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NEW APPROACHES IN GROUNDWATER REHABILITATION

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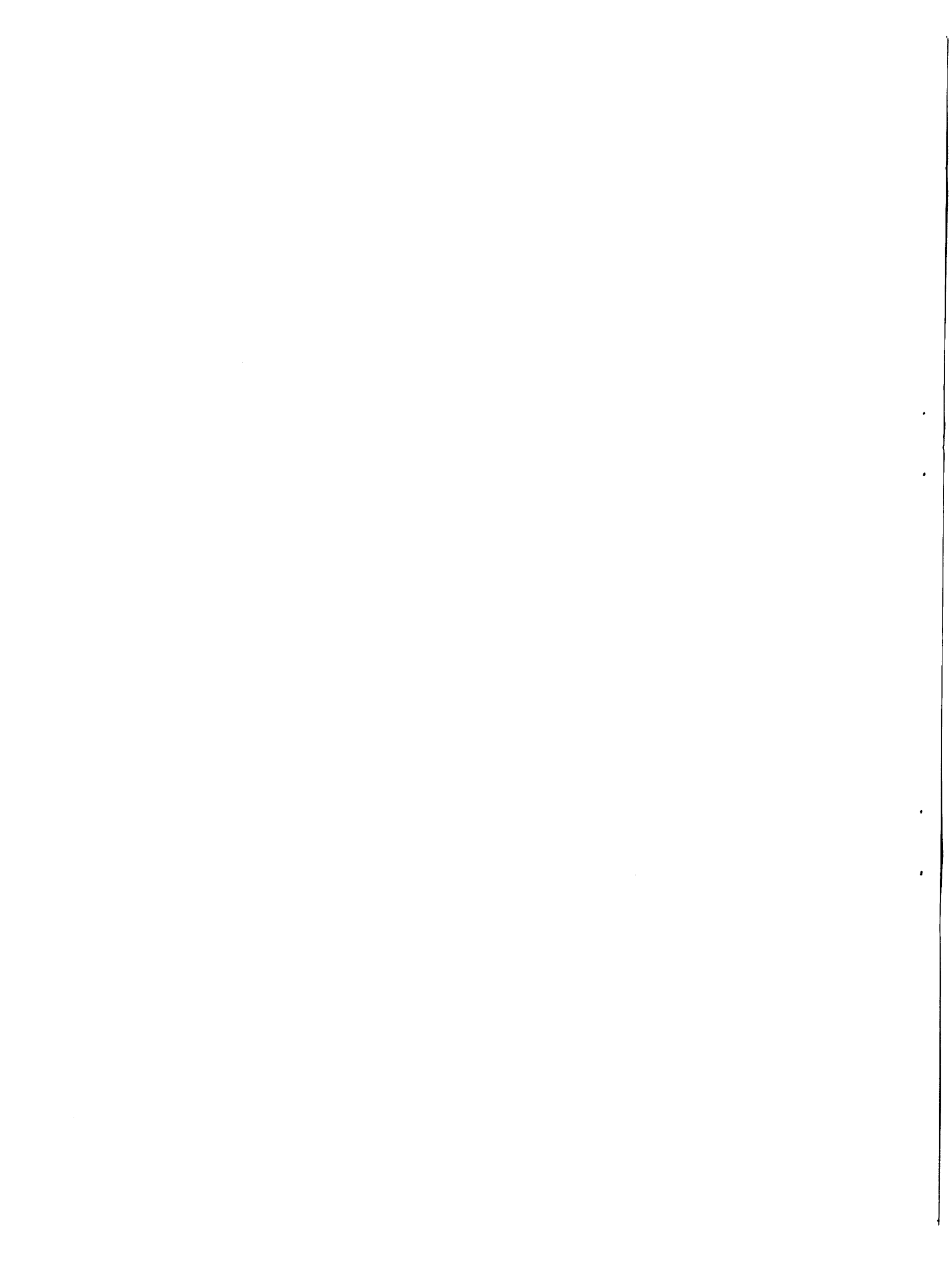
NEW APPROACHES IN GROUNDWATER REHABILITATION

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ABSTRACT

A large proportion of contaminated land and groundwater is the result of many decades of industrial production and modern agricultural practices, carelessness and accidents. A number of contaminants like Chlorinated Hydrocarbons, Benzene, toluene, ethylbenzene, xyclene, Pesticides, Polycyclic aromatic hydrocarbons, Polychlorinated biphenyls and heavy metals are found in soil and water samples of contaminated sites.

The (environmental and/or human health) risk varies according to specific characteristics of contaminants. A risk assessment is used in deciding whether or not eliminate or reduce the risks posed by a contaminated site. If the risks need to be reduced, a remediation strategy must be developed to address them. There is a need of an adequate site characterization and a thorough understanding of the subsurface system targeted for remediation.

The suitability of a remediation method depends on many factors including: contaminated media, contaminants, remediation objectives, current status of the site, location of the site, time available to complete the treatment, and money available to pay for the treatment. In many cases combinations of technologies (treatment trains) have been determined to be a most effective solution.

This report is an overview of information on available conventional and innovative remediation technologies. Information provided includes an introduction to the types , the properties and the migration of the most frequent contaminants. The general strategies are briefly defined and discussed.

The general principles and techniques of in situ and ex situ technologies for the remediation of contaminated soil and groundwater are described. This includes conventional civil engineering-based methods (excavation, containment, hydraulic measures), process-based methods and innovative concepts: treatment walls, bioremediation and monitored natural attenuation. The general applicability and the limitations of these methods are discussed.

I. GROUNDWATER CONTAMINATION

A. CONTAMINATION SOURCES

A large proportion of contaminated land is a historical legacy from past industrial practice associated with coal and metal mining, petroleum and chemical industries, metal-plating, manufactured gas plants and coal gasification. The (underground) storage, the industrial sewage systems and the industrial and municipal landfills are important sources of soil and groundwater contamination. But also facilities like dry-cleaners play an important role.

The input of contamination had been taken place at points or on larger areas, the contaminants could have been liquids or solids, the contamination process could have happened as an accidental spill or a leakage over a long period.
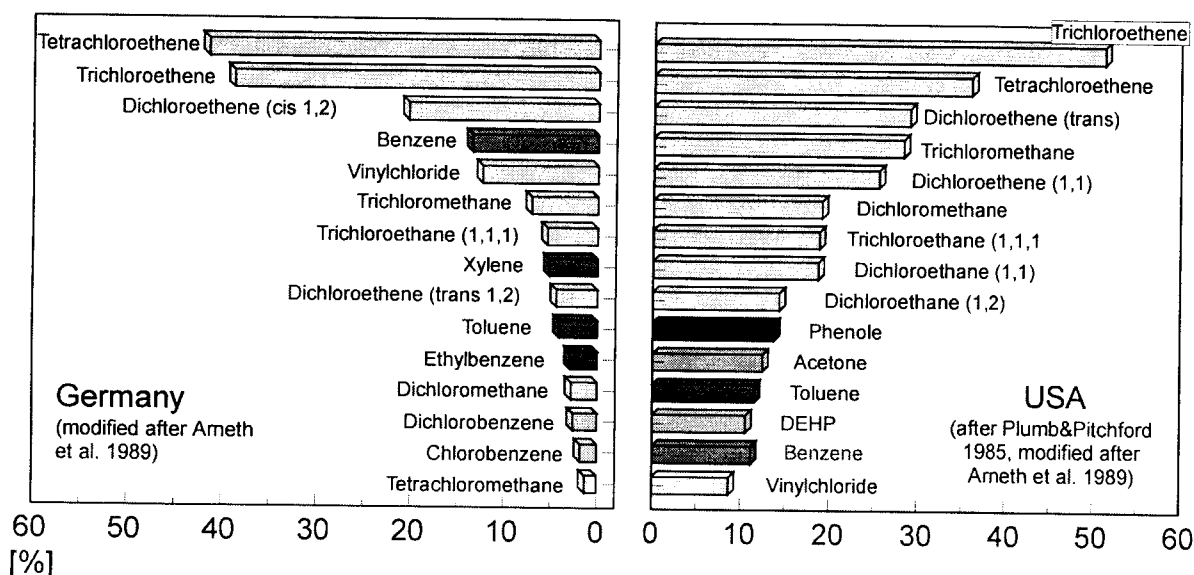
B. TYPES OF CONTAMINANTS

Fig. 1: Groundwater Contaminants Frequently Found in Groundwater Plumes

The contaminants fall into the following main categories:

- Volatile organic compounds (VOCs)
  Chlorinated VOCs
  Benzene, toluene, ethylbenzene, and xyclene (BTEX)
- Semivolatile organis compounds (SVOCs)
  Pesticides
  Polycyclic aromatic hydrocarbons (PAHs)
  Polychlorinated biphenyls (PCBs)
- other VOCs and other SVOCs
- Metals
- Inorganics

