Remediation Technologies Handbook

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Acknowledgements

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FOREWORD

As part of the decision-making process aimed at selecting the most suitable remediation technologies applicable on a contaminated site, not only is it essential to carry out an in-depth assessment/comparison of the different applicable technologies, but also a strict and thorough analysis of the environmental context where the contaminant was found should be considered indispensable.

The assessment of the environmental context, combined with the definition of the chemical-physical and toxicological characteristics of the contaminants, as well as any potential migration path and receptors present on the site, make up the **(Preliminary or Final) Conceptual Model set forth by Legislative Decree 152/06** (the Italian Environmental Consolidated Act, aligned with international laws, regulations and best pracices in the field of environmental management).

Eni Rewind S.p.A., in order to guide the reader to understand the most suitable site-specific remediation technologies, has drafted these **Guidelines** based on over twenty years of experience in the remediation sector in Italy and, as of 2018, worldwide, accompanied by a rigorous collection of technical-scientific knowledge and direct consultation of Italian and international institutional sources, field operators and scholars.

In particular, these Guidelines have been developed through a **simple and informative narration of the remediation technologies** used, based on the geology and hydrogeology and on the type of related contaminants; furthermore, the document includes layouts, diagrams, charts, infographics and pictures of the main types of treatments applied mainly on Eni sites.

Moreover, these guidelines are addressed at once to an audience that rarely approaches the complex topic of subsoil remediation, as well as field operators, Control Units and the different stakeholders that wish to learn more about quintessentially technical and system-related aspects, in the interest of sustainability.

Lastly, ample space was given to both **mature and consolidated remediation techniques** and **innovative technologies**. The document includes those technologies that have been applied in recent times, that have reached an on-field application stage, and for which the market or institutions have expressed interest. It does not include those technologies that are still in their early development stage, on which only single academic research results are available.

In order to approach the complex world of environmental remediation, from an integrated and multidisciplinary perspective, and to provide, at the same time, added value in selecting the most suitable remediation technologies, the Handbook is structured as follows:

- Chapter 1 devoted to the classification of the typical environmental context of a contaminated site, with a particular focus on certain findings related to the subsoil and its main characteristics;
- Chapter 2 dedicated to the characteristics of the main contaminants, including the emerging ones, such as PFAS;
- Three sections dedicated to: a preliminary classification of the main elements to take into account when selecting a remediation technique (**Chapter 3**); a general classification of the remediation technologies currently used and the related chemical-physical or biological processes related to them (**Chapter 4**); a selection worksheet with the main techniques, which, starting from the consolidated Remediation Technologies Screening MATRIX drafted by ISPRA, can implement further elements to explore the technology applicability in terms of subsoil particle size, average remediation times and related costs (**Chapter 5**);

- Chapter 6 containing specific description datasheets on the main consolidated remediation techniques;
- A digression on a selection of innovative remediation techniques (**Chapter 7**);
- A presentation of the main innovative technologies and methods developed by Eni (**Chapter 8**).

Lastly, **Chapter 9** contains the complete bibliography used to develop the contents of this Handbook.

1.0 ENVIRONMENTAL CONTEXT

The remediation of a polluted site is aimed, according to the environmental Italian legislation, to eliminate the pollution from the environmental matrices or reducing the concentrations of pollutants in the soil, subsoil, underground and surface waters within the contamination threshold (CSC), established for the designed use, or at the risk threshold concentration values (CSR) defined based on a specific Risk Analysis.

A remediation process can be schematically reduced to the following phases:

- following the occurrence of a potential contamination event communicate it to the competent bodies and, where necessary, the adoption of appropriate Emergency Safety Actions (MISE);
- preliminary definition of the Conceptual Model of the site;
- preparation of a specific Characterization Plan, even if the preliminary investigations have already ascertained that the Contamination Threshold Concentrations (CSC), established by the local law, have been exceeded;
- definition of the definitive conceptual model of the site, following the characterization investigations;
- elaboration of the site-specific Risk Analysis, in order to define the acceptable Risk Threshold Concentrations (CSR) for that site. If the concentrations detected on site are lower than the CSC, the site is classified as "NOT contaminated" and does not require any remediation;
- otherwise, the site is classified as "contaminated" and, following the drafting and approval of a suitable Remediation Project, is subject to remediation in order to bring the concentrations of pollutants within the values of CSR or CSC;
- obtaining the certification of successful remediation, following a positive opinion of the testing activities.

Eni Rewind, Eni's environmental company that operates in line with the principles of the circular economy to enhance resources (soils, water, waste), sees remediation as an opportunity for the Country System and for the territories in environmental, economic and social terms.

Eni Rewind plans, in agreement with local institutions and stakeholders, projects for the areas to be remediated in order to make them available for new value-added projects.

The company promotes the application of increasingly innovative and sustainable remediation technologies. In compliance with the environmental legislation, a strong attention is paid to the application of technologies in situ that Eni Rewind prefers as they allow the remediation of soils and aquifers in their natural location, without using to excavation and disposal operations, minimizing impacts of remediation interventions.

To better understand the environmental remediation process, it was therefore considered appropriate to investigate some knowledge elements relating to the soil - subsoil - aquifer system and its main characteristics. **Figure 1-1** shows a rendering of the soil-subsoil system in presence of a free aquifer.

In particular, starting from the ground level, a distinction is made between:

A. A surface portion, called **unsaturated area** (ventilation or vadose area): inside it, the interstitial spaces are empty, and can contain gas or water in variable proportions, and, in any case, not saturated. Liquid movement is mainly vertical, due to gravity (percolation);

B. An intermediate area, called **capillary fringe** area: it is located above the groundwater table, and is characterized by oscillations at groundwater level, with potential movement of the contaminants present in the solution, which are distributed to the portion of soil affected by the oscillation. In this area, water is retained by capillary forces;

C. A deeper area, called **saturated area**: inside it, the pores are saturated with water. Liquid movement is mainly horizontal and is caused by the difference of hydraulic load under the control of gravity.

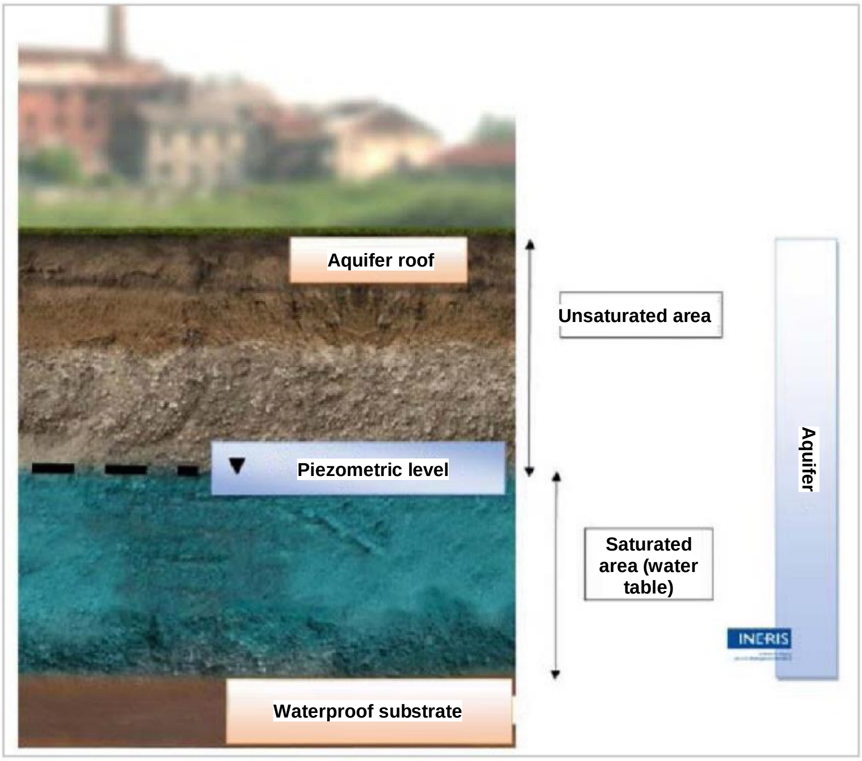
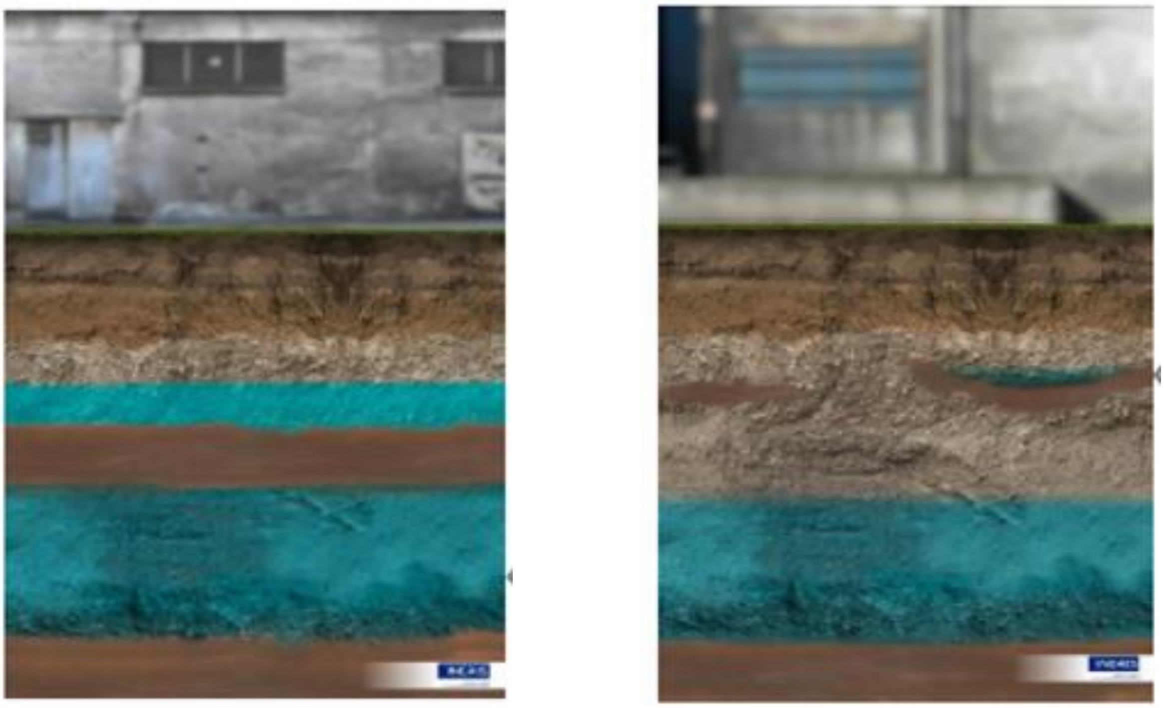


Figure 1-1 Soil-subsoil system diagram – free aquifer (Source: Guide méthodologique relatif au Plan de Conception des Travaux (PCT), INERIS 2019 - edited)



Enclosed aquifer
Perched water table

Figure 1-2 Confined aquifer and perched water table variants (source: Guide méthodologique relatif au Plan de Conception des Travaux (PCT), INERIS 2019)

The soil-subsoil system, rendered in **Figure 1-3**, is a complex system within which the contaminant _can be found in four different phases_:

I. Adsorbed phase, in which the contaminant molecules bind to the soil particles through a chemical or physical mechanism;

II. Volatile or gaseous phase, in which the contaminant molecules volatilize, undergoing a transition from the liquid state (evaporation) or, theoretically, also from the solid state (sublimation) to the aeriform one;

III. Dissolved phase (water-soluble), in which the contaminant molecules are found in solution, or dissolved in hygroscopic water;

IV. Liquid phase (non soluble) (NAPL), i.e. the contaminant is present as a pure product.

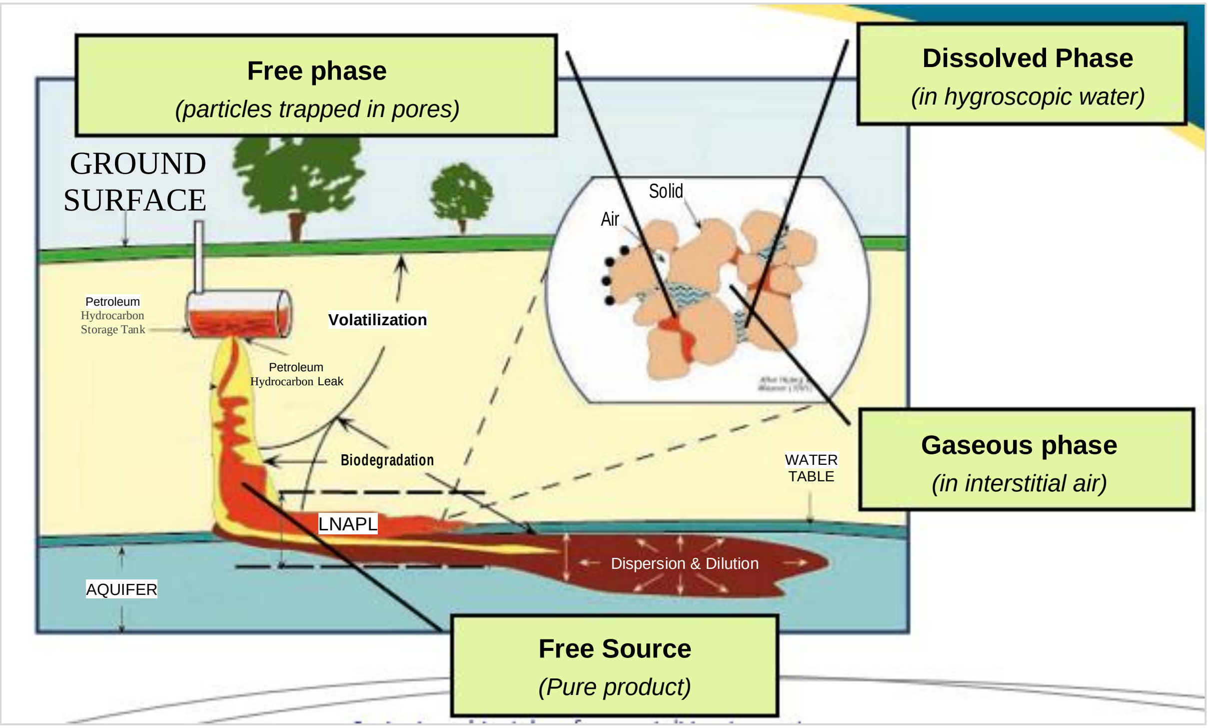


Figure 1-3 Subsoil phases diagram (Source: Tecnologie per la bonifica di siti contaminati: fondamenti teorici ed applicazioni, MWH, 2014)

Consequently, in the subsoil, contaminants may be transported, adsorbed, volatilized, and be subject to chemical and/or biological transformations.

The main processes that affect the contaminants' behaviour and mobility are the following:

- _Hydrodynamic processes:_ they affect the mobility of substances - and contaminants in particular - in the aquifers. They are mainly based on the lithology, permeability and hydraulic gradient;
- _Biotic processes_: they are essential for organic contaminant and nutrient degradation;
- _Abiotic processes:_ they affect both the transport of the substances by interacting with the stationary phases and their speciation. Some examples could be adsorption, ionic exchange, hydrolysis, etc.

Based on their characteristics, contaminants can be classified as organic (such as hydrocarbons) or inorganic (such as metals). Particularly relevant from an environmental standpoint, concerning subsoil pollution, are **organic compounds.**

The parameters that affect their behaviour and mobility in the subsoil are:

- Vapour pressure and Henry0s Law Coefficient (H);
- Water solubility (S), inversely proportional to molecular weight;
- Diffusion Coefficients in Air (Da) and Water (Dw);
- Distribution Coefficient (Kd);
- The solute's density and viscosity, compared to the solvent;
- Degradation Constant (λ).

The following elements should also be taken into account:

- Soil retention capacity;
- Contamination source type;
- Pollutant volume.

The following paragraphs briefly describe the behaviour of organic compounds in the unsaturated and saturated areas of the subsoil.

1.1 Unsaturated area

This paragraph briefly illustrates the behaviour of the characteristic phases of organic compounds in the unsaturated zone that distinguishes the subsoil.

The unsaturated area comprises two main phases.

- Volatile phase: volatile compounds may migrate from the contamination source, expanding in gaseous form (evaporation) in the unsaturated area, returning into the atmosphere or creating the known indoor vapours. The intensity of the evaporation and gas dispersion is, among the other factors, directly proportional to the soil permeability. However, part of the vapours is also adsorbed and diluted by the infiltration water, and migrates into the water table in soluble form;
- Liquid phase: the liquid mass percolation is mainly characterized by a vertical motion; the distribution and speed in the subsoil are mainly affected by the pollutant’s density and viscosity.

1.2 Saturated area

This paragraph briefly illustrates the behaviour of the characteristic phases of organic compounds in the saturated zone that distinguishes the subsoil.

The saturated area comprises three main phases:

- Volatile phase: it requires a significant presence of the pollutant's volatile fraction in the groundwater. Its migration is both toward the unsaturated area and within the saturated portion;
- Miscible phase: it occurs in contact with the piezometric surface;
- Non-miscible phase: based on the density, there may be two types of products: LNAPL (*Light Non Aqueous Phase Liquid*, lighter than water) and DNAPL (*Dense Non Aqueous Phase Liquid*, heavier than water), as shown in the following figure.
    - LNAPL compounds tend to float on the water table surface, generating sections more or less extended and separated from one another (supernatant phase). They move vertically and horizontally (i.e. in the main groundwater flow direction);
    - Since they are heavier than water, DNAPL compounds develop a slow and mainly vertical flow, until they encounter a low level of hydraulic conductivity (such as the permeable bottom of the aquifer).

Figure 1-4 shows a simplified diagram of the behaviour of the main contaminants in the subsoil.

In order to assess the distribution and diffusion paths of the contamination during the classification phase, complex hydrogeological and provisional models are often drafted, and their level of representation of the actual subsoil status is based on the number and quantity of data and information available.

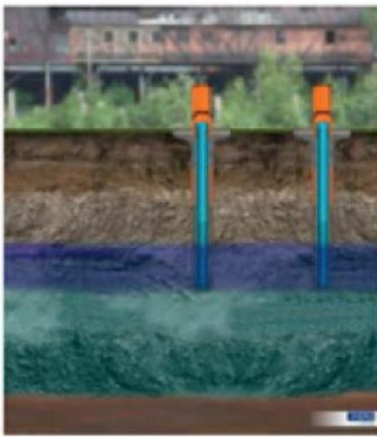
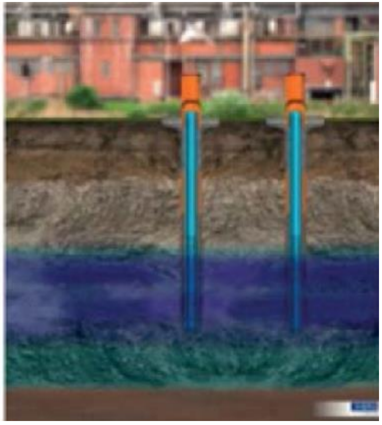
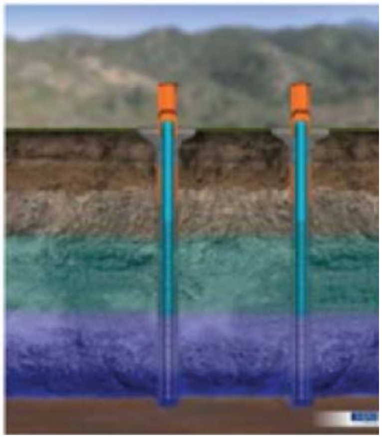
	Example of contamination resulting from the presence of a free organic supernatant phase on the water table (LNAPL)
	Central example of contamination resulting from one or more soluble substances
	Example of contamination resulting from the presence of an organic phase deposited on the bottom of the aquifer (DNAPL)

Figure 1-4 Examples of pollutant distribution in an even aquifer (source: Guide méthodologique relatif au Plan de Conception des Travaux (PCT), INERIS 2019 - edited)

2.0 CONTAMINANTS CHARACTERISTICS

Knowing the main chemical-physical, toxicological and environmental characteristics of site-specific contaminants is particularly crucial to define the most suitable remediation technologies.

The following paragraphs summarize the most significant characteristics, for the purposes of these Guidelines, concerning the two main classes of contaminants analysed herein:

- Organic compounds;
- Inorganic compounds.

The main characteristics related to the entire category will be described for each class of chemical compounds, followed by a table listing the qualitative information on the main chemical-physical-toxicological parameters (focusing on each pollutant).

It should be noted that the information was mainly obtained from the following sources:

- ISS-INAIL Database (last update in March 2018) and related supporting documents;
- Decontamination Database (ISS);
- Carcinogenic Substances Database (ISS).

Specific graphic symbols comparable to one another were identified to represent the main chemical/physical/toxicological characteristics of the concerned contaminants. The following key was used in each summary table:

High
Medium
Low

💧 liquid
solid
☁ gas

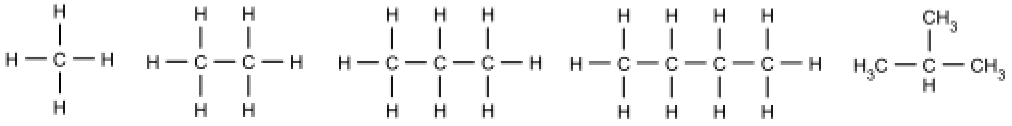
🔥 flammable
non-flammable
★★ Class. 2 IARC

★★★★ Class. 4 IARC
★★★ Class. 3 IARC
★ Class. 1 IARC

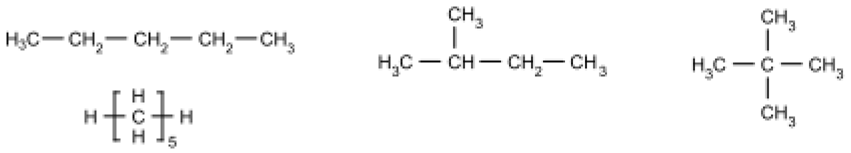
2.1 Organic compounds

Hydrocarbons

Hydrocarbon compounds are organic molecules mainly obtained from fossil fuels, which contain carbon and hydrogen atoms; many compounds used in basic and fine chemistry are obtained from crude-oil refining and are also used as motor and heating fuels. **Figure 2-1** shows some hydrocarbon organic compound molecules.



methane. CH_4 ethane, C_2H_6 propane. C_3K_8 butane. C_4H_{10} isobutane C_4H_{10}



n-pentane, CsH_{12} isopentane, CsH_{12} neopentane, CsH_{12}

Figure 2-1 Molecules of the main hydrocarbon organic compounds

A first distinction between the many different hydrocarbon compounds can be made based on their physical status (state of aggregation) at ambient pressure and temperature conditions, which in turn depends on the molecular weight:

- Solid or semi-solid hydrocarbons, with higher molecular weight;
- Liquid hydrocarbons, with intermediate molecular weight;
- Gas hydrocarbons, with lower molecular weight;

From a chemical standpoint, hydrocarbons can be divided into two main classes:

- Aromatic Hydrocarbons: having “aromaticity”, a chemical property given by a benzene ring, which makes them particularly stable;
- Aliphatic Hydrocarbons: without aromaticity and with branching.

The characteristics are summarized in Table **2-1**.

The environmental fate of a hydrocarbon mixture is strongly affected by its chemical composition and structure, and its distribution in the environment varies significantly over time.

The single mixture compounds are divided into the different environmental matrices in varied proportions and are subjected to specific degradation processes. In addition, given their heterogeneity and complexity, it is not possible to attribute a single toxicity value to the entire hydrocarbon mixture. Therefore, the environmental law provides for specific chemical testing aimed at determining the individual contributions in the hydrocarbon mixtures (e.g., MADEP "speciation" tests).

Table **2-1** summarizes the main chemical/physical/toxicological characteristics of these compounds.

In particular, from an environmental standpoint, hydrocarbon compounds with carbon-hydrogen only molecular structures have a lower density than water, and, for this reason, they can be found in pure form (LNAPL - Light Non Aqueous Phase Liquids) in nature and as suspended solids in groundwater.

Volatility *(Henry's Law Coefficient, vapour pressure, boiling point)*	◓ Light hydrocarbons, ◓ Heavy hydrocarbons
Physical status	☁ 💧 ⬡
Solubility *(Solubility, Soil/Water Partition Coefficient, Octanol/Water Partition Coefficient)*	◓ in water, ◓ in polar substances
Diffusion *(Diffusion Coefficient in Air and Water)*	◓
Carcinogenicity *(IARC Classification, International Agency for Research on Cancer)*	★★ ★★
Flammability	🔥

Table 2-1 Hydrocarbon Characteristics

Aromatic Organic Compounds (BTEXS)

Aromatic compounds mean a set of chemicals with a specific molecular structure, called benzene ring. The best-known compound is Benzene, an organic chemical essential for "fine chemical" industrial processes, which is liquid, transparent, highly flammable and characterized by a sweet and aromatic smell, and which easily evaporates into the air at ambient temperature. Benzene comprises 6 carbon atoms and 6 hydrogen atoms, as seen in **Figure** 2-2.

