GLOSSARY OF CHEMICAL AND RELATED TERMS USED IN CONTAMINATED LAND PRACTICE
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INTRODUCTION

This glossary sets out some of the chemical and related terms used in contaminated land practice. It is based on UK practice and it should be noted that slightly different terminology or contaminant groupings may be used in other countries.

CONTAMINANT GROUPINGS

It has become common practice in contaminated land discussions to group chemicals together. Reasons for the groupings include:

- they tend to occur together in contaminated land;
- analytical techniques may be similar;
- they have similar physical properties;
- they are similar chemically.

Use of chemical groupings can save time in discussions, for example, with analytical laboratories. However, it should not be assumed that everyone will have the same understanding of the definition/members of a group. Examples of groups and possible definitions are as follows:

ADE Average daily exposure – used in assessment of possible effects of contamination in land

Aliphatics Organic hydrocarbons (chemicals containing carbon and hydrogen and/or other species) with straight or branched chains but no aromatic ring structures.

Aromatics Hydrocarbons containing one or more six carbon, benzene rings.

BTEX Benzene, toluene, ethyl benzene, xylenes. These are typically the major components of the aromatic fraction of petrol.

Chlorinated aliphatics Aliphatic compounds with chlorine atoms attached to one or more carbon atoms. Examples include vinyl chloride, dichloromethane, trichloromethane, tetrachloromethane (i.e. methane with one to four hydrogens substituted by chlorine), trichloroethene, tetrachloroethene, 1,2 dichloroethane – all these examples are also VOCs and also may be referred to as chlorinated solvents.

Chlorinated aromatics Aromatic compounds containing chlorine, e.g. chlorobenzenes, hexachlorobenzene, PCBs, PCDDs, PCDFs, chlorophenols, chloronaphthalene.

DNAPLs Dense non aqueous phase liquids. Any chemical or mixture of chemicals that can form a separate phase which sinks through water (i.e. is denser than water and is present in sufficient quantity that it is not all dissolved into any available water, e.g.

local groundwater). Chlorinated solvents such as tetrachloroethylene (C_2Cl_4) and tetrachloroethane ($C_2H_2Cl_4$) are DNAPLs. See also LNAPLS and NAPLS.

DROs   Diesel range organics such as diesel oil, heavy hydrocarbons of low volalility.

Dry residue   Total solids in a water determined by evaporation to dryness at a specified temperature, expressed as mg/litre. See also SS.

EC   Electrical conductivity, units are likely to be milli- or micro- Siemens. See also total dissolved solids (TDS).

Heavy   Literally metals with a high specific gravity, for example >5.
metals   More generally potentially toxic metals, typically transition metals such as cadmium, chromium, copper, lead, mercury and nickel. However, other elements can be included such as selenium, boron, arsenic ….

LNAPLs   Light non aqueous phase liquids. Any chemical or mixture of chemicals that can form a separate floating phase on water (i.e. is less dense than water and is present in sufficient quantity that it is not all dissolved into any available water, e.g. local groundwater). BTEX compounds are LNAPLs.

MTBE   Methyl tertiary butyl ether an oxidant used in petrol – especially unleaded petrol.

NAPLS   Non aqueous phase liquids (see DNAPLS and LNAPLS). Note: some non aqueous phase liquids may be of similar density to water and thus be neutrally buoyant (no tendency to float or sink). However, they may have different temperature coefficients of expansion and thus become DNAPLS or LNAPLS depending on temperature.

PAHs   Polycyclic aromatic hydrocarbons, species with two or more benzene rings fused together with at least two common carbons e.g. naphthalene (2 rings), anthracene and phenanthrene (3 rings) and benzo(a)anthracene, chrysene and pyrene (4 rings) and benzo(a) pyrene with 5. Fluoranthene, benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene are examples of more complex systems including a five membered ring.

PCBs   Polychlorinated biphenyls. Biphenyl consists of two benzene rings linked through one carbon atom on each ring. In chlorinated biphenyls, some or all of the remaining the carbon sites are chlorinated. There are 209 different PCBs (different congeners) depending on the degree of chlorination and the position of the chlorines on the benzene rings. Contamination will consist of a mixture of PCB congeners of different degrees of chlorination and different toxicities. PCBs were used as heating fluids and cooling fluids (the latter, for example, in transformers, capacitors etc) .

PCDDs   Polychlorinated dibenzo-p-dioxins. A class of chlorinated compounds containing two benzene rings linked at two carbon atoms through oxygen atoms.

PCDFs   Polychlorinated dibenzo-furans (furans include five membered rings, four carbons and an oxygen).

Phenols   A class of aromatic hydrocarbons in which one or more hydroxyl groups (OH) are attached directly to a benzene ring. The simplest member of the class, phenol

consists of a benzene ring with a single hydroxyl group. It is also known as carbolic acid.

SS   Suspended solids. In water and waste water treatment, solids that could be removed by filtration. May include both organic and inorganic solids. Usually expressed as mg solids per litre of water. See also TDS and Dry residue.

SVOCs   Semi volatile organics compounds. SVOCs will include some PAHs.

Tars   By-products of the distillation of coal and other organics. Likely to be rich in PAHs.

TDS   Total dissolved solids determined by evaporation to dryness, expressed as mg/litre. May be determined by evaporating a water sample to dryness (see Dry residue) but often estimated from electrical conductivity by multiplying the electrical conductivity by a constant (which depends on the concentration range).

TEM   Toluene extractable material. An indicator of the quantity of low volatility organics in a sample. The sample is extracted with toluene and the extract allowed to evaporate and the residue weighed. May be useful for coal tars etc. Elemental sulphur is extractable and will be included in the TEM. Now seldom used.

