rocks where they were diluted by the groundwater and gradually dispersed through the ground. Percolation through rock does improve their polluting strength but such processes are not entirely reliable and any risk of polluting groundwater in this manner is not now acceptable.

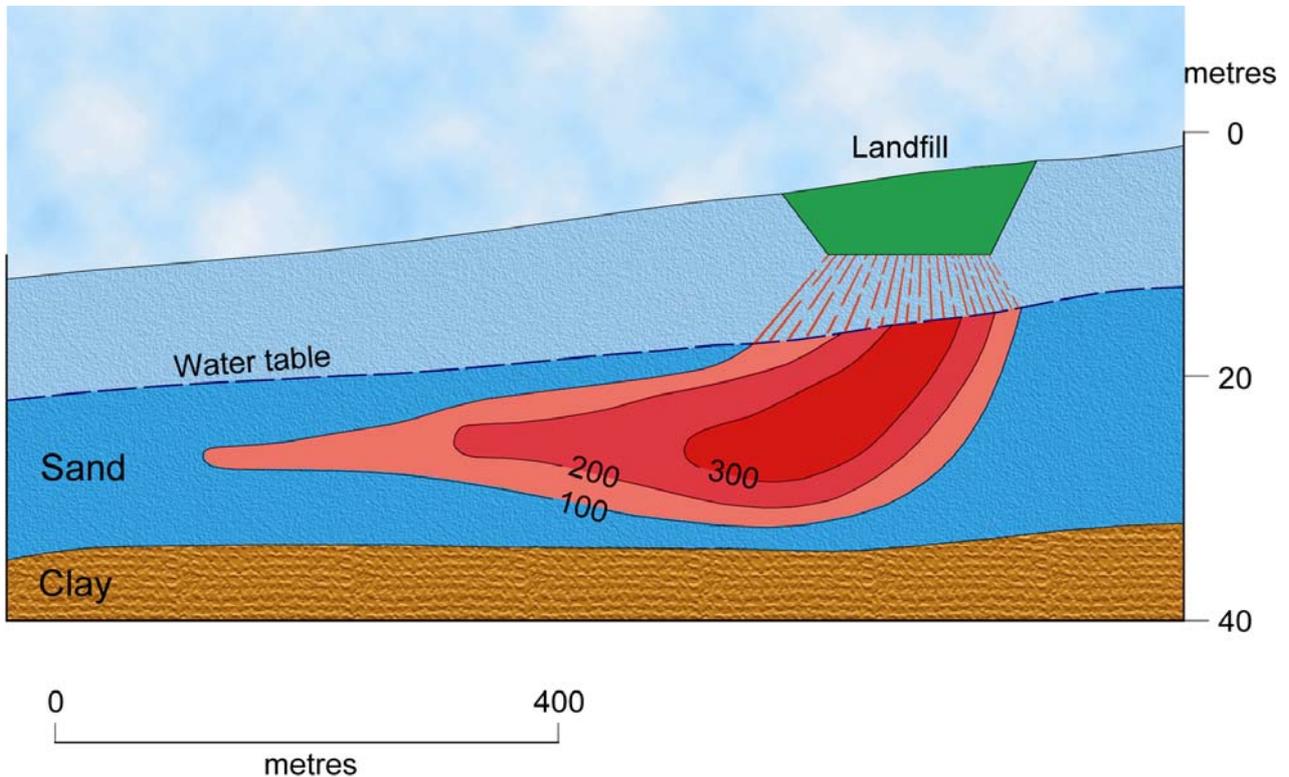
Instead landfills are lined with clay and flexible synthetic membranes, intended to prevent leachate escaping and contaminating groundwater. The leachate is drained to collecting

sumps for subsequent treatment. Methane is also collected and either vented to the atmosphere, or used for heating, even the generation of electricity.

The current disposal practice is designed to create very compact dense waste which effectively reduces its contact with water.