C. NATURE OF CONTAMINANTS

The physical state of contaminants is one of the factors determining the possibilities of clean-up. Contaminants may be present as pure **particulate pollutants** equal in size to, or smaller or larger than the non-pollutant soil articles. Contaminants may also have been **adsorbed** onto soil particles, or be present in organic soil particles, such as plant material and humic substances. They may also be present as a **solid- (or**

pure liquid) phase in the pores of soil particles. Finally they may partly be present as **dissolved** components in an aqueous phase in the pores of soil particles, and partly **adsorbed** onto the pore walls in such particles.
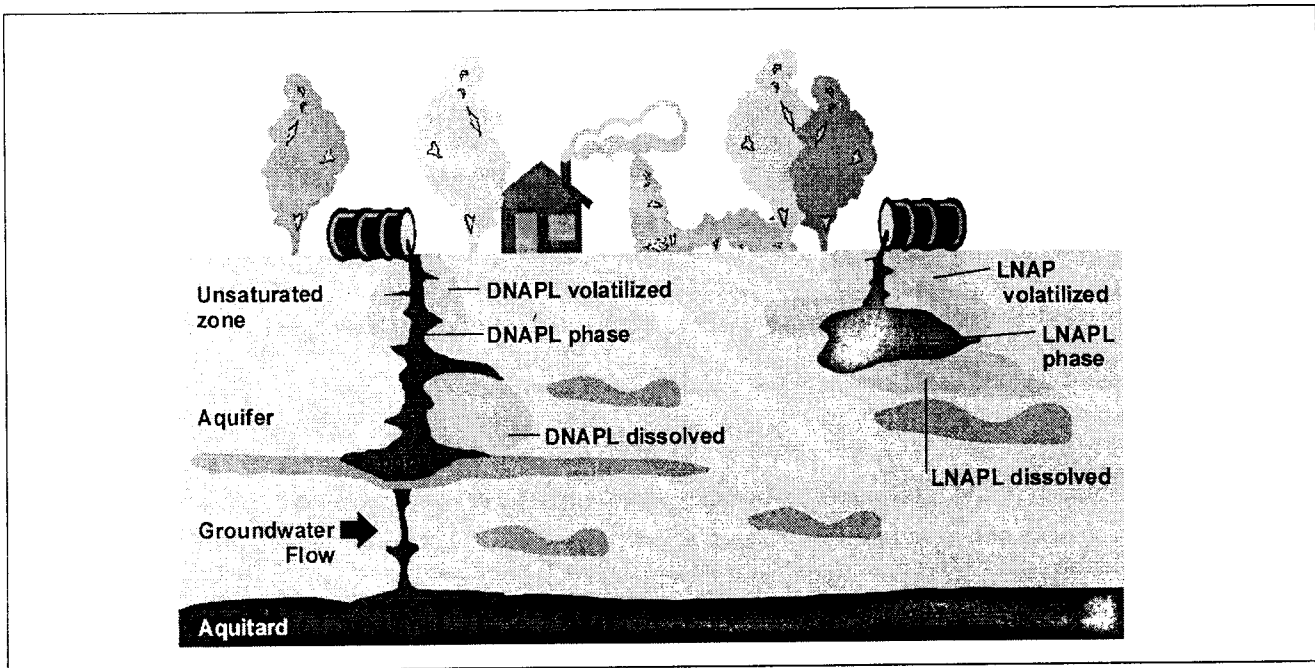

Fig. 2: NAPL Contamination

Non-Aqueous Phase Liquids (NAPLs) comprise simple or complex mixtures of nonpolar substances that are effectively immiscible with water with densities greater or less than water. They form discrete globules with high surface tensions, due to the capillary pressure between the NAPL and water, which is of fundamental importance with respect to their transport and fate in the subsurface.

Dense Non-Aqueous Phase Liquids (DNAPLs) are comprised of denser fraction compounds, such as some chlorinated solvents, wood preservative waste, coal tar waste, and pesticides. As a result of widespread production, transportation, use, and disposal of hazardous DNAPLs since the 1940s, many sites are contaminated with DNAPLs.

Light Non-Aqueous Phase Liquids (LNAPLs) are comprised of lighter fraction compounds, primarily petroleum distillates, and are commonly associated with underground storage tank releases and petroleum spills.

D. MIGRATION OF CONTAMINANTS

The migration conditions in an aquifer will be governed by the specific physico - chemical characteristics of the contaminants, such as solubility, specific gravity, adsorption coefficient, and biodegradability.

DNAPL migrates downward down through the vadose zone along preferential pathways through water column, contaminating soil, bedrock, and groundwater and typically the free-phase DNAPL accumulates as pools in low points atop the surface of the less permeable horizon. Hydrocarbons are preferentially trapped in the coarsest layers underground thus inducing rapid migration, e.g. downstream through gravel beds.

LNAPLs accumulate as pools on reaching the water table where further migration is controlled by the groundwater hydrodynamics. They have a low solubility and are not easyly biodegradable

Migrating NAPLs may leave behind a trail of residual contamination within the soil pore space. Coupled with the low water solubilities of many of the constituent NAPL contaminants, this means that clean-up

using technologies which rely on the occurrence of the target compounds in the aqueous or gaseous phase may at best be slow and at worst, ineffective. The implementation of appropriate existing remediation strategies and the development of new technologies requires a good understanding of the dissolution processes governing the exchange of NAPLs with the soil aqueous, gaseous and solid phases.

The direction and the speed of contaminants migration depend directly on local natural underground parameters, eg. pH/ oxidation/reduction potential, contents of silt and clay and humic substances and on the key aquifer characteristics (hydraulic conductivity, transmissivity, flow direction, type of aquifer, level of watertabel, hydraulic gradient etc.)

Taking as an example five very common products of the petroleum or chemical industries, a mixture of gasoil/ benzene/ phenol/ naphtalene/ tetrachloroethylene, considering only water solubility and specific gravity as dispersion parameters, one obtains five different types of behaviour and thus five responses in the terms of migration through the aquifer.

II. REMEDIAL DESIGN

A. INVESTIGATION AND RISK ASSESSMENT

Suspect sites are first subject to a preliminary investigation. The history of the site is studied in order to yield indications about the nature of the contaminants. Soil and groundwater are sampled. Information on geologic profiles and site conditions are collected.

Site-specific field measurement and modeling techniques should allow a reliable field scale quantification of the contaminant source strength (type, level and location) as well as the characterization of the contaminant plume.

The most common approach to source strength characterization is based on soil and groundwater samples which are obtained from boreholes, ditches, piles etc. Transport mechanisms controlling the contaminant propagation in the subsurface are commonly estimated from groundwater samples obtained at various distances downstream of the source zone.

A risk assessment is usually used in deciding whether or not to eliminate or reduce the (environmental and/or human health) risks posed by a contaminated site. The environmental risk varies according to specific characteristics of contaminants. Concentrations of contaminants are compared with quality criteria. If contamination exceeds these values, a further and more extensive investigation must be carried out. If the risks need to be reduced, a remediation strategy must be developed to address them.

B. REMEDIATION PLANNING PROCESS

A careful consideration of all aspects during the planning phase helps to save money in the later construction and remediation phase. With small amounts of money substantial changes of the strategy and remediation pattern are still possible.

A comprehensive remediation plan is elaborated that describes all remediation measures necessary to achieve groundwater protection standards and/or to prevent the further migration of contaminants into the groundwater.

To assess the applicability and potential performance of remediation methods, information is required on the contaminants present (e.g. types, concentrations, speciation, and distribution) and the physical, chemical, and biological properties of the material to be treated. In most cases this involves collecting supplementary data beyond that necessary for the risk assessment and initial remedy selection.

Treatability studies are likely to be required to select, design, and implement the remedy. In general, the suitability of a remediation method depends on many factors including: contaminated media, contaminants,

remediation objectives, current status of the site, location of the site, time available to complete the treatment, and money available to pay for the treatment.

The selection of remedial options is critically dependent upon the goals which are set for site remediation. Goals can be defined on various levels, e.g. reduction of potential or reduction of actual risk. The selected remedial options are on the other hand dependent upon the remediation strategy: e.g. a risk reduction/management strategy may suggest the use of pump and treat systems, physical and/or hydraulic containment systems.

Prioritizing the selected remedial options should consider the primary and secondary effects of taking a particular option; its environmental effects; its achievability and sustainability. The primary effect is defined by the remediation goal. Secondary environmental effects include, e.g. the generation of emissions, residual waste products, and the consumption of energy and materials.

C. APPROACHES TO REMEDIATION

The two basic approaches to remediation are:

- Elimination of the risks by removing or destroying contaminants
- Control of risks to an acceptable level by reducing contaminant concentrations or by containing the contaminants, such as installing barriers between the contaminants and potential receptors.

The remediation strategy developed for a particular site may combine both approaches and several different methods.

Remediation methods may be classified as

- **civil engineering-based remediation methods**, such as **excavation, containment** using sealing systems and vertical barriers,
- hydraulic / **pump and treat** (P&T) measures and
- process-based methods.