TPH   Total petroleum hydrocarbons. May be subdivided into aliphatic and aromatic (benzene ring containing) species and by number of carbon atoms e.g. aliphatic C_5 - C_8, C_9 - C_{16}, C_{17} - C_{35} and aromatic C_6 - C_8, C_9 - C_{16}, C_{17} - C_{35}.

VOCs   Volatile organic compounds. Any organic compound which evaporates easily at ambient temperatures. VOCs may cause stratospheric ozone depletion. Examples include chlorinated solvents and benzene.

OTHER TERMS

ADI   Acceptable daily intake (used in health assessments).

ALARP   As Low As Reasonably Practicable – a principle used when assessing control measures taking into account the practicalities of the task in hand.

ALARA   As Low As Reasonably Achievable.

Anthropogenic   Man-made or influenced.

BAT   Best Available Techniques - these are required to be considered (under EC Directive 96/61) in order to avoid or reduce emissions resulting from certain installations and to reduce the impact on the environment as a whole. BAT is required when licensing major potentially polluting industries under the IPPC legislative regime. BAT takes into account the balance between the costs and environmental benefits.

BPEO   Best Practicable Environmental Option. BPEO has been defined by the Royal Commission on Environmental Pollution (RCEP) as "*the outcome of a systematic consultative and decision making procedure which emphasises the protection and conservation of the environment across land, air and water. The BPEO procedure establishes for a given set of objectives, the option that provides the most benefits or*

the least damage to the environment, as a whole, at acceptable cost, in the long term as well as in the short term".

CERCLA   Comprehensive environmental response, compensation and liability Act, 1980 (USA).

CLEA   Contaminated land exposure assessment tool, a key risk assessment tool for use with the Part IIA Statutory Guidance on contaminated land.
See:
https://www.gov.uk/government/publications/contaminated-land-exposure-assessment-clea-tool

Contaminant   In contaminated land usage "contaminant" and "pollutant" both mean a substance relevant to the Part 2A regime (of the Environmental Protection Act) which is in, on or under land and which has the potential to cause significant harm to a relevant receptor, or to cause significant pollution of controlled waters.
For in depth review, see:
https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/223705/pb13735cont-land-guidance.pdf

COSHH   Control of substances hazardous to health regulations, 2002 (UK).

EA / EPA   Environment Agency (UK); Environmental Protection Agency (USA).

Ingestion   Contaminant entering the stomach and gastrointestinal tract through eating contaminated food or hand to mouth contact.

Inhalation   Breathing in through the nose or mouth, a significant health pathway for fine particulate (dust) matter and vapours.

IRIS   Integrated risk information system useful source of data on health hazards of chemicals (USA EPA).

LEL, UEL   Lower, Upper explosive limit. Volume concentration of a gas in air at which an explosion can occur. An explosion may not occur if there is too little of the gas (lower limit) or too little air (i.e. too much gas - upper limit). These limits will be important for gases such as methane and hydrogen but should be used with caution as many factors can influence explosivity.

Linkage   For the purposes of contaminated land, a contaminant (or pollutant) linkage is a source - pathway - receptor linkage. If one or more linkages which can cause significant harm or significant possibility of significant harm to a receptor are present on a site then it may be legally contaminated land in the England and may require remediation. Note: contaminated land will be defined differently in different countries (different legal jurisdictions).

LOAEL   Lowest observed adverse effect level. A term used in toxicology, the lowest dose at which some adverse effect is seen.

MAC   Maximum acceptable concentration, an upper limit on concentrations of chemicals in water (or soil) – used as a control values in certain jurisdictions.

MCL   The USEPA has established Maximum Contaminant Levels (MCLs) for concentrations of certain contaminants in public drinking water supplies.

MTR   Maximum tolerable risk.

NOAEL,   No observed adverse effect level, see also LOAEL.

NOEL   No observed effect level.

Pathway   A route or means by or through which a receptor is or could be exposed to a contaminant.

Phase 1   Desk study
Phase 2   Intrusive ground investigation
Phase 1   Remediation
           Further phases of verification and monitoring are likely to be required.

PPE   Personal Protective Equipment. Often erroneously considered as the only necessary defence against contamination. PPE should be used only as a last line of defence after other procedures such as elimination or reduction of risk of exposure.

RBCA   Risk-based corrective action. A procedure for contaminated land assessment developed in the USA but now used more widely.

Receptor   A person, system or thing which could be harmed by a contaminant such as human health, other living organisms, ecological systems, property or controlled waters. Formerly referred to as a target.

RfC, RfD   Reference concentration or dose.

SPOSH   Significant possibility of significant harm (see UK Statutory guidance on contaminated land).

Target   See receptor

TDI   Tolerable daily intake. A dose parameter used in health risk modelling.

AN OVERVIEW OF SOIL & GROUNDWATER CONTAMINATION & REMEDIATION TECHNOLOGIES

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INTRODUCTION

There are hundreds of thousands of natural and manmade chemicals that could be present in the ground. It is impracticable in terms of both time and cost to investigate for all such chemicals. Therefore before doing any physical investigations at a site, for example, boreholes or trial pits to obtain samples for analysis it is normal practice to carry out a Desk Study sometimes known as a Phase 1 investigation.

In the Desk Study, the former uses of the site are reviewed using all the information that can be obtained, for example, maps (current and older), web searches, plant records, interviews with past and present employees, local libraries (maps and related data can be purchased on-line as package). If the desk study shows no evidence of current or former uses of the site that could cause or have caused contamination then it may be reasonable to take no further action. However, if the study shows that contamination may be present or there are sensitive receptors (see Glossary) then an intrusive investigation may be necessary. This will involve boreholes, trial pits etc. and is sometimes referred to as a Phase 2 investigation. Samples obtained from the intrusive investigation will be analysed for a list of chemicals developed from the Desk Study.