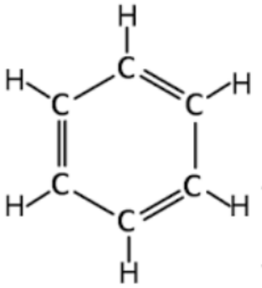


Figure 2-2 Benzene Molecule

The main compounds derived from Benzene (generally indicated with letter B in the BTEXS class) are: toluene (T), ethylbenzene (E), xylenes (m-xylene, o-xylene, p-xylene - X) and styrene (S).

In particular, from an environmental standpoint, BTEXS are volatile and soluble compounds with high diffusivity in air and water.

Among the BTEXS, according to the IARC (International Agency for Research on Cancer) Carcinogenicity Classification, benzene is certainly the compound with the higher toxicity. Breathing in a very high quantity of benzene can lead to death. The main effect of a chronic exposure to benzene is bone tissue damage and a decrease in bone marrow cells. The characteristics are summarized in **Table 2-2.**

Volatility *(Henry's Law Coefficient, vapour pressure, boiling point)*	⏲
Physical status	💧
Solubility *(Solubility, Soil/Water Partition Coefficient, Octanol/Water Partition Coefficient)*	⏲
Diffusion *(Diffusion Coefficient in Air and Water)*	⏲
Carcinogenicity *(IARC Classification, International Agency for Research on Cancer)*	★ benzene, ★★ ethylbenzene and styrene, ★★★ toluene e xylenes
Flammability	🔥

Table 2-2 BTEX Characteristics

Aromatic Polycyclic Hydrocarbons

The IPA acronym includes many organic compounds with two or more aromatic rings condensed to one another. IPA compounds are often present in the atmosphere, due to the incomplete combustion of organic material and the use of fuel oil, gas, coal and wood for energy production. The most significant man-made sources include accidental spillage and vehicle emissions, followed by heating systems, thermal power plants and incinerators.

IPA compounds are often associated to suspended particulate matter and, in particular, to particles with aerodynamic diameter smaller than 2 microns, which can easily reach the lung alveolar area, and from there the blood and tissues. In addition, some molecules have recognized mutagenic and carcinogenic characteristics (e.g. benzo(a)pyrene).

From an environmental standpoint, IPA compounds can be generally divided into two categories, depending on their chemical/physical characteristics:

- IPA with lower molecular weight: volatile and soluble;
- IPA with higher molecular weight: non-volatile and insoluble in water.

IPA's characteristics are summarized in **Table 2-3**, while **Figure 2-3** shows the molecular structure of Benzo(a)pyrene.

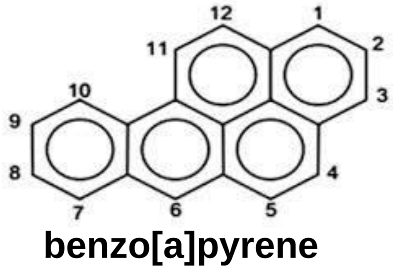


Figure 2-3 Benzo(a)pyrene molecule

Volatility *(Henry's Law Coefficient, vapour pressure, boiling point)*	Heavy IPA, Light IPA
Physical status	
Solubility *(Solubility, Soil/Water Partition Coefficient, Octanol/Water Partition Coefficient)*	Heavy IPA, Light IPA
Diffusion *(Diffusion Coefficient in Air and Water)*	
Carcinogenicity *(IARC Classification, International Agency for Research on Cancer)*	★ Benzo(a)pyrene ★★ Benzo(a)anthracene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Chrysene, Dibenzo(a,i)pyrene, Dibenzo(a, l)pyrene, Dibenzo(a,h)pyrene, Indenopyrene, Naphthalene ★★★ Benzo(g,h,i)perylene, Dibenzo(a,e)pyrene, Pyrene ,Acenaphthene, Anthracene, Phenanthrene, Fluoranthene, Fluorene, Perylene Not Classified: Acenaphthylene
Flammability	🔥

Table 2-3 IPA Characteristics

Chlorinated Organic Compounds

Chlorinated hydrocarbon compounds (or chlorinated solvents) are synthetic molecules obtained from hydrocarbons by the addition of a halogen, chlorine (Cl).

Generally, chlorinated organic compounds are particularly stable, and thus significantly persistent in the porous aquifers. This property is given by the Carbon-Chlorine bond: the presence of chlorine significantly reduces the reactivity of the other bonds present in the organic molecules and decreases the biodegradability and the natural mitigation potential. This means that, once they penetrate into the environment, halogenated hydrocarbons are very difficult to degrade, with consequent accumulation in the environment. This is worsened by the fact that the majority of them are hydrophobic, i.e. insoluble in water.

Generally, chlorinated compounds are volatile elements with high density and low viscosity. Since their density is higher than water and since they are very difficult to mix with ground water, they can be deposited in the lower sections of the aquifer as pure fluids (DNAPL, *Dense Non Aqueous Phase Liquids*). Due to these characteristics, they are very difficult to remove.

Considering the complexity of removing these compounds, **Figure 2-4** below shows the classic degradation chain of Tetrachloroethylene (PCE – 1,1,2,2-tetrachloroethylene) to Vinyl Chloride (VC - more carcinogenic than PCE from a toxicologic) and the Ethene compound.

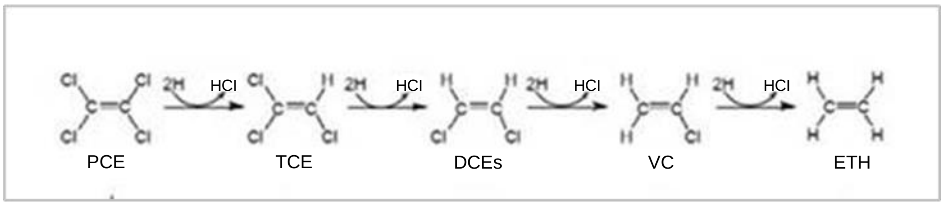


Figure 2-4 Tetrachloroethylene degradation chain

In turn, chlorinated compounds can be divided as follows:

- Non-carcinogenic Chlorinated Aliphatic Compounds;
- Carcinogenic Chlorinated Aliphatic Compounds;
- Carcinogenic Halogenated Aliphatic Compounds.

The characteristics of these compounds are summarized in **Table** 2-4

Volatility *(Henry's Law Coefficient, vapour pressure, boiling point)*	
Physical status	💧
Solubility *(Solubility, Soil/Water Partition Coefficient, Octanol/Water Partition Coefficient)*	
Diffusion *(Diffusion Coefficient in Air and Water)*	

Carcinogenicity *(IARC Classification, International Agency for Research on Cancer)*	★ 1,2 – Dichoropropane, Vinyl Chloride, Trichloroethylene ★★ 1,2,3 – Trichloropropane, 1,1,2,2 – Tetrachloroethane, Dichloromethane, Trichloromethane, 1,2 – Dichloroethane, Tetrachloroethylene (PCE), 1,2 – Dibromethane, Bromodichloromethane ★★★ 1,1,1 – Trichloroethane, 1,1,2 – Trichloroethane, Chloromethano, 1,1 – Dichloroethylene, Hexachlorobutadiene, Dibromochloromethano, Tribromomethane (Bromoform) Not Classified: 1,1 – Dichloroethane, 1,2 – Dichloroethylene
Flammability	🚫🔥

Table 2-4 Chlorinated Organic Compounds Characteristics

Ethers (MTBE and ETBE)

Methyl-t-butyl ether (or MTBE) is an ether that looks like a transparent liquid with a peculiar smell at ambient temperature. It is a synthetic organic compound obtained from methanol and 2-methyl-2-propanol, which is used as gasoline additive to increase the octane number, in place of tetraethyl lead, since it is cheaper and less toxic. However, it is quite soluble in water and it is not retained in the soil surface layers. For this reason, once it reaches ground water, it scatters easily and is poorly degraded. In humans, it can cause skin rashes, but it does not pose a risk of acute toxicity.

Ethyl-t-butyl-ether (or ETBE) is an ether, an organic compound whose characteristics are very similar to MTBE. Just like MTBE, it can be used to increase the octane number as gasoline additive. It is obtained from the reaction of ethanol and isobutene. From a technical standpoint, ETBE's characteristics are similar to MTBE.

The structure of the two MTBE and ETBE molecules is shown in **Figure** 2-5**.**

They are not regulated by Legislative Decree 152 of 2006; however, their limit is governed by ISS Regulation (resumed by M.D. 31/2015, specific for Fuel Sales Points). Their characteristics are summarized in **Table** 2-5**.**

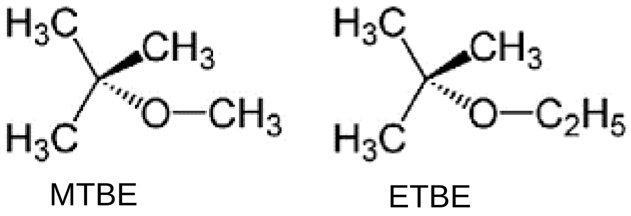


Figure 2-5 MTBE and ETBE molecules

Volatility *(Henry's Law Coefficient, vapour pressure, boiling point)*	
Physical status	💧
Solubility *(Solubility, Soil/Water Partition Coefficient, Octanol/Water Partition Coefficient)*	
Diffusion *(Diffusion Coefficient in Air and Water)*	
Carcinogenicity *(IARC Classification, International Agency for Research on Cancer)*	★★★ MTBE Not Classified: ETBE
Flammability	🔥

Table 2-5 MTBE and ETBE Characteristics

Perfluoro-Alkyl Substances (PFAS)

Perfluoro-Alkyl substances (PFAS) - among the most significant emerging contaminants - are organic compounds comprises by a variable-length fluoride-rich alkyl chain (generally between 4 and 14 carbon atoms) and by a hydrophilic functional group - generally a carboxylic or sulphonic acid.

Among the hundred molecules in this family, the ones mostly used and studied are perfluoro-octanoic acid (PFOA) and perfluoro-octane sulphonic acid (PFOS).

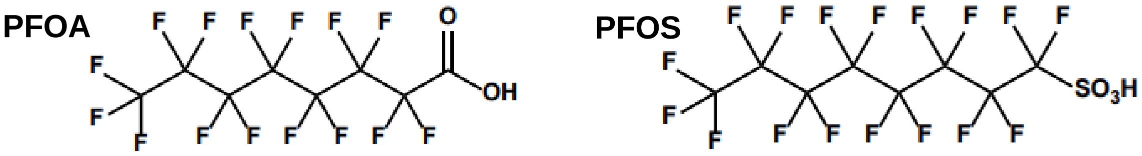


Figure 2-6: PFAS Molecular Structure

They are water and grease-repellent, from a thermal standpoint; in addition, since they are very surface-active, they are very useful in industrial application and consumer goods fields. Since the 1950s, their main applications include metallurgy, plastics, textile and paper.

Given their intrinsic characteristics, these compounds are very persistent, bio-accumulative and toxic organic pollutants. Indeed, they tend to be transferred to trophic chains and, lastly, to humans, especially through the food chain.

They can remain in the air for days on end and be transported before falling to the ground and contaminating water. The main sources of exposure may be ingesting contaminated drinking water or food with high levels of these compounds in them (e.g. fish and seafood) or contaminated by packaging that contains them. The general population may also be exposed by inhaling air containing particles or touching contaminated surfaces or soil, especially children. Based on scientific literature, in those industries that produced or used PFOA and PFOS, workers may have been exposed to high quantities of these compounds, which can be found in their blood. The population residing near those plants may have been exposed to PFOA and PFOS through drinking water and/or food.

The available studies suggest that a higher level of PFOA and PFOS in the blood may be related to an increase of the quantity of cholesterol and uric acid in the blood and an increased risk of high pressure. The target organ seems to be the liver, even in studies on animals.

Although some studies suggest a possible correlation with testicular and kidney cancer, due to the inconsistencies observed, exposure to PFOA and PFOS and human cancer could not be linked in a conclusive way.

Their characteristics are summarized in **Table** 2-6.

Volatility *(Henry's Law Coefficient, vapour pressure, boiling point)*	
Physical status	⬡
Solubility *(Solubility, Soil/Water Partition Coefficient, Octanol/Water Partition Coefficient)*	
Diffusion *(Diffusion Coefficient in Air and Water)*	
Carcinogenicity *(IARC Classification, International Agency for Research on Cancer)*	Under study
Flammability	🚫🔥

Table 2-6 PFAS Characteristics

2.2 Inorganic compounds

Although among the inorganic substances that may cause environmental contamination, there are also compounds such as Fluorides, Sulphates, Nitrides, Boron and Cyanide, the main contaminants belong to the **Metals family.**

Metals comprise those chemicals that form basic oxides and react with acids to create Salts. Metals are characterized by high malleability and ductility, high reflectivity, and good heat and electric conductivity. They also feature highly symmetrical and compact crystalline structures and are among the most numerous chemicals.

At ambient temperature and atmospheric pressure, they are in solid form, except for Mercury, which is liquid. This family includes:

- Aluminium;
- Arsenic;
- Iron;
- Manganese;
- Lead;
- Mercury;
- Zinc;
- Total Chromium;
- Copper.

The characteristics of the metals are summarized in **Table** 2-7.

Volatility *(Henry's Law Coefficient, vapour pressure, boiling point)*	◔, ◔ mercury
Physical status	□, 💧 mercury
Solubility *(Solubility, Soil/Water Partition Coefficient, Octanol/Water Partition Coefficient)*	◔
Diffusion *(Diffusion Coefficient in Air and Water)*	◔
Carcinogenicity *(IARC Classification, International Agency for Research on Cancer)*	★ Arsenic, Beryllium, Cadmium, Chromium VI, Nickel ★★ Lead ★★★ Selenium, Mercury, Total Chromium Not Classified: Aluminium, Antimony, Silver, Cobalt, Iron, Manganese, Copper, Tin, Thallium, Vanadium, Zinc.
Flammability	🚫🔥, 🔥 Pure aluminium powder

Table 2-7 Metals Characteristics

2.3 Other substances

Tetraethyl Lead

Tetraethyl Lead is a toxic compound belonging to the organic metal class. In the past, it was used as additive in gasoline to increase the octane number; however, due to its toxicity, it was replaced with other substances.

Tetraethyl lead is a viscous transparent liquid, obtained from the reaction of ethyl chloride with a lead-sodium allow, whose characteristics are summarized in **Table** 2-8. The molecular structure is shown in **Figure** 2-7.

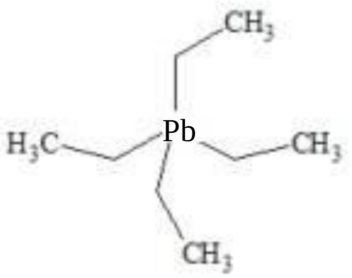


Figure 2-7 Tetraethyl Lead Molecule

Volatility *(Henry's Law Coefficient, vapour pressure, boiling point)*	◠
Physical status	💧
Solubility *(Solubility, Soil/Water Partition Coefficient, Octanol/Water Partition Coefficient)*	◠
Diffusion *(Diffusion Coefficient in Air and Water)*	◠
Carcinogenicity *(IARC Classification, International Agency for Research on Cancer)*	★★★
Flammability	🔥

Table 2-8 Tetraethyl Lead Characteristics

3.0 PRELIMINARY ASSESSMENT ELEMENTS

The right definition and subsequent implementation of the remediation activities must be preceded by an accurate characterization of the polluted site and the area subject to the effects of pollution.

Choosing the most suitable technique between the possible remediation technologies cannot disregard an in-depth assessment and balancing of the different technical-strategic interests at play, and the analysis of the different general and, first and foremost, site-specific variables, such as:

- The status of the sites (abandoned or active);
- Possible redevelopment projects already defined for the site;
- The desirable environmental protection level to be achieved;
- The existence of reliable techniques to obtain and achieve such protection level over time;
- The environmental sustainability of the remediation techniques selected;
- The design, implementation, management, monitoring costs, etc. to be borne in the different intervention phases.

The most evolved formulation to inspire this balance of interests is given by the definition of the "**Best Available Techniques"** (**BAT**), set forth in Directive 96/61/EC and implemented into Italian Legislation (Legislative Decree 152/2006, Section 4, Title V, Annex 3):

- "techniques": both the techniques employed and the plant design, construction, maintenance, operation and closing methods;
- "available": the techniques developed on a scale that allows their application in cost/effective and technically feasible conditions, within the related industrial sector, by taking into account costs and benefits, regardless of the fact that they have been applied or produced in that Member State, as long as the manager can have access to them at reasonable conditions;
- "best": the most effective techniques to obtain a high level of overall environmental protection.

In particular, the choice of the most suitable remediation technique must be aimed at:

- Favouring those techniques that permanently and significantly reduce the pollutants' concentration, toxic effects and mobility;
- Favouring in-situ or on-site ex situ techniques;
- Favouring those techniques that immobilize the pollutants;
- Favouring those techniques that allow the treatment and reuse of different or excavation materials on site for backfill;
- Including the reuse of soil and materials treated off-site;
- Favouring the use of organic materials of suitable quality;
- Avoiding any additional risks, such as air, surface water and soil/groundwater matrix pollution;
- Avoiding hygiene and health hazards to the population during the interventions.

Based on the consolidated experience in environmental remediation developed, the main factors to select the Best Available Technology are summarized below, grouped in 3 macro-categories:

- pollutant's nature;
- site-specific factors;
- applicable technologies.

3.1 Pollutant's nature

Among the factors related to the contaminants' intrinsic nature, the following aspects should be taken into account:

- chemical-physical characteristics;
- spatial distribution (depth and extension) and concentrations;
- polluting mass phase fractioning (free, adsorbed, dissolved and gaseous phases);
- toxicity / flammability / explosiveness;
- stability / mobility / persistence;
- biodegradability.

3.2 Site specific factors

Among the factors related to the site's nature, the following aspects should be taken into account:

- section affected by pollution and value of the site;
- presence of sensitive receptors;
- decontamination target to be reached, based on the site's intended use and calculation of the objectives;
- geological and hydrogeological context;
- aquifer's closeness and vulnerability, site's hydrogeology, meteorology and existence of underground water extraction points;
- nature and type of activities carried out on the site;
- utilities accessibility and availability;
- presence of underground and above-ground structures.

3.3 Applicable technologies

Among the factors related to the available technologies, the following aspects should be taken into account:

- **technical feasibility**, development level, limits and confidence level;
- presence of **adverse effects** and accident risk;
- treatment **costs** and remediation **times**;
- level of **environmental sustainability**.

4.0 REMEDIATION TECHNOLOGIES CLASSIFICATION

The **different remediation techniques** can be preliminary classified based on the following criteria:

- Type of intervention (on site – ex situ);
- Nature of the chemical-physical or biological processes employed;
- Effects on the contaminants.

Often, in several contaminants in different phases are present, and the single contaminant (LNAPL, dissolved, etc.) can be detected in the subsoil, different remediation techniques may be applied at the same time or at subsequent stages.

Here is a short introduction on the types of remediation techniques that can be adopted; for more information on the main elements used to define the most suitable site-specific remediation technology, and a detailed description of the main remediation techniques, see Chapters 5 and 7 of these Guidelines.

4.1 Type of intervention implemented

The classification system usually adopted to identify the type of intervention defines, based on the contaminated matrix treatment site:

- **on-site interventions**: carried out without handling or removing the soil;
- **on-site ex-situ interventions**: with handling and removal of polluted material and soil, which are treated on site, and possible reuse of the soil treated;
- **off-site ex-situ interventions**: with handling and removal of polluted material and soil off-site, by sending the material and soil to authorize treatment plants or to the landfill.

Among the different in-situ interventions outlined in these Guidelines, there is also contamination containment, generally as MISE action, consisting in the implementation of operations aimed at limiting the pollutant's migration potential.

In particular, if, on one hand, ex-situ interventions are characterized by greater flexibility in terms of process control and management, on the other side, they generate a higher environmental impact, therefore limiting the site usage during the remediation operations.

A first selection of the type of intervention can be made considering the main site characteristics, in terms of contamination extension, soil characteristics, presence of constraints and/or receptors and based on the deadline to revert the area back to its intended use. By way, of example, the bottom of **Table** 4-1 summarizes some assessment elements, related to the site characteristics, based on which the most suitable intervention technique should be adopted (Colombano et. al, 2010 - edited).

	SITE CHARACTERISTICS				
	Contamination distribution	**Subsoil characteristics**	**Structural constraint**	**Closeness of receptors**	**Intervention execution times**
EX SITU	Limited vertical and horizontal extension	Very uneven, with preferential flows	No structural constraints in the affected area	No sensible receptor immediately close-by	Quick reversion to its intended use
IN SITU	Broad vertical and horizontal extension	Even, permeable or moderately permeable	Presence of structures within the contaminated area	Sensitive receptors near-by that need to be preserved	Indefinite reversion times to its intended use

Table 4-1 Preliminary intervention type assessment based on the main site characteristics

4.2 Nature of the biological - chemical/physical processes employed

Remediation treatments can be classified based on the process or mechanism nature:

- biological;
- chemical;
- physical.

Biological remediation techniques include those treatments whose purpose is the organic molecules degradation, thanks to the metabolic activity of indigenous micro-organisms present in the subsoil or introduced therein.

The goal is increasing microbial growth, whilst ensuring the presence of nutrients and suitable environmental conditions (such as pH, temperature, etc.) to speed up the processes.

This category also includes those processes known as *Phytoextraction* (within the broadest *Phytoremediation* category, which are based on the plants' capacity of extracting contaminants from the soil and concentrating them mainly on the aerial sections (stem and leaves). Once the contaminant is accumulated, the plants must be sent to a controlled disposal. This technique is particularly suitable to treat the more recalcitrant inorganic compounds (e.g. heavy metals), generally found in the first meter of the subsoil.

On the other hand, chemical-physical methods exploit the chemical and physical properties of the contaminant, or contaminated matrix, to reduce the contaminants concentration and/or contain it.

Chemical treatments involve the transformation of the pollutant chemical state, which can lead to a reduction of their concentration/toxicity and/or increase/reduction of their mobility respectively. Depending on the operating principle, we can have:

- Reduction: "reducing" chemical agents are used to modify the chemical compounds structure and obtain a lower toxicity compared to the related oxidised forms;

- Oxidation: thanks to the oxidizers contained in the mixtures often injected into the environmental matrix involved, the organic pollutant is transformed, at the end of the oxidation process, into carbon dioxide and water, or, in any case, its toxicity is reduced;
- Fixation: used mainly to reduce the mobility of the contaminants (e.g. heavy metals) by injecting chelating chemical agents. The latter, bond to the pollutants, accumulate in certain portions of the soil, and are therefore removed and treated;
- Extraction: solvent injections are used to transfer the pollutant from the solid phase to the liquid one and are then removed from the subsoil and treated.

Physical treatments are aimed at changing the pollutants physical status, with their consequent transfer between the different soil phases. The main mechanisms are:

- Solidification/Stabilization: the use of special chemical agents of different nature determines the formation of a stable mass with reduced permeability;
- Thermal treatments: heat is used to increase the volatility, burn, degrade or melt the pollutants, generating inorganic compounds (e.g. CO2, nitrogen oxides and sulphur). This category also includes the ventilation technique, which consists in creating a solid amorphous matrix, full of non-volatilized pollutants.

4.3 Effects on the contaminants

Based on the type of expected effects on the contaminants, the remediation types are divided as follows:

- Immobilization: it includes technique to modify the mobility and/or toxicity of the pollutants, through two types of processes:
  - *Pollutant modification*: that is, changing the behaviour or toxicity through chemical reactions;
  - *Receiving environment modification*: including the permeability and porousness reduction.
- Transformation and/or separation: it can occur through the chemical, thermal, physical and biological processes previously described.

5.0 SCREENING MATRIX

In these Guidelines, specific **Screening Matrices were used to select the most suitable remediation techniques applicable to soil and underground water.**

The following internationally and nationally renowned models - suitably modified - were used:

- The screening matrix created by ISPRA;
- The screening matrix developed by the *Federal Remediation Technologies Roundtable*.

It is hereby specified that the decision-making support instruments described below are not exhaustive, since the state of the art on remediation technologies is constantly being updated. This aspect, along with the future site definition, often significantly affect the choice of the most suitable technologies to be applied.

The "remediation" techniques mentioned are the ***most potentially applicable*** strategies while drafting the remediation project, divided by contamination matrix (soil/groundwater), treatment site (in situ/ex situ), treatment mechanism (biological/chemical/physical/thermal).