Furthermore, the waste is covered with a layer of clay to prevent, or at least reduce, the ingress of surface water. This practice reduces the rate of decomposition. It may be decades before leachate and gas are produced, especially in the large and deep sites that are now favoured. Recent views are that water should not be excluded and that ideally landfills should be very efficient bioreactors with high rates of leachate formation and accelerated rates of decomposition. A landfill should reach a final stable unpolluting state within out about 30 years. This could mean that it is necessary to irrigate the waste with water or recycle the leachate to encourage decomposition.

Landfill operators are required to have a licence from one of the environment agencies and to adhere to waste management licensing regulations. Landfills must be designed and constructed to high engineering standards and ensure containment of waste products and thereby provide long-term protection of the environment. However, although much is known about the processes in a landfill, monitoring facilities around sites and the assessment of the performance of sites are relatively undeveloped. There are no well-defined standards of performance.



Migration of a plume of leachate from a landfill. The high chloride concentrations in the groundwater (the units are milligrams per litre) show the extent of the plume. Landfills are now designed so that leachates are contained in the structure and collected for appropriate disposal. Contamination of underlying aquifers should not occur.

The efficacy of the long-term containment of wastes has yet to be demonstrated and the overall risk to groundwater quality remains uncertain. However, although landfills are potential threats to groundwater quality, any pollution that occurs is localised and quite dissimilar to the more widespread pollution that arises from agriculture and from urban areas. Nevertheless, reducing the polluting impact of landfills remains a prime consideration.



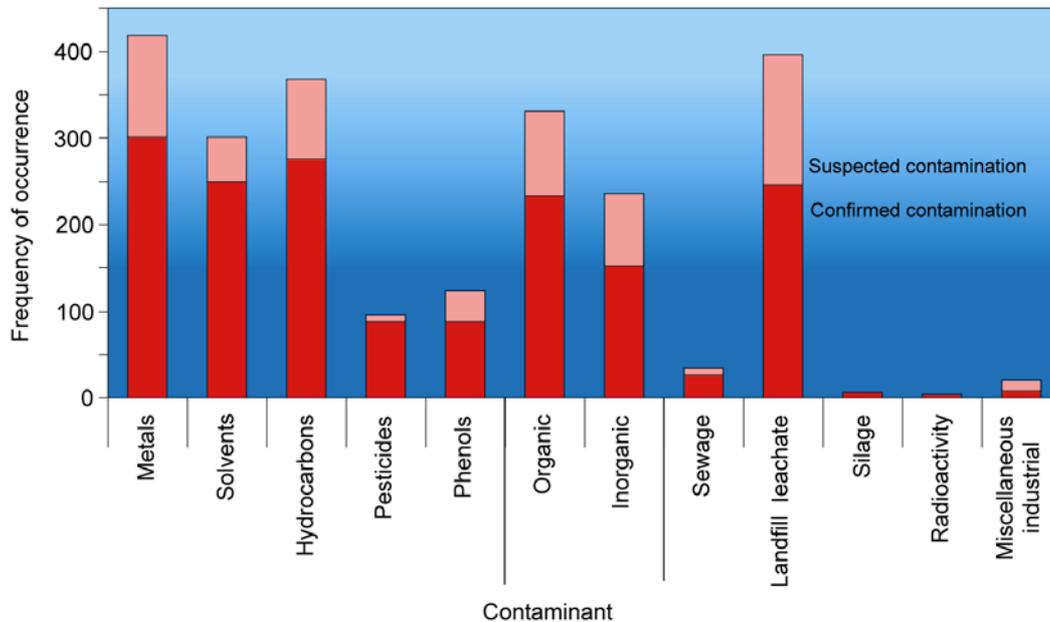
Laying a liner of synthetic membrane for a new landfill.

Contaminated land and urban pollution

Contaminated land and urban pollution are legacies of the Industrial Revolution and the subsequent industrial expansion. For over 200 years, industrial wastes have been disposed of, and spilled in and near urban areas, and many contain potential groundwater contaminants. Initially they were mainly mining and foundry wastes, essentially inorganic compounds, but eventually they included tars, phenolic wastes, oils and, more recently, complex synthetic organic compounds. These and similar substances have contaminated large areas of land particularly in urban areas but also around mines, military installations and old landfills.