If, as a result of the Phase 2 investigation, chemicals are suspected which were not identified in the Desk Study then it may be necessary to widen the scope of the investigation and carry out further rounds of sampling and analysis.

When commissioning analyses and considering the results it is often helpful to group contaminants which have similar chemical or physical properties or tend to occur together. Examples of typical contaminant groupings are given in the Glossary. See, for example, chlorinated solvents, PCBs and heavy metals.

During and after the Phase 1 (desk study) and Phase 2 (intrusive ground investigation) studies a conceptual model of the site will be developed and refined. This a model of the site including its setting (location, receptors etc), geology, hydrogeology, sources of contamination etc. This model and the results of the Phase 1 and 2 assessments will enable a risk assessment to be carried out for any contaminants found or expected on the site. If as a result of the risk assessment unacceptable contamination is found then the site may need to be remediated (Phase 3) (note: there may be several, sources, receptors and pathways at a site and all must be considered). During the remediation, it will be necessary to ensure that the remedial processes are properly verified and that an appropriate monitoring regime is put in place to confirm the continuing satisfactory performance of the remedial scheme.

CONTAMINANT PROPERTIES

There are a number of general physical and chemical properties of contaminants that can affect their behaviour in the ground and the choice and effectiveness of remedial technologies.

Solid contaminants - solubility

Contaminants may be dumped on soils as solids and/or they may be precipitated in the soil as a result of change of pH or redox conditions e.g. as low solubility hydroxides or as sulphides (redox - crudely the availability of oxygen or chemicals that behave like oxygen in the ground).

If a chemical is soluble in water it will tend to dissolve in the groundwater. It will then move with the groundwater flow. The rate of migration may be reduced by sorption (partitioning) of the contaminant on to the soil. The spread of contamination also will be increased by diffusion and dispersion.

However, it should not be assumed that all soluble chemicals would be fully dissolved. They may be present above the groundwater table or the soil may be of such low permeability (e.g. clays) that sufficient water cannot reach the chemicals to fully dissolve them. This can be a dangerous situation if later development of the site introduces more water and so mobilises previously relatively localised contamination.

Binding (sorption) to the soil
The simplest form of a chemical in the ground is in solution in the groundwater. However, chemicals can also bind to the soil itself. For example, heavy metals may bind to clays (clays carry a negative charge which is balanced by exchangeable cations, e.g. metal ions).

Many organic chemicals can bind to soils – especially the organic content of the soil. Thus a petrol spill may bind strongly to peat type material in a soil.

Binding of chemicals to soil will retard their movement relative to that of the groundwater (just as in chromatography). This retardation may be substantial so that chemicals may remain close to their source (for example, where they were dumped)

Volatility
Chemicals may tend to evaporate from the soil (i.e. they may have a high vapour pressure at soil temperatures). This will lead to loss from the soil by vapour movement with the result that there can be ingress to buildings and exposure at the surface, e.g. by inhalation. Vapour and gas movement may be enhanced by atmospheric pressure changes – low atmospheric pressure may draw gas and vapour from partially saturated soils (soils above the groundwater level).

Partitioning
The above brief discussion of solubility, sorption and volatility considers separately the components of a process known as partitioning. When a small amount of a contaminant enters a soil it will divide between the soil, and the water and gas phases of the soil. Some will sorb on the soil, some will dissolve into the groundwater, and some will evaporate into the soil gas space (N.B. generally there will be no gas below the groundwater table and usually, for this region, only the dissolved and sorbed phases need be considered). The amount of contaminant held in each of the soil phases (solid, liquid and gas) will depend on the solubility, soil partition coefficient and the volatility. Once the local capacity of these three phases to take up the contamination has been exhausted (i.e. no more can dissolve in the water, sorb onto the soil or evaporate into the soil gas space) the contaminant will be present as a free phase e.g. as a solid or as free non aqueous phase liquid (NAPL).

Density
Liquid contaminants which are of modest/low solubility and which are less dense than water will tend to sink through the soil until they reach the groundwater table. They will then float on the groundwater and tend to spread out sideways from the initial point(s) of contamination. Free phase liquids (i.e. liquids which are present at above local solubility limits) which are less dense than water are referred to as Light non aqueous phase liquids (LNAPLS). BTEX compounds are examples of LNAPLS (see Glossary for definition of terms).

Free phase liquid contaminants which are denser than water and so sink through groundwater are referred to as DNAPLS. Examples include chlorinated solvents and some PAHs (for PAHs this may depend on ground temperature).

DNAPLS such as chlorinated solvents are denser than water and will sink through soil and groundwater until they reach a soil layer such as clay which is too fine for them to enter (surface tension effects produce a capillary entry pressure and a deep pool of DNAPL will be necessary to force entry into a fine soil). If/once a fine soil is reached, DNAPLs may move sideways following the slope of the fine soil surface and ultimately collect at any low points. Note: chlorinated and brominated (halogenated) chemicals tend to be denser than water; chlorine and bromine atoms are heavier than oxygen atoms).

Viscosity

Both high and low viscosities may be significant. Low viscosity liquids such as chlorinated solvents can move rapidly through all but fine soils (rapidly, that is for soils – this will depend on the permeability of the soil to the particular fluid. Actual timescales mu be months to decades).

Very high viscosity materials such as tars may appear to be solids but, if buried, the pressure of the overlying soil may cause them to squeeze up to the surface as tar boils so that an apparently remediated site becomes a problem site some years later.