The conventional **civil engineering-based methods**, may be an essential precursor to the application of a process-based method involving ex situ treatment. Furthermore, civil engineering-based methods, such as vertical barriers and lowering the water table, can also be essential to the application of an in situ treatment, such as soil vapor extraction.

Hydraulic measures are often essential components of remediation systems. The extraction or infiltration of groundwater may be used to:

- control groundwater levels, enabling excavation to take place
- control groundwater levels in conjunction with physical barriers as part of a remediation strategy
- control groundwater levels and flow directions so that in situ treatment can be applied
- extract groundwater for ex situ treatment and return the treated water to the ground
- infiltrate water as part of an in situ treatment process.

Process-based methods may be applied **ex-situ** (after contaminated soil or groundwater has been removed for the treatment) or **in situ** (without removing the contaminated media). Ex situ treatment may be performed **onsite** using for example mobile or transportable treatment systems or **off-site** fixed treatment facilities.

The processes are frequently combined in **treatment trains**. A treatment train is a sequential combination of technologies or unit processes which treat recalcitrant matrices more effectively than any single technology could. E.g. soil washing becomes the prelude to chemical or biological treatment. Integrated strategies consisting e.g. of P&T for hydraulic control and dissolved plume mass removal combined with source targeted technologies have been determined to be a most effective long term solution in many cases.

Different mobility of the components of a mixture of contaminants will require different methods, strategies and priorities of remediation. Underground, the substances, which are lighter than water, float on the

watertable, whereas others, denser than water, sink into the aquifer, polluting the deep water layers. E.g. gasoil and naphtalene are virtually immiscible in water and tetrachloroethylene is poorly soluble, but the more soluble phenol and benzene will rapidly contaminate the water downstream. That means that for each of these products, which possibly come from the same source, the operational remediation features will be different, all natural conditions remaining the same.

When a pure **oily phase**, light or dense, is present, the double pumping system, including a withdrawal from the aquifer where the oil is assumed to be concentrated, usually is a suitable process for removing the pollutant. The contaminated water is treated.

When the contaminant is rather **well dissolved** in the water, the pumping of contaminated water from the dispersion plume stops its extension of confinement, protecting the downstream part of the aquifer.

The clean-up of contaminated **source zones** in many cases is hardly achievable at reasonable costs. As a consequence concepts which focus on the control of the groundwater plume rather than the elimination of the source have received increasing attention during the recent years.

Strategies for remediation of contaminated groundwater (and soil) are rapidly changing. A few years ago many considered contaminated aquifers biologically inactive systems which could only be remediated by very drastic and expensive methods. Nowadays, one has become aware that the natural microbial population in soil and groundwater react actively when confronted with pollution, and thus offer new ways to protect groundwater.

For compounds which are sufficiently biodegradable, natural attenuation can be a valid concept, whereas reactive barriers are needed in cases where the natural attenuation leads to an unacceptably long aquifer reactive zone. Most likely, appropriate combinations of both concepts may lead to cost-effective groundwater remediation measures specifically suitable to large industrial areas, where the source zones are often poorly defined or hardly accessible.

Much of the current research on groundwater remediation has focussed on the removal of contaminated water form the subsurface and treating it at the surface. While the removal of the contaminants is desirable, the costs often are prohibitive and rarely are contaminants concentrations lowered to the required regulatory levels. This has been particularly evident for standard "pump and treat" approaches.

In-situ chemically reactive permeable barriers or treatment zones and natural attenuation are being considered as a low cost and effective alternative for the treatment of contaminated sites.

The application of an in-situ approach to subsurface remediation increases the emphasis on adequate site characterization and thorough understanding of the subsurface system targeted for remediation.

The following chapters provide an overview of the available remediation methods, including several innovative evolving technologies.

III. CIVIL ENGINEERING-BASED METHODS

A. CONTAINMENT

A method that is currently in wide use is to contain the contamination where it occurs. In its ultimate form this requires the complete encapsulation of the contamination by the provision of surface cover and in-ground vertical and horizontal barriers. Primary functions are the control of leachate production, the control of soil fluid movement and the limitation of surface water ingress

Containment can be used to prevent further migration of the contaminants, but does not provide a means for correcting the problem in the long term. Further, the effectiveness of containment technologies decreases with depth and geologic complexity, such as fractured aquifers.

Vertical Containment Barriers (VCBs) are used **to isolate** the contaminated material from contact with groundwater and to **control the migration** of contaminated groundwater and soil gas. They are frequently

used in conjunction with hydraulic measures to control the groundwater plume or with an active or passive system to control gas emissions.

When used as the primary remediation method, vertical barriers must be designed to last for decades. No matter how well designed and installed, barriers perform satisfactorily only for a limited time. Because experience is limited, predicting performance is difficult.

VCBs include slurry walls, grout curtains and sheet piling:

- Aquifers with sandy surficial soil and underlain by an impermeable layer of fine grain deposits or bedrock are most amenable to **slurry wall** construction. The trenches are constructed by using cement-bentonite or soil-bentonite mixtures. Synthetic liners are additionally used in some projects.

- **Grout curtains** are constructed by injecting grout (liquid, slurry, or emulsion) under pressure into the ground through well points.

- Construction of **steel piling** involves driving interlocking sections of steel sheet piling into the ground. The piles are driven down into the consolidated zone

B. EXCAVATION

Excavation to remove source materials at hot spots represents one of the most common alternatives for remediation. The excavated soil is treated in on site or off site soil treatment facilities:

- soil washing,
- thermal treatment,
- biological treatment,
- solidification.

Excavation for ex-situ treatment can be very costly, with costs increasing and efficiency decreasing with depth. This strategy is used in the case of urgent social, economical or environmental needs, e.g. the remediation of the contact zone of an inhabited site.

C. PUMP- AND- TREAT (P&T)

Cleanup of groundwater by P&T methods is probably the longest established and most commonly used in-situ remediation technology. P&T involves extracting contaminated groundwater through recovery wells or trenches and treating the extracted groundwater by ex situ (aboveground) processes, such as air stripping, carbon adsorption, biological reactors, or chemical precipitation and reintroducing to the aquifer. Variables in the design of a typical P&T system include:

- the number and production rate of groundwater extraction points (determined by such factors as the extent of contamination and the productivity of the contaminated aquifer

- the ex situ treatment processes employed (determined by such factors as system throughput and the contaminants that require remediation)

- the discharge location for treatment plant effluent (determined by such factors as location of the site and regulatory requirements.

P&T is complex because whilst pumping may remove NAPL pools on or below groundwater, the pumping process itself may enhance diffusion gradients and contaminant mass transfer of soil-sorbed compounds and/or residually saturated NAPLs within the vadose zone, promoting the growth of existing NAPL pools or creating new pools. Groundwater extraction often causes an initial decrease in contaminant concentrations in the extracted water, followed by a leveling of concentrations, and sometimes a gradual decline that is generally expected to continue over decades. The failure of P&T has been attributed to the failure of the flowing water to remove the residual saturated (i.e. immobile) phase of the contaminant from the soil.

IV.   PROCESS-BASED METHODS

A. EX SITU METHODS FOR SOLIDS AND LIQUIDS

Several methods are available for the ex situ treatment of solids and liquids. Treatment aims to remove, destroy, or modify contaminants, rendering them unavailable to potential human or environmental targets. Whether an ex situ method can be applied at a site is determined by the nature and the distribution of the contaminants, and by physical, chemical, and in some cases, biological properties of the media to be treated.

The decision to treat contamination onsite or offsite depends on a number of factors, including the availability and cost of on- and off-site facilities; available time scales; and site specific factors, such as the location of the site relative to off-site treatment centers, space available for on-site treatment and temporary storage, and availability and capacity of local services, such as power, drainage, and water supply.

To assess the applicability and potential performance of ex situ treatment methods, information is required on the contaminants present (e.g. types, concentrations, and distribution) and the physical, chemical, and biological properties of the material to be treated. The data on applicability and performance should be tailored to meet the specific requirements of the method, or methods, intended for use. In most cases, this involves collecting supplementary data beyond that necessary for the risk assessment and initial remedy selection. Treatability studies are likely to be required to select, design, and implement the remedy.

Many ex situ treatment methods are specific to particular types of contaminants and are sensitive to variations in feedstock composition.

Factors that can limit the effectiveness of ex situ methods of treatment include:

- inappropriate particle size preventing effective contact between treatment reagents and contaminants;
- heterogeneous feedstock leading to variable performance and quality of the treatment product;
- inappropriate matrix types, such as clay or humic soils in soil washing technologies or overly coarse material in thermal treatment technologies
- complex contaminant mixture leading to antagonistic or unproductive reactions, or interference in the main process reactions; and
- sub-optimal processing conditions leading to poor or variable performance.

B. EX SITU METHODS FOR LIQUIDS (GROUNDWATER)

Treatment methods developed for drinking water, sewage treatment, and industrial effluent can be adapted, provided that the physical, chemical, and biological properties of the liquid to be treated and the design and operational requirements of the treatment system have been considered. Several methods have been specially developed for the treatment of contaminated groundwater.