Land contaminated in this manner can give rise to a range of liquid and gaseous pollutants, and the more soluble and mobile infiltrate to the water table. Below many industrial sites there are plumes of contaminated groundwater slowly moving down the hydraulic gradient.

It has been estimated that over 500 square kilometres of contaminated land exist in the UK, distributed over more than 50 000 sites, although only some pose a threat to the quality of groundwater. A particular risk arises when sites



The frequency that particular contaminants occur in groundwater in England and Wales. The data are from a survey by the Environment Agency of groundwater pollution.

are redeveloped, as this disturbs and may remobilise pollutants.

Land is contaminated when substances are present at concentrations that could be harmful to humans, animals or the environment as a whole. To pose a risk there must be a source of contamination, a pathway that allows the contaminant to migrate, and a specific location (or target) which may be affected. To put this in a groundwater context with a typical example, old gasworks produced coal, or 'town', gas until the mid-1960s, contaminating the ground underlying the works with compounds including coal tar, phenols, cyanides, heavy metals and sulphur compounds. These substances were dissolved by infiltrating water and the groundwater became contaminated over a much greater area. If the groundwater flowed to a borehole or well used as a source of drinking water, then the risk sequence was completed.

The decontamination of such a site may involve pumping and treating the groundwater, as well as the removal of the contaminated soil to landfills, or the treatment of the soil on site by one of the remedial methods available. Such land reclamations are obviously extremely costly.

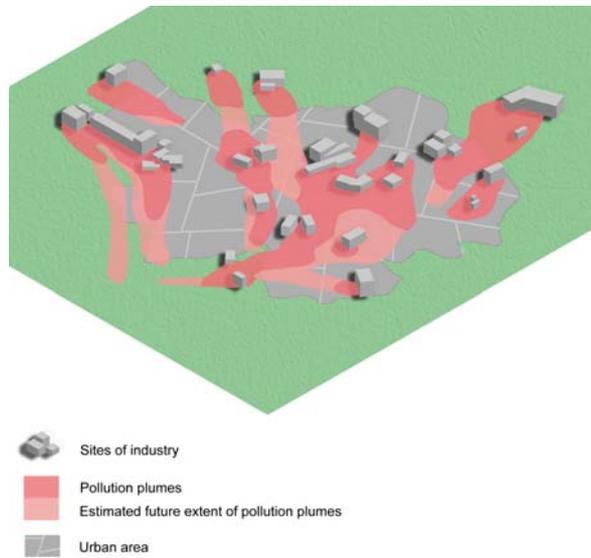
The scale and nature of the problem of contaminated land in urban areas and around industrial complexes remains uncertain. Currently this is being assessed by the environment agencies. There is not a national register of contaminated land but local authorities are compiling their own registers, and have powers to investigate potential problems and

require remediation where a risk to the environment or public health can be demonstrated. The onus for cleaning-up contaminated land, however, is with the owner.

Generally it can be assumed that urban areas are centres of groundwater pollution from industrial zones, railways, and possibly leaking sewers. Studies of the quality of groundwater below the cities of Birmingham and Coventry revealed that pollution by organic and inorganic compounds was extensive. The predominant organic pollutants were chlorinated hydrocarbon solvents. There was a close correlation between land use and the pollutants identified. Widespread contamination of groundwater by solvents in the Chalk below Luton has also been recorded.

A survey of the extent of groundwater pollution in England and Wales, by the Environment Agency, revealed that the main sources of pollution were landfills, the chemical and metal processing industries, and gas works, power stations and petrol service stations. The pollutants most frequently recorded were metals (particularly arsenic, copper and chromium), organic compounds and landfill leachates. The Chalk and the Triassic sandstones in the Midlands and north-west England were the aquifers particularly affected.