Environmental degradation

Heavy metals are obviously permanent and if released in the environment will remain there, though they may be sorbed on clay soils so that they are effectively immobile.

Organic materials may biodegrade. Hydrocarbons such as BTEX compounds tend to degrade more rapidly under aerobic conditions (more rapidly – again actual timescales may be months to decades). BTEX degradation can be sufficiently rapid that the plume from a spill, for example a leaking tank under a garage forecourt, may reach a limiting length of less than about 100 m. Under aerobic conditions BTEX compounds may be biodegraded to non-detect levels within this distance. Chlorinated solvents can be dechlorinated under anaerobic conditions to hydrocarbons – though rates tend to be slow and it will be important to look for toxic degradation products such as vinyl chloride which is both very volatile and a carcinogen.

Speciation

Chemicals also can change their speciation in the ground. For example from low redox (e.g. anaerobic) to higher redox conditions (e.g. aerobic):

- sulphur may be found as: sulphide (anaerobic), organic sulphur compounds, elemental sulphur, sulphate (aerobic), etc.
- nitrogen may be present as: organic nitrogen, ammonia, nitrogen, nitrite, nitrate, etc.
- carbon may be present as: methane (CH_4), organic carbon, carbon dioxide (CO_2), bicarbonate, carbonate ion, etc.

The form in which these elements occur will vary with the redox and pH conditions. These conditions can change as a result of construction work, for example, a rise in the local groundwater level could prevent entry of atmospheric oxygen so producing locally reducing conditions and hence promoting the formation sulphide, ammonia and methane. The change of speciation is often as a result of bacterial activity – bacteria gaining energy from the movement of electrons.

REASONS FOR REMEDIATION

The Statutory Guidance issued under the Environmental Protection Act 1990 requires that land can be defined as 'Contaminated land' only if there is:

- a source of contamination;
- a receptor that can be damaged by the contamination;
- a pathway between contaminant and receptor;

and that there is at least a significant possibility of significant harm to a receptor.

In the terminology of the Guidance, a contaminant linkage is said to exist if there is a source, a receptor and a pathway between them. In England following from the definition of contaminated land, remediation does not specifically require the removal of the source (though this may be preferred by some of those responsible for remediation as it gives more certainty). What is required is the breaking of linkages.

Receptors include:

- human health;
- ground and surface waters (often referred to as controlled waters)
- other living organisms or ecological systems;
- crops, garden produce, owned animals including livestock, etc.;
- buildings, service pipes and cables, other property;
- commercial operations if contamination prevents their use.

Remediation also may be undertaken:

- to enhance land value;
- to enhance a company's image or limit damage to it;
- for aesthetic reasons.

A contaminant can reach a receptor only if there is a pathway from the contaminant source(s) to the receptor(s). For human health typical pathways are:

1) ingestion of soil, for example, by children playing on the ground;
2) ingestion of garden produce and any soil adhering to it;
3) dermal (skin) contact with soil;
4) inhalation of contaminated soil as dust;
5) inhalation of indoor air;
6) inhalation of outdoor air;
7) inhalation of vapour, for example, during showering;
8) dermal contact with contaminated water, for example, during showering;
9) ingestion of drinking water.

In the UK it would be rare for contaminated water to be put into supply without treatment and thus pathways 7, 8 and 9 normally will not be of significance for a human health assessment. However, some caution is necessary in relation to distribution pipes passing in or near contaminated sites. Polythene water pipes are permeable to some contaminants such as BTEX, diesel oil, heating oils etc. Thus clean water from a works can become contaminated during distribution. There have been a number of incidents of drinking water become tainted particularly as a result of leakage of domestic heating oil into the ground. Fortunately this may give an unpleasant taste to the water and thus a warning to the consumer at concentrations below levels at which there may be health impacts. The government's drive to reduce water leakage has led to a programme of pipe renewal – often using polythene type piping and thus increasing the risk – though polythene pipes incorporating a thin, organics proof, metal foil are now used.

Pathway 2 may be cut by prohibiting the growing of vegetables and animal grazing on the site - though many would not regard this as remediation. More generally, a designed clean cover layer over the site can cut the soil related pathways 1 to 4 – though if the contaminants include gases or volatile materials then the cover layer must include a suitably impermeable element and some forced or natural ventilation (this may be particularly important under the footprint of the building to prevent indoor air contamination). If a remedial scheme relies on capping a site then it will be most important to consider the long-term effect of human impacts and natural processes such as freezing/thawing and drought/flooding on the performance of the cap. Also it may be appropriate to include a warning layer should holes be dug in the cap.

It follows that as regards human health in many instances remediation can be achieved by a cover layer over the site if this is practicable.

However, a cover layer will not deal with groundwater contamination. This is often a very important consideration. The pathways for groundwater contamination will depend on the local geology and hydrogeology. Data on this may be obtained from the Environment Agency's groundwater vulnerability maps. For contaminated sites underlain by continuous (non-fissured), low permeability clay the potential for groundwater contamination is likely to be low. In contrast sites on chalk or gravel may present a high risk for groundwater contamination.

REMEDIATION TECHNOLOGIES
There are a large number of proven and developing soil and groundwater remediation technologies. They can be divided for discussion purposes into five generic types of remedial action:
- passive containment,
- active containment (permeable reactive barriers);
- monitored natural attenuation;
- in-situ treatment (i.e. treatment in-place);
- ex-situ treatment (i.e. excavation of soil, treatment and replacement, treatment at surface and re-injection, removal of groundwater or soil from the site etc.).