The variables analysed take into account the type of contamination (significant contaminants pursuant to the regulation in force), the grain size for the soil matrix (coarse/fine) and the level of permeability for the groundwater matrix (high/low).

Lastly, attention is given also to those parameters that are important in the decision-making process, such as the residues generated by the remediation activities (residual streaming), and the intervention times and costs.

5.1 Soil Screening Matrix

				POLLUTANTS									
				Inorganic compounds		Organic compounds							
PROCESS	RESIDUAL STREAMING	REMEDIATION TIMES	COSTS	Metals (except for mercury)		Light hydrocarbons / Aromatic compounds		Heavy hydrocarbons (C>12)		IPA		Volatile chlorinated aliphatic compounds	
			Lithology	sandy / gravelly	loamy / clayey	sandy / gravelly	loamy / clayey	sandy / gravelly	loamy / clayey	sandy / gravelly	loamy / clayey	sandy / gravelly	loamy / clayey
Biological treatments on site													
Bioventilation	Vapour/Liquid	B	15-50 €/ton of treated soil	☹	☹	☺	😐	☺	😐	☺	😐	😐	😐
Aided bioremediation	-	A	25€ -75/ton of treated soil	😐	😐	☺	☺	☺	☺	☺	☺	☺	☺
Plantbased sewage-treatment	Vapour/Solid	A	15-40 €/m² of treated soil surface*	😐	😐	😐	😐	😐	😐	😐	😐	😐	😐
Biological treatments ex situ													
Landfarming	Vapour/Liquid	M	20€ -60/ton of treated soil	☹	☹	☺	😐	☺	😐	☺	😐	😐	😐
Biopile	Vapour	B/M	50€ -80/ton of treated soil	☹	☹	☺	😐	☺	😐	☺	😐	😐	😐
Chemical-physical treatments on site													
Soil Vapour Extraction	Vapour	B	25€ -60/ton of treated soil	☹	☹	☺	😐	☹	☹	☹	☹	☺	😐
Solidification/Stabilization	Solid	M	25€ -70/ton of treated soil	☺	☺	☹	☹	☹	☹	☹	☹	☹	☹
Soil-flushing	Liquid	A	40€ -120/ton of treated soil	☹	☹	☺	😐	☺	😐	☺	😐	😐	😐
Chemical oxidation	Sol./Liq./Vap.	B	30€ -90/ton of treated soil	☹	☹	☺	😐	☺	☺	☺	😐	☺	😐
Chemical-physical treatments ex situ													
Soil-washing	Solid/Liquid	B	100€ -400/ton of treated soil	☺	😐	☺	😐	☺	😐	☺	😐	☺	😐
Excavation and disposal	-	B	50-250 €/ton of excavated soil	☺	☺	☺	☺	☺	☺	☺	☺	☺	☺
Thermal treatments on site													
Vapour extraction/stripping	Vapour/Liquid	B	30€ -100/ton of treated soil	☹	☹	☺	😐	😐	😐	☺	😐	☺	😐
Vitrification	Vapour/Solid	B	250€ -800/ton of treated soil	☺	😐	☺	😐	☺	😐	☺	😐	☺	😐
Thermal treatments on site/ex situ													
Thermal desorption	Vapour	B	100-250 €/ton (on site); 100-400 €/ton of treated soil (ex-situ)	☹	☹	☺	😐	☺	😐	☺	😐	☺	😐

☺	applicable
😐	applicable with low efficiency
☹	not applicable

KEY: A=high/i; M=medium/i; B=short/low
(*)=excluding the application of topsoil

5.2 Groundwater Screening Matrix

				POLLUTANTS							
				Inorganic compounds		Organic compounds					
PROCESS	RESIDUES GENERATED	REMEDIATION TIMES	COSTS	Metals		Aromatic compounds		Carcinogenic halogenated aliphatic compounds		Hydrocarbons	
			Degree of permeability	high permeability	low permeability	high permeability	low permeability	high permeability	low permeability	high permeability	low permeability
Natural Mitigation	-	A	12€ -65/m^2 of treated water surface	😐	😐	😐	😐	😐	😐	😐	😐
Biological treatments on site											
Plantbased sewage-treatment	Solid	A	15-40 €/m^2 of treated water surface	😐	😐	😐	😐	😐	😐	😐	😐
Biosparging	-	M	10€ -50/m^3 of treated water	☹	☹	☺	😐	☹	☹	😐	😐
Bioremediation	-	A	25-60 €/m^3 of treated water	😐	😐	☺	☺	☺	☺	☺	☺
Bioaugmentation	-	A	25-60 €/m^3 of treated water	😐	😐	☺	☺	☺	☺	☺	☺
Biological treatments ex situ											
Activated sludge processes	Semi-solid/Liquid	A	40€ -200/m^3 of treated water	☹	☹	☺	😐	☺	😐	☺	😐
Slurry bioreactors	Semi-solid/Liquid	A	60€ -200/m^3 of treated water	☹	☹	☺	😐	☺	😐	☺	😐
Chemical-physical treatments on site											
Air-Sparging	Gas	M	15€ -55/m^3 of treated water	☹	☹	☺	😐	☺	😐	☺	😐
Reactive permeable barriers	Solid	A	200-1500€/m^2 of barrier surface	☺	☺	☺	☺	☺	☺	☺	☺
Multi Phase Extraction	Liquid/Gas	M	40€ -100/m^3 of drawn/treated liquids	😐	😐	😐	☺	😐	☺	😐	☺
Chemical oxidation	Possible by-products	B	30€ -90/m^3 of treated water	☹	☹	☺	😐	☺	😐	☺	😐
Hydraulic barriers	Liquid	B	10-100 €/m^3 of drawn/treated water	☺	😐	☺	😐	☺	😐	☺	😐
Chemical-physical treatments ex situ											
Chemical precipitation	Solid/Liquid	A	*	☺	☺	☹	☹	☹	☹	☹	☹
Oxidation	Solid/Liquid	A		☺	☺	😐	😐	😐	😐	😐	😐
Clariffloculation	Solid/Liquid	A		☺	☺	☺	☺	😐	😐	☹	☹
Adsorption	Liquid	A		☹	☹	😐	😐	😐	😐	😐	😐
UV oxidation	Gas	A		☹	☹	☺	☺	😐	😐	😐	😐
Stripping	Liquid	A		☹	☹	😐	😐	😐	😐	☺	☺
Reverse osmosis	Solid/Liquid	A		☺	☺	☹	☹	☹	☹	☹	☹

KEY: A=high/i; M=medium/i; B=short/low
(*)= cost included in each remediation treatment mentioned in the matrices

☺	applicable	😐	applicable with low efficiency	☹	not applicable

6.0 MAIN REMEDIATION TECHNOLOGIES

This chapter describes the main remediation technologies presented in the Screening matrices in detail, divided based on the following criteria:

- type of intervention (on site – ex situ);
- nature of the processes employed (biological - chemical/physical - thermal).

The datasheets drafted and divided by technology are structured as follows:

- General description of the remediation technology classification and main operating criteria;
- Another section providing additional in-depth analyses on:
  - technology conditions and application limits;
  - basic system components and main development parameters. Alternatively, the required instruments and operating phases, if the technology does not require any specific system configuration;
  - technology application pros and cons;
  - any related technologies.

Lastly, each datasheet is accompanied by images and tables or diagrams, to better understand the remediation technologies and their practical applications.

*Remediation Technologies On site - Biological Processes**

*(*) The **Bioventing** technology is summarized as a related technology in the Soil Vapour Extraction datasheet (chemical-physical process), and the **Biosparging** technology was included in the Air Sparging datasheet (chemical-physical process).*

6.1 Bioremediation

Definition and general criteria

***Bioremediation* (or Bioreclamation)** is a remediation technique that can be applied to unsaturated soil, to the capillary fringe area and to groundwater, to clean up organic compounds ((aromatic, aliphatic) hydrocarbon), nitrobenzene, chlorobenzene, phenols, aromatic amines, certain pesticides and plant protection products), certain metals and other inorganic compounds.

This technique exploits the natural capacity of the micro-organisms present in the subsoil (or specifically introduced therein) to degrade organic contaminants, provided that the microbial colonies growth conditions are optimal (pH, temperature, redox potential, oxygen quantity, nutrients, etc.). They feed off polluting organic compounds and transform them into carbon dioxide, water and/or biomass.

Inorganic contaminants and metal cannot be biodegraded; however, some experimental techniques show that the micro-organisms' action can be used to change their valence state and induce their absorption, grounding, precipitation, build-up and concentration within the biomass, with consequent reduction of their concentration in the affected environmental matrix.

Micro-organisms can be divided into:

- Aerobic: the require oxygen for metabolic processes;
- Anaerobic: the do not require oxygen for metabolic processes.

Depending on the type of micro-organism and based on the contaminant present, biodegradation processes can occur according to **four main metabolic reaction classes**:

- Aerobic oxidation: through the micro-organisms, the contaminants surrender their electrons, which are acquired by oxygen and oxidizing, and are then transformed into carbon dioxide, water and biomass;
- Anaerobic oxidation: through the micro-organisms, the contaminants surrender their electrons, which are acquired in sequence, once the redox potential is reduced, from the following final electron acceptors: nitrates, manganese (IV), iron (III), sulphates and carbon dioxide. Contaminants are then metabolised to methane, limited quantities of carbon dioxide and traces of hydrogen gas;
- Anaerobic reductive dechlorination: it entails the replacement of a chlorine atom with an hydrogen atom, and it is very effective in some chlorinated compounds (such as PCE, TCE, DCE);
- Cometabolism: a secondary effect of the biodegradation action. The compounds are not directly degraded by the micro-organism action, but rather by enzymes (mono-oxygenase) generated following the degradation of other compounds present.

The more applied bioremediation technique is the so-called ***Enhanced Bioremediation* (Biostimulation)**, which entails the stimulation of biodegradation processes by adding nutrients (nitrogen, phosphorous, etc.) and/or other reagents (oxygen, lactate, etc.) to the existing system, to provide the energy required by the micro-organisms to grow, survive and promote the degradation processes. It can be achieved at the following conditions:

- Aerobic conditions: oxygen is provided in gas form by pumping air or adding pure oxygen or products with a slow oxygen release. Using pure oxygen helps create optimal, constant and more stable conditions for the degradation processes.

  The compounds efficiently processed are aromatic hydrocarbons, nitrobenzene, non-chlorinated phenols, IPAs, aromatic amines and some chlorinated solvents. At a lower rate, aerobic degradation can also be effective for lightly chlorinated PCB, chlorinated phenols, cresols and some pesticides and plant protection products.

  Figure 6-1 shows the biodegradation operating principle.

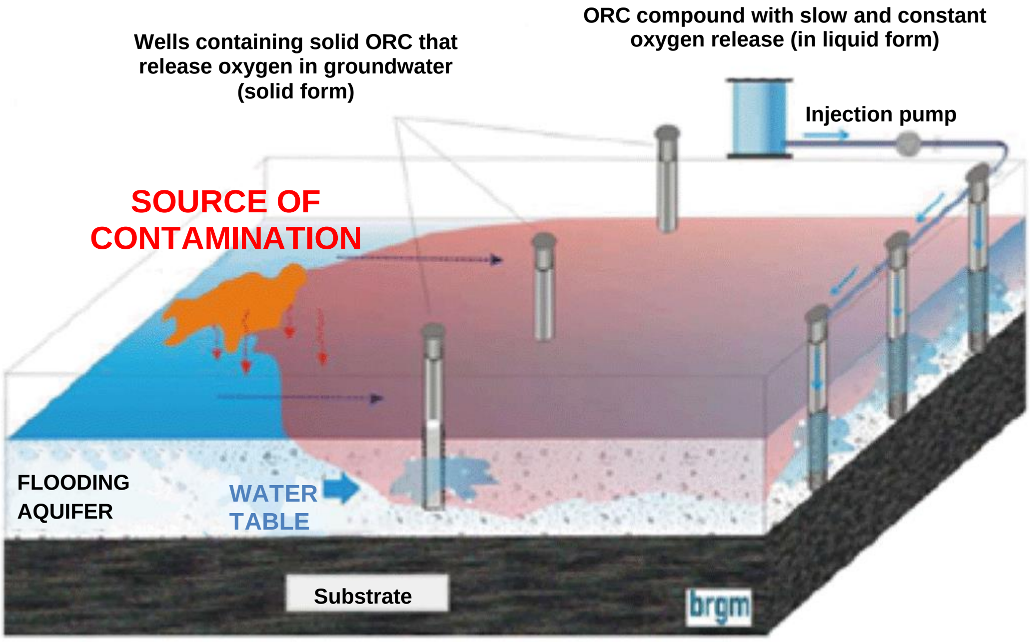


Figure 6-1 On-site biodegradation principle diagram (Source : Quelles techniques pour quels traitements - Analyse couts-benefices Rapport Final, BRGM, 2010 ©BRGM/RP-58609-FR - Edited)

- anaerobic conditions: the system requires the addition of nutrients (nitrates, iron (II), sulphates, carbon dioxide, methanol, ethanol, molasses, sugar, fat acids, oil, chitin, hydrogen) and electron donors. These components are mainly injected in liquid or gaseous form.

  The pollutants most effectively treated with anaerobic processes are chlorinated aliphatic compounds (PTC, TCE, dichloroethylen), toluene, IPA, nitrobenzene, chlorobenzene, non-chlorinated phenols, aromatic amines, PCB and other organic chlorinated pollutants (pesticides, etc.). With greater difficulty, anaerobic degradation can occur also in o-xylene and m-xylene, chlorinated phenols, plant protection products, some metals and inorganic compounds.

Conditions and application limits

The **Bioremediation technique is particularly suitable** and applicable under the following conditions:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- presence of organic compounds;
- extension of soil and/or groundwater contamination plume.

SUBSOIL CHARACTERISTICS

- presence of uniform soil with loamy-sandy to gravelly particle size, characterized by medium-high hydraulic conductivity (K $>10^{-5}$ cm/s);
- pH preferably within the 6 – 8 range;
- soil / groundwater temperature > 10°C;
- soil humidity >10% in volume.

Conversely, **the Bioremediation technique is not suitable or applicable** when the following conditions occur:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- High concentration of treatable organic contaminants;
- Not suitable for inorganic contaminants, except for ammoniacal nitrogen;
- High concentration of heavy metals, chlorinated compounds, long-chain hydrocarbons or inorganic salt;
- presence of product in separated phase.

SUBSOIL CHARACTERISTICS

- presence of fine particle size with low hydraulic conductivity (k $< 10^{-5}$ cm/s);
- presence of excessively uneven and/or layered soil;
- excessively acid or basic pH;
- low soil humidity.

Table 6-1 shows the level of effectiveness of Bioremediation in relation to the environmental conditions listed above.

PARAMETER	VERY EFFECTIVE	MODERATELY EFFECTIVE	INEFFECTIVE
CONTAMINATION CHARACTERISTICS			
TYPE OF CONTAMINANT	Aerobic Process: aromatic hydrocarbons, nitrobenzene, non-chlorinated phenols, IPAs, aromatic amines and some chlorinated solvents Anaerobic Process: chlorinated aliphatic compounds (PTC, TCE, dichloroethylen), toluene, IPA, nitrobenzene, chlorobenzene, non-chlorinated phenols, aromatic amines, PCB and other organic chlorinated pollutants (pesticides, etc.)	Aerobic Process: lightly chlorinated PCB, chlorinated phenols, cresols and some pesticides and plant protection products Anaerobic Process: o-xylene and m-xylene, chlorinated phenols, plant protection products, some metals and inorganic compounds	High concentration of organic contaminants; Inorganic contaminants, heavy metals, chlorinated compounds
CONTAMINATION PHASE	Dissolved contaminant	Adsorbed contaminant	Product in separated phase
CONTAMINATION DISTRIBUTION			
PLUME EXTENSION	Any extension	-	-
POLLUTANT LOCATION	Near groundwater table	In shallow aquifers	In confined deep aquifers
SUBSOIL CHARACTERISTICS			
LITHOSTRATIGRAPHY	Even soil with loamy-sandy to gravelly particle size	Poorly layered, loamy-sandy and gravelly soil	Silt and clay, and soil with very fine particle size
HYDRAULIC CONDUCTIVITY (K)	$>10^{-4}$m/s	$10^{-5}\div10^{-4}$m/s	$<10^{-5}$ cm/s
OVERALL LEVEL OF HETEROGENEITY	Limited or isotropic	Moderate	High

Table 6-1 Bioremediation degree of effectiveness

Basic system components and main development parameters

The **basic system components** to implement a Bioremediation intervention comprise:

- Multiple vertical (valved piezometers, direct push, etc.) or horizontal injection stations (injection drainage, trenches, irrigation systems);
- A reagent/nutrient storage and distribution system with a different layout based on their form (gas, liquid or solid) (booster pump, storage tank, water mixing system, pump, meters, etc.);
- If required, a wastewater recovery and treatment system: vertical (gas extraction needles) or horizontal gas extraction points (extraction discharges), an extraction network to connect the different extraction points and the extractor, different extraction units (volumetric, intermediate, centrifugal extractor), a water separator (or demister) and a gas treatment system;
- If required, a wastewater recovery and treatment system: vertical extraction points (vertical wells, horizontal wells, pumps, piping, trenches), water treatment system (and a re-infiltration system, if required);
- Solid and liquid waste (resulting from the treatment) storage system;
- Piezometric monitoring network to monitor the groundwater flow and quality.

The main parameters to take into consideration when developing and sizing a Bioremediation system stem from a characterization of the site and the related chemical/physical processes, and a thorough knowledge of the source of contamination (geometry, plume concentration, contaminant degradability level).

In particular, to design the system, the following parameters are required:

- Environmental matrix characteristics: permeability, porousness, organic matter content, organic carbon content, humidity, temperature, pH, redox potential, nutrient content (ammoniacal nitrogen, total nitrogen, nitrate, nitrite, total phosphorous), dissolved oxygen, sulphates, ferric and ferrous iron, methane, dissolved manganese;
- Contaminants characteristics: solubility, vapour pressure, Henry's Law Coefficient, boiling point, air/water/soil partition coefficient, concentration, half-life and degradation rate);

in order to define:

- The injection well's range of action depends on the type of booster used;
- The number, spacing and characteristics of the injection points (depth, diameter, trenches, wells...);
- Injection frequency and method (continuous or intermittent);
- The nutrients and additives (electron acceptors and donors) injection points' effective range based on their capacity.

Technology application pros and cons

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
DEGREE OF DEVELOPMENT, RELIABILITY AND DIFFUSION	🙂	Reliable and tested technique. Technique that can be used to support traditional physical extraction techniques (SVE, MPE, AS, etc.) once they reach their application limits;
	😐	Contaminant concentration abatements higher than 90% are very hard to achieve. This process requires high-profile skills, and the performance is extremely variable, depending on the specific site conditions. Probable “rebound” effect: when the treatment is interrupted, concentrations are low, but they can significantly increase a few months later.
APPLICABILITY BASED ON THE TYPE OF CONTAMINANT	🙂	Applicable to a wide range of organic contaminants not in high concentration.
	☹	Not suitable to high concentrations of heavy metals, chlorinated compounds, long-chain hydrocarbons or inorganic salt, and in case of products in separated phase.
APPLICABILITY BASED ON THE SUBSOIL CHARACTERISTICS	🙂	Suitable for soil with loamy-sandy to gravelly particle size, characterized by medium-high hydraulic conductivity.
	☹	Not suitable for soil with fine particle side and low hydraulic conductivity, or excessively uneven and/or layered soil.
APPLICABILITY BASED ON THE SITE CHARACTERISTICS	🙂	It can be applied under buildings (horizontal drilling) and in case of pollution at great depths (several tens of meters).
	☹	The use of oxygen may pose health, safety and environmental risks (fire, suffocation in enclosed spaces and explosion).

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
REMEDIATION TIMES	🙁	The duration of bioremediation treatment is often crucial. In addition, *post operam* monitoring is required to ensure the intervention's success.
INTERVENTION COSTS	🙂	Reduced intervention costs. Both groundwater and soil can be treated at the same time, with further cost benefits.
COMPATIBILITY WITH OTHER TECHNOLOGIES	🙂	Compatible with other remediation methods.
ENVIRONMENTAL SUSTAINABILITY	🙂	Generation of limited issues in the subsoil. However, in case of unsaturated soil, the circulation of water-based solutions in the soil can increase the contaminants mobility, and consequently affect the underlying groundwater. In case of high concentration of iron and manganese, the micro-organisms growth may cause the well/piezometer filter clogging, especially in case of bacteria that reduce iron. In anaerobic conditions, metabolites even more dangerous than the original contaminants may develop.

🙂 Good 😐 Medium 🙁 Low

Table 6-2 Bioremediation pros and cons

Related technologies

The **main** Bioremediation-related active type on site technologies that exploit the natural contamination degradation capacity of micro-organisms are:

- ***Bio-venting:*** on site remediation technology that entails the injection of air in unsaturated soil to increase the quantity of oxygen and stimulate the biodegradation action by indigenous bacteria. This technology is described in detail in Paragraph 7.11;
- ***Bio-sparging***: on site remediation technology that uses indigenous micro-organisms to biodegraded the organic components in the saturated area through air injections. This technology is described in detail in Paragraph 7.4;
- ***Bio-slurping***: technology that combines bio-venting and free-product vacuum pumping elements, in order to retrieve the free product from groundwater, and, at the same time, stimulate the degradation process by indigenous micro-organisms on the unsaturated portion. This technology is described in detail in Paragraph 7.8;
- ***Bioaugmentation*****:** it consists of integrating the existing system by introducing micro-organisms selected based on the population present on site (indigenous bacteria) or lab-isolated bacteria known for their capacity to degrade specific contaminants (allochtonous bacteria), in order to speed up the biodegradation processes. This approach is effective to degrade petroleum-based hydrocarbons, chlorinated aliphatic hydrocarbons, chlorobenzene, aromatic hydrocarbons, IPA and phenols. With greater uncertainty and limitations, this technique may also be applied to some PCB and pesticides.

6.2 Monitored Natural Attenuation (MNA)

Definition and general criteria

Natural contamination attenuation is a technique of **environment self-purification** obtained by reducing the concentrations of pollution load thanks to a series of physical, chemical and biological phenomena naturally developed in saturated and unsaturated soil, such as, by way of example: biodegradation, dispersion, dilution, adsorption, volatilization, and chemical/biological transformation and/or destruction processes.

For this reason, MNA can be seen as a "passive" remediation technique, although highly **pollutant-specific.**

Since it is slower than active processes - and therefore unsustainable beyond a certain period of time - it can be applied even to large sites with a low pollutant concentration and without free products.

As defined by the *Environmental Protection Agency* (EPA), this contamination management approach entails long-term monitoring.

It actually requires the development of a well-structured project, entailing:

- **complete and exhaustive site characterization**, in order to develop its conceptual model and gather suitable field data to assess the actual existence of natural mitigation, as well as establish if the existing processes are sufficient to ensure the remediation of the pollution phenomenon (e.g. through mass balance and the use of specific indicators);
- full **control over the source** of contamination;
- drafting of a **Risk Analysis** to assess if the mitigation will be sufficient to protect the receptor against contamination-related risks and to establish the remediation objectives;
- assessment of the **remediation times** based on the objectives set;
- long-term **monitoring plan**;
- **corrective or emergency action** plan.

Conditions and application limits

The **MNA is particularly suitable** and applicable under the following conditions:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Presence of volatile or semi-volatile organic compounds (light hydrocarbons, BTEX, halogenated and chlorinated solvents) and some inorganic compounds;
- Presence of reduced contaminant concentrations;
- Limited to broad contamination extension, preferably with an even distribution.

SUBSOIL CHARACTERISTICS

- Presence of even soil;
- Mostly applied to saturated portions, although effective also on unsaturated areas;
- Areas even at quite great depths.

A necessary condition for the technology to be applicable is a complete and exhaustive site characterization and proof that the remediation objectives have been achieved within reasonable times.

Conversely, **MNA is not suitable or applicable** when the following conditions occur:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Presence of pollutants with a low volatility degree and/or reduced biodegradability;
- Presence of free product;
- Uneven pollutant distribution;
- High pollutant concentrations.

SUBSOIL CHARACTERISTICS

- Presence of uneven soil;
- Conditions under which the pollutants may migrate before their degradation;
- Conditions under which the hydrogeological and geochemical conditions may vary over time, with possible mobilization of previously-stabilized pollutants.

Table 6-3 shows the level of effectiveness of Natural Mitigation in relation to the environmental conditions listed above.