Contaminated waters may contain only one or a small number of contaminants present over a relatively narrow concentration range, or they may contain complex mixtures of contaminants at wide-ranging or very high concentrations. In addition, these concentrations may fluctuate over time, and the volumes of liquid to be treated and time scales may vary considerably. The relatively short-term nature of remediation projects, compared to conventional water and wastewater treatment and the complex conditions have implications for cost, which will be higher for the remediation technology.

1.   Air stripping

Stripping with air or steam is used to remove dissolved volatile organic compounds from water. Air stripping involves transferring a dissolved substance from the liquid to the gas phase whereas steam stripping is essentially a distillation process in which the volatile contaminants are removed. The driving force of the removal is the concentration difference between the liquid an the air phases.

Air stripping can be accomplished using aeration tanks, cascade aerators, spray basis, or packed towers. The stripped water is collected at the bottom of the tower and the emissions may be treated by activated carbon. Factors that control stripping efficiency include tower height and diameter, the air-to-water ratio and the temperature. Packed towers include an aeration system, devices to insure that the mass transfer occurs optimally, and packing material (polypropylene).

2. Carbon adsorption

Adsorption is a physical mechanism based on the properties of some porous materials to fix molecules on their surface. Specific surface governs this mechanism. Adsorption on activated carbon is a widely used method for removing organic pollutants dissolved in water. Adsorption capacity values vary depending on the compounds to be removed. For instance, adsorption capacity of chlorophenol is six times higher than that of butylacetate in same conditions.

3. Resin Adsorption

Resin adsorption is a physical-chemical process in which dissolved substances are removed from solution by synthetic or natural materials. The resins may be ionic or nonionic; the nonionic materials form stronger bonds which are harder to reverse. Therefore, weak ionic or nonionic resins are more widely used. Synthetic resin adsorbs dissolved substances by trapping and holding the solutes in its molecular structure. In comparison to activated carbon, resin adsorption is more selective for some compounds; non ionic resin polymers readily sorb low molecular weight lipophilic substances as the alcyl benzenes. Capital costs are low, operating cost are high.

4. Ion Exchange

Ion exchange is an adsorption process which has been demonstrated for removal of most inorganic dissolved salts, some organic dissolved substances and some low molecular weight lipophilic compounds.

5. Filtration

Filtration is an effective method that separates low levels of solids from an aqueous phase by passing through a semi-permeable medium. For contaminated groundwater granular media (sand) filters are used to filter suspended solids by gravity or auxiliary pressure. The filter bed is regenerated by back washing and removing solids by flocculation or sedimentation.

6. Reverse Osmosis

Reverse Osmosis (RO) is a filtration process by which inorganic salts and some organic substances are removed from solution by passing the contaminated groundwater through a semi-permeable membrane under pressure. The contaminants are concentrated on one site of the membrane while water passes through. The osmotic pressure of the contaminated groundwater is counteracted by the applied pressure so that the solute con be concentrated, Most commonly used membranes include cellulose acetate, polyamides, and polysulfones. Organic compounds of low molecular weight are not removed by RO. The removing efficiency of organic compounds usually decreases with an increase in polarity and hydrogen bounding with the filter.

7. Chemical or UV Oxidation

UV/oxidation processes combine the use of ultraviolet light (UV) and chemical oxidants such as ozone (O_3) and hydrogen peroxide ($H_2 O_2$) to destroy organic contaminants in groundwater. In most UV/oxidation processes, high intensity UV radiation is combined with $H_2 O_2$ to oxidize organic contaminants to Carbon dioxide and water. Through direct photolysis the UV reacts with the $H_2 O_2$ to generate hydroxyl radical (OH). The hydroxyl radical attack the organic molecules resulting in the destruction of the parent organic compound. The reaction is aided by the direct photolysis of the organic molecule by the UV light which can break or activate certain atomic bonds making the molecule more susceptible to oxidation.

A wide variety of organic contaminants are susceptible to destruction by UV/oxidation, including petroleum hydrocarbons, halogenated solvents, phenol, pentachlorophenol, pesticides, dioxines, glycols, PCBs, explosives like TNT, RDX, and HMX, creosote, VC, BTEX and other organic compounds. UV has most often been used for contaminant concentrations in groundwater below 500 mg/l. UV/Oxidation processes

con be configured in batch or continuous flow operations. A key advantage of the technology is that it is a destruction process, as opposed to air stripping or carbon adsorption, for which contaminants are extracted and concentrated in a separate phase.

The process is only efficient at rather low wavelengths (<200 nm). The stream treated must provide for good transmission of UV light, should be relatively free of heavy metal ions and have low alkinity and carbonates. The cost may be higher than competing technologies because of energy requirements.

8. Biological degradation

Biological treatment uses the action of microorganisms to metabolize the contaminants present. Under aerobic conditions, contaminants may be completely converted to carbon dioxide, water and additional microorganisms. Thus, biological treatment is considered to be true destruction process. However some of the contaminants which are present in groundwater are not readily biodegradable. The main reason is that the microorganisms are limited by a lack of degradation steps. The combination of several processes can be an answer to this problem.

9. Ion exchange

This process is employed for removing dissolved anions in contaminated groundwater. Removal method can be percolation through specific resins or clays.

C. IN SITU METHODS FOR SOILS

In situ treatment methods avoid the above-ground environmental impacts and costs associated with excavation. Some methods are particularly attractive for application on operating sites and other sites where buildings and structures need to be preserved.

In situ technologies for treating soil can be classified like their ex situ counterparts on the basis of the underlying treatment principle, such as physical separation and biological degradation. In addition, a distinction can be made between those methods that seek to remove, destroy, or stabilize contaminants by introducing a treatment agent into the ground, and those that act directly on the ground, such as electroremediation and in situ vitrification.

In situ treatment methods may be combined with P&T methods to treat contaminated groundwater. Soil flushing, in situ bioremediation, and soil vapor extraction may be combined in an integrated remediation scheme. Heat may be introduced to aid bioremediation or vapor extraction.

Accurate identification of all contaminants present, combined with treatability data, is essential because of the danger that a treatment adopted to remedy some contaminants could lead to adverse or counterproductive reactions with other contaminants. This may result in increased toxicity or mobility. An understanding of the physical characteristics of the site is essential for all in situ techniques, especially those requiring infiltration of treatment agents.

The effectiveness of in situ treatment methods is determined by a variety of factors, including:

- Nature, extent, and distribution of contaminants;
- Contact achieved between contaminants and treatment agents, often the extent to which the contaminants can be solubilized (conductivity and penetration can be enhanced by a variety of means;
- Control over processing conditions in the ground which are not visible, especially when working at considerable depth,
- extent to which treatment agents can be delivered to the site of action
- ability to effectively remove treatment products and excess agents from the ground; and
- time available for treatment in terms of access to the site and natural factors, such as groundwater flow rates.

Minimal information is available on the long-term effectiveness of in situ treatment methods that do not remove or destroy contaminants. In situ techniques are likely to be most effective when applied to specific

types of contaminants in homogenous ground conditions or at least well defined heterogeneous ground conditions. In situ treatment may have significant implications on the engineering properties of the ground and hence on any subsequent construction work (e.g. infiltration may affect the stability of neighboring buildings).

In-situ remediation relies on enhancing the rate of release of contaminants from the soil-sorbed and NAPL-phases into the aqueous or gaseous phases, from which they can be removed.

The primary mechanisms believed to be responsible for solid-solution exchange of organic chemicals can be classified into physically and chemically based categories. Chemically based mechanisms are very stable and may be irreversibly sorbed under prevailing environmental conditions so they are generally to be considered to be unavailable to loss by biodegradation, volatilization or leaching. The potential to remove such contaminants from soil using in-situ technologies may be limited.

There are several physical or diffusive mass transfer rate-limiting mechanisms that are responsible for the slow release of contaminants from the soils, involving the physical trapping of organic molecules within soil micropores, the retarded intraparticle diffusion and the intraorganic matter diffusion.

Unfortunately, the release kinetics of organic contaminants into these environmentally mobile forms usually decline over time, such that the dissipation of an organic substance from soil is essentially bi-phasic – an initial period of relatively rapid loss is followed by a longer, much slower one. Consequently, there are limitations to the economic efficiency and the overall success of remediation technologies.

Optimal NAPL dissolution and desorption of soil-sorbed chemical residues will occur in the presence of freely flowing water (or air) which effectively maximizes the diffusion gradient between NAPL globules, or the soil solids, and the bulk solution phase. In many soils a proportion of contaminants may occur within the soil matrix where water does not commonly flow, or may do so only at very slow rates. (non homogeneous distribution of contaminants within soils and associated spatially distributed fluid flow pathways and velocities)

1. In Situ Stabilization/Solidification:

is a process of alteration of organic or inorganic contaminants to an immobile state by injection or infiltration of stabilizing agents into a zone of contaminated soil or groundwater. Contaminants are physically bound or enclosed within a stabilized mass, or their mobility is reduced through chemical reaction. Excellent understanding of the hydrogeologic regime is essential. Best applied to moderate to high permeability soils. May be used for a variety of organic and inorganic contaminants.