The suitability of a treatment method for a given site will be influenced by a combination of the characteristics of the site and the remedial technologies. Important characteristics of the site will include:
- the types of contaminants at the site, their distribution and depth;
- the surface conditions (open land, hard standing, housing, offices, industry etc.);
- the subsurface conditions (type of soil, depth to the groundwater, likely depth of contamination);
- the surrounding environment (houses, parks, industry);
- the time available for remediation (immediate problems, decommissioning or redevelopment).

Significant factors in evaluating any potential treatment option will include:
- its availability;
- its state of development;
- its demonstrated reliability and effectiveness;
- its perceived environmental impacts;
- its cost.

Large sites may permit the use of relatively new technologies after suitable testing, while small sites generally will be best addressed with proven, easily available techniques.

Two types of remedial action were widely used during the 1980s. These were the excavation and removal off-site (dig and dump, generally to a landfill) of impacted soil and the containment of

impacted soils and groundwater at the site. There has been a regulatory drive in many countries to promote/require contaminant treatment rather than removal or containment. However, dig and dump and containment are still regularly used in the UK (though there is now requirement treatment of contamination before landfill so as to reduce its volume, toxicity, etc.).

The following provides an overview of current techniques, their advantages and disadvantages.

CONTAINMENT
Passive containment
In Europe and North America, containment usually consists of placing a new cover (cap) across the affected area to minimise rainwater infiltration through or to the impacted soil, and will often include some form of barrier wall (cut-off wall) around the periphery of the affected area to prevent the impacted groundwater leaving the site. The procedure does not reduce or remove any contaminant and is generally only used on large sites where the contaminants are difficult to treat and/or excavating them would produce a serious threat (e.g. from dust or vapours). The costs of this approach are relatively high plus long term water treatment may be required (the barrier walls around a site make it effectively a pond). In addition, the legal implications (management, maintenance, etc.) of a long-term containment/landfill site may be onerous.

Capping has been seen as a cheap remedial solution whereby a small thickness of clean soil is placed over impacted soil to provide a separation layer between the affected soil and the environment and people/animals etc. This is not appropriate. A cover layer must be properly engineered to provide protection. It must be of suitable thickness and it may be necessary to include a capillary break layer to prevent upward movement of contamination during dry seasons. Also it will be necessary to provide safe route for utilities or any future underground works on the site.

Permeable reactive barriers (active containment)
An alternative procedure to passive containment is to accept or exploit any natural groundwater flow in the region of a contaminant source and use it to bring the contaminants into a purpose designed (for the particular contaminants) reactor system which removes or destroys the contaminants present in the water as it flows through the reactor. A Permeable reactive barrier (some times known as a reactive treatment zone) is effectively an underground chemical reactor system. It may be necessary to have underground collector and distributor system for the water if the natural geology does not provide them.

In principle, permeable reactive barriers should completely enclose all identified pathways from the contaminant sources to the receptors. Possible configurations of the reactor include:
- Treatment zones in the region of the source through which all the contaminated groundwater flows and which reduce contaminant concentrations to levels at which natural intrinsic remediation can operate in zones down gradient of the source. A typical example might be a trench filled with reactive material. The trench may encircle the source or be down-gradient of it so that contaminated groundwater leaving the source zone is intercepted;
- Systems which focus the flow for example funnel and gate systems. The funnel is created with an impermeable barrier wall in the ground and directs the flow to the reactive zone;
- Columns of chemicals mixed into the ground with an auger – the columns positioned to intercept the contaminated groundwater flow;
- The use of lines injection wells to introduce chemicals into the natural groundwater flow;
- The use of passive wells containing replaceable canisters etc. of treatment chemicals that may dissolve into the natural groundwater flow.

If space is available (i.e. all receptors are at some distance) the input concentration to the reactive

system may be reduced by selecting the position of the reactive zone in relation to the contaminant source so that in-ground natural attenuation may be exploited upstream and/or downstream of the reactive treatment zone.

It should be noted that permeable reactive barriers often will be used as pathway control mechanisms to prevent contaminants from a source reaching a receptor rather than as source clean-up technologies (at least in the short/medium term).

MONITORED NATURAL ATTENUATION
Until about 30 years ago it was assumed that much of the contamination disposed to ground would be so diluted, dispersed and naturally degraded that it would be of little consequence (a long discredited idea that dilution could be the solution to pollution). Unfortunately although this may have worked in a few situations it resulted in numerous incidents of serious contamination many of which are still causing problems. Natural processes in the ground therefore became largely discredited and dilute and disperse, as this type of technology was called, lost much credibility. However, it is now apparent that:

- In many countries the cost of cleaning the legacy of contaminated sites is so high as to potentially have a major impact of quality of life in other areas. For example, it has been estimated that in the Netherlands it would require the entire gross national product for the next 20 years. Contaminated land would then kill by deprivation of resources to health, transport and the entire social fabric of society rather than direct chemical interaction.
- Many remedial technologies, during the works, will increase exposure and therefore themselves bring potential health and ecological effects.
- Additional road movements and construction work associated with dig and dump and other technologies requiring soil excavation and movement can and do kill.
- Disturbing contaminated land can exacerbate problems.

Natural attenuation may be defined as those natural processes which can immobilise, retard, or degrade contaminants present in the soil or ground water. There is considerable interest in natural attenuation and in particular in identifying the factors which control it. It is often proposed as a low cost option. However, with the present state of knowledge it is unlikely that natural attenuation could be accepted by a regulator in England without substantial supporting monitoring data. Unfortunately if required over long times, monitoring can be very expensive and so although there may be no construction costs natural attenuation may still entail considerable operational costs. In time, if costs can be reduced, it may become a preferred remedial method.