PARAMETER	VERY EFFECTIVE	MODERATELY EFFECTIVE	INEFFECTIVE
CONTAMINATION CHARACTERISTICS			
TYPE OF CONTAMINANT	Volatile and semi-volatile organic compounds light hydrocarbons, BTEX, halogenated solvents, chlorinated solvents	Some pesticides, explosives (trinitrotoluene), phenols and some inorganic compounds.	High contaminant concentrations may hinder the process. High metal concentrations are incompatible with this technique
CONTAMINATION PHASE	Contaminants dissolved in water, adsorbed in soil particles or vapour form		Not applicable with NAPL present
CONTAMINATION DISTRIBUTION			
PLUME EXTENSION	From limited to extended	An uneven pollutant distribution affects the	Excessively extended plume.

PARAMETER	VERY EFFECTIVE	MODERATELY EFFECTIVE	INEFFECTIVE
CONTAMINATION CHARACTERISTICS			
		treatment effectiveness	
POLLUTANT LOCATION	Mostly applicable in saturated portions, even at great depths	-	-
SUBSOIL CHARACTERISTICS			
LITHOSTRATIGRAPHY	Even soil	Slightly uneven soil	Uneven soil
HYDRAULIC CONDUCTIVITY (K)	Medium to high permeability		Very low permeability
OVERALL LEVEL OF HETEROGENEITY	Limited or isotropic	Moderate	High

Table 6-3 MNA degree of effectiveness

Required elements

The required elements include only the monitoring piezometers, whose position is strictly related to the hydrogeology and the pollutants' behaviour. Therefore, the following is required:

- Piezometers upstream to monitor the site natural conditions;
- Piezometers on the source of contamination and downstream, along the plume direction, in order to assess the source behaviour and its impact;
- Side piezometer to assess the plume lateral expansion;
- Remote sentinel piezometers to monitor the source containment and its impact.

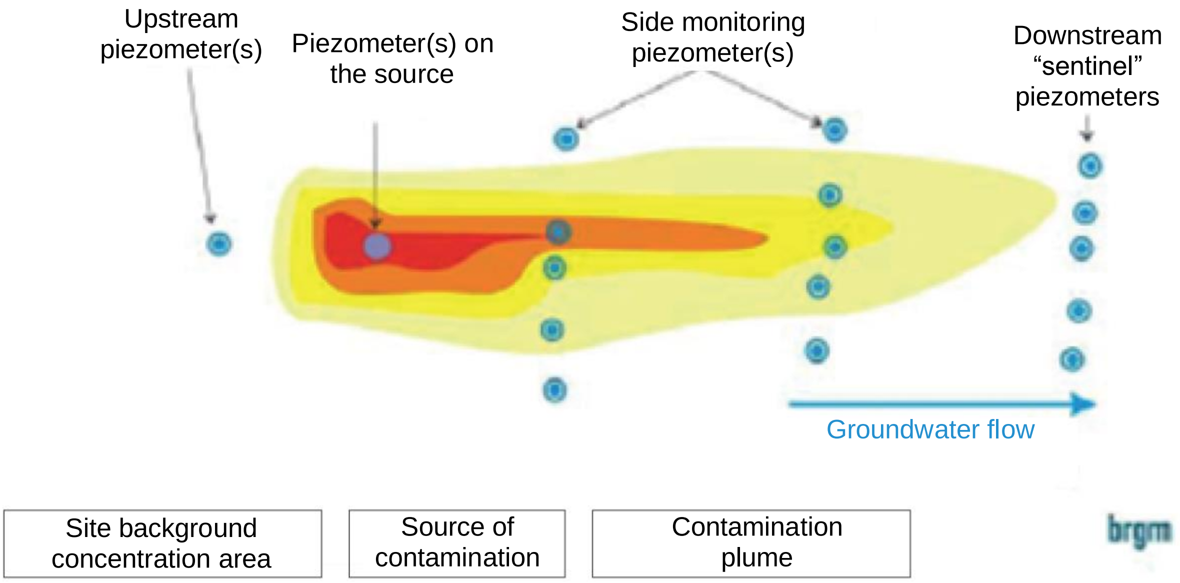


Figure 6-2 Location of the MNA monitoring piezometers (Source: Quelles techniques pour quels traitements - Analyse couts-benefices Rapport Final, BRGM, 2010 ©BRGM/RP-58609-FR - Edited)

Technology application pros and cons

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
DEGREE OF DEVELOPMENT, RELIABILITY AND DIFFUSION	🙂	This technique is easy to install and has virtually no logistic issues.
	😐	The remediation performance is highly variable; however, it is not uncommon to register performances higher than 70% in optimal conditions. Strategies with coded protocols only for very few types of contaminants.
APPLICABILITY BASED ON THE TYPE OF CONTAMINANT	🙂	Very effective processes in degrading many kinds of organic compounds, in transforming them into less hazardous products and in immobilizing both organic compounds and heavy metals.

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
	🙁	In some cases, the formation of more toxic and/or mobile intermediate compounds may occur (e.g. TCE's degradation into vinyl chloride). Not applicable with free products.
APPLICABILITY BASED ON THE SUBSOIL CHARACTERISTICS	🙂	Suitable to even soil with variable particle size and permeability.
APPLICABILITY BASED ON THE SITE CHARACTERISTICS	🙂	Applicable in the majority of logistic contexts.
REMEDIATION TIMES	🙁	Since this is a "passive" remediation technique, it requires fairly long times to establish natural mechanisms.
INTERVENTION COSTS	😐	No installation costs required, except for the monitoring piezometers. However, the monitoring costs can be significant, especially over a long time.
COMPATIBILITY WITH OTHER TECHNOLOGIES	🙂	Compatible with active remediation methods.
ENVIRONMENTAL SUSTAINABILITY	🙂	No system disturbance. No waste to be disposed of/treated or emissions.

🙂 Good 😐 Medium 🙁 Low

Table 6-4 MNA pros and cons

Related technologies

There are no MNA-related technologies.

6.3 Phytoremediation

Definition and general criteria

Phytoremediation techniques are environmental restoration tools that exploit vegetation such as grass, forbs, shrub as well as tree species to treat the contamination caused by heavy metals, organic compounds and radioactive elements, both in unsaturated and saturated matrices, and in soil with medium-coarse particle size.

It is based on natural processes pertaining to the plant capacity to absorb nutrients and other molecules that can be accumulated or metabolised by them. This depollution technique can potentially provide a more sustainable alternative to other remediation technologies.

Plants are used in a remediation context to:

- Extract pollutants from the subsoil and accumulate them in the plant tissue;
- Extract pollutants from the subsoil and decompose them;
- Modify the subsoil and/or pollutants characteristics;
- Create a more favourable environment to pollutant degradation.

Phytoremediation occurs through the following processes:

- Rhizodegradation: it consists in the contaminant decomposition through the biological activity of the organisms (bacteria and mildew) that occupy the rhizosphere, that is the portion of soil affected by roots (which extends, according to Shimp et al. 1993, for 1-3 mm around the roots surface). The contaminants treated are mainly organic compounds (TPH, chlorinated solvents and PCB). The types of plants adopted are both grassy plants and tree species, with typical humid environment plants being particularly effective;
- Phytostabilization: it consists in the absorption/accumulation in roots, deposit and/or immobilization in the roots area. The contaminants treated are heavy metals. The types of plants adopted are both grassy plants and tree species, with water plants and typical humid environment plants being particularly effective;
- Phytodegradation: it consists in the absorption and subsequent transformation of the contaminant through plant-based processes. The contaminants treated are some organic compounds (TPH, chlorinated solvents, BTEX and phenols). The types of plants adopted are both grassy plants and tree species, with water plants and typical humid environment plants being particularly effective;
- Phytostimulation (or rhizoremediation): at root level, the symbiotic association of plants and micro-organisms leads to the contamination degradation to a non-toxic or reduced toxicity form. On one site, roots provide the nutrients and the substrate; on the other, the micro-organisms degrade the pollutant. This process can be enhanced by using additives that stimulated the degradation growth and action, or by introducing fungal and/or bacterial strains in the rhizosphere (Bioaugmentation, Kuiper et al, 2004)
- Phytoextraction: it consists in extracting the contaminant and then accumulating it in the plant tissue. The contaminants treated are mainly heavy metals and radionuclides. The types of plants adopted are both grassy plants and tree species, with water plants and typical humid environment plants being particularly effective;

- Phytovolatilisation: it consists in the absorption and subsequent release of the contaminants into the atmosphere by transpiration (Contaminants may be subjected to chemical modifications before being released). The contaminants treated are both organic compounds (such as chlorinated solvents and MtBE) and inorganic compounds (such as mercury, arsenic, selenium and silver). The types of plants adopted are both grassy plants and tree species, with water plants and typical humid environment plants being particularly effective;
- Evapotranspiration: the standard evapotranspiration process grants some hydraulic control over the contaminated site. The contaminants treated are those soluble in water. The types of plants adopted are both grassy plants and tree species, with typical humid environment plants being particularly.

The different types are shown in **Figure** 6-3.

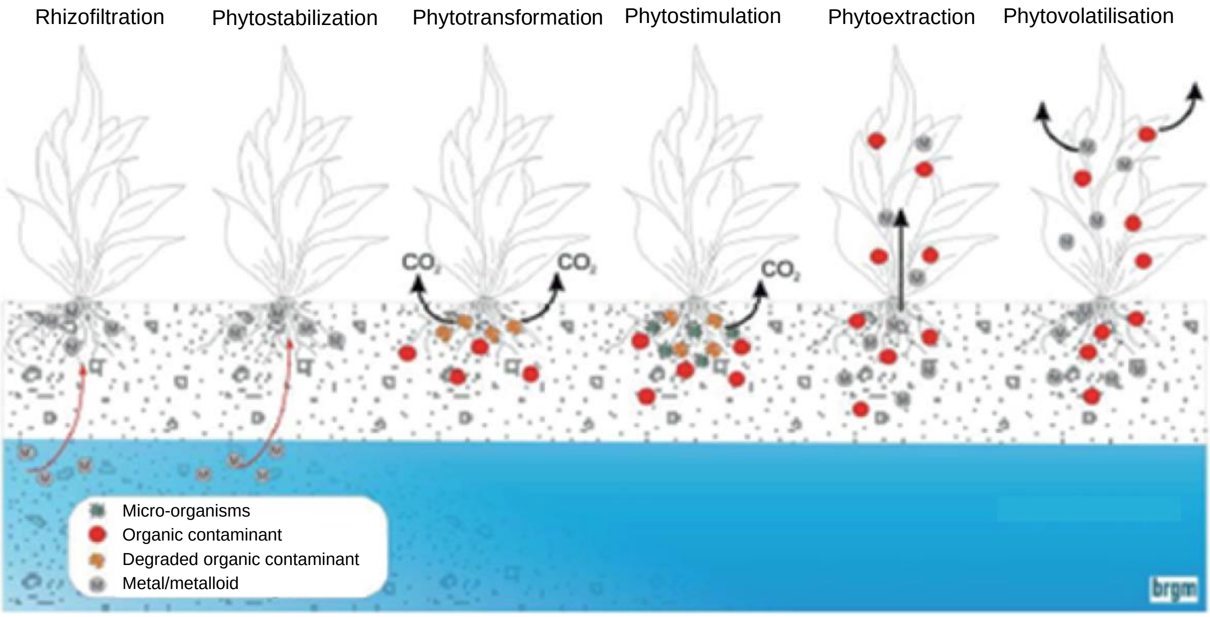


Figure 6-3 Phytoremediation types (Source: Quelles techniques pour quels traitements - Analyse couts-benefices Rapport Final, BRGM, 2010 ©BRGM/RP-58609-FR - Edited)

At the end of the treatment, the plant biomass is collected and the aerial part full of metals is separated from the roots and undergoes a disposal process (landfill or incinerator).

Conditions and application limits

Phytoremediation is particularly suitable and applicable under the following conditions:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Presence of inorganic compounds (heavy metals and radioactive elements) and organic compounds, both in unsaturated and saturated areas;
- Presence of low contaminant concentrations on vast areas an on sites contaminated by more than one pollutant;
- Contamination depth < 1 m and evenly distributed; in some cases, greater depths can be reached by using tree species with highly developed roots systems (e.g. poplars).

SUBSOIL CHARACTERISTICS

- Soil with medium-high permeability (from loamy-sandy to sandy);
- pH range between 4 and 9.

Conversely, **Phytoremediation is not suitable or applicable** when the following conditions occur:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Presence of phyto-toxic elements and non-phytoavailable metals;
- Contamination depth > 1 m and unevenly distributed.

SUBSOIL CHARACTERISTICS

- Soil with low permeability;
- pH lower than 4 and higher than 9.

Table 6-5 shows the level of effectiveness of Phytoremediation systems in relation to the environmental conditions listed above.

PARAMETER	VERY EFFECTIVE	MODERATELY EFFECTIVE	INEFFECTIVE
CONTAMINATION CHARACTERISTICS			
TYPE OF CONTAMINANT	Soluble and bioavailable inorganic contaminants (heavy metals and radioactive elements) Organic compounds (chlorobenzene, pesticides)	Organic contaminants (IPA, chlorinated aliphatic and halogenated hydrocarbons, BTEX, non-chlorinated and chlorinated phenols, aromatic amines)	Inorganic contaminants (non-bioavailable metals) Organic compounds (nitrobenzene, dioxins and furans, PCB)

<table>
<tr><th>PARAMETER</th><th>VERY EFFECTIVE</th><th>MODERATELY EFFECTIVE</th><th>INEFFECTIVE</th></tr>
<tr><td colspan="4">CONTAMINATION CHARACTERISTICS</td></tr>
<tr><td>CONTAMINATION PHASE</td><td>Contaminant in adsorbed phase
Low concentrations</td><td>Contaminant in adsorbed phase and non-bioavailable form
Contaminant in dissolved phase
Medium-low concentrations</td><td>Contaminant in gaseous phase
High concentrations and presence of phyto-toxic elements (e.g. Cu)</td></tr>
<tr><td colspan="4">CONTAMINATION DISTRIBUTION</td></tr>
<tr><td>PLUME EXTENSION</td><td colspan="2">Extended with even contamination distribution</td><td>Extended with uneven contamination distribution</td></tr>
<tr><td rowspan="2">POLLUTANT LOCATION</td><td>In unsaturated area/capillary fringe/saturated area at max. 80 cm of depth</td><td>In unsaturated area/capillary fringe/saturated area between 0.8-1 m of depth</td><td>In unsaturated area/capillary fringe/saturated area at > m of depth</td></tr>
<tr><td colspan="3">In some cases, greater depths (2-3 m) can be reached by using tree species with highly developed roots systems (e.g. poplars).</td></tr>
<tr><td colspan="4">SUBSOIL CHARACTERISTICS</td></tr>
<tr><td>LITHOSTRATIGRAPHY</td><td>Soil with medium-coarse particle size (from sandy-loamy to sandy) and pH higher than 4 and lower than 9</td><td>Soil with medium-fine particle size</td><td>Soil with fine particle size and pH close to 4 and 9</td></tr>
<tr><td>HYDRAULIC CONDUCTIVITY (K)</td><td>>10E-5 m/s</td><td>10E-6÷10E-5 m/s</td><td><10E-6 m/s</td></tr>
<tr><td>OVERALL LEVEL OF HETEROGENEITY</td><td>Limited or isotropic</td><td>Moderate</td><td>High</td></tr>
</table>

Table 6-5 Phytoremediation effectiveness

Required elements and design parameters

The **required elements** to implement a phytoremediation system are essentially those related to the cultivation of **plant species** (farming equipment) and the plants themselves.

The main parameters used to plan the interventions are:

- Choice and selection of the plant species (based on the type of contamination present and the climatic conditions);
- Pollutant transfer speed;
- Plant productivity (which, among other things, is related to climatic conditions and soil characteristics);
- Transpiration rate;
- Plant species layout and density;
- Irrigation system;
- Agronomic system;
- Monitoring system.

Here are some examples of plant species effective on contaminants in specific environmental contexts:

CONTAMINATED SOIL:

- Acer-pseudoplatanus (Mountain Maple) → Zinc, Cadmium, Lead;
- Eucalyptus globulus (Eucalyptus) → Cadmium, Zinc, Copper, Lead, organic contaminants;
- Populus nigra (Black Poplar) → Cadmium, Lead, organic contaminants;
- Robinia pseudoacacia (Robinia) → Heavy metals, organic contaminants;
- Zea mays (corn or maize) → Heavy metals, organic contaminants;
- Agrostis stolonifera (Creeping bentgrass, perennial grass) → Heavy metals, Arsenic, hydrocarbons.

CONTAMINATED WATER:

- Robinia pseudoacacia (Robinia) → Heavy metals, organic contaminants;
- Populus nigra (Black Poplar) → Cadmium, Lead, organic contaminants;
- Cannabis sativa → Cadmium, Chromium, Nickel, Lead, Zinc, organic contaminants and radio-nuclides;
- Pteris vittata (fern) → Arsenic;
- Phalaris arundinacea (Reed canary grass) → Heavy metals, organic contaminants, nutrients.

Here are some of the **phytotechnology applications**:

- *Phytobarriers*: they are employed to block the contamination in the air (thanks to the aerial filter) and in surface groundwater (thanks to the roots' action);
- *Phytodehydration*: through the plants transpiration process, a gradual substrate dehydration is obtained. This process can also affect the level of contamination, by reducing its hazardousness;
- *Phytocapping*: it's a surface covering system with topsoil and plants to control percolation. It is employed in landfill, as an alternative to traditional systems.

Technology application pros and cons

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
DEGREE OF DEVELOPMENT, RELIABILITY AND DIFFUSION	😐	This technology is not particularly widespread; however, it has shown very promising results when applied in optimal conditions. The plants' efficiency (especially in case of deciduous species) is related to seasons (i.e. it is reduced during the non-vegetative period), and they may be subject to parasites. Some pollutants may migrate during the treatment phases.
APPLICABILITY BASED ON THE TYPE OF CONTAMINANT	😐	Effective both on inorganic contaminants (heavy metals and radioactive elements) and organic contaminants (hydrocarbons, chlorinated solvents, IPA, MtBE, pesticides, landfill percolation). However, concentrations must be low and heavy metals must be soluble and bioavailable.
	☹	Applicable only at limited depth (<1 m), based on the roots characteristics of the species.
APPLICABILITY BASED ON THE SUBSOIL CHARACTERISTICS	☺	Effective in soil with medium-coarse particle size (from sandy-loamy to sandy) and medium-high permeability.

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
APPLICABILITY BASED ON THE SITE CHARACTERISTICS	☹	Not applicable with pH lower than 4 and higher than 9.
REMEDIATION TIMES	☹	Long intervention times (3-5 years).
INTERVENTION COSTS	☺	In general, the costs are low, especially in relation to the remediation area, which can be very big.
COMPATIBILITY WITH OTHER TECHNOLOGIES	☹	Phytoremediation is applied in contexts where other remediation techniques wouldn't be as effective. It can be used as supporting technology after another initial treatment requiring a finishing intervention.
ENVIRONMENTAL SUSTAINABILITY	☺	It does not entail any complex system (and does not cause disturbance to the subsoil); however, the plant fractions resulting from the different treatment cycles must be removed. Increased aesthetic value of the area and reduction of noise and foul smell. Limitation of the greenhouse effect thanks to the CO2 absorption. Production of renewable energy thanks to the potential recovery of energy from biomasses.
	😐	Potential contamination of the trophic chain.

☺ Good 😐 Medium ☹ Low

Table 6-6 Phytoremediation pros and cons

Related technologies

There are no Phytoremediation-related technologies.

Remediation Technologies On site - Chemical-Physical Processes

6.4 Air Sparging (AS)

Definition and general criteria

AS is a remediation technique suitable to treat volatile and semi-volatile organic compounds (halogenated and non-halogenated) in even soil with medium-coarse particle size and medium-high permeability, on capillary fringe/saturated areas.

This technology consists in injecting pressurized air into the groundwater, through wells suitably meshed in the saturated area (generally with 2" diameter, with filtering section between 0.15 and 3 m, placed 1.5-6 m below the water table).

The physical operating principle includes:

- Transfer of volatile pollutants from the aqueous phase to the vapour phase (***stripping***, primary effect), followed by their migration within the unsaturated medium above and by their removal;
- Increase of the quantity of oxygen dissolved in the groundwater, which leads to an increase of the microbial degradation of the contaminants (secondary effect).

In case of volatile compounds, the **AS** requires an additional *Soil Vapour Extraction* (**SVE**) system since the vapour generated (with a high pollutant concentration), once they leave the groundwater free surface, migrate into the unsaturated medium above. Through the SVE system, the vapour generated is directed into special extraction devices, conveyed by activated carbon filters, and then released into the atmosphere after being treated, in compliance with the limits set forth by current regulations.

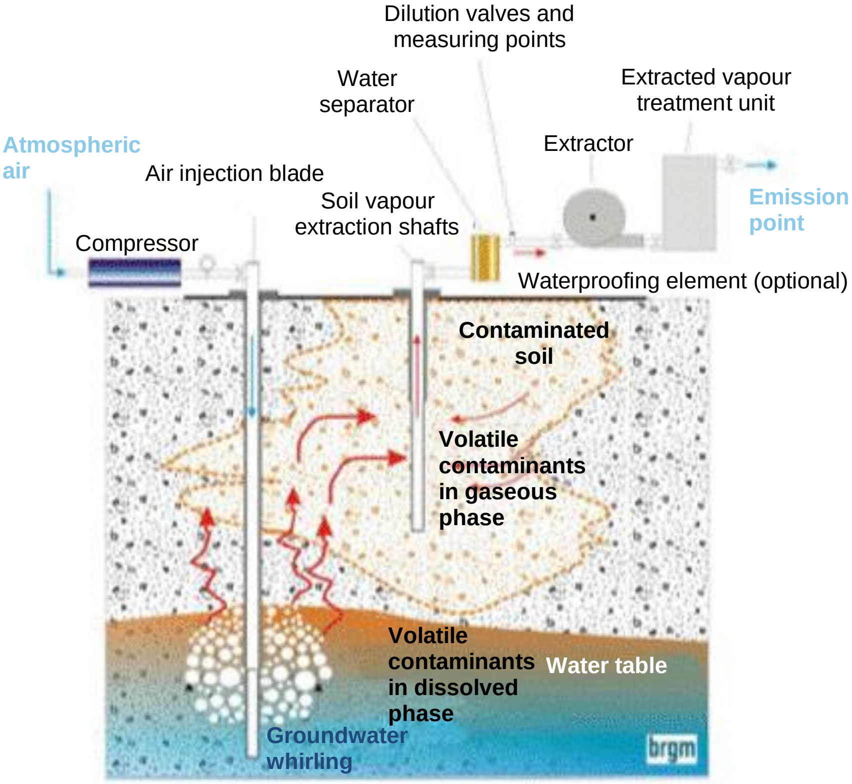


Figure 6-4 AS - SVE operating diagram (Source: Quelles techniques pour quels traitements - Analyse couts-benefices Rapport Final, BRGM, 2010 ©BRGM/RP-58609- FR - Edited)

Conditions and application limits

The **AS is particularly suitable** and applicable under the following conditions:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Presence of volatile and semi-volatile organic compounds;
- Limited contamination extension (small plume) and located near the groundwater table.

SUBSOIL CHARACTERISTICS

- Presence of uniform soil with loamy-sandy to gravelly particle size, characterized by medium-high hydraulic conductivity;
- Saturated area depth between 2 m and 15-20 m.

Conversely, the **AS is not suitable or applicable** when the following conditions occur:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Presence of pollutants with a low volatility degree and/or reduced biodegradability and very soluble contaminants;
- Presence of free product;
- Widespread contamination (large plume) located near the bottom of a free aquifer.

SUBSOIL CHARACTERISTICS

- Presence of confined aquifers and/or limited aquifer thickness (<3m);
- uneven soil with low permeability;
- Presence of foundations or enclosed spaces where pollutant vapour build-up may be generated;
- Presence of high concentration of dissolved iron Fe2+ in the subsoil.

Table 6-7 shows the level of effectiveness of the AS systems in relation to the environmental conditions listed above (source: USACE, 2008 - edited).