2. In Situ Soil Flushing (in situ soil washing):

Injection or infiltration of a solution into a zone of contaminated soil or groundwater to mobilize or solubilize NAPLs, followed by downgradient extraction of groundwater (flushing solution mixed with the contaminants) and above ground treatment and/or re-injection. Solutions may consist of surfactants, co-solvents, acids, bases, solvents, or plain water. Surfactants enhance mobility of hydrophobic organic compounds by lowering interfacial tension between water an NAPL; co-solvents increase the solubility. Any variety of configurations of injection wells, directional wells, trenches, infiltration galleries and extraction wells or collection trenches may be used to contact the flushing solution with the contaminated zone.
Contaminants treated are VOCs, SVOCs, petroleum hydrocarbons, PCBs and pesticides. The method may enhance existing pump and treat systems but can increase plume size and concentrations. It is difficult to recover surfactants and to remove contaminants from extracted groundwater with surfactants.

3. In Situ Oxidation

In situ chemical oxidation is based on the delivery of chemical oxidants to contaminated media. Strong oxidants like hydrogen peroxide, potassium permanganate ($KMnO_4$) or Fentons Reagent (whereby hydrogen peroxide is applied with an iron catalyst creating a hydroxyl free radical) are used. The hydroxyl free radical is capable of oxidizing complex organic compounds. Oxidants are injected or recirculated through a well or injector head directly into the subsurface, mixed with a catalyst. Best for compounds with unsaturated carbon-carbon bonds, like VOCs, SVOCs and petroleum hydrocarbons.
In situ oxidation needs low capital and energy. It may require large quantities of oxidizing agent. Incomplete oxidization or formation of intermediate contaminants is possible, other carbon sources compete for oxidant.

Successful implementation of this technology requires an effective means for disperging the oxidant to the subsurface contaminated regions.

4. Electrokinetics

Electrokinetics is a process that separates and extracts heavy metals and organic contaminants from saturated or unsaturated soils, sludges and sediments. A low intensity direct current is applied across electrode pairs that have been implanted in the ground on each side of the contaminated soil. The electrical current causes electroosmosis and ion migration, which move the aqueous phase contaminants in the subsurface from one electrode to the other. Contaminants in the aqueous phase or contaminants desorbed from the soil surface are transported towards respective electrodes depending on their charge. The contaminants may then be extracted to a recovery system or deposited at the electrode. Surfactants and complexing agents can be used to increase solubility and assist in the movement of the contaminant. Also reagents may be introduced at the electrodes to enhance contaminant removal rates.

5. Soil Vapor Extraction

Soil vapor extraction (SVE) is a process that physically separates contaminants from soil. Therefore, SVE systems are designed to remove VOCs from soil beneath the ground surface in the unsaturated zone. By applying a vacuum through a system of underground wells, contaminants are pulled to the surface as vapor or gas. Vapor wells can be placed either vertically or horizontally. Vapors extracted by the SVE process are typically treated using carbon adsorption, incineration, catalytic oxidation, or condensation. Carbon adsorption is the most commonly used treatment for contaminated vapors and is adaptable to a wide range of volatile organic compounds.

Soil vapor extraction often fails and leaves contaminants sorbed to solids in the vadose or in the saturated zone. SVE is very effective for the removing the labile fractions of contaminants located in the vapor and free liquid phases or adsorbed to the external surfaces of the soil matrix. But it will not be effective for removing contamination trapped in the interior of the soil matrix. Because the quantity trapped in the interior of the soil matrix may exceed surface contamination by 1-2 orders of magnitude, SVE cannot be relied upon to return long-contaminated soils to their pristine conditions.

Enhancements for soil vapor extraction are used as follows:

Thermal Enhancement: Use of steam, heated water, hot air or radio frequency (RF) or electrical resistance/ alternating current (AC) heating to alter temperature-dependent properties of contaminants in situ to facilitate
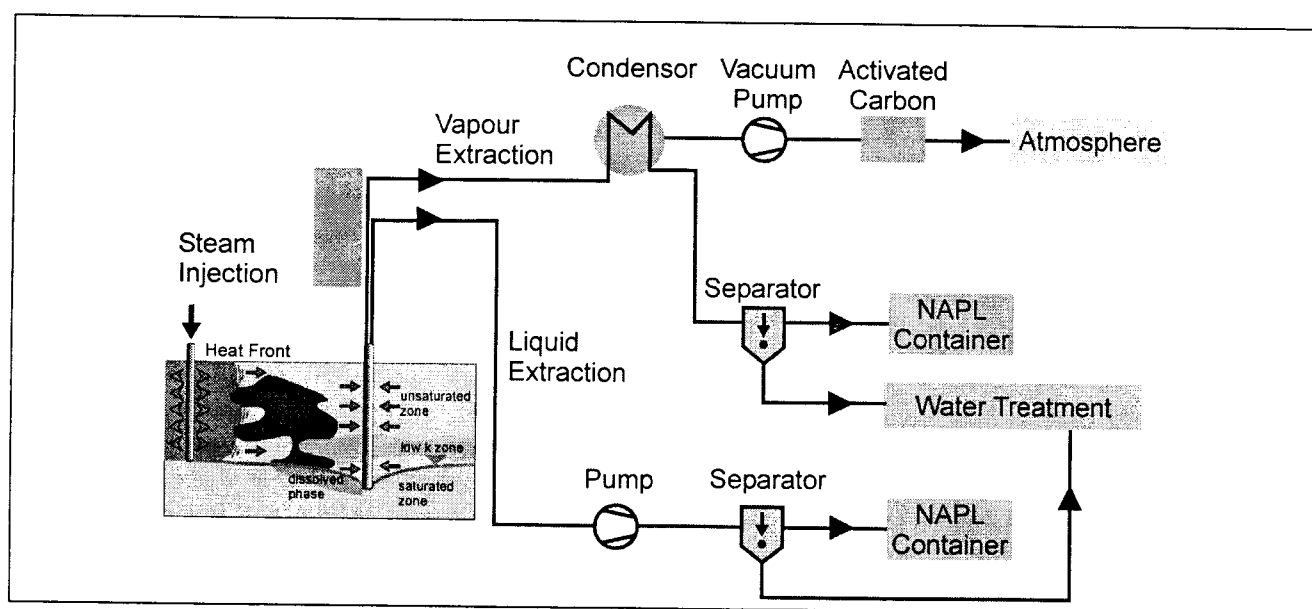

Fig. 3: Process Diagram Steam Enhanced *in situ* Remediation

their mobilization, solubalization, and removal. VOC and SVOC may be vaporized; they then rise to the vadose zone where they are removed by vacuum extraction and treated. Steam best applied to moderate to high permeability geologic materials. RF and AC heating may be applied to low permeability, clay rich geologic materials as the clay will preferentially capture the RF or AC energy.

At temperatures achieved by steam injection, organic compounds will readily oxidize over periods of days to weeks. By introducing both heat an oxygen, this process has effectively destroyed petroleum and solvent contaminants. After the free organic liquids are gone, this oxidation will continue to remove low-level contamination. The oxidation of contaminants at steam temperatures is extremely rapid (e.g. two weeks for naphthalene) if sufficient oxygen is present.

At the leading edge of the heat front the contaminants come in contact with the cold soil and condense again. This may result in a NAPL saturation above residual and subsequent downward migration of the liquid NAPL. Therefore most of the contaminant leaves the system as a liquid removed from the water surface.

Thermal enhancement could increase the size of the plume and temporarily destroy biomass, but reduce the treatment time for difficult soils (clay, silt). Good understanding of hydrogeologic conditions is essential for all applications.

Hydraulic and Pneumatic Fracturing are techniques adapted from petroleum industry to create enhanced fracture networks to increase soil permeability to liquids and vapors and accelerate contaminant removal. Especially useful for vapor extraction, but also for biodegradation and thermal treatments.

Hydraulic fracturing involves injection of high pressure water into the bottom of a borehole to cut a notch; a slurry of water, sand and thick gel is pumped at high pressure into the borehole to propagate the fracture of the initial notch. The gel biodegrades, leaving a highly permeable sand-filled lens that may be up to 60 feet in diameter.

Pneumatic fracturing involves injection of highly pressurized air to extend existing fractures and create a secondary fracture network. The fractures are created through the use of fluid pressure to dilate a well borehole and open adjacent cracks. Once fluid pressure exceeds a critical value, a fracture begins to propagate. Fractures may remain open naturally, or they may be held open by permeable materials (typically sand), injected during fracture propagation. The fractures serve as avenues for bioremediation, steam or hot air injection or contaminant recovery and can also improve pumping efficiency and the delivery for other in situ processes. Mostly applicable for unconsolidated sediments and bedrock.