It should be noted that passive containment, active containment and natural attenuation all leave the contamination in the ground – though with the latter two procedures there will be some on-going removal. This may affect the value of the contaminated land and, if the land is to be sold after remediation, technologies which offer complete source removal (if such a state exists – and it does not) may give a better overall return.

Finally it should be noted that active containment and natural attenuation procedures which do not destroy the contamination but merely sorb or precipitate it are actually achieving no more than allowing the movement of the contamination from one location to another – though it may be more secure in the second location. Before permitting such procedures a regulatory agency may require recovery procedures to be identified – particularly if the procedures are used for 'permanent' – non-degradable contaminants such as heavy metals.

IN-SITU TREATMENT
In-situ soil treatment technologies include the following technologies which range from common practice to little more research concepts:

- pump and treat   widely used in the USA, now recognised as often very slow;
- bioremediation   widely used for hydrocarbon contamination;
- soil vapour extraction   commonly used for volatiles;
- soil washing   initially tried in-situ, but now used more ex-situ (used, for example, on the London Olympics site);
- steam stripping   generally in-situ but rarely used;
- electrokinetics   after initial flurry of interest usage is now limited;
- vitrification   occasional applications for specialist purposes;
- microwave heating   research level.

All in-situ techniques require that the distribution of the contaminants in the soil is reasonably known, that the soil is generally relatively homogeneous and in many cases that it is relatively sandy (permeable) as many of the methods work better in sandy soils than in clayey soils. Unfortunately these conditions are found on rather few sites and thus much in-situ remediation must be undertaken on less than ideal sites.

Pump and treat
In some jurisdictions, for example the USA and the Netherlands clean-up strategies were initially directed at removing or permanently reducing the strength of the source of contamination as containment was disapproved (it was argued that a containment ultimately must fail and thus a contained site is a chemical timebomb - an emotive and thus powerful argument in the anxiety driven concern for the clean-up of contaminated land).

One of the most widely used procedures in the USA for source reduction was pump and treat. Basically this consists of pumping contaminated groundwater from the contaminated area, treating it and returning to either surface water (streams etc.) or to the ground by re-injection via wells. Chemical agents such as surfactants or could be added to enhance the contaminant removal.

However, it was soon found that the contaminant removal rate in many pump and treat systems rapidly reduced to very low levels so that clean-up of a source might take hundreds of years and costs could be massively higher than originally predicted. The reasons for the rapid reduction in removal rates include the heterogeneity of most natural soils. Contaminants may be trapped in low permeability zones of the soil and/or the bulk of the groundwater flow may be through narrow high permeability (e.g. gravel) bands etc. thus leaving the remaining contaminated ground largely unaffected.

Pump and treat is still occasionally used but generally as method to reduce the spread of contamination from a source rather than as a source removal technology.

Bioremediation
In-situ bioremediation (see also ex-situ bioremediation), uses bacteria to destroy/breakdown organic contaminants (it cannot destroy metals though it may possibly reduce their mobility, for example by precipitating them as sulphides). Typically aerobic bacteria breakdown organic contaminants faster than anaerobic bacteria. Therefore for effective bioremediation it is necessary to get oxygen into the soil for example by injecting air or by using chemical oxygen sources.

Bioremediation is still a relatively young technology but has considerable potential in terms of cost and effectiveness for certain chemicals. Petroleum spirit, diesel, jet fuel, light mineral oils, benzene, toluene, xylene and ethyl benzene are all generally readily biodegradable by stimulating indigenous micro-organisms. The rate of degradation decreases as chemical compounds become more complex, so that polycyclic aromatic hydrocarbons (PAHs, for example, tars), polychlorinated biphenyls (PCBs),

and similar chemicals and pesticides are not readily biodegradable. Chlorinated solvents such as carbon tetrachloride, trichloroethylene are also difficult to biodegrade. Some companies have developed specific micro-organisms to degrade some of these chemicals. However, if bacteria are introduced they must be able to survive and function in the contaminated soils – in competition with the bacteria naturally present in this soil.

In-situ bioremediation works best in sandy soils, at sites where the geology is uniform and well defined. Sites with well-defined point sources of contamination (e.g. a leaking tank) are more amenable to in-situ bioremediation than sites with multiple and ill-defined sources of contamination. It is often a preferred approach when the contamination is on-site, not affecting any off-site location and there is time available to use bioremediation (a minimum of a few months).

When contaminated groundwater is being bioremediated, it is usually recirculated, with oxygen, hydrogen peroxide and/or nutrients being added before the water is re-injected. In-situ bioremediation is being increasingly used in conjunction with other techniques such as vapour extraction and air sparging (see below) to provide overall remediation of a site.

Some of the problems encountered during in-situ bioremediation include:
- clogging of soils with fines and microbial growth;
- maintenance of stable oxygen concentrations over time and throughout the contaminated zone;
- clay minerals which have sorbed compounds such as hydrocarbons and remain as long term sources from which the organics are only slowly released;
- residual contamination in the vadose zone (unsaturated) above the water table;
- seasonal or shorter term fluctuations in the groundwater level.

Soil Vapour Extraction
Soil vapour extraction, forced air venting, or in-situ air stripping revolves around the extraction of air containing volatile chemicals from unsaturated soil. The vapour laden air is withdrawn under vacuum from recovery or extraction wells, while fresh air is allowed to flow in from above. The soil surface immediately above the impacted area may be covered with a plastic sheet to promote air flow more fully through the source zone. It was used in the early to mid-1980s at service stations which had experienced leaks, but its use quickly spread to the remediation of other chemical compounds, such as trichloroethylene, benzene, xylene etc.