PARAMETER	VERY EFFECTIVE	MODERATELY EFFECTIVE	INEFFECTIVE
CONTAMINATION CHARACTERISTICS			
TYPE OF CONTAMINANT	Volatile and semi-volatile (*): BTEX, MOGAS and AVGAS, halogenated solvents, chlorinated solvents	Diesel and aviation fuels, acetone	Degraded fuels, lubricant oil, hydraulic and dielectric oil, PCB. “Old” contamination
CONTAMINATION PHASE	Dissolved contaminant	Adsorbed contaminant	Free product
(*)The pollutant volatility is determined by the vapour pressure, Henry’s Law Coefficient, its composition and its boiling point.			
CONTAMINATION DISTRIBUTION			
PLUME EXTENSION	Small	Medium	Large
POLLUTANT LOCATION	Near groundwater table	In shallow aquifers	In an enclosed aquifer or near the bottom of a free aquifer and with reduced aquifer thickness (<3 m)
SUBSOIL CHARACTERISTICS			
LITHOSTRATIGRAPHY	Even soil with big particle size (sand and gravel), even silt	Poorly layered, loamy-sandy and gravelly soil, very fissured clay	Silt and clay, highly organic soil, fissured substrate, layered soil and confinement elements

PARAMETER	VERY EFFECTIVE	MODERATELY EFFECTIVE	INEFFECTIVE
CONTAMINATION CHARACTERISTICS			
HYDRAULIC CONDUCTIVITY (K)	>10E-4 m/s	10E-5÷10E-4 m/s	<10E-5 m/s
OVERALL LEVEL OF HETEROGENEITY	Limited or isotropic	Moderate	High

Table 6-7 AS effectiveness

Basic system components and main development parameters

The **basic system components** to implement an AS intervention, supported by a SVE system to recover stripped vapour, comprise (Johnson et al., 1993; Suthersan S., 1997):

- One or more vertical or horizontal ventilation shafts;
- One compressor;
- One or more vertical or horizontal air extraction wells;
- One fan or vacuum pump;
- The related *interconnecting* networks;
- A water separator;
- One flue gas treatment unit;
- Piping and related instruments;
- Monitoring piezometers;
- Eectric control panel.

The main parameters to consider when developing an AS system are described in the following table **Table** 6-8 (Source: Marley and Bruell, 1995 – edited).

PARAMETER	RANGE OF VALUES*
Well diameter (inc)	1-4
Meshed section length (m)	0.15-3
Filter top depth below the water table (m)	1.5-6
Air injection flow (m3/h)	2.2-68
Injection pressure (kPa)	380-2700
Overpressure (KPa, with respect to the hydrostatic pressure)	38-1970
Sparging-affected area (m)	1.5-7.5
Ratio between the SVE and the AS affected areas	0.16-7.4
(*) = source: Marley e Bruell, 1995 – edited	

Table 6-8 Main parameters of an AS system

The **main configurations that can be adopted** are the following:

- Nested wells distributed along the entire plume length or in the source area (typical case of SVE technology pairing);
- Linear well orientation perpendicular to the underground water flow direction (sparging curtain), located inside the plume or immediately downstream from it;
- Horizontal wells (especially in case of subsurface thin and long plume, and in sections with limited access);
- Enclosing the contaminated area with sparging wells;

The injection wells should be 2 times less distant than the RoI (Radius of Influence).

Technology application pros and cons

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
DEGREE OF DEVELOPMENT, RELIABILITY AND DIFFUSION	🙂	Reliable and tested technique. Easy to install and reduced logistic disturbance.
	😐	Contaminant concentration abatements higher than 90% are very hard to achieve. Probable "rebound" effect: when the treatment is interrupted, concentrations are low, but they can significantly increase a few months later.
APPLICABILITY BASED ON THE TYPE OF CONTAMINANT	🙂	Applicable to many volatile and semi-volatile pollutants.
	☹	Difficult to apply to very soluble compounds, and impossible to treat semi-volatile pollutants with limited aerobic biodegradability. Insufficient extraction power on free products denser than water (DNAPL).
APPLICABILITY BASED ON THE SUBSOIL CHARACTERISTICS	🙂	Suitable to even soil with coarse particle size and medium-high permeability.

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
	☹	Not suitable to uneven soil with fine particle size, high content of organic matter and low permeability.
APPLICABILITY BASED ON THE SITE CHARACTERISTICS	😐	It can be applied below the foundation; however, it poses a risk of build-up in enclosed spaces (if present). The limited range of action of each injection point may require the construction of a significant quantity of injection wells to achieve satisfying results.
REMEDIATION TIMES	😐	Relatively fast in optimal conditions.
INTERVENTION COSTS	😐	Reduced intervention costs. However, the emissions into the atmosphere resulting from the SVE technology - often combined - require suitable air treatments (additional costs)
COMPATIBILITY WITH OTHER TECHNOLOGIES	🙂	Compatible with other remediation methods (e.g. SVE/ BV).
ENVIRONMENTAL SUSTAINABILITY	🙂	Generation of limited issues in the subsoil. No waste generation.

🙂 Good 😐 Medium ☹ Low

Table 6-9 AS pros and cons

Related technologies

Introducing air directly into the saturated area is only one of the possible variants of the flexible sparging technology.

The **main variants** are:

- ***Bio-sparging***: this process is similar to AS; however, the purpose of air insufflation is not the stripping/volatilisation processes, but rather oxygenating the groundwater and saturated area;
- ***Gas-sparging***: in the presence of trichloroethylene, methane injections (1% or 4% in air, for continuous or intermittent introduction respectively, Alvarez-Cohen et al. 1992; Hazen et al., 1994), propane (Wackett et al., 1989), or even natural gas (a mixture of methane, ethane, propane and traces of superior alkanes, Wilson e Wilson, 1985) may be evaluated, to exploit them as carbon substrates for compound biodegradation. On the other hand, the use of ammonia (Dinee et al., 1990), nitrogen oxide (0.07% in air) or triethyl phosphate (0.007%) increased the biodegradation action by indigenous micro-organisms (Hazen et al., 1994), acting as sources of nitrogen and phosphorous;
- ***Pneumatic/hydraulic fracturing***: soil and rock fracturing during a remediation intervention has been implemented to increase air permeability, and, specifically, to increase the flow in compact and hardened formations (e.g. limestone) or with a low degree of heat conductivity (silt and clay);
- ***In-well aeration***: by conveying air in the lower section of a water well piping, air bubbles ascend inside the column, developing a vapour-liquid and liquid-vapour mass transfer (Hinchee, 1994);
- ***Steam stripping***: using steam fosters the development of thermal gradients that accelerate the VOC volatilisation in the saturated area (Evans, 1991).

Given its widespread use, the following paragraphs include some detailed considerations on the *Biosparging* (BS) technology.

The mechanism - similar to AS - entails the injection of air into the saturated area. The main difference is given by the flow values used, which are about 1/3÷1/5 with respect to the AS, therefore preventing water stripping and the consequent release of vapours.

BS is extremely effective in treating medium weight petroleum substances (e.g. gas oil, petrol, aviation gas), and non-halogenated volatile and semi-volatile compounds. Just like the AS technology, it CANNOT be applied soil with low permeability and high clay content.

This technology CANNOT be applied in the following cases:

- Presence of free product, since it can migrate following the piezometric increase induced;
- If the aquifer is enclosed, because the input air would be trapped in the groundwater;
- There are closed spaces in the site, where pollutants may build up.

Given its characteristics, its effectiveness is closely linked to two factors (Province of Milan, 2004):

- Contaminants biodegradability;
- Quantity of bacteria present;
- Soil permeability.

Lastly, the following table summarizes the significant benefits resulting from the adoption of a BS system rather than an AS system:

PARAMETER	**BENEFITS COMPARED TO AS**	
INTERVENTION COSTS	☺	BS can more cost-effective, because the co-installation of a SVE system (and extracted vapour treatment) may not be required.
SYSTEM CHARACTERISTICS	☺	BS employs significantly lower air injection rates and more flexible configurations.

Table 6-10 Advantages of the BS system

6.5 Hydraulic Barriers

Definition and general criteria

To date, hydraulic barriers are one of the most used groundwater contamination reduction systems, although they were initially a containment technique.

This technology consists in a series of table wells (called "barrier wells") mainly located across the water outflow, whose action creates piezometric vacuum cones, attracting the contamination plume and preventing its migration into the surrounding environment.

Often, hydraulic barriers are paired with a drained water treatment system, hence the term ***Pump&Treat*** (P&T), as shown in **Figure 6-5**.

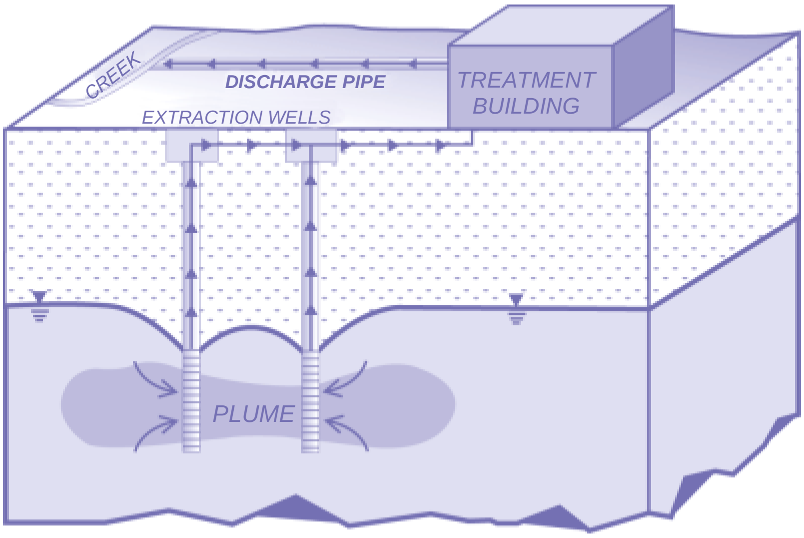


Figure 6-5 Treatment diagram with P&T (Source: U.S. EPA)

If on-site treatment is used, water can then be released into the sewage system or in a surface water body or reintroduced into the aquifer through re-injection wells.

Unfortunately, the treatment is often successful at the initial implementation phases, but then the performance drops drastically over time, entailing the presence of significant residual contamination.

Due to these limitations, the P&T method is now used mainly to recover the product and control the contaminant plume migration.

Conditions and application limits

Hydraulic barriers are particularly suitable and applicable under the following conditions:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Contamination dissolved in water (or as free product).

SUBSOIL CHARACTERISTICS

- Presence of soil with medium and medium-high permeability, even mildly uneven;
- Presence of groundwater, even superficial.

Conversely, **Hydraulic Barriers are not suitable or applicable** when the following conditions occur:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Contamination in unsaturated soil.

SUBSOIL CHARACTERISTICS

- Highly uneven soil with low permeability (permeability < 10^{-5} m/s);
- Aquifers with fracturing permeability;
- Very productive aquifers (due to high costs).

Table 6-11 shows the level of effectiveness of P&T systems in relation to the environmental conditions listed above.

PARAMETER	VERY EFFECTIVE	MODERATELY EFFECTIVE	INEFFECTIVE
CONTAMINATION CHARACTERISTICS			
TYPE OF CONTAMINANT	All types of contaminations		-
CONTAMINATION PHASE	Dissolved or LNAPL		DNAPL
CONTAMINATION DISTRIBUTION			
PLUME EXTENSION	Small-medium size		Very large
POLLUTANT LOCATION	Saturated soil and groundwater		Unsaturated soil

PARAMETER	VERY EFFECTIVE	MODERATELY EFFECTIVE	INEFFECTIVE
SUBSOIL CHARACTERISTICS			
LITHOSTRATIGRAPHY	Even or mildly uneven soil with medium and medium-coarse particle size		Uneven soil with fine particle size or fractured aquifers
HYDRAULIC CONDUCTIVITY (K)	>10E-6 m/s		<10E-6 m/s
OVERALL LEVEL OF HETEROGENEITY	Moderate or isotropic		High

Table 6-11 P&T systems effectiveness

Basic system components and main development parameters

To design a P&T system, it is necessary to:

- trace the aquifer geometry and characteristics (permeability, heterogeneity, storage coefficient, groundwater level, etc.);
- draft a piezometric map;
- define the contaminant concentration in groundwater;
- define the contaminant plume extension.

These data will help define:

- the extraction points' range of action;
- the number, spacing and characteristics of the pumping points (depth, diameter, well, etc...);
- the pump type and power;
- the water treatment unit size;
- in case of re-injection into the groundwater: the number, spacing and characteristics of the injection points (depth, diameter, well, etc...);
- the effects on possible surface water near-by;
- variation of the groundwater level based on the flow and the different conditions (transitional regime, high water table, low water table, etc.);
- voncentration evolution and pollution plume.

The construction of a hydraulic barrier entails an accurate planning, so that the vacuum cones created by the single wells penetrate each other to capture the entire contamination plume.

In order to keep the containment system operation under control, a set of monitoring wells downstream the system is also required: an increase of the pollutant concentration in the monitoring wells is the first sign of issues in the table wells.

The **basic system components** to implement a P&T intervention comprise:

- An extraction network comprising suitably slotted vertical wells in the saturated area or draining trenches;
- A monitoring piezometers network;
- Electric or pneumatic submerged pumps;
- Water/oil separator (if present in the supernatant product);
- A drained groundwater treatment unit (in case of on-site treatment);
- Waste storage (in case of supernatant product and/or if water is not sent to the sewage system/re-injected into the water table);
- Piping and related instruments (litre-counter, pressure switches, etc.);
- Electric control panel.

Technology application pros and cons

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
DEGREE OF DEVELOPMENT, RELIABILITY AND DIFFUSION	🙂	Reliable and tested technique. Relatively simple and quick to configure, with minimum subsoil disturbance. It allows obtaining hydraulic confinement.
	😐	It requires complete control over the groundwater flow direction, to prevent the risk of pollution diffusion.
APPLICABILITY BASED ON THE TYPE OF CONTAMINANT	🙂	Effective with all kinds of contaminants.
APPLICABILITY BASED ON THE SUBSOIL CHARACTERISTICS	🙂	Applicable in several environmental contexts (capillary fringe and saturated area). Suitable for even or slightly uneven soil with medium-fine particle size and medium-low permeability (not lower than 10^{-7} m/s).

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
	🙁	Not suitable for soil with fine particle size and low permeability.
APPLICABILITY BASED ON THE SITE CHARACTERISTICS	😐	Applicable underneath existing buildings. The range of action of each injection shaft may require the construction of a significant quantity of wells to achieve satisfying results. It also requires the installation of monitoring wells downstream of the hydraulic barrier.
REMEDIATION TIMES	🙁	Long remediation times possible and inability to reduce the pollutant value below a certain balance value, often higher than limit concentrations
INTERVENTION COSTS	😐	It can be a fairly inexpensive treatment; however, depending on the plume extension, many extraction points may be required and the quantity of pumped and treated water may be consistent, with consequent cost increase.
	🙁	Costs may be high in case of water draining and storage.
COMPATIBILITY WITH OTHER TECHNOLOGIES	🙂	It is often used as securing activity, paired with other technologies to reach the remediation objectives.
ENVIRONMENTAL SUSTAINABILITY	😐	Often, the quantity of water pumped is higher than that actually contaminated. Pumped water must be treated.
	🙁	In case of storage, the need to discharge the water entails further reduction of the environmental sustainability.

🙂 Good 😐 Medium 🙁 Low

Table 6-12 Pros and cons

Related technologies

The P&T system is often used as securing activity, paired with other remediation interventions both on unsaturated soil and on the groundwater (AS, SVE, dig&dump, etc.).

The above is due to:

- The inability to reduce the pollutant value below a certain balance value, often higher than limit concentrations;
- The effectiveness on the dissolved phase only.

6.6 Permeable Reactive Barriers (PRB)

Definition and general criteria

The term **"PRB (Permeable Reactive Barrier)"** comes from the U.S. EPA (1998); this passive technology can be applied for the remediation of dissolved contaminants in groundwater. The treatable contaminants include chlorinated hydrocarbons, trace metals and anionic pollutants (sulphates, nitrates, phosphates, Arsenic).

It consists in building a trench in the downstream hydrogeological subsoil of the soil requiring remediation, filled with a reactive material (i.e. capable of degrading pollutants to non-toxic or less toxic substances). This passive treatment exploits the natural gradient of the groundwater that passes through the reactive medium located inside the barrier. The plume that passes through the barrier is in contact with the material that constitutes and reacts with it. The chemical-physical processes taking place allow degrading, immobilizing or adsorbing the contaminant in the pass-through stage. The operation is outlined in **Figure 6-6**.

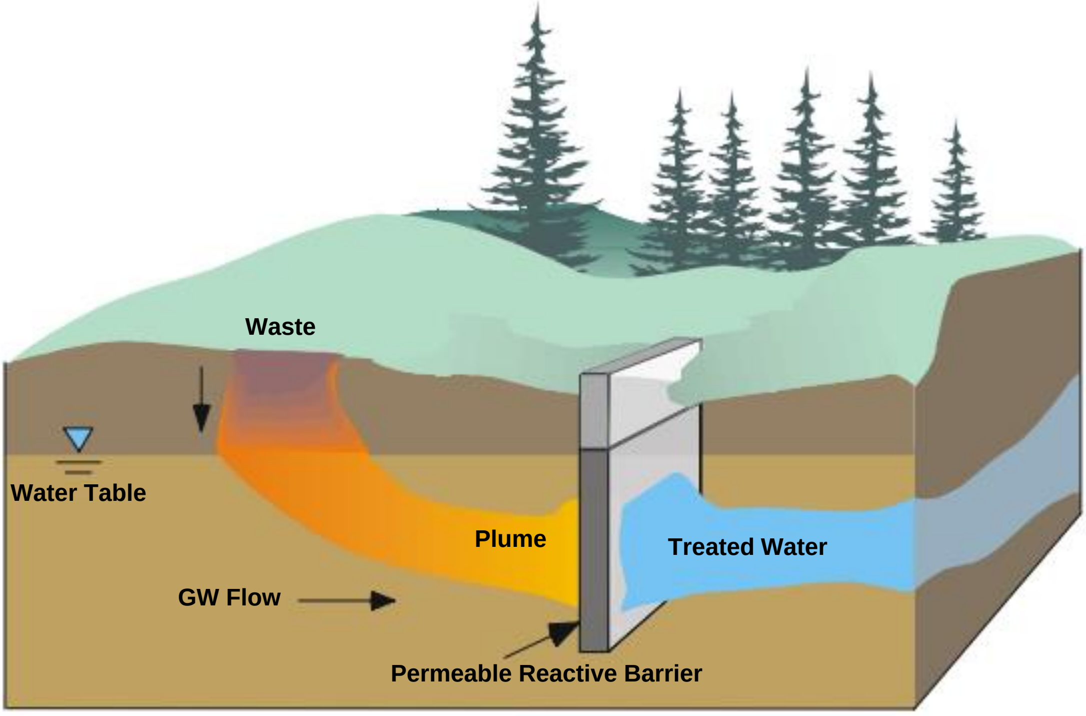


Figure 6-6 Permeable Reactive Barriers Diagram (source: EPA, 1998)

For the intervention to be effective, the entire plume must be conveyed across the barrier reactive element, characterized by a higher level of permeability than the aquifer, in order to prevent bypassing the barrier in any direction.

The reactions between contaminants contained in water and the reactive substrate can be of two types:

- absorption in the solid surface: contaminants are subtracted from the moving liquid phase and are absorbed by the solid substrate, which generally comprise i activated carbon - effective especially on apolar organic compounds - or natural or artificial zeolites.
- degradation: depending on the type of reactive material used, a chemical or microbiological degradation of the contaminants in liquid phase is developed. The degradation may be total or partial, with formation of intermediate products with different toxicity compared to the initial compounds.

Conditions and application limits

The **PRB is suitable and applicable** under the following conditions:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Presence of wide-ranging contamination dissolved in groundwater;
- Particularly suitable for contamination within 15 m from the ground level.

SUBSOIL CHARACTERISTICS

- Even aquifer, no preferential permeability paths;
- Presence of a waterproof layer deeper than 25-30 m;
- Good soil excavation conditions and no construction works issues.

Conversely, **PRB is not suitable or applicable** when the following conditions occur:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Presence of poorly soluble contamination;
- Presence of supernatant product;
- Contaminations > 15 m deeper than the ground level.

SUBSOIL CHARACTERISTICS

- Areas with preferential groundwater flow paths or low hydraulic gradient;
- Presence of lithologies with more than 20% of fine fractions.
- Porous and uneven soil with low permeability and high organic substance content;
- Significant cationic exchange capacity.

Table 6-13 shows the level of effectiveness of the PRB systems in relation to the environmental conditions listed above.

PARAMETER	**VERY EFFECTIVE**	**MODERATELY EFFECTIVE**	**INEFFECTIVE**
CONTAMINATION CHARACTERISTICS			
TYPE OF CONTAMINANT	(Chlorinated) organic and inorganic compounds (trace metals and anionic pollutants)	Aromatic hydrocarbons IPA, non-chlorinated phenols	PCB, Mercury, some pesticides
CONTAMINATION PHASE	Dissolved contaminant	Poorly dissolved contaminant	Free product
CONTAMINATION DISTRIBUTION			
PLUME EXTENSION	Little to mildly extended plume		Excessively extended plume
POLLUTANT LOCATION	< 15 m from the ground level.		> 15 m from the ground level.
SUBSOIL CHARACTERISTICS			
LITHOSTRATIGRAPHY	Fairly even soil with sandy particle size	Fairly uneven soil with sandy particle size	Soil with a high content of organic matrix Uneven soil with medium-fine particle size (sandy-loamy, loamy, loamy-clayey)
HYDRAULIC CONDUCTIVITY (K)	High	Medium	Low
OVERALL LEVEL OF HETEROGENEITY	Limited or isotropic	Moderate	High

Table 6-13 Permeable Reactive Barrier's Effectiveness

Lab testing and configuration/construction types

There are many different types of reactive materials applied until now or currently being studied on lab scale.

The **tests** to perform comprise both static testing (batch tests) and dynamic testing (column testing), and should preferably involve water samples collected on site, given the importance of the water geochemical characteristics in determining the treatment's efficiency.

- *Batch tests* are usually employed in the initial screening phase of the reactive material (rapid, inexpensive and easily manageable tests), and they also help obtaining information on the reaction paths more easily and better verify mass balances.

- On the other hand, *column tests* are conducted on the material selected in the batch tests, in order to estimate the contaminants and the intermediate compounds halving times. These tests allow obtaining information on the system's behaviour under conditions that are very similar to those on site, and also on the process kinetics in more representative conditions than in batch testing. From the degradation kinetics, we can calculate the residence time necessary to reach the required concentration, and therefore, based on the groundwater speed, the thickness of the reactive medium.

Reactive barriers are generally implemented based on two different **layout configurations,** depending on the size of the area to be treated, on the aquifer characteristics and on the type of reactive material required:

- *Continuous barrier*: it comprises a cell that extends without interruptions, so as to intercept the plume in its entire extension, without affecting the site flow conditions. The plume, as shown in **Figure 6-7**, passes through the barrier below the natural gradient, without any speed variations.

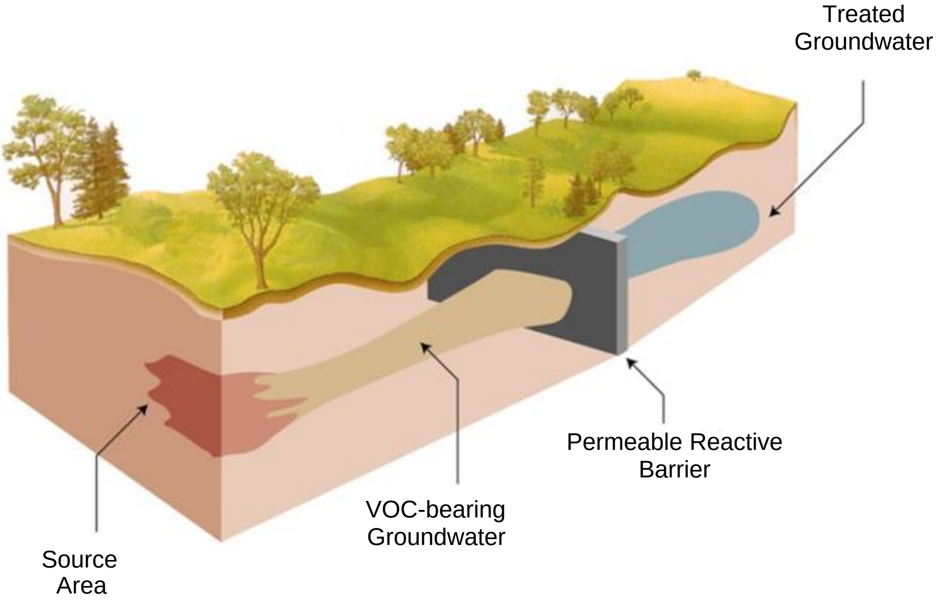


Figure 6-7 Continuous barrier's operation (source: Professor Petrangeli Papini)

- *"Funnel and gate"*, which can be divided into "single gate" or "multiple gates". The first case - shown in **Figure 6-8** - includes:
  - Two external low permeability sections (funnels), comprising one or more plastic diaphragm (e.g. made of concrete-bentonite) or pilings that convey the plume toward the central area;
  - An internal permeable section (gate), comprising a trench and containing the reactive material.