A few cases have involved blast-enhanced fracturing.

Air Sparging (AS) expands the remediation capabilities of SVE to the saturated zone. One of the limitations of SVE alone is that it does not effectively address contaminated soils within the capillary fringe and below the groundwater table. AS involves injecting air or oxygen under pressure into the saturated zone to volatilize contaminants in groundwater. The injected air removes adsorbed VOCs in soil and dissolved contaminants in groundwater as the air rises through the formation. Volatilized vapors migrate into the vadose zone where they are extracted by vacuum, generally by a soil vapor extraction system. Most applicable for volatile organic contaminants relatively moderate to high permeability geologic materials.

AS is also used to supplement P&T systems. For example, AS may be added to remediate specific portions of a contaminated plume that are not treated effectively by P&T alone or to accelerate cleanups. AS can also be used to promote biodegradation in saturated and unsaturated soils by increasing subsurface concentration of oxygen.

Dual-phase extraction (DPE) like AS combines soil and groundwater treatment for cleaning up VOC contamination. By removing both contaminated water and soil gases from a common extraction well under vacuum conditions, simultaneous treatment can be achieved, reducing both the time and cost of

treatment. DPE provides a means to accelerate removal of NAPL and dissolved groundwater contamination. Three basic types of DPE have been developed including:

- Drop-tube entrainment extraction: Extraction of total fluids (liquid and soil vapor) via vacuum applied to a tube inserted in the extraction well. Groundwater and vapors are removed from the extraction well in a common pipe manifold, separated in a gas/liquid separator, and treated.

- Well-screen entrainment extraction: Extraction of groundwater and soil vapors from a common borehole screened in the saturated and vadose zones. Groundwater is aspirated in the vapor stream at the well screen, transported to the treatment system in a common pipe manifold, separated a gas/liquid separator, and treated.

- Downhole-pump extraction: Extraction of groundwater using a downhole pump with concurrent application of vacuum to the extraction well. Groundwater and soil vapors are removed in seperate pipe manifolds and treated.

Use of DPE is most advantageous for sites contaminated with volatile compounds and for soils with moderate to low hydraulic conductivity.

Bioslurping is an in situ remediation technology, adapted from vacuum dewatering techniques used in construction projects, that is being developed and tested for the cleanup of LNAPL contamination. Bioslurping simultaneously employs vacuum-enhanced extraction/recovery to remove the free-phase LNAPLs from the water table and capillary fringe, vapor extraction to remove high volatility vapors from the vadose zone and bioventing to stimulate biodegradation of less volatile hydrocarbons in unsaturated and capillary zones. By removing free product and addressing residual contamination in the same step, bioslurping can increase efficiency and lower cost and treatment times when compared to phased hydrocarbon remediation techniques.

The main components of a bioslurping system include:
- Recovery (slurper) wells with slurp tube
- Vacuum pump capable of extracting liquids and vapors (usually a liquid ring pump)
- Liquid/vapor and oil/water separation units
- Water and vapor treatment units

The above mentioned technologies supporting the soil vapor extraction can also be used for the enhancement of methods that need a higher mobility of the contaminants.

D. IN SITU METHODS FOR GROUNDWATER

In situ treatment of groundwater requires water to pass through a treatment zone where injection of agents in solution or in gaseous form cause degradation or promote natural degradation of contaminants; or a solid substrate exists that supports physical separation of the contaminants by adsorption, chemical or biological degradation, or reduction in toxicity.

These two processes may be used in combination. In situ treatment of groundwater may be combined with in situ treatment of the unsaturated zone. Soil vapor extraction coupled with microbial treatment is an example of this type of combination. In situ groundwater treatment also may be combined with P&T operations. The flow of groundwater through or to the treatment zone may be the result of natural gradients; induced by pumping from vertical or horizontal wells, or by infiltration of water; or achieved through injection of heated water or steam.

In situ groundwater remediation requires a thorough understanding of the hydrogeology of the site and its environs, and in many cases requires the prior removal or containment of the source of the contamination and removal of free product. As for all in situ methods, ensuring contact between contaminants and the treatment agent is major practical difficulty. Contaminants may be adsorbed onto mineral surfaces and held in capillary pores. Effective long-term treatment requires that these contaminants be released to the

groundwater. A variety of means may be used to promote the movement of contaminants through the subsurface. These include hydrofracturing, electrokinetic techniques, injection of steam or hot water, and surfactant flushing.

Because contaminant mobility is different at each site, any in situ treatment method must take into account the characteristics of the contaminant present. Contaminants partition between liquid, soil, and vapor phases, characteristic of the contaminants, aquifer materials, organic content, and other geochemical factors. For many contaminants, these associations vary and may not be completely reversible. Modeling groundwater and contaminant movement is often required to design the treatment system.

Significant amounts of groundwater flow – both vertically and horizontally – may occur through limited parts of the aquifer, and the direction and rate of flow may be markedly different at different depths. This can result from spatial variability in the permeability of water, or as a result of density or other contaminant characteristics. Thus, neither the bulk water flow nor the distribution of contaminants can be assumed to be homogeneous.

Technical specifications should ensure:
- appropriate controls over treatment agents and other materials used during treatment;
- proper provisions for locating, installing, operating, and maintaining injection wells, barrier systems, and associated storage facilities;
- satisfactory monitoring arrangement, particularly to determine the end point of treatment.

Care is required in the selection and design of an in situ groundwater treatment system to ensure that:
- any chemical introduced into the ground during treatment does not itself become a pollutant;
- mobilization of contaminants other than those that are primary object of the treatment or are naturally present is prevented; and
- treatment end products are not more harmful than the original compounds.

1. In-Well Vapor Stripping

In-well vapor stripping (in situ vapor or in situ air stripping), is a technology for the in situ remediation of groundwater contaminated by VOCs. The in-well stripping process, an extension of air sparging technology, involves the creation of a ground-water circulation cell around a well through which contaminated ground-water is repeatedly cycled until sufficient contaminant removal has taken place. The air stripping well is a double-cased well („well-within-a-well") with hydraulically separated upper and lower screened intervals within the same saturated zone (aquifer). The lower screen, through which groundwater enters, is placed at or near the bottom of the contaminated aquifer and the upper screen, through which ground-water is discharged, is installed across or above the water table.

Air is injected into the inner casing, decreasing the density of the contaminated groundwater and allowing it to rise within the inner casing. This constitutes a type of air-lift pumping system, similar to that found in an aquarium filter system. Through this air-lift pumping, volatile contaminants in the groundwater are transferred from the dissolved phase to the vapor phase by the rising air bubbles through an air stripping process. Contaminated vapors can be drawn off and treated above ground (similar to a soil vapor extraction system) or discharged into the vadose zone, through the upper screened interval, to be degraded via in situ bioremediation.

The ground-water, which has been partially stripped of volatile contaminants, continues to move upward within the inner casing and is eventually discharged into the outer casing, moving through the upper screened interval into the vadose zone or the upper portion of the aquifer. Once returned to the subsurface, ground-water flows vertically downward, eventually reaching the lower portion of the aquifer where it is cycled back through the well into the lower screened interval, replacing the water that rose due to the density gradient.

In the in-well vapor stripping process, contaminants that are dissolved in ground-water are transferred to the vapor phase, which is generally easier and less expensive than ground-water to treat. Ground-water is not removed from the subsurface, but is circulated back into the well to facilitate further vapor removal. The

vapors can be removed using the same stripping well, or, if applicable, can be discharged into the vadose zone for in situ bioremediation.

Most of the field applications of this technology have involved halogenated (VOCs), such as TCE, and petroleum products/constituents such as benzene, toluene, ehtylbenzene, and xylene. Applications of in-well stripping to non-halogenated VOCs, semi-VOCs (SVOCs), pesticides and inorganics have been proposed based on modifications of the basic remedial process.

The three main types of in-well vapor stripping systems include:

- NoVOCs™
- Unterdruck-Verdampfer-Brunnen (UVB) or „vacuum vaporizer well"- system
- Density Driven Convection (DDC) system

No VOCs

The NoVOCs™system uses a compressor to deliver the air to the contaminated water column. The bubble-water mixture rises to a point where optimum volatilization has occurred, where it encounters a deflection plate. At this point the air bubbles combine. The water flows out of the well through the upper screen and the coalesced bubbles are drawn off by vacuum for above ground treatment for VOCs. In addition, one modified NoVOCs™ system is purported to allow removal of metals from ground-water through in situ fixation using common water treatment chemicals.

UVB

The UVB system supplements air-lift pumping via a submersible pump to maintain flow at a standard rate. In addition, the UVB system employs a stripper reactor to facilitate transfer of volatile compounds from aqueous to gas phase before the water is returned to the aquifer. This device, located just below the air diffuser, „consists of fluted an channelized column that facilitates transfer of volatile compounds to gas phase by increasing contact time between two phases and by minimizing coalescence of air bubbles".