Usually the effect on groundwater is localised near the site in question, although in urban areas where there are many potential sources of pollution, contamination is widespread, as in Coventry and Birmingham. Cleaning-up



The contamination of groundwater below an urban area in the Midlands. The map shows the present and estimated future contamination of groundwater by chlorinated hydrocarbon solvents.

contaminated groundwater is of growing interest but the cost of clean-up, is set against the benefits that accrue, is also an important consideration. In some situations, for example where the groundwater is not likely to be used for drinking, less stringent levels of 'clean-up' may be appropriate. The question that must be answered is: does the contamination pose a potential risk to human health, or the environment, on the basis of current and anticipated use of the site or area?

Remedies for pollution

If groundwater is contaminated by a relatively small-scale source of pollution such as a spill of hydrocarbons, the question is: how can the quality be restored or at least improved to an acceptable standard?

The first concern is to determine the distribution of the contaminant in the aquifer, whether it is in the unsaturated zone or the saturated zone or both, and whether it is entirely in solution or there is a non-aqueous phase. Answers to these questions will suggest a possible remediation strategy as shown below.

Despite the availability of these techniques, restoring an aquifer to its original pristine state is difficult if not impossible. When a contaminated aquifer is pumped, the groundwater flows preferentially through the more permeable horizons and consequently these are cleaned relatively easily and quickly. However, contaminants that have penetrated into less permeable horizons and the smaller pore spaces may be virtually unaffected. When pumping stops, contaminants from these zones diffuse into

the permeable zones that have been cleared. The more permeable fractures in the Chalk represent only 1 or 2% of the total rock volume while the relatively immobile water in the matrix represents 25 to 40%; in this situation the cleaning process can take a very long time. Similarly, if nutrients are injected to encourage biodegradation they may penetrate only slowly into the less permeable horizons.

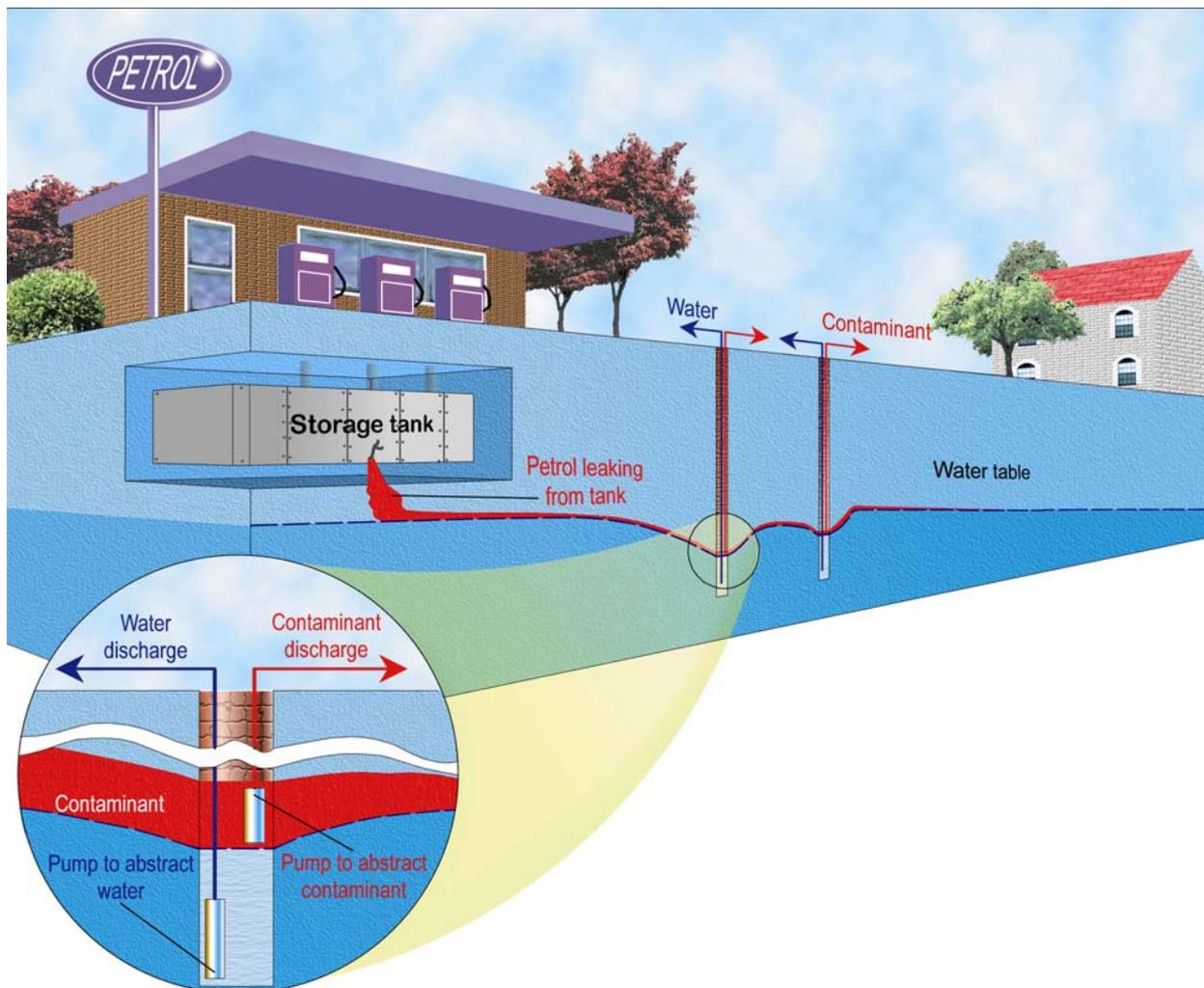
The difficulty of cleaning an aquifer emphasises the need to minimise all forms of pollution. Where it does occur, the problem should be tackled at or as near the source as possible and as soon as possible after the event. It must be accepted that with existing technology, groundwater quality often cannot be restored within a reasonable time and at a reasonable cost. Nevertheless, wherever pollution occurs in an aquifer it should be contained and treatment initiated, bearing in mind the use made of the groundwater, any health risk that exists and cost.