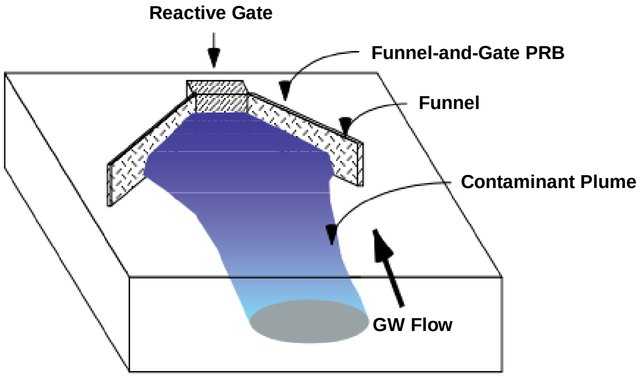


Figure 6-8 Funnel and Gate's Operation (source: EPA, 1998)

Regardless from the layout configuration selected, the reactive element may be suspended or butted into the waterproof substrate. The second solution is always preferable, in order to prevent the contaminated water from vertically or laterally bypassing the barrier.

There are several techniques to create the reactive area, such as:

- Creation of a trench with inverted boom excavators, log grapples or continuous movement excavators;
- Laying of the reactive material with caissons, removed once the reactive material replaces the soil;
- Laying of the reactive material with a spindle.

Technology application pros and cons

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
DEGREE OF DEVELOPMENT, RELIABILITY AND DIFFUSION	☹	Although it's a mechanically reliable process, this technology is not very widespread. The formation of precipitates, related to the reaction between the contaminants and the reactive medium, may compromise the system's long-term effectiveness.
	☺	Physical-chemical processes, if correctly sized, may have performances >95%; generally, biological processes have lower performances.
	😐	The barrier's continuity and effectiveness must be constantly monitored by checking the hydraulic conductivity and movements of the surrounding soil, which might affect the works stability and the quality of groundwater downstream from it.

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
APPLICABILITY BASED ON THE TYPE OF CONTAMINANT	🙂	Applicable to a wide range of organic and inorganic contaminants.
APPLICABILITY BASED ON THE SUBSOIL CHARACTERISTICS	🙁	Not suitable to areas with preferential groundwater flow paths or low hydraulic gradient aquifers. Difficult to apply in case of deep pollution (deeper than 15 m from the ground level).
	🙂	Excellent treatment for distributed and/or hardly locatable sources.
	🙂	Applicable in active production areas; in general, the area can be used during environmental remediation operations.
REMEDIATION TIMES	🙁	There are no long-duration field tests capable of providing guarantees on the longevity of the barrier's reactive properties or its reduced permeability due to precipitation phenomena. Long-term maintenance/monitoring interventions must be implemented.
INTERVENTION COSTS	😐	Low operating and maintenance costs; however, the reactive material can be costly.
COMPATIBILITY WITH OTHER TECHNOLOGIES	🙂	Compatible with other remediation technologies.
ENVIRONMENTAL SUSTAINABILITY	🙂	Applicable on site, therefore it does not require any contaminated water extraction or handling (except during the excavation - installation phase). In this passive system, water moves, pushed by a natural hydraulic gradient, and reaches the treatment area without any additional power supplied.
	🙁	Excavation soil to be disposed of. For granular active charcoal barriers, the waste reactive material must be disposed of.

🙂 Good 😐 Medium 🙁 Low

Table 6-14 Permeable Reactive Barrier's pros and cons

Related technologies

Worthy of notice is the existence of barriers that use mixed chemical-biological treatments: in case of chemical degradation, the solid material may be granular iron, even combined with other solid materials, such as silica sand, which may act as medium for the growth of indigenous bacteria. In this case, by adding nutrients and oxygen at suitable quantities and times, the bacterial growth is stimulated to support the biological degradation.

Based on these principles, three different categories of permeable reactive barriers are identified:

- ***Chemical barriers:*** they are based on the transformation of contaminations into less harmful compounds, and they do not require reactive material reclamation;

- ***Absorbing barrier***: the two more representative materials that can be used in this kind of barriers are activated charcoal and natural zeolites;

- ***Biological barrier***: "bioremediation" is essentially based on the nutritional/energy support provided to micro-organisms already present on the site to be contaminated or specifically introduced therein.

6.7 Electrokinesis

Definition and general criteria

Electrokinesis is an on-site remediation technique applied both on unsaturated and saturated areas, to separate and extract:

- heavy metals;
- radionuclides;
- inorganic molecules (nitrates, sulphates and cyanide);
- explosives;
- organic compounds, such as petrol-based products (fuels and lubricant oil), DNAPL, halogenated solvents (TCE), BTEX and aromatic polycyclic hydrocarbons (IPA).

This technology is based on the application of continuous and constant current at low intensity (600mA) between two electrodes stuck into the ground; the potential difference between the two electrodes generates a migration of the contaminants dissolved in water in ionic form toward the respective electrodes (anode and cathode), where they are retrieved.

In addition, the presence of an electric field in the soil fosters the development of a pH gradient, redox reactions, heat generation and electrolysis processes.

There are several electrokinetic treatments:

- electro-osmosis: it consists in water moving from the anode to the cathode;
- electromigration: it consists in the transport of ions and ionic complexes to the opposite charge electrode (cathode and anode);
- electrophoresis: it consists in the transport of charged particles or colloids under the influence of an electric field; contaminants are transported in adsorbed form.

The electrolysis operating diagram is shown in **Figure 6-9**.

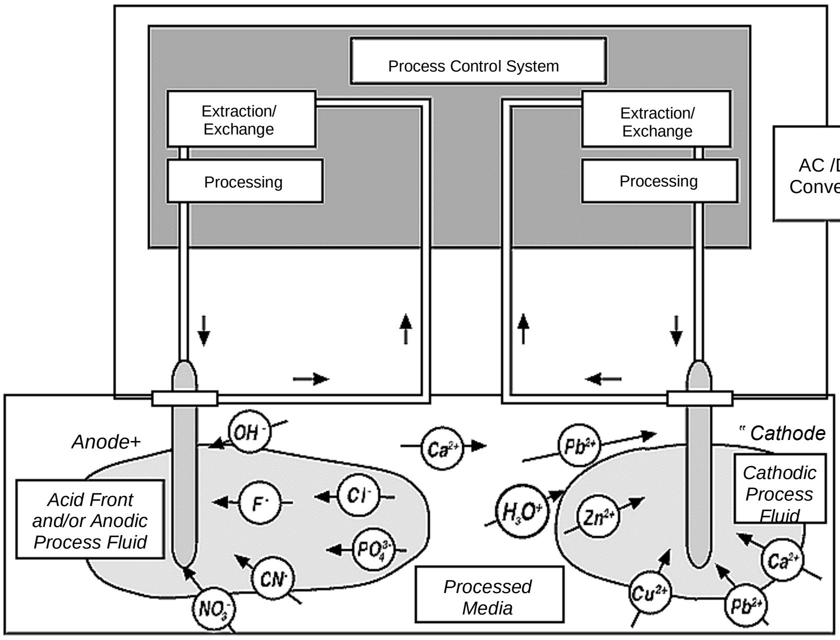


Figure 6-9 Electrokinesis Diagram (Source: FRTR, EPA)

Conditions and application limits

Electrokinesis is particularly suitable and applicable under the following conditions:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Polar and soluble compounds, thanks to their high mobility. The most suitable compounds for this treatment are heavy metals;
- The process can also be applied to a wide range of concentrations (from a few ppm to tens of thousands ppm);
- Presence of DNAPL;
- Contamination depth < 20m.

SUBSOIL CHARACTERISTICS

- Presence of even soil with fine particle size (silt and compact clay); less efficient, although possible, also in case of quartz sand;
- Medium-low hydraulic conductivity;
- Low cationic exchange capacity and saltiness;
- Deposits with low electric conductivity levels.

Conversely, **Electrokinesis is not suitable or applicable** when the following conditions occur:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Low concentrations of ions to be removed lead to a low efficiency;
- Premature precipitation of chemical species next to the cathode;
- Contamination depth greater than 20 m.

SUBSOIL CHARACTERISTICS

- Soil with coarse particle size and medium-high hydraulic conductivity;
- Uneven soil and subsoil anomalies;
- High pH that causes the precipitation of certain metals and progressive pore clogging;
- Acidity conditions and electrolytic deterioration;
- High cationic exchange capacity and saltiness;
- Deposits with high electric conductivity levels.

Table 6-15 shows the level of effectiveness of the Electrokinesis technology in relation to the environental conditions listed above.

PARAMETER	VERY EFFECTIVE	MODERATELY EFFECTIVE	INEFFECTIVE
CONTAMINATION CHARACTERISTICS			
TYPE OF CONTAMINANT	Inorganic compounds: heavy metals, radionuclides, toxic inorganic molecules (cyanide, sulphates, nitrates), explosives	Polar organic compounds: petrol-based products (fuels and lubricant oil), DNAPL, halogenated solvents, BTEX, PAH	Apolar compounds and zerovalent metals
	Concentrations from a few ppm to several thousands ppm		
CONTAMINATION PHASE	Dissolved and adsorbed compounds (in case of electrophoresis)		-
CONTAMINATION DISTRIBUTION			
PLUME EXTENSION	Limited-moderate		High
POLLUTANT LOCATION	in unsaturated and saturated area, within 20 m from the ground level.		Over 20 m from the ground level

PARAMETER	**VERY EFFECTIVE**	**MODERATELY EFFECTIVE**	**INEFFECTIVE**
SUBSOIL CHARACTERISTICS			
LITHOSTRATIGRAPHY	Even soil with fine particle size (silt and clay) Subsoil humidity level between 14 and 18%. Low cationic exchange capacity and saltiness.	Fairly even soil with medium-fine particle size (quartz sand)	Even soil with coarse particle size (sand and gravel). Humidity level > 10%. High cationic exchange capacity and saltiness.
HYDRAULIC CONDUCTIVITY (K)	Low	Medium	High
OVERALL LEVEL OF HETEROGENEITY	Limited or isotropic	Moderate	High

Table 6-15 Electrokinesis effectiveness

Basic system components and possible configurations

The **basic system components** to implement an electrokinesis intervention comprise:

- Electrodes (anodes, cathodes) fixed to a support system powered by electricity, and comprising conductive and corrosion-resistant materials (titanium, platinum, special alloys, graphite);
- Extraction/cationic exchange system;
- Cathodic treatment fluid injection;
- Extraction/anionic exchange system;
- Anodic treatment fluid injection;
- Extracted product treatment/recirculation;

  If required: a waterproof cover for the entire area to be treated and a gas treatment system;
- A water monitoring system;
- Solid and liquid waste (resulting from the treatment) storage.

The possible configuration may be one- or bidimensional (hexagonal, square, triangular), depending on:

- ➢ Number and cost of electrodes per area to be treated;
- ➢ Position and size of any inactive field areas;
- ➢ Processing time required.

Technology application pros and cons

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
DEGREE OF DEVELOPMENT, RELIABILITY AND DIFFUSION	😐	Lab test results on low hydraulic conductivity soil highlighted 75-95% of metal recovery. Emerging processes and techniques; in addition, it requires a very accurate monitoring of groundwater to prevent the plume diffusion.
	🙂	Relatively simple system.
APPLICABILITY BASED ON THE TYPE OF CONTAMINANT	🙂	Suitable for polar and soluble compounds. The most suitable compounds for this treatment are heavy metals. Applicable also to other inorganic compounds (radionuclides, toxic inorganic molecules, explosives) and to organic compounds (petrol-based products, DNAPL, halogenated solvents, BTEX, PAH).
APPLICABILITY BASED ON THE SUBSOIL CHARACTERISTICS	🙂	Suitable to even soil with fine particle size and medium-low permeability.
	🙁	Not suitable for uneven soil with coarse particle size and high permeability.
APPLICABILITY BASED ON THE SITE CHARACTERISTICS	😐	Waste or underground structures with high electric conductivity may render this technique ineffective.
REMEDIATION TIMES	😐	The treatment time required depends on the contaminant transport speed. Adsorption, precipitation and complexing interfere with transport, delaying it, and, in turn, transport depends on the type of soil, pH conditions and presence of organic substances.

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
INTERVENTION COSTS	😐	The costs are strongly affected by the type of soil to be treated, its conductivity, type of pollutants, electrodes spacing and process. Even the cost of electricity and long-term monitoring affect the final cost.
COMPATIBILITY WITH OTHER TECHNOLOGIES	🙂	Surfactants or complexing agents may be used to increase the pollutants' solubility and therefore their mobility. Some reagents can also be used to increase recovery rates.
ENVIRONMENTAL SUSTAINABILITY	😐	The application of an electric field may cause soil overheating and therefore drying. Metal electrodes may dissolve during electrolysis reactions and generate further metal pollution in the soil. No on-/off site contamination recovery required.

🙂 Good 😐 Medium ☹ Low

Table 6-16 Electrokinesis pros and cons

Related technologies

The main variants to the traditional electrokinesis technique - recently developed and patented - are:

- *Electrochemical Geooxidation (ECGO):* system used to mineralize organic compounds and immobilize inorganic ones through electric currents. It can be applied both on unsaturated and saturated areas;
- Lasagna™ Process: layered structure technology combining electro-osmosis and treatment areas, used both on inorganic and organic compounds and mixed waste;
- Electroacoustic Technique: it employs an acoustic source, in addition to the electric one, located mid-way between the potential electrodes. It is used mostly on clayey soil contaminated by heavy metals and NAPL;
- *Permeable Electrochemical Oxidation Reactor (PEOR):* it employs a permeable electrochemical oxidation reactor (Van Cauwenberghe, 1997).

6.8 Multi Phase Extraction (MPE)

Definition and general criteria

MPE systems that contain multiple system configurations (***TPE, DPE, Bioslurping***), are suitable to treat volatile organic compound contamination, present in the unsaturated area/capillary fringe/saturates area at the same time, in soil with medium-low permeability.

The simultaneous multi-phase extraction through vertical and horizontal wells consists in exerting a significant negative pressure on the unsaturated area, at the capitally fringe level, and on the saturated area upper portion, with the purpose of extracting vapour from the soil, any supernatant product and the dissolved phase.

This technology can be applied also on aquifer with low transmissivity, and, in these cases, it can also be used as hydraulic containment system.

Here is a short description of the possible system configurations.

Dual Phase Extraction (DPE)

The DPE technique, shown in **Figure 6-10**, includes the extraction of gases and liquids (NAPL and groundwater) from the well, through two separated pipes and two pumps or fans.

- Liquids are extracted through an electric or pneumatic submerged pump located inside the casing. They are then treated in the above-ground system;
- Vapours are extracted by creating a low- or high-level of vacuum, generated by a vacuum pump installed on the well head. On the surface, they are first input in a water separator, and then the aeriform phase is treated.

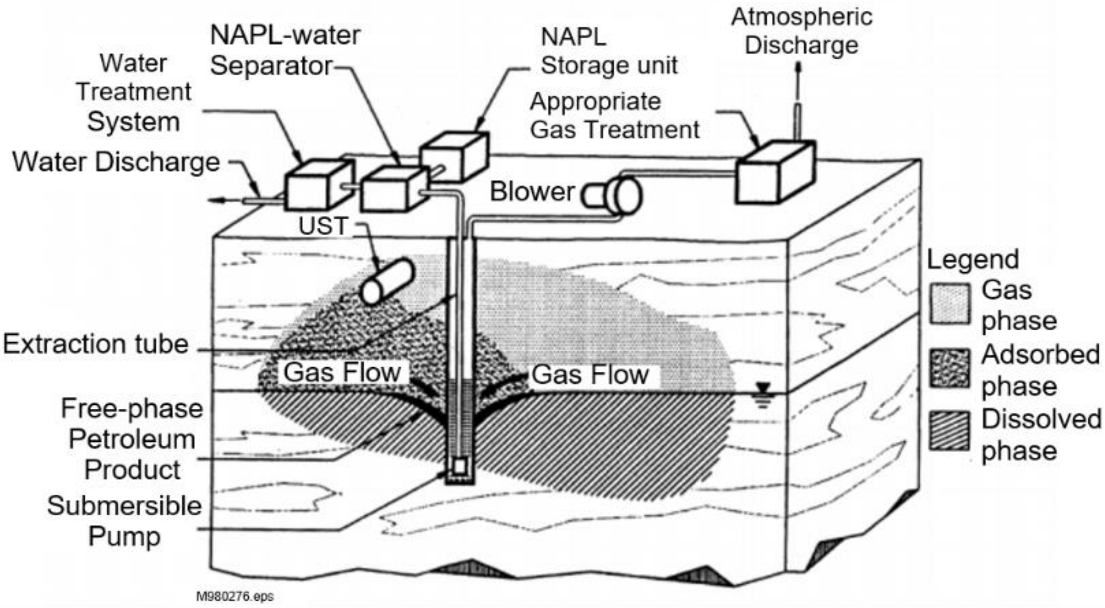


Figure 6-10 DPE Technology Diagram (Source: After USEPA 1995)

An alternative to the configuration shown in **Figure 6-10,** is the so-called Dual Pump, i.e. two pumps inside the same (large) well at different heights, if the purpose is recovering only hydrocarbons.

Two Phase Extraction (TPE)

The TPE technique, shown in **Figure 6-11,** entails the extraction of gases and liquids (NAPL and groundwater) from the well through a single pipe (*drop tube*), aided by the action of a blowing or suction pump that generates a high level of vacuum.

Once the extracted mixture of phases reaches the surface, it first passes through the gas/liquid separator (and possibly through an oil/water separator), and then each single phase (gases and liquids) is treated separately.

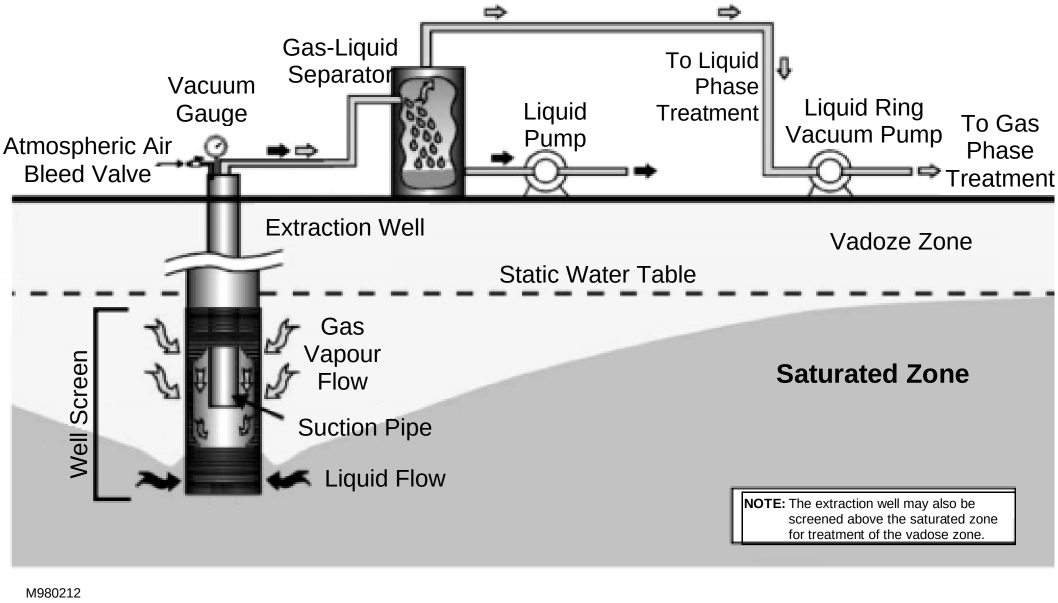


Figure 6-11 Tpe Diagram (Source: After EPA 1997)

Bioslurping

This technique, visible in **Figure 6-12**, is actually a variant of the TPE, designed to improve the LNAPL product recovery, and enhance the biodegradation in the unsaturated portion, caused by the soil oxygenation via bioventing.

It entails the use of a suction tube, located on the LNAPL-water interface, to create a pressure gradient that causes the 3 phases (gas, liquid, LNAPL) to enter the well, without generating any smearing effects (i.e. the product retention in the unsaturated area and its stationing in the unsaturated area, following the water table oscillations).

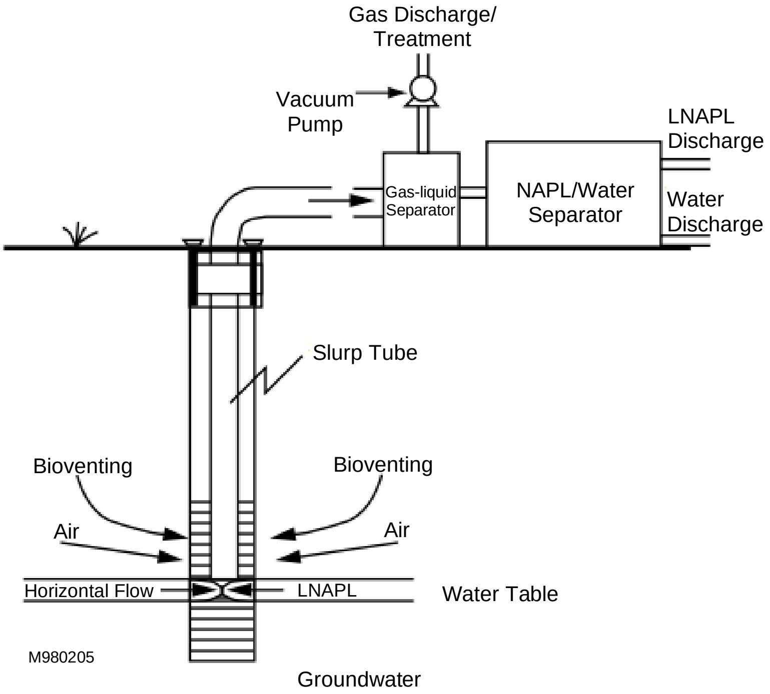


Figure 6-12 Bioslurping Diagram (Source: After AFCEE 1994b)

Conditions and application limits

The **MPE is particularly suitable** and applicable under the following conditions:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Presence of volatile organic compounds and petrol-based hydrocarbons;
- Contamination in two or three phases, including supernatant product;
- Recent contamination or, in any case, not too old.

SUBSOIL CHARACTERISTICS

- Presence of sandy-loamy soil, silt or loamy clay with medium-low permeability, even fairly uneven;
- Presence of groundwater, even superficial;
- Soil with limited organic matter content.

Conversely, **MPE is not suitable or applicable** when the following conditions occur:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Presence of very soluble and highly volatile pollutants;
- Supernatant product thickness < 1 cm and density very close to 1;
- Strong space-time variations of the supernatant thickness;
- Old contamination.

SUBSOIL CHARACTERISTICS

- Very uneven soil with high permeability (coarse sand and gravel) or with permeability $< 10^{-7}$ m/s;
- Groundwater level > 7-10 m;
- Presence of high quantities of organic matter and high level of humidity.

Table 6-17 shows the level of effectiveness of MPE systems in relation to the environmental conditions listed above.

PARAMETER	VERY EFFECTIVE	MODERATELY EFFECTIVE	INEFFECTIVE
CONTAMINATION CHARACTERISTICS			
TYPE OF CONTAMINANT	Volatile compounds* and petrol-based hydrocarbons in particular. Recent contamination.	Semi-volatile compounds	Non-volatile compounds. "Old" contamination
CONTAMINATION PHASE	Dissolved or gaseous contaminant LNAPL	Adsorbed contaminant	DNAPL NAPL thickness < 1 cm and density very close to 1
(*)The pollutant volatility is determined by the vapour pressure, Henry's Law Coefficient, its composition and its boiling point.			
CONTAMINATION DISTRIBUTION			
PLUME EXTENSION	Small-medium size	Medium size	Large
POLLUTANT LOCATION	In unsaturated soil, capillary fringe areas and in saturated area surface portions	In shallow aquifers	In groundwater at > 7-10 m of depth
SUBSOIL CHARACTERISTICS			
LITHOSTRATIGRAPHY	Even soil with medium-fine particle size (sandy-loamy, loamy, loamy-clayey)	Fairly uneven soil with sandy particle size	Very organic soil with coarse particle size with a very high level of humidity, fissured substrate and layered soil.

PARAMETER	**VERY EFFECTIVE**	**MODERATELY EFFECTIVE**	**INEFFECTIVE**
CONTAMINATION CHARACTERISTICS			
HYDRAULIC CONDUCTIVITY (K)	<10E-5 m/s	10E-5÷10E-4 m/s	>10E-4 m/s <10E-7 m/s
OVERALL LEVEL OF HETEROGENEITY	Limited or isotropic	Moderate	High

Table 6-17 MPE technology effectiveness

Lastly, it should be noted that the MPE technology can be applied more effectively than traditional systems (SVE, water draining and treatment) in low-medium permeability conditions. This is due to the fact that:

- An enhanced retrieval action is developed by applying the vacuum system;
- The so-called "superposition" principle applies, due to the vacuum action summed to the piezometric negative pressure, thus generating higher air/water flow values.