DDC

The DDC system emphasizes the enhancement of bioremediation and involves the discharge of extracted vapors into the vadose zone for degradation by naturally-occurring microorganisms. Nutrient solutions may be added to the DDC well as a concentrated slug. Oxygen is supplied to both the saturated subsurface and the vadose zone promoting natural aerobic processes.

The overall effectiveness of the system depends upon the time available for mass exchange between dissolved and vapor phase, the concentration gradient, the temperature of the operating system. The interface area of the bubble (bubble size), and the contaminant gas-liquid partitioning (mass transfer coefficient). The technology employs readily available equipment and materials. The technology is limited to treatment of VOCs in the saturated zone and the capillary fringe, modification of the basic remedial process are proposed for application to SVOC. May be used in unconfined or confined aquifers; process has been applied to geologic materials of wide ranging permeability.

2. *Permeable Reactive Barriers (PRB)*

A PRB, (or passive barrier, passive treatment wall, treatment wall, trench), consists of an in-ground trench that is backfilled with a reactive medium to provide passive treatment of contaminated groundwater passing through the trench. The treatment wall is placed at strategic location to intercept the contaminant plume. The selection of the reactive medium is based on the targeted contaminants and the hydrogeologic setting of the site. Zero-valent iron is the most common medium used in PRBs to date. Examples of other reactive media include, microorganisms, zeolite, activated carbon, peat, phosphate, bentonite, limestone, and amorphous ferric oxide.

Raw zeolite has a high adsorptive capacity for positively charged contaminants. Surface-altered zeolite is selective for major classes of soluble organics such as benzene and trichloroethylene, inorganic cations such

as lead and cadmium, and inorganic anions such as chromate and arsenate. The properties of the zeolite can be tailored for specific needs.
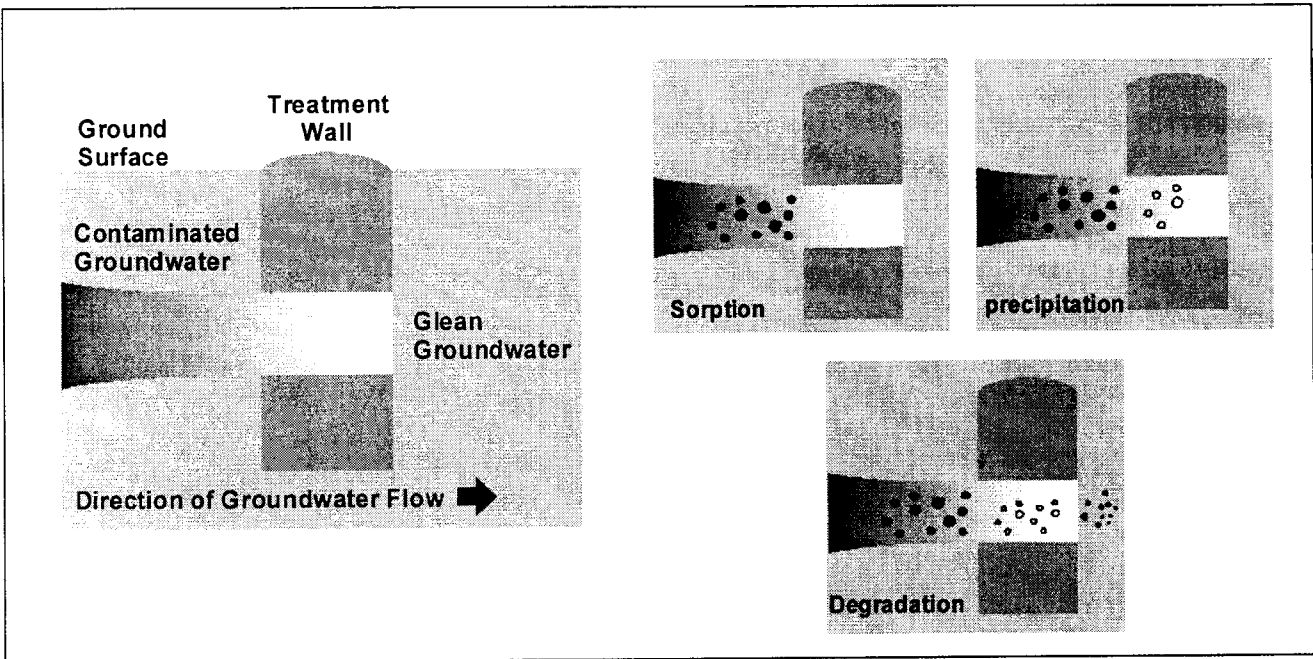

Fig. 4: Treatment Walls

Different fillings do their job through different processes: sorption, precipitation, degradation:

Sorption barriers contain fillings that remove contaminants from groundwater by adsorbing or chelating contaminants to the barrier surface.

Precipitation Barriers contain fillings that react with contaminants in groundwater as they seep through the wall. The "insoluble" precipitation products are left trapped in the barrier and clean ground water flows. A precipitation barrier filled with limestone placed across the path of an acid, lead-contaminated ground water neutralizes the acid. This causes the lead to change to a solid form that is trapped in the barrier.

Degradation barriers cause reactions that degrade the contaminants in the groundwater (oxidation, reduction). For example, fillings of iron granules degrade certain volatile compounds. Walls may also be filled with a mixture of nutrients and oxygen sources which stimulate the activities of microorganisms.

The reactions that take place in the barriers are dependent on parameters such as pH, oxidation/reduction potential, concentrations, and kinetics.

Much research and testing has been done on **the use of iron** for the treatment of chlorinated contaminants. As the iron is oxidized, the toxic component of the contaminant (usually the chlorine atom) is removed from the compound. The iron granules are a by-product of manufacturing process so their use as a barrier wall material has the added benefit of the recycling the material. Iron can be used to degrade many common chlorinated organic compounds such as trichloethylene (TCE), tetrachloroethylene (PCE), dichloroethene (DCE), and 1,1,1-trichloroethane (TCA). The understanding of the fundamental mechanisms of the metal enhanced degradation is far from complete understanding, direct corrosion on the iron surface was selected as the most probable.

Choice of treatment wall is based on specific contaminant. Hydrogeologic setting is critical to application; geologic materials must be relatively conductive and a relatively shallow aquitard must be present to provide a basement to the system. Groundwater flow should have a high degree of preference, and groundwater

quality must support the desired reaction without imposing additional loading of the reactive media or creating undesirable by-products.

Reactive walls downgradient of contaminated areas are currently being discussed as an alternative method to traditional groundwater remediation technologies. PRBs may be used to treat contaminated groundwater **at the boundary of a site**, or to restore the groundwater **throughout a site.**

The volume of groundwater treated by a PRB is typically much lower than it would be for a P&T system at the same site because PRBs treat only the groundwater that passes through the barrier, while P&T systems actively extract groundwater from an aquifer, usually at multiple locations throughout the plume.

The **most important advantage** of this innovative technology for passive in situ-treatment of contaminated groundwater are the comparatively low costs associated with operation and maintenance (O&M). PRB systems may be configured as **funnel and gate** designs. In such configurations groundwater flow is routed by two or more permeable walls through a permeable reactive zone.

Besides the treatment of organic compounds there are also successful projects with other contaminants (e.g. Chromium, Arsenic), but there is a need for research on deeper installations (>50 feet), other reactive media and the reactivity lifetime. The replacement of treatment units is discussed. Issues of concern include the system long term performance, and the potential for remobilization or generation of secondary products more toxic than those initially present.

3. Bioremediation

Bioremediation is a managed or spontaneous process in which microbiological processes are used to degrade or transform contaminants to a less toxic or nontoxic form, thereby mitigating or eliminating contamination. Microorganisms (yeast, fungi, or bacteria) depend on nutrients and carbon to provide the energy needed for their growth and survival. Degradation of natural substances in soils and sediments provides the necessary food for the development of microbial populations in these media. Bioremediation technologies harness the natural processes by selecting or promoting the enzymatic products and microbial growth necessary to convert the target contamination to nontoxic end products.

Many organic contaminants, like petroleum, can be biodegraded by microorganisms in the underground environment. For example, biodegradation process can effectively cleanse soil and groundwater of hydrocarbon fuels such as gasoline and BTEX compounds. Biodegradation also can break down chlorinated solvents, like TCE, in the groundwater but the processes involved are harder to predict and are effective at a smaller percentage of sites compared to petroleum contaminated sites. When chlorinated compounds are biodegraded, it is important that the degradation be complete, because some products of the breakdown process can be more toxic than the original compounds.

In the presence of sufficient oxygen (**aerobic conditions**) and nutrients, microorganisms will ultimately convert many organic contaminants to carbon dioxide, water and microbial cell mass. In the absence of oxygen (**anaerobic conditions**), the electron acceptor is a compound other than molecular oxygen, such as sulfate, nitrate, or carbon dioxide, and the contaminants will be ultimately metabolized to methane, limited amounts of carbon dioxide, and a trace amount of hydrogen gas. Oxygen, if present, is the electron acceptor used preferentially, as it provides maximum energy yield to the microorganisms, maximizing cell production and microorganisms growth, per unit amount of electron donor used. Thus, aerobic bioremediation generally proceeds more quickly and provides a more complete degradation of the organic compounds than anaerobic bioremediation.