On-site treatment of groundwater pumped from an aquifer contaminated by chlorinated hydrocarbons.

There are four basic remediation methods:

- Containment of the pollution, that is, prevent it spreading by using physical barriers such as sheet piles, cement grouts and impermeable membranes.
- Removal of the contaminated water by pumping and then treating it to an appropriate quality. The water can then be either re-injected into the aquifer or used directly for water supply.
- Removal of the volatile fraction of a contaminant by a process called 'bioventing'. Soil gas is removed by vacuum pumping from a borehole. This circulates air which volatilises and assists in the degradation of organic contaminants. The method removes volatile contaminants from an aquifer that are present at less than the residual saturation level.
- Bioremediation to deal with organic contaminants. The technique is intended to encourage bacteria to grow by adding nutrients to the contaminated zone. Organic matter is degraded into simple compounds such as water and carbon dioxide. Alternatively, specific bacteria can be introduced to metabolise a particular contaminant. The process can be encouraged by injecting air into the contaminated zone from a borehole. This stimulates aerobic biodegradation. Under favourable conditions, bioremediation can occur as a result of natural processes in an aquifer. Indigenous microbes will degrade organic contaminants if a supply of nutrients is present for their metabolism.



Dealing with groundwater contamination. Petrol leaking from a fractured storage tank contaminates groundwater. It flows down the hydraulic gradient, is intercepted by boreholes, and pumped to the surface where it is recovered. The boreholes contain two pumps. The lower pump abstracts water and creates a hydraulic gradient towards the borehole. The upper pump abstracts the contaminant, in this case petrol. The groundwater that is abstracted may have to be treated before being used or re-injected into the aquifer.

Mine drainage

Coal and metalliferous mines can be hundreds of metres deep, with the workings well below the natural water table. Consequently, deep mining is only possible if mines are drained by pumping. At the time of maximum coal output from mines in England and Wales some 450 million cubic metres of water were pumped each year for drainage purposes. The collieries of South Wales and Scotland were particularly wet, pumping 8 and 10 cubic metres of water respectively, per tonne of coal mined, although the average drainage-output ratio for collieries in England and Wales as a whole was 2 cubic metres per tonne of coal.