Basic system components and main development parameters

The **basic system components** to implement a MPE intervention comprise:

- An extraction network comprising suitably slotted vertical wells in the unsaturated and saturated area;
- A monitoring piezometers network;
- Multiphase flow suction blades (slurp tubes, as per the TPE configuration) tightly connected to the well head and usually adjustable in height;
- Electric or pneumatic submerged pumps (as per the DPE configuration)
- One fan or vacuum pump;
- Multiphase flow water/gas separator;
- Water/oil separator (in case of supernatant product);
- Extracted vapour treatment unit;
- A drained groundwater treatment unit;
- Interconnecting networks;
- Piping and related instruments;
- Electric control panel.

The main parameters to consider when developing an MPE system are described in the following **Table** 6-18. Concerning the characteristics of the extraction wells, the reference standards were mainly drafted by ASTM; AWWA and U.S: EPA.

PARAMETER	MOST COMMON RANGE OF VALUES
Vertical extraction well diameter (‘’)	4-8
Monitoring piezometer diameter (‘’)	4-6
Window length and its positioning (m)	Based on the contamination depth and thickness
Affected area (m)	2-8
Extraction capacity (m3/h)	10-100
Vacuum generated (mmHg)	Low (approx. 100-300) High (approx. 300-650)

Table 6-18 MPE system parameters

The **main configurations that can be adopted** are the following:

- vertical well clusters distributed within the source area;
- similar to barrier wells for hydraulic containment purposes (in case of low transmissivity aquifers).

Technology application pros and cons

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
DEGREE OF DEVELOPMENT, RELIABILITY AND DIFFUSION	🙂	Reliable and tested technique. Relatively simple and quick to configure, with minimum subsoil disturbance. It allows obtaining hydraulic confinement. Contaminant concentration abatements higher than 95% can be achieved. Limited “rebound” effect, thanks to the elimination of the LNAPL/air/water phases (i.e. the potential contamination release sources).
	😐	It requires complete control over the groundwater flow direction, to prevent the risk of pollution diffusion.

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
APPLICABILITY BASED ON THE TYPE OF CONTAMINANT	🙂	Applicable to volatile pollutants, and to petrol-based hydrocarbons in particular. Suitable to recover LNAPL.
	🙁	Unsuitable to treat non-volatile pollutants and DNAPL. Unsuitable for supernatant product thickness < 1 cm.
APPLICABILITY BASED ON THE SUBSOIL CHARACTERISTICS	🙂	Applicable in several environmental contexts (unsaturated area, capillary fringe and saturated area). Suitable for even or slightly uneven soil with medium-fine particle size and medium-low permeability (not lower than 10^{-7} m/s).
	🙁	Not suitable to uneven soil with coarse particle size, high permeability, high content of organic matter and high level of humidity. Unsuitable to treat groundwater located at >7-10 m from the ground level. Its effectiveness is strongly affected by frequent water table oscillations.
APPLICABILITY BASED ON THE SITE CHARACTERISTICS	😐	The limited range of action of each injection point may require the construction of a significant quantity of injection wells to achieve satisfying results. It can be used to treat even the subsoil under existing buildings.
REMEDIATION TIMES	😐	Relatively fast in optimal conditions.
INTERVENTION COSTS	😐	Extracted vapour/water treatment costs can be considerable. Numerous extraction points may be required, with consequent cost increase.
COMPATIBILITY WITH OTHER TECHNOLOGIES	-	This technology allows replacing traditional draining/treatment/product recovery/venting techniques in low-medium permeability conditions and in less even soils.

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
ENVIRONMENTAL SUSTAINABILITY	😐	Extracted vapour/water treatment systems required.

🙂 Good 😐 Medium 🙁 Low

Table 6-19 MPE pros and cons

Related technologies

The MPE remediation technology (in DPE, TPE and Bioslurping configuration) is just one of the many possible variants of the flexible multiphase extraction technology.

The **main variants** are:

- ***Pump-skimming***: in case of supernatant product, the groundwater is drained, generating a dragging cone. Products in separated phase accumulate in the cone centre by gravity, facilitating their surface recovery;
- ***Hydraulic containment:*** it comprises clusters of extraction wells, generally placed perpendicularly to the groundwater flow direction, that intercept the plume and prevent its circulation off-site;
- ***Trench drains***: place perpendicularly to the groundwater flow direction, for the entire length of the contamination source; they are employed in limited depth conditions. They generally comprise a trench of set of drain pipes, and extraction pumps or skimmers (in case of supernatant product).

6.9 Chemical Oxidation

Definition and general criteria

On-site chemical oxidation treatments consist in injecting a mix comprising a suitable oxidising agent into the contaminated matrix, to allow a complete transformation of the organic pollutant into carbon dioxide and water, or its partial transformation into substances with a simpler and more easily degraded molecular structure.

Its most common application is groundwater remediation with direct reagents injection into the aquifer; however, the reagents can also be injected into the unsaturated area.

The most commonly employed oxidising compounds are hydrogen peroxide, ozone, potassium permanganate and sodium, plus other oxidizer (sodium persulphate, peracetic acid, hypochlorites).

This type of technology is often used when biologic treatments do not work correctly, due to a high concentration or changing nature of contaminants in the source area.

Figure 6-13 shows the diagram of the technology described above.

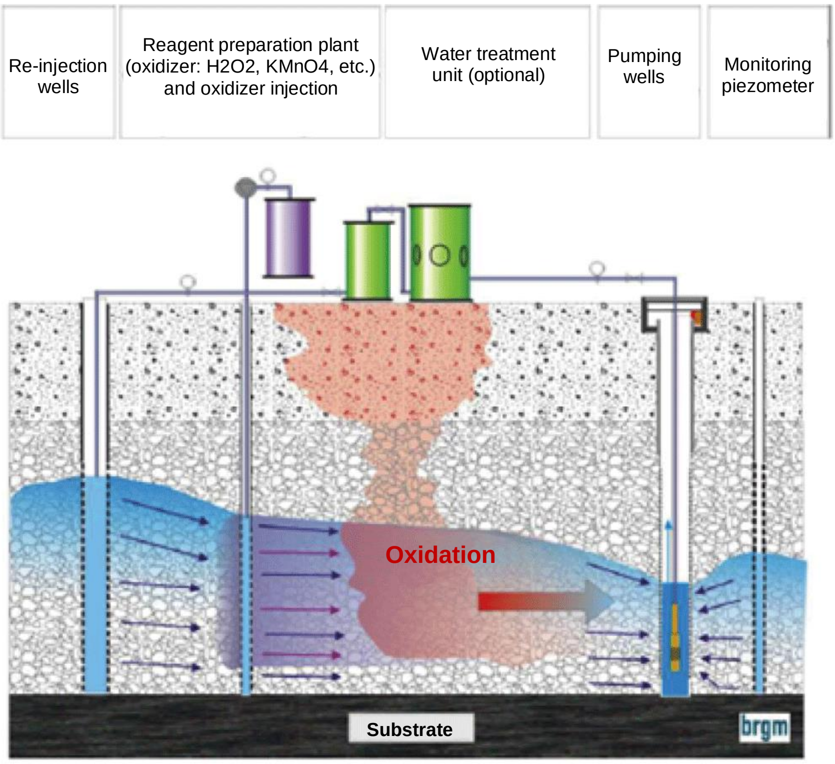


Figure 6-13 Chemical oxidation diagram (Source: Quelles techniques pour quels traitements - Analyse couts-benefices Rapport Final, BRGM, 2010 ©BRGM/RP - 58609-FR – Edited)

Conditions and application limits

Chemical oxidation is particularly suitable and applicable under the following conditions:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Contamination even at high concentration or in case of separated phase (LNAPL);
- Oxidisable contaminants;
- Contamination in the saturated area (also widespread).

SUBSOIL CHARACTERISTICS

- Even lithology;
- Moderately permeable soil;
- Limited concentration of organic matter.

Conversely, **chemical oxidation is not suitable or applicable** when the following conditions occur:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Presence of non-oxidisable contaminants;
- Widespread contamination in the unsaturated area.

SUBSOIL CHARACTERISTICS

- Very variable lithology;
- Soil with fine particle size;
- Permeability lower than 10E-7 m/s;
- Presence of organic matter greater than 20%.

Table 6-20 shows the level of effectiveness of Chemical Oxidation in relation to the environmental conditions listed above.

PARAMETER	VERY EFFECTIVE	MODERATELY EFFECTIVE	INEFFECTIVE
CONTAMINATION CHARACTERISTICS			
TYPE OF CONTAMINANT	VOC, SVOC, HC, BTEX, IPA, PCB, chlorinated compounds		Inorganic compounds
CONTAMINATION DISTRIBUTION			
CONTAMINATED MATRIX	Capillary fringe, saturated soil, groundwater		Unsaturated soil
SUBSOIL CHARACTERISTICS			
LITHOSTRATIGRAPHY	Even soil with big particle size (sand and gravel), even silt		Silt and clay, highly organic soil

PARAMETER	VERY EFFECTIVE	MODERATELY EFFECTIVE	INEFFECTIVE
CONTAMINATION CHARACTERISTICS			
HYDRAULIC CONDUCTIVITY (K)	>10E-6 m/s		<10E-7 m/s
OVERALL LEVEL OF HETEROGENEITY	Limited or isotropic		High

Table 6-20 Chemical Oxidation effectiveness

Basic system components and main development parameters

The reagents application methods are the following:

- Injection into some monitoring wells already installed on site;
- Direct injection into the soil with a Geoprobe system and direct-push technology;
- Injection by building dedicated injection wells, usually with a smaller diameter than monitoring wells. These wells are never used for water sampling purposes.

As indicated above, oxidizers are mainly used for groundwater contaminations.

The **basic system components** to implement a chemical oxidation intervention in the saturated area comprise:

- One or more injection wells (already present or newly-built);
- One or more monitoring wells;
- One high-pressure pump;
- the related *interconnecting* networks;

if the compounds used generated gaseous intermediate products (e.g. when hydrogen peroxide is injected), it may be necessary to install wells with gas extraction systems connected to an air treatment system.

If ozone is used, any air sparge wells already installed may be used.

Furthermore, as shown in the image below, treated water may be re-injected upstream of the hydraulic system, to perform several treatment cycles.

The success of a chemical oxidation intervention mainly depends on the effective interaction between the reagent injected and the contaminant, and the effective introduction of oxidizers in the entire area to be treated. Both factors are strongly affected by site-specific conditions.

For its correct sizing, performing pilot on-field tests is essential to estimate, among other parameter:

- The injection well range of action;
- The oxidizer's stability;

- Possible by-products to be monitored;
- Minimum quantity of reagents to inject.

Technology application pros and cons

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
DEGREE OF DEVELOPMENT, RELIABILITY AND DIFFUSION	🙂	Easy to install and reduced logistic disturbance.
	😐	Quick abatement; however, the intervention's success is very dependent on an accurate design phase.
APPLICABILITY BASED ON THE TYPE OF CONTAMINANT	🙂	Applicable to many pollutants categories, even at high concentrations.
	☹	Unsuitable to treat non-oxidisable pollutants.
APPLICABILITY BASED ON THE SUBSOIL CHARACTERISTICS	🙂	Suitable to even soil with medium-coarse particle size and medium-high permeability.
	☹	Mainly applicable to the saturated area. Not suitable to uneven soil with fine particle size, high content of organic matter and low permeability.
APPLICABILITY BASED ON THE SITE CHARACTERISTICS	🙂	Suitable to treat large areas without interrupting on-site activities. It can be also employed to treat the soil underneath existing buildings, if the aquifer at greater depth than the utilities.
REMEDIATION TIMES	🙂	Relatively fast in optimal conditions.
INTERVENTION COSTS	😐	In case of high concentrations, costs may be significant. For some reagents, the intervention needs to be paired with vapour extraction systems.

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
COMPATIBILITY WITH OTHER TECHNOLOGIES	🙂	Not compatible with Bioremediation interventions (usually carried out at a later time).
ENVIRONMENTAL SUSTAINABILITY	😐	It eliminates the risks and costs related to transporting large quantities of polluted soil. Groundwater chemism alteration, with the risk of by-product generation. Partial or total distribution of the micro-organisms naturally present.

🙂 Good 😐 Medium ☹ Low

Table 6-21 Chemical Oxidation pros and cons

Related technologies

The treatment with oxidizers is mainly followed by ***Bioremediation*** because it is hardly able to bring the concentrations below the reference CSC. Usually, chemical oxidation is applied to reduce the dissolved phase concentrations, after removing a free phase, and before a bioremediation treatment.

6.10 Soil Flushing (SF)

Definition and general criteria

The **SF** technology consists in treating the organic and inorganic compounds, both in the unsaturated and saturated areas, on even soil with medium-high permeability (from sandy-loamy to gravelly) on site, by removing them through a chemically-implemented flushing.

The operating principle, shown in **Figure 6-14**, is based on soil flushing via water injection or seepage (often with the addition of additives to help remove the contaminants, such as surfactants, chelating agents, solvents) in a series of wells/trenches located upstream of the contaminated area. This flushing generates two different mechanisms:

- Contaminant extraction or suspension;
- Dragging of the fine fraction (<2 mm), where the contamination is often bonded.

Apart from improving the solubilization, this system also affects the speed of chemical-physical reactions, such as desorption-adsorption, biodegradation, complexing and precipitation.

Following the leaching action, the watery fluid is removed downstream of the treated area, in outlet shafts, trenches or drains, and then treated before being re-injected on site or discharged into the sewage system/surface watercourses. Sometimes, in addition to systems such as the Pump&Treat, it can be used together with physical barrier systems (plastic diaphragms, jet grouting, etc.).

The **main additives** used are:

- Surfactants, such as detergents, emulsifiers and foams: used in particular to remove hydrophobic contaminants (petrol-based products, aromatic solvents, chlorinated products, PCBS, chlorinated pesticides and semi-volatile organic compounds);
- Acid solutions: used to remove metal molecules and certain organic compounds (e.g. ethers);
- Basic solutions: used to remove organic pollutants (e.g. NAPL and phenols) and certain heavy metals (e.g. tin, zinc and lead);
- Complexing agents: used to remove heavy metals;
- Co-solvents: to remove organic compounds with a low solubility.

Once the contaminants have been removed, the agents used to remove them can be recycled (Sims R.C et al., 1984).

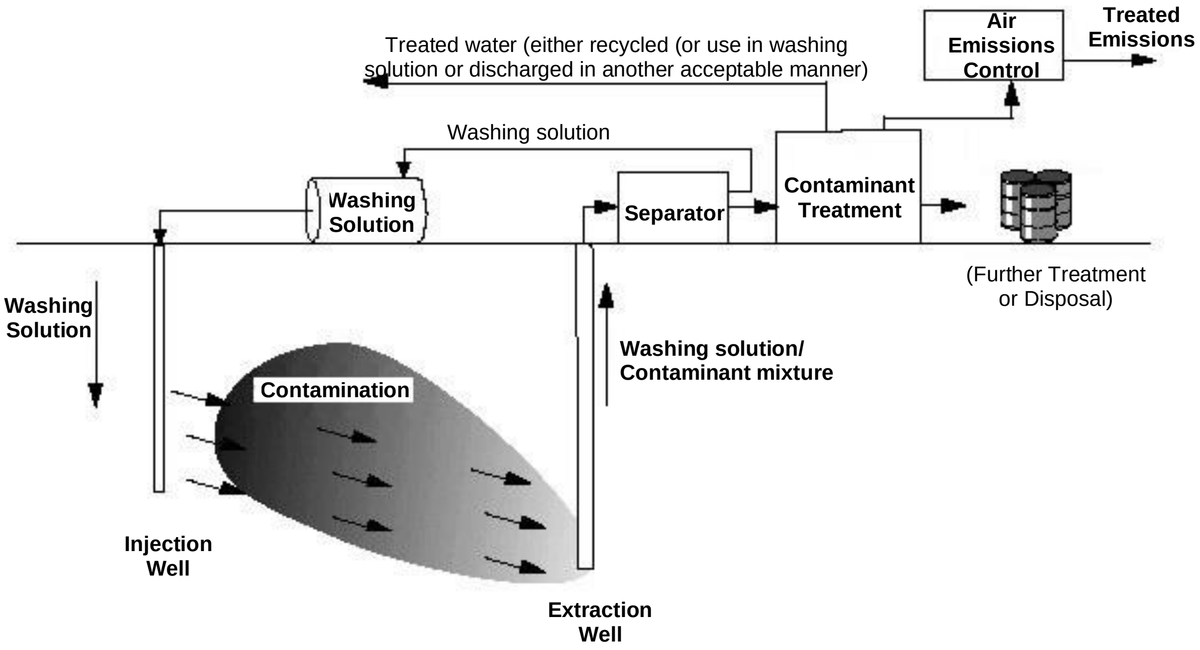


Figure 6-14 Soil Flushing diagram (source: EPA,1996)

Conditions and application limits

SF is particularly suitable and applicable under the following conditions:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Presence of inorganic compounds (metals, cyanide, corrosive substances, radioactive isotopes) and organic compounds (volatile and semi-volatile, PCBS, non-halogenated pesticides, dioxins and furans, cyanide, corrosive substances);
- Possible presence of NAPL;
- Localized and limited contamination with a reduced depth from the ground level.

SUBSOIL CHARACTERISTICS

- Even soil with medium-high permeability (from loamy-sandy to gravelly);
- Soil with limited organic matter content;
- Limited cationic exchange capacity and clayey fraction.

Conversely, **SF is not suitable or applicable** when the following conditions occur:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Presence of poorly water-soluble and highly adsorbable contaminants;
- Widespread and extended contamination located at great depth.

SUBSOIL CHARACTERISTICS

- Uneven soil with medium- low permeability;
- Soil with high organic matter and carbonate content;
- Significant cationic exchange capacity and clayey;
- Presence of underground man-made obstructions.

Table 6-22 shows the level of effectiveness of the SF systems in relation to the environmental conditions listed above (source: Roote, 1997 – edited).

PARAMETER	VERY EFFECTIVE	MODERATELY EFFECTIVE	INEFFECTIVE
CONTAMINATION CHARACTERISTICS			
TYPE OF CONTAMINANT	Inorganic and organic contaminants very soluble in water and poorly adsorbable, with limited vapour pressure values, high density and reduced viscosity	Inorganic and organic contaminants mildly soluble in water, mildly adsorbable, with moderate vapour pressure/density/viscosity values	Inorganic and organic contaminants poorly soluble in water, very adsorbable, with high vapour pressure values and low density
CONTAMINATION PHASE	Contaminant in dissolved phase	NAPL	Contaminant in gaseous phase
CONTAMINATION DISTRIBUTION			
PLUME EXTENSION	Small and localized	Medium size	Widespread and extended
POLLUTANT LOCATION	In unsaturated area/capillary fringe/saturated area at limited depth	In unsaturated area/capillary fringe/saturated area at medium depth	In unsaturated area/capillary fringe/saturated area at great depth Presence of underground man-made structures
SUBSOIL CHARACTERISTICS			
LITHOSTRATIGRAPHY	Even soil with medium-coarse particle size (from sandy-loamy to gravelly) with low organic matter content	Slightly uneven soil, with medium particle size and moderate organic matter content	Even soil with fine particle size and high content of organic matter and carbonates

PARAMETER	VERY EFFECTIVE	MODERATELY EFFECTIVE	INEFFECTIVE
CONTAMINATION CHARACTERISTICS			
			Significant cationic exchange capacity and clayey
HYDRAULIC CONDUCTIVITY (K)	>10E-5 m/s	10E-7÷10E-5 m/s	<10E-7 m/s
OVERALL LEVEL OF HETEROGENEITY	Limited or isotropic	Moderate	High

Table 6-22 Soil Flushing effectiveness

Basic system components and main development parameters

The **basic system components** to implement a SF intervention comprise:

- Additives storage tank and water mixing system;
- Solution injection system, comprising vertical wells or horizontal trenches, injection tunnels and dispersant areas;
- A contaminated flushing liquid recovery system, comprising wells, trenches and drains;
- A system to treat contaminated water before re-injecting it into groundwater, discharging it into the sewage system/surface watercourse or reusing it in the flushing cycle;
- A possible additive recovery system;
- A monitoring piezometers network;
- Interconnecting networks;
- Piping and related instruments;
- Electric control panel.

The **main configurations that can be adopted** to flush the soil are the following:

- If the area to be treated is completely unsaturated, the solvent may be sprayed on the soil directly (spray irrigation) or through trenches;
- If the area to be treated includes also saturated portions, injection wells and extraction shafts can be implemented to recover the contaminated solutions.

Technology application pros and cons

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
DEGREE OF DEVELOPMENT, RELIABILITY AND DIFFUSION	☹	In optimal conditions, the intervention's effectiveness is generally lower than 80%. It is still an experimental technique.
APPLICABILITY BASED ON THE TYPE OF CONTAMINANT	☺	Technique that can be applied to a large number of organic and inorganic compounds, including heavy metals, PCB and radioactive contaminants, both in unsaturated and saturated portions. Applicable also with NAPL present.
	☹	Not suitable to poorly water-soluble and highly adsorbable contaminants
APPLICABILITY BASED ON THE SUBSOIL CHARACTERISTICS	☺	Effective on even soil with medium-coarse particle size and medium-high permeability.
	☹	Not suitable to uneven soil with medium-fine particle size and medium-low permeability, with high organic matter and carbonate content, and significant cationic exchange capacity and clayey fraction. Not feasible at great contamination depth and with widespread pollution.
APPLICABILITY BASED ON THE SITE CHARACTERISTICS	😐	The area must be suitably enclosed. The presence of underground man-made structures may interfere with the flushing action.
REMEDIATION TIMES	☹	Long intervention times, due to the reiteration of several flushing cycles and continuous monitoring.
INTERVENTION COSTS	☹	Generally high costs.

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
COMPATIBILITY WITH OTHER TECHNOLOGIES	🙂	Additional technologies required to recover, remove and treat the drained solution (e.g. geochemical fixation, P&T).
ENVIRONMENTAL SUSTAINABILITY	😐	The use of solvents - e.g. surfactants - may alter the soil chemical-physical characteristics. Possible reduction of the soil porousness, due to the bio-growth. Waste production and drained solution treatment/recycling system required (even for large volumes).

🙂 Good 😐 Medium ☹ Low

Table 6-23 Soil Flushing pros and cons

Related technologies

There are similar remediation techniques that are more effective and reliable and that allow greater control over the process.

Such as ***Soil Washing (SW)***, a (on-site and off-site) remediation technology.

It consists in removing the contaminant from the soil - after previously extracting it from the contaminated area and sifting it to divide coarse and fine fractions that will be treated - by washing it with solvents. This technology is described in **Figure 6-15.**

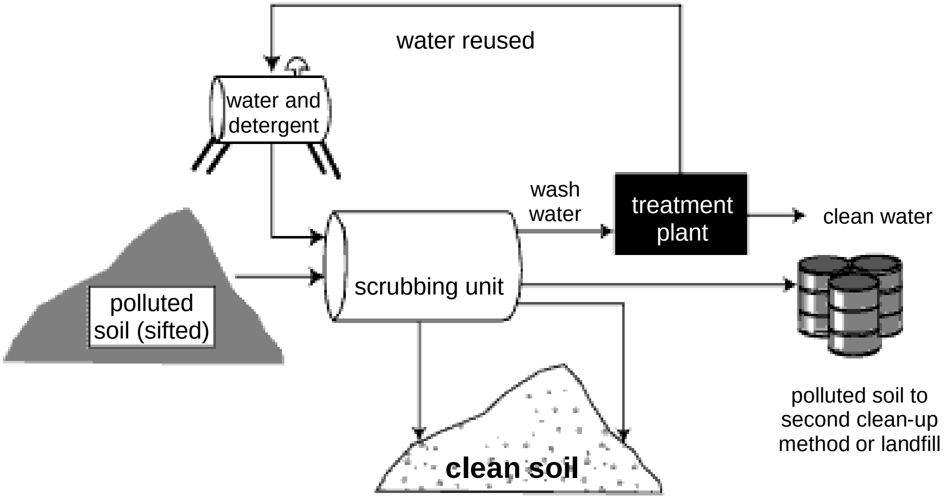


Figure 6-15 Soil Washing diagram (source: EPA)

SW is mainly applied on uneven soil to concentrate the finer fractions, which are generally more polluted. It is effective on petrol-based hydrocarbons, VOCS, SVOCS, halogenated pollutants and on recalcitrant compounds, such as IPA, PCB, dioxins and furans, pesticides and metals/metalloids.