Enhanced bioremediation technologies increase biodegradation rates by supplying nutrients and electron acceptors, or control other factors that can be rate-limiting, e.g. temperature, pH. Enhanced in situ remediation involves the percolation or injection of groundwater or uncontaminated water mixed with nutrients and saturated dissolved oxygen, using injection and extraction wells. Placement of the wells is dependent on the area of contamination and the permeability of the formation. An infiltration gallery or spray irrigation is typically used for shallow contaminated soils, and injection wells are used for deeper contaminated soils.

Bioventing systems treat soil in situ by injecting atmospheric air into unsaturated soil. The air provides a continuous oxygen source, which enhances the growth of microorganisms naturally present in the soil and accelerates the natural processes. **Biosparging** enhances bioremediation by injecting a gas under pressure into the saturated zone to transfer volatile compounds to the unsaturated zone for biodegradation.

Research is underway at a number of facilities using exogenous, specialized microorganisms or genetically engineered microbes to optimize bioremediation. This approach, referred to as **bioaugmentatation,** may be appropriate for ex situ bioremediation projects, but has yet to be proven effective in situ. The inoculation of a specialized microbial population into the environment may not produce the desired degree of degradation for a number of reasons. Limiting factors may include soil conditions, substances or other organisms that are toxic or inhibitory to the growth and activity of the inoculated organisms. In addition, adequate mixing to ensure contact of the organisms with the specific organic constituent may be difficult. The effectiveness in controllable environments (e.g. bioreactors) has been demonstrated, in uncontrolled environments such as the subsurface is much more difficult to achieve, demonstrate and assess.

Contaminants that are readily biodegradable under aerobic conditions include

- Petroleum hydrocarbons, BTEX, gasoline
- VOCs
- Pesticides
- Organic solvents

Many of the more persistent contaminants are resistant to microbial remediation, because of

- their toxicity to the organisms,
- preferential feeding of microorganisms on other substrates,
- unfavorable environmental conditions
- lack of capability to use the compounds as a source of carbon and energy.

Alteration of the environmental conditions can often stimulate development of appropriate microbial populations that can degrade the organic compounds. Such changes may include adjusting the concentration of the compound, pH, oxygen concentration, or temperature, or adding nutrients or microbes that have been acclimated to the compound. PCBs and PAHs can be transformed or partially metabolized as a second substrate. Though they might not be suitable for growth substrate, they may be degraded by **co-metabolism,** where microorganisms growing on one compound produce an enzyme which transforms another compound on which they can not grow.

Most bioremediation technologies have focused on the addition of oxygen to facilitate the biodegradation. **Alternate electron acceptors** can be used for bioremediation in the saturated zone. A variety of oxy-anions can substitute for oxygen, including nitrate, sulfate and salts of iron III. Various types of anaerobic bacteria exist in nature that can use the anaerobic electron acceptors.

4. Natural Attenuation

Natural Attenuation (NA) makes use of natural processes to contain the spread of contamination and reduce the concentration and amount of pollutants at contaminated sites. It includes a variety of physical, chemical, and biological processes that act without human intervention to reduce the mass (through destructive processes such us biodegradation and chemical transformations), toxicity, mobility, volume, or concentration of contaminants in soil or groundwater.

Biodegradation is a process in which naturally occurring microorganisms degrade hazardous substances into less toxic substances. In most subsurface environments aerobic and anaerobic biodegradation of contaminants occur. Once the contaminants are degraded, the microorganism populations decline because they have used their food sources.

In situ precipitation of heavy metals and sulfates is a method based on stimulation of sulfate reducing bacteria (SRB) in aquifers and groundwater by supplementing an appropriate electron donor. In the presence

of a suitable electron donor, for instance acetate, SRBs reduce sulfates to sulfites and further to sulfides, which form stable and rather insoluble metalsulfides. The applicability has to be evaluated case by case in lab scale treatability testing in batch and column experiments.

NA processes may reduce contaminant concentrations (through simple **dilution or dispersion**); or bind contaminants to soil particles so the contamination does not spread or migrate very far (adsorption). The effects of dilution and dispersion appear to reduce contaminant concentration but do not destroy the contaminant. **Adsorption** occurs when contaminants attack or sorb to underground particles. Fuel hydrocarbons tend to repel water, as most oily substances do. When they have an opportunity to escape from the groundwater by attaching to organic matter and clay minerals that also repel water, they do so. This is beneficial because it may keep the contaminants from flowing to an area where they might be a threat. Sorption, like dilution and dispersion, appears to reduce the concentration and mass of contamination in the groundwater, but does not destroy the contaminants.

NA is an in situ treatment method, it is used as one part of a site cleanup that also includes other strategies. The processes contributing to NA are acting at varying rates and degrees of effectiveness, depending on the types of contaminants present, and the physical, chemical and biological characteristics of the soil and groundwater.

In certain situations, natural attenuation is an effective option and the most appropriate way to remediate some contamination problems. NA is sometimes mislabeled as a "no action" approach. However, NA is really a proactive approach that focuses on the confirmation and monitoring of natural remediation (Monitored Natural Attenuation, MNA). Hydrocarbons are good candidates for NA.

Responsibly proposed natural attenuation at a groundwater remediation site requires demonstration that the processes mentioned will occur at a sufficient rate to remediate the plume prior to impact at a receptor.

Therefore a site assessment must identify the following:

- Soil characteristics such as soil type, hydraulic conductivity and organic content
- Groundwater characteristics such as direction, gradient and velocity of flow, temperature, pH and dissolved oxygen content inside and outside the plume
- Horizontal and vertical extent of contamination in soil and groundwater, historical behavior of the plume, and the ability for attenuation of the plume under site conditions
- A detailed review of receptors and migration pathways in the area surrounding the site.

The rates of natural processes are typically slow. Long-term monitoring is necessary to demonstrate that contaminant concentrations are continually decreasing at a rate sufficient to ensure they will not become a health threat. The NA sites need to be well-characterized.

IV.   INFORMATION SOURCES

http://umweltbundesamt.de/altlast/
Results of recent research and development projects sponsored by BMBF and UBA are presented. BMBF published TERESA, a technology database on CD

http://clu-in.org

The Hazardous Waste Clean-UP Information System provides information about innovative site characterization and treatment technologies. Download of recent documents and access of databases designed to aid those responsible for contaminated site remediation is possible.

http://www.epareachit.org

The Remediation And Characterization Innovative Technologies database combines information from three established US EPA databases to give users access to comprehensive information about treatment and characterization technologies and their applications.

http://www.frtr.gov

The Federal Remediation Technologies Roundtable is a forum for joint activity regarding the development and demonstration of innovative technologies for contaminated site remediation. Links to case studies and Performance Reports for various technologies implemented at SUPERFUND sites can be found.

http://www.gwrtac.org

The Groundwater Remediation Technologies Analysis Center is a specialized US technology transfer and information center focusing on groundwater remediation, providing an easily accessible and reliable source of current information . There are several downloadable Technical Reports.

http://www.rtdf.org

The remediation Technologies Development Forum is a consortium of partners from government, industry, and academia working to develop safer, more effective, and less costly technologies.

http://www.gnet.org

The Global Network of Environment and Technology (GNET) provides daily news and up-to-date information on current environment and technology issues. Resources include the free interactive database TechKnow: http://www.techknow.org

http://www.epa.gov/ORD/SITE

SUPERFUND Innovative Technology Innovation (SITE) Program information, including electronic versions of the SITE Profiles Document (presenting information regarding SITE Program technologies) and selected information can be viewed and downloaded at the SITE Program Home Page

http://www.epa.gov/etv

The Environmental Technology Verification was created to accelerate the entrance of new environmental technologies into the marketplace by verifying their performance.

http://.clarinet.at

CLARINET is a Concerted Action within the Environment and Climate Program of the European Commission, DG Research. The Project is coordinated by the Austrian EPA. The main goal is to identify how contaminated land can be managed effectively and sustainably. CLARINET develops technical recommendations to facilitate decision making and establishes and co-ordinates a network for information exchange.

http://nicole.org

The overall objective of the Network for Industrially Contaminated Land in Europe (NICOLE) is to proactively develop, enhance and communicate concepts/strategies and technologies for the responsible management of soil and groundwater problems. The industry-led network was formed to establish a mechanism for increasing sharing of information between companies on their knowledge and understanding of the science and technology aspects of their problems and possible solutions

ANCORE is a platform for the exchange of innovative know-how in the field of applied research.

http://www.prb-net.org

The Permeable Reactive Barrier (PRB) Network establishes a communication framework for the exchange of ideas and technology relating to PRB