Vacuum extraction is only applicable at sites where volatile compounds are the primary contaminants in the soil. Compounds should satisfy certain characteristics (vapour pressures greater than 1.0 mm of mercury at 20°C and a Henry's Law constant greater than 0.01). While compounds such as trichloroethylene (TCE) meet these criteria, some care is necessary about their breakdown products such as cis-1,2 dichloroethylene and vinyl chloride, which may also be present in the ground and be of concern at lower concentrations (e.g. toxicity) than the original TCE.

Soil vapour extraction is particularly attractive for sites where areas of contamination are large and deep (greater than about 6m), or when the contamination is beneath a building. Vapour extraction is more suitable in relatively permeable soils (hydraulic conductivity must be higher than 10^{-8}m/s and preferably higher than 10^{-5}m/s). Well spacing is usually based on the estimated radius of influence of an individual well, which can vary from 5 to 30m. The extraction wells are usually designed to penetrate the unsaturated zone or contaminated stratum, although in some applications, the only lower region of the well is slotted. Remediation is usually started at the most impacted area.

The extent to which treatment of the extracted vapours is required will depend upon the contaminants and their concentrations, local regulations and the local environmental setting. In North America, the

most common forms of treatment are carbon adsorption, catalytic incineration, flare incineration or condensation. The costs can be significant and may be up to 50% of the overall treatment cost. At some sites, it may be possible to vent the gases into an industrial furnace or similar unit.

There have been several developments in soil vapour extraction. One of the simplest is the use of air sparging (injection) wells that force air into the soil or strata beneath the water table. In order for an air-sparging/vapour extraction system to be successful:

- the aquifer must be a water table aquifer (i.e. unconfined, not trapped below layers of low permeability soils such as clays);
- the aquifer must be coarse and permeable (hydraulic conductivity of at least 10^{-5}m/s), so that the air that is injected can move up through the water in the pore spaces;
- the compounds to be treated must be relatively insoluble (otherwise they will preferentially partition into the water phase rather than the gas phase) and amenable to air stripping, such as TCE (trichloroethylene), TCA (trichloroethane), benzene etc.

The vapour extraction system is started first, and then as the exhaust gas VOC (volatile organic compounds) concentrations decline, air is injected at a rate such that it can be recovered by the vapour extraction system. The time required for remediation can be significantly reduced in comparison with sites where air sparging is not used.

Another development in soil vapour extraction is the dual phase well, by which both soil gases and contaminated groundwater are removed from an extraction well under vacuum. It is claimed that the process is applicable to a wide variety of chlorinated and non-chlorinated solvents and degreasers, petroleum hydrocarbons and semi-volatile compounds.

Electrical heating has been used to increase the effectiveness of a vacuum extraction.

Steam stripping

In-situ steam stripping was first used as a remedial method in the Netherlands in the early 1980s, with steam being injected to treat 2m by 2m columns of soil at a former gas plant. A demonstration steam stripping plant was built in California to treat a 1000m^2 site where petroleum hydrocarbons had leaked from underground storage tanks. The soil was treated in 430 blocks of about 2m^2 and total petroleum hydrocarbon concentrations reduced from between 100 ppm and as high as 15,000 ppm down to less than 100 ppm. Steam stripping is becoming more widely used for organics which can be mobilised at steam temperatures.

Soil Washing

In-situ soil washing was investigated in the early 1980s to treat permeable soil that was impacted with hydrocarbons, PCBs etc. Initial laboratory tests with water were ineffective, but the process was significantly improved with the use of surfactants. However, when the process was used in the field with surfactants, the results were disappointing.

In-situ leaching with hydrochloric acid was used in the Netherlands in 1987 to remediate 30,000m^3 of soil with high cadmium concentrations (total of about 700 kg). The overall treatment cost was estimated at about £45/m^3 at then current prices. Acid leaching is unlikely to be used today as it may mobilise other species and so add to the problems.

In-situ soil washing and leaching have tended to be replaced by various on-site washing processes, partly due to limited in-situ effectiveness but also due to the difficulty of recovering the surfactants and leaching liquids used and the risk of increasing the mobility of any contaminants that are not recovered.

Electrokinetics

As is evident from the above examples, many remedial methods work better in permeable sandy soils. One method which has been used with some success over the past decade (initially in the Netherlands) to treat contamination at sites with clayey/silty soils is electrokinetics. Anodes and cathodes are placed in the soil. An electrical current is then applied causing various compounds to move towards the electrodes. The system can reportedly remove inorganic contaminants like heavy metals, cyanides, nitrates and polar organics from both soil and groundwater.

Vitrification
In-situ vitrification is a thermal treatment process which converts contaminated soil into a durable glass by melting the soil by electrical heating. The process has been under development in the USA since about 1980 when it was initiated as a method for in-situ stabilisation of high level radioactive wastes. Electrodes are placed in the soil and the soil heated to over 2000°C, well above the initial melting temperature of soils. A hood placed over the area being treated is used to draw off gases for treatment.

Microwave heating
This has been used at a demonstration level to heat 30 tons of soil impacted with jet fuel, chlorinated hydrocarbons and waste oil. The heating apparently greatly increased the effectiveness of soil the vapour extraction system at the site.

EX-SITU TREATMENT
Ex-situ treatment processes include:
- excavation
- bioremediation
- solidification of soil
- soil washing
- thermal treatment
- steam stripping
- solvent extraction
- volatilisation (aeration)

From the above list it can be seen that several of the treatment methods can be used both in-situ and ex-situ.