Table 6-24 shows the SW system pros/cons compared to the SF system in a nutshell:

PARAMETER	SW PROS/CONS COMPARED TO SF	
DEGREE OF DEVELOPMENT, RELIABILITY AND DIFFUSION	☺	In optimal conditions, the intervention's effectiveness is generally around 95%. Extensively tried and tested technique.
APPLICABILITY BASED ON THE SITE CHARACTERISTICS (SUBSOIL AND LOGISTICS)	☺	The SW is applicable regardless of the site characteristics, even if it is not very effective in case of fine materials. It is effective both on even and uneven soil of any particle size (although it is more effective on coarse particle sizes). It can be used with any solution, because there is not risk of worsening the natural characteristics of the underlying soil.
REMEDIATION TIMES	☺	The intervention can be faster than SF (although by a few months).
INTERVENTION COSTS	☺	It is more cost-effective than SF; furthermore, non-contaminated coarse-fractions can be reused on site, to reduce topsoil costs.

PARAMETER	SW PROS/CONS COMPARED TO SF	
ENVIRONMENTAL SUSTAINABILITY	☹	It is an off-site technology that generates significant quantities of residues to be treated and disposed of, and significant water volumes. Atmospheric emissions and noise pollution may be relevant.

☺ Good 😐 Medium ☹ Low

Table 6-24 Soil Washing pros and cons

6.11 Soil Vapour Extraction (SVE)

Definition and general criteria

SVE is a remediation technique suitable to treat volatile and semi-volatile organic compounds in even soil with medium-coarse particle size and medium-high permeability, on the unsaturated portion (hardly applicable if the groundwater is at less than 2 m from the ground level).

The operating principle, shown in **Figure** 6-16, is based on the generation of an underground air flow, through the application of a pressure gradient via horizontal trenches or vertical and horizontal wells, followed by the extraction of the unsaturated material.

The volatile compounds released by the soil evaporate until the pores are saturated; the ventilation causes the air to circulate and the renovation of polluted air in the pores. This phenomenon alters the chemical balance between the different phases (air, water, soil); therefore, while passing through the contaminated area, air is "charged" with contaminants, and vapours are recovered by the extraction points and treated on the surface.

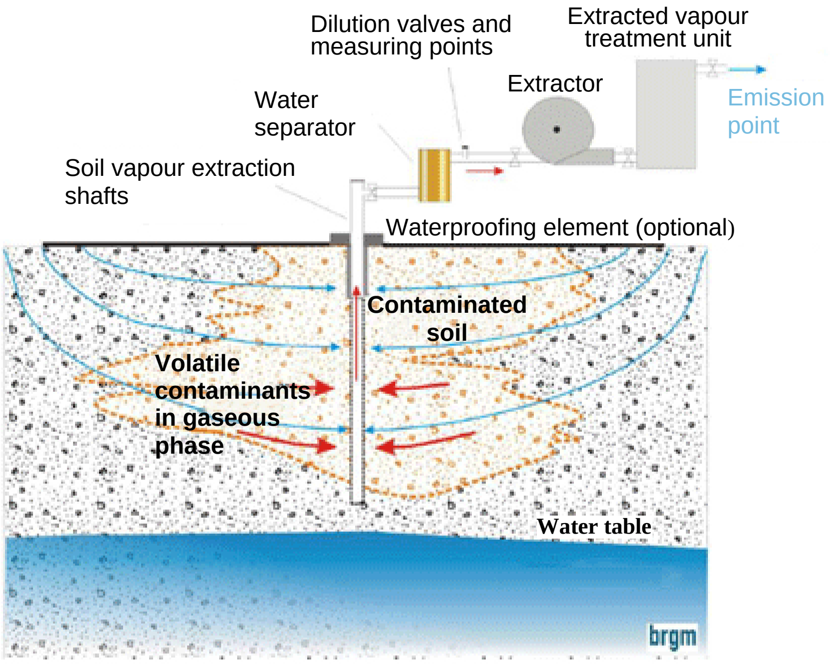


Figure 6-16 SVE Diagram (Source: Quelles techniques pour quels traitements - Analyse couts-benefices Rapport Final, BRGM, 2010 ©BRGM/RP-58609-FR - Edited)

The SVE technology is based on the extraction and recovery of the underground interstitial air, by applying a negative pressure on the unsaturated soil portion.

The negative pressure helps remove the more volatile hydrocarbon fraction, and attracts air from the outside, with consequent oxygenation of the unsaturated soil portion. The solid matrix decontamination process exploits two properties of hydrocarbon compounds: volatility and biodegradability.

The SVE technology is often used in combination with other remediation techniques, such as the Air Sparging, aimed at treating volatile and semi-volatile organic compounds in the saturated portion. The vapour generated (with a high pollutant concentration), after leaving the free groundwater surface, migrate to the unsaturated medium above them, where they are attracted by special vacuum devices, conveyed through activated charcoal filters, and then released into the atmosphere, after being treated, in compliance with current regulations.

Conditions and application limits

The **SVE is particularly suitable** and applicable under the following conditions:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Presence of mainly volatile organic compounds, and, to a lesser extend, semi-volatile organic compounds;
- Recent contamination or, in any case, not too old.

SUBSOIL CHARACTERISTICS

- Presence of uniform soil with sandy-loamy to gravelly particle size, characterized by medium-high permeability;
- Depth of the underlying saturated area > 2-3 m;
- Soil with limited organic matter content and low humidity level.

Conversely, **SVE is not suitable or applicable** when the following conditions occur:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Presence of pollutants with a low volatility degree, low permeability and/or reduced biodegradability;
- Presence of NAPL in low permeability sections;
- Old contamination.

SUBSOIL CHARACTERISTICS

- Uneven soil with low permeability (silt and clay);
- Groundwater level< 2-3 m;
- Presence of high quantities of organic matter and soil humidity.

Table 6-25 shows the level of effectiveness of the SVE systems in relation to the type of organic pollutant (source: USACE, 2002 - edited).

POLLUTANT	TESTED EFFECTIVENESS	POTENTIAL EFFECTIVENESS	UNEXPECTED EFFECTIVENESS
ORGANIC	Halogenated VOC Non-halogenated VOC Non-halogenated SVOC	Halogenated SVOC	Organic cyanide Organic corrosive compounds Dioxins Explosives PCB Dioxins
INORGANIC	-	-	Volatile metals Non-volatile metals Asbestos Inorganic cyanide Radioactive materials Organic corrosive compounds
REACTIVE	-	Oxidizers Reductants	-
VOCS = volatile organic compounds *SVOCS = semi-volatile organic compounds*			

Table 6-25 SVE technology effectiveness

Basic system components and main development parameters

The **basic system components** to implement a SVE intervention comprise:

- One or more vertical or horizontal air extraction wells or trenches;
- One fan or vacuum pump;
- The related interconnecting networks;
- A water separator
- Extracted vapour treatment unit;
- One treatment or storage unit for water resulting from the water separator;
- Piping and related instruments.

The treatment's effectiveness is increased by adding also air insufflation wells to facilitate the air flow induction in the basic operating system.

The main parameters to be considered when developing a SVE system are described in the following **Table** 6-26. Concerning the characteristics of the extraction wells/trenches, the reference standards were mainly drafted by ASTM; AWWA and U.S: EPA.

PARAMETER	MOST COMMON RANGE OF VALUES
Vertical extraction well diameter (‘’)	4-6
Monitoring piezometer diameter (‘’)	¾-2
Pipe diameter in case of horizontal trenches (mm)	101-203
Total trench width (mm)	Pipe diameter+600 mm
Window length (m)	Based on the contamination depth. In any case, to be placed at a safe distance from the groundwater table
Ventilation-affected area (m)	5-20/30
Extraction capacity (m3/h)	17-170
Well head negative pressure (atm)	0.4-0.9

Table 6-26 SVE technology parameters

The **main configurations that can be adopted** are the following:

- Nested wells distributed inside the source area (typical case of AS technology pairing);
- Horizontal trenches (especially in case of *contamination and groundwater very close to the surface)*.

Technology application pros and cons

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
DEGREE OF DEVELOPMENT, RELIABILITY AND DIFFUSION	🙂	Reliable and tested technique. Easy to install and reduced logistic disturbance.
	😐	Contaminant concentration abatements higher than 90% are very hard to achieve.
APPLICABILITY BASED ON THE TYPE OF CONTAMINANT	🙂	Applicable to many volatile and semi-volatile pollutants.
	☹	Not suitable to treat semi-volatile pollutants with reduced aerobic biodegradability and non-volatile contaminants.

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
APPLICABILITY BASED ON THE SUBSOIL CHARACTERISTICS	🙂	Suitable to even soil with medium-coarse particle size and medium-high permeability. Suitable to treat contaminations at great depth (dozens of meters).
	🙁	Suitable only to the unsaturated portion. Not suitable to uneven soil with fine particle size, high content of organic matter and humidity level, and low permeability. Unsuitable with groundwater at < 2-3 m from the ground level.
APPLICABILITY BASED ON THE SITE CHARACTERISTICS	🙂	Suitable to treat large areas without interrupting on-site activities. It can be used to treat even the soil under existing buildings.
REMEDIATION TIMES	🙂	Relatively fast in optimal conditions (from 6 months to 2 years).
INTERVENTION COSTS	😐	Low cost-benefit ratio; however, extracted vapour treatment costs may be considerable.
COMPATIBILITY WITH OTHER TECHNOLOGIES	🙂	Compatible with other remediation methods (e.g. BV, AS/ BS).
ENVIRONMENTAL SUSTAINABILITY	😐	It eliminates the risks and costs related to transporting large quantities of polluted soil. Extracted vapour treatment system required.

🙂 Good 😐 Medium 🙁 Low

Table 6-27 SVE technology pros and cons

Related technologies

Extracting air from the unsaturated area with the SVE system is only one of the possible variants of the flexible venting technology.

The **main variants** are:

- ***Bioventing***: air (or other gases) injection during venting, combined with the nutrient additives, triggers the pollutant biodegradation, which increases the purification performance on the unsaturated area, and reduces the quantity of gaseous pollutants to be treated;
- ***Passive venting***: Vapour transfer is made at different pressure levels (especially when the groundwater level raises) (Card G., 1996), without injecting air or developing a negative pressure;
- ***Dual Phase Extraction, Slurping or Multi Phase Extraction***: it consists in applying a significant negative pressure on the unsaturated portion right above the groundwater surface, aimed at extracting the vapours from the subsoil, the supernatant (in case of floating product) and the dissolved phase. For details, see Paragraph 6.8;
- ***Pneumatic frackling + SVE:*** if the soil to be treated has an insufficient air permeability for the extraction, pneumatic frackling can be used to increase the air flow and accelerate vapour extraction;
- ***On-site Soil Heating + SVE:*** Vapour or hot air are injected through injection wells, thus increasing the contaminants (also semi-volatile) volatilisation and extraction.

Given its widespread use, the following paragraphs include some detailed considerations on Bioventing (BV) technology.

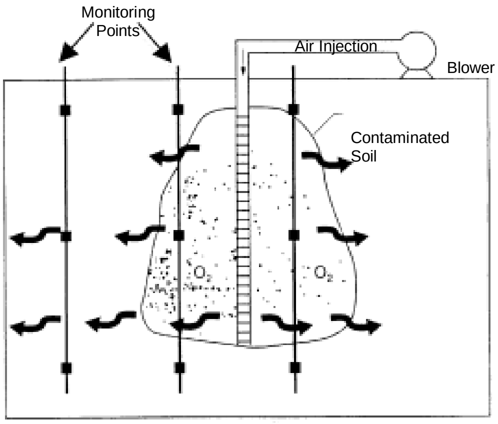


Figure 6-17 BV operating diagram
(Source: AFCEE,1994 / USACE 2002)

As shown in **Figure 6-17,** the mechanism entails the injection of gases (mainly oxygen) into the unsaturated portion at low flow (2÷14 m3/h), in order to nourish indigenous micro-organisms, and lower the groundwater hydrostatic level. Along with the oxygen, other nutrients and co-substrates can be injected or input.

Just like the SVE technology, it CANNOT be applied soil with low permeability and high clay content.

Given its characteristics, its effectiveness is closely linked to two factors (Province of Milan, 2004):

- Contaminants biodegradability;
- Air permeability of the soil to be treated.

Table 6-28 shows the level of effectiveness of the BV system in relation to the type of organic pollutant.

VERY EFFECTIVE	MODERATELY EFFECTIVE/INEFFECTIVE
Petrol-based compounds and hydrocarbons (gasoline, fuel oil, lubricant oil, petrol, BTEX) Halogenated organic compounds (vinyl chloride, trichloroethylene)	Double-ring aromatic compounds (e.g. naphthalene)

Table 6-28 BV effectiveness

Despite the fact that the benefits generated by the joint use of the SVE and BV are significantly higher than their individual use (usually the SVE technology is applied first, to remove the volatile fraction, and then the BV, to degrade the less-volatile compounds), the BV has more benefits compared to the SVE, as shown in the following **Table** 6-29:

PARAMETER	BENEFITS COMPARED TO SVE	
APPLICABILITY BASED ON THE TYPE OF CONTAMINANT	☺	BV can be applied on poorly-volatile substances (e.g. fuel constituents, both petrol and diesel).
INTERVENTION COSTS	☺	BV is more cost-effective, because the extracted vapour treatment may not be required.
SYSTEM CHARACTERISTICS	☺	BV employs significantly lower air flows.

Table 6-29 BV pros

6.12 Soil Solidification/Stabilization

Definition and general criteria

The technology in question is the result of the interaction of soil geotechnical consolidation technology and soil inertization usually employed in the environmental preservation field for contaminated soils and waste. It is generally known as **"deep soil mixing".** The treatment has the following purposes:

- Reducing the surface of the material exposed to the contact with rainwater or percolation;
- Reducing the material permeability to limit seepage;
- Reducing the contaminant's solubility following the formation of precipitates;
- Enhancing the formation of chemical bonds between the contaminants in the material to be treated and the reagents used to treat them.

Generally, the process comprises **two steps**:

1. Step1 - stabilization: transformation of toxic compounds into compounds with a very low solubility (and therefore more stable from a chemical standpoint) through chemical reactions. Stabilization does not necessarily improve the physical and mechanical characteristics of the material treated; in general, it retains its initial physical form. However, the contaminant's toxicity or mobility are reduced, thanks to chemical immobilization processes;
2. Step 2 - solidification: entrapment of the toxic compounds into a solid mass, to make the contaminated material more stable from a physical and dimensional standpoint. This process does not necessarily entail chemical reactions between the material and the stabilizing agent.

The treatment is performed by entrapping the contaminants into a solid matrix physically, or chemically, to reduce their solubility, mobility and toxicity. The immobilization mechanisms may vary: adsorption or complexing, precipitation, ionic exchange, solid solution formation and incorporation in the crystalline structure. It is mainly applicable to inorganic contaminants and waste, also in case of medium-fine materials.

This method is applied on the material on site, with specific machinery, similar to those usually employed for soil geotechnical consolidation. Drilling is carried out with propeller tools to reach the depth of the material to be treated. Then, when the drilling tools rise back up, the inerting mix (concrete, silicate, thermoplastic blends or polymers) is injected and mixed with the soil to be treated. An inerting mix forced (high-pressure, such as "jet grouting") injection tool can be used instead of the propeller tool, for a more penetrating mixing action with the contaminated soil, thanks to the break-up action promoted by high pressure. In order to be certain that the entire volume of contaminated soil has been treated, drilling is overlapped, at variable distances, based on the machine potential and on the site-specific range of action.

Because this technology immobilizes the contaminants, rather than removing or degrading them, it is often considered a permanent securing technology, rather than a remediation technique. As stated above, it may also be applied to waste.

The operating diagram is shown in **Figure 6-18.**

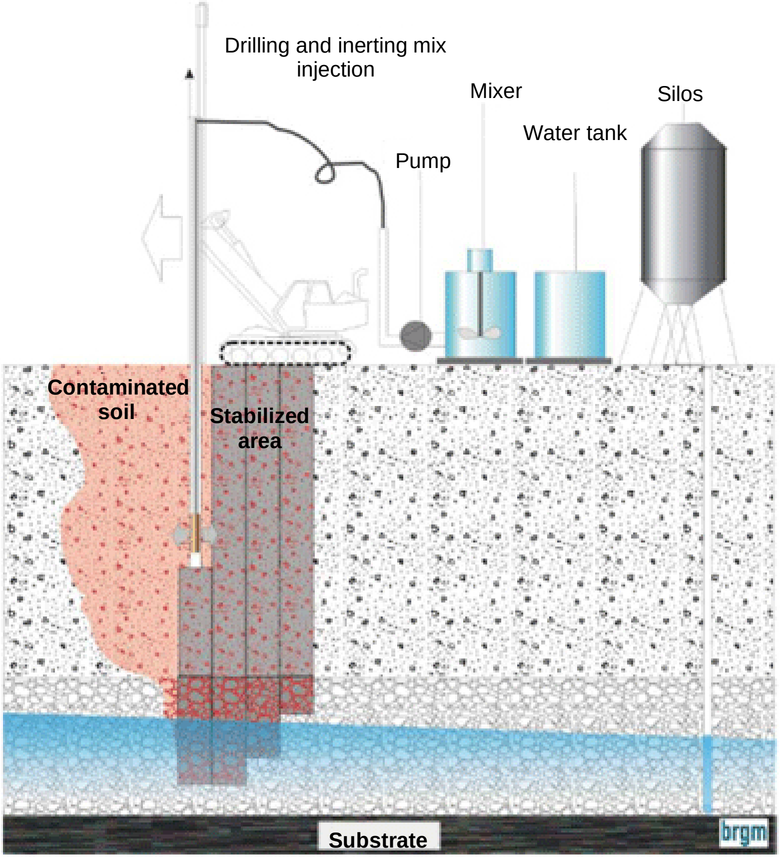


Figure 6-18 Solidification and Stabilization diagram (Source: Quelles techniques pour quels traitements - Analyse couts-benefices Rapport Final, BRGM, 2010 ©BRGM/RP-58609-FR - Edited)

Conditions and application limits

Solidification/stabilization is suitable and applicable under the following conditions:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Presence of inorganic compounds;
- the application to organic compounds should not be excluded, even if with limited effectiveness.
- This technology may also be applied to waste (e.g. sludge), in addition to contaminated soil.
- On average, contamination at depths < 40-45 m from the ground level.

SUBSOIL CHARACTERISTICS

- Presence of granular and loamy / clayey dissolved soil;
- It is preferable that the contaminated soil is located in an unsaturated area;

Conversely, **stabilization/solidification is not suitable or applicable** when the following conditions occur:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Presence of organic pollutants only;
- Very deep contamination.

SUBSOIL CHARACTERISTICS

- Saturated soil: the presence of groundwater may cause leaching of the injected mixtures and related contaminants, with potential groundwater contamination;
- Subsoil contamination with high content of erratic boulders or very consistent surroundings (e.g. rocks).

Table 6-30 shows the level of effectiveness of Solidification/Stabilization systems in relation to the environmental conditions listed above.

PARAMETER	VERY EFFECTIVE	MODERATELY EFFECTIVE	INEFFECTIVE
CONTAMINATION CHARACTERISTICS			
TYPE OF CONTAMINANT	Inorganic compounds, soil and waste	Applicable also to certain organic compounds, albeit less appropriate	Volatile organic compounds

PARAMETER	**VERY EFFECTIVE**	**MODERATELY EFFECTIVE**	**INEFFECTIVE**
CONTAMINATION CHARACTERISTICS			
CONTAMINATION PHASE	Free product, dissolved or adsorbed contaminant		Gaseous phase
CONTAMINATION DISTRIBUTION			
PLUME EXTENSION	Small in the unsaturated area	Moderate in the unsaturated area	Widespread in the unsaturated and saturated area
POLLUTANT LOCATION	Near the ground level, at 0-20 m of depth	Medium deep soil, up to 40-45 m	Deep soil, beyond 40-45 of depth
SUBSOIL CHARACTERISTICS			
LITHOSTRATIGRAPHY	Dissolved soil with big particle size (sand and gravel), or fine particle size (loamy-clayey)	-	-
HYDRAULIC CONDUCTIVITY (K)	10E-4 m/s ÷10E-5 m/s	-	-
OVERALL LEVEL OF HETEROGENEITY	Limited or isotropic	Moderate	High, presence of very compact soil and rocks

Table 6-30 Solidification/Stabilization effectiveness

Basic system components and main development parameters

The **basic system components** to implement a Solidification/Stabilization intervention comprise:

- A drilling and injecting machine for the hydraulic binder mixtures, such as those employed in geotechnical soil consolidation (jet grouting);
- Silos to store water, additives and hydraulic binders;
- Binders mixing and injection mix preparation system;
- Compressed air supply compressor;
- High-pressure pump;
- The related *interconnecting* networks.

The main parameters to consider when applying the Solidification/Stabilization technology are described in the following **Table** 6-31.

PARAMETER	MOST COMMON RANGE OF VALUES
Reachable treatment depth (m from ground level)	30-45
Diameter of the treated material columns (m)	0.4-1.0
Dry hydraulic binder percentage with respect to the dry soil to be treated (%)	15-30
Injection pressure with jet grouting technology (MPa)	30-50
(source: P. Berbenni, C. Di Toro, 2003.)	

Table 6-31 Solidification/Stabilization parameters

Technology application pros and cons

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
DEGREE OF DEVELOPMENT, RELIABILITY AND DIFFUSION	🙁	Although this technology has been applied for quite some time in the geotechnical field in a reliable and tested manner, its application in the environmental field is quite limited. This technology is mainly used abroad (USA)
	😐	It is hard to monitor the technology's correct application (to be sure that the entire contaminated soil has been treated), and its long-term duration in case of freeze/thaw cycles, acid precipitations and other subsoil erosive phenomena.
APPLICABILITY BASED ON THE TYPE OF CONTAMINANT	🙂	Applicable to inorganic contaminants.
	🙁	Not suitable to volatile contaminants.

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
APPLICABILITY BASED ON THE SUBSOIL CHARACTERISTICS	🙂	Suitable to dissolved granular and loamy/clayey soil. Applicable up to 30 -45 m of depth from the ground level.
	☹	Applicable only on the unsaturated portion, in order to prevent the mixture and the contaminants from leaching, with consequent worsening of the groundwater quality.
APPLICABILITY BASED ON THE SITE CHARACTERISTICS	😐	Not applicable in limited spaces, due to the dimensions of the drilling machine and supporting equipment. It cannot can be used to treat the soil under existing buildings or structures.
REMEDIATION TIMES	😐	Based on the contamination extension (both in terms of surface and depth). They are basically related to the drilling/injection times. An additional period must be considered at the end of the injections for post-operam monitoring
INTERVENTION COSTS	☹	The overall intervention costs are significantly affected by drilling costs, especially if the jet grouting technology is employed, and if a significant depth from the ground level must be reached.
COMPATIBILITY WITH OTHER TECHNOLOGIES	☹	Not compatible with other technology; once applied, it leads to consolidation and solidification of the subsoil.
ENVIRONMENTAL SUSTAINABILITY	🙂	No excavation or contaminated soil handling required. It eliminates the costs related to transporting large quantities of polluted soil. No impacting systems or equipment required

🙂 Good 😐 Medium ☹ Low

Table 6-32 Solidification/Stabilization technology pros and cons

Related technologies

The solidification/stabilization technology has no related technologies. Worthy of mention is the possibility to inject organic reagent mixtures, instead of inorganic ones (hydraulic binders). The organic reagents with known application purposes are of thermoplastic (e.g. bitumens, polyethylene) or polymeric nature (e.g. urea, formaldehyde), or micro-encapsulated compounds. In any case, the most common applications involve the use of hydraulic binders, while those with organic reagents have a limited development.

Remediation Technologies Ex Situ - Biological Processes

6.13 Landfarming / Biopile

Definition and general criteria

Landfarming and **Biopile** are two ex situ biological remediation techniques to treat unsaturated soil contaminated by organic substances; they can be implemented both on- and ex situ.

Their common **operating treatment** is the stimulation of the biodegradation processes exerted by indigenous micro-organisms that can feed off the hydrocarbon chains and degrade the organic contaminants contained in the soil to be reclaimed.

The effectiveness of a biological soil treatment depends on several factors, such as:

- soil characteristics: microbial population density, pH, water content, temperature, nutrient concentration, texture;
- contaminants characteristics: volatility, chemical structure, concentration and toxicity;
- climate conditions: temperature, rainfall, wind.

The two technology differ from a dimensional and operational standpoint:

- in **Landfarming**, soil is spread on a large surface, and aeration is performed directly by the atmosphere. Bioremediation can be accelerated by mechanically handling the soil at regular intervals to oxygenate