Coal seams and mudstones in the Coal Measures contain pyrite (ferrous sulphide) which was subject to oxidation by air as the water table was lowered, the process being supported by sulphur-oxidising bacteria. As a result, water draining from coal mines can be very acidic, with pH values of 2 or 3, due to sulphuric acid, and high concentrations of sulphate and iron, as well as other metals, in solution. Similar waters form in metalliferous mines and in mine wastes.

The discharge of such waters to rivers is detrimental. The iron precipitates as ferric hydroxide when the pH rises above 6, following reactions with the river sediments and mixing with alkaline waters in rivers, and when bacterial oxidation of the ferrous compounds occurs. The iron precipitate discolours the rivers leaving



Contamination of the River Esk in East Lothian by ferruginous groundwater discharging from an abandoned coal mine.

unsightly ochrous deposits and the oxidation process leads to the depletion of the oxygen in the river water.

Ferruginous waters discharging from disused mines have been a problem for decades, but with the closure of so many coalmines, beginning in the 1950s and continuing into the 1990s, the problem has been accentuated. As mines closed, pumping stopped or was reduced and groundwater levels recovered. The rate of recovery depends very much on the rate of flow into the workings and their extent. In some cases complete recovery may take several decades. As well as contaminating rivers, rising acidic ferruginous groundwater may in the future contaminate aquifers overlying the Coal Measures such as the Permian Basal Sands, the Magnesian Limestone and the Permo-Triassic sandstones. The rise of water levels can also lead to subsidence as a result of the weakening and eventual collapse of strata left to support the roof in shallow workings. The corrosion of engineering structures that contain Portland Cement and the flooding of landfills are other problems.

The quality of the discharge from disused mines improves gradually with time as the rising groundwater flushes the acidic oxidation products out of the Coal Measures, but the process can take many years.

Increasingly widespread pollution by such acidic ferruginous waters seems to be inevitable unless expensive treatment methods are introduced or pumping from some mines is continued to control the discharges. The circulation of contaminated ferruginous waters through artificially constructed wetlands, which improves their quality, is being investigated as a relatively cheap solution to the problem.

Responsibility for pollution by acid mine-waters is very unclear. Mine owners who permit pollution from abandoned mines are given indemnity under the Water Resources Act of 1991 and, in Scotland, the Control of Pollution Act of 1974. The Environment Act 1995 removed this defence but only for mines abandoned after 1999. This leaves the legal responsibility and the problem unresolved.

The rebound of groundwater levels in coalfields

The recovery of groundwater levels in coalfields that are no longer mined has caused serious environmental problems in many areas and potential future problems in others. The coalfields in Scotland afford numerous examples, a case in point being the Dalquharran Colliery in Ayrshire, where pumping for drainage purposes ceased in 1977. Groundwater levels recovered and water began discharging from the mine in 1979 at rates

rising to 13 Ml/d. The water flowed into the River Girvan. As it contained 1200 mg/l of iron, 100 mg/l of aluminium and 6000 mg/l of sulphate, the effect on the ecology of the river was devastating. The problem was ameliorated by adding lime to the outflow and controlling the rate so as to link it to the flow of the river, thereby ensuring dilution.

The mine workings in the Durham Coalfield are extensively interconnected. While the collieries were operating, groundwater levels were maintained some 150 metres below the ground surface by pumping almost 100 Ml/d from nine

pumping shafts. The quality of the water was quite good and most was discharged into the River Wear providing nearly 50% of the flow in dry spells. Once this pumping stops, the rising groundwater will dissolve the oxidation products of pyrite in the Coal Measures to give an acidic water, with large concentrations of metal ions in solution, which will discharge ultimately into the river system. The Permian aquifers that overlie the Coal Measures are also likely to be contaminated. Complete recovery of groundwater levels in the Durham Coalfield may take 30 or 40 years.