Excavation, treatment and disposal (dig, treat and dump)
Excavation and off-site disposal at a licensed landfill is the most basic and was the most commonly used technique to deal with contaminated soil UK. However, legislation (originally from the EU Landfill Directive) now prohibits the disposal of bulk contaminated soil to landfill. Contaminated soil must receive some prior treatment for example to reduce its volume or its toxicity. Dig and dump can be particularly attractive when the time to remediate is limited and the contamination is shallow and the land surface can be lowered so that there is no need to import clean fill to replace the disposed soil. However, if it is being contemplated, it should be recognised that long-term liability issues may be involved (in some jurisdictions, though not the UK if appropriate duty of care procedures are followed a disposer remains responsible for his waste even in a landfill). There are also public perception issues that wastes are not destroyed, only transferred to another location (though note that wastes such as metals cannot be destroyed). In addition, as landfill costs rise (and taxes are applied – they are substantial in the UK), it becomes an increasingly expensive option.

Bioremediation
Bioremediation can be used at a site to treat organically (hydrocarbons, etc.) impacted soil which is excavated, treated and then replaced. This technique is largely derived from land farming, used for

many years at refineries to treat petroleum wastes. Contaminated soil is spread out over a prepared surface in a layer up to approximately 0.6m in thickness. Nutrients are added and the soil is then regularly mixed using agricultural type equipment to break up the soil, allow air ingress and improve the contact between the contaminants and the nutrients. Water may be added if necessary. The bio-pile may be covered to limit vapour escape. Water percolating through the soil can be recycled or treated and discharged.

Bioremediation has been used to treat contaminated soils at former gasworks sites, wood treatment plants and refineries. The soil may take between several months and a year to treat. The time taken to treat is longer for compounds with increasing molecular weight and a greater number of aromatic rings (e.g. benzene degrades much faster than benzo(a)pyrene).

Solidification / stabilisation
Portland cement and cementitious/pozzolanic materials may be mixed with water and contaminated soil and the mixture allowed to harden. The resulting solid material can be relatively durable, of low permeability and relatively leach resistant. The contaminants in the soil are not destroyed but their potential impact on the environment is reduced as they are physically and/or chemically bound in the matrix.

The process is more accepted as a means of stabilising heavy metals than organic compounds, because of concerns that organics can interfere with the solidification process. This concern is being partly alleviated through protocols which have been published to assess the longevity of cement-based solidified wastes, and case histories where stabilisation/solidification has been used to stabilise soil impacted with PCBs, and even volatile and semi-volatile organics. However, in these cases, the proportion of cement used has often been increased (from a waste:cement ratio of 3:1 to 5:1 more commonly used up to as high as 1:1.

There are a large number of potential stabilising materials, including Portland cement, ground granulated blast furnace slag, kiln dust, lime and fly ash. Most contractors use additional proprietary stabilising agents and/or chemical fixatives, which are intended to help the fixation process. Prior to any full-scale use, laboratory tests will be required to assess the performance of the cement/waste system. Stabilisation is most often done in-situ

Soil washing
Soil washing using semi-transportable equipment was developed in Holland and Germany during the mid-1980s and has been used at a number of sites in the UK. The process basically consists of the separation of the fine particles, usually smaller than about 60 micron by washing, because much of the contamination may be sorbed on the fine particles. There are many different soil washing processes; the key differences lie in the method used to separate the fine particles from the coarser fraction. These vary from special vibrating screens to patented surfactants. Most soil washing techniques are viable only if there is less than about 20% fines in the soil. Soil washing alone is not a complete treatment process, it is a process which concentrates the contaminants to be treated into a part of the soil fraction. Soil washing has been used on soils contaminated with petrochemical residues, heavy metals, PCBs, cyanides and pesticides. The cost to set up a large plant is considerable, so the process is best suited to large sites or at a treatment hub (a site set-up to provide contaminated soil treatment services).

Thermal treatment
Impacted soils can be removed from the ground and exposed to heat to destroy organic compounds. Treatment techniques vary from high temperature incineration to lower temperature thermal stripping followed by vapour destruction. Costs to set up an incinerator are so high that it is feasible only at a large site (several thousand tons of contaminated soil). Mobile low temperature thermal strippers are available to provide a more economical means of treating soils impacted with the more volatile

petroleum hydrocarbons, e.g. gasoline, diesel, jet fuel etc. In these processes the soil is heated only sufficiently to volatilise the organics, which are then passed as a gas stream to a separate furnace for high temperature incineration. The procedure has been successfully used to treat PCB impacted soil and for this it is markedly cheaper than bulk incineration.

The rate at which soil can be treated is typically in the 5 to 20 tonnes/hr range. The feasibility of using thermal treatment is influenced by the particle size distribution of the soil, its moisture content, and most of all by the local air emissions regulations. It is often the most expensive remedial method, but also the most thorough form of treatment though the treated soil may be sterile and heavy metals naturally present in it may show increased mobility.

Steam stripping
Steam heating and extraction of mobilised contaminants may be used ex-situ in a similar way to the in-situ process.

Solvent extraction
Solvents are used in two patented American processes to treat soils contaminated with organic compounds, such as petroleum sludges, PCB contaminated soil, etc. They are best suited to highly impacted soil and sludges at industrial sites.

Volatilisation
Many contaminant chemicals are volatile and vapour release may occur during the processes of excavation, treatment and replacement of contaminated soils. Worker exposure etc. must be prevented / monitored during all contaminated land work.

On occasion spreading soil on the ground to promote volatilisation has been used as a remedial technology. It is difficult to justify such an uncontrolled procedure.

Other remedial technologies
There are a plethora of other remedial techniques, in various stages of development and application. Many are contaminant specific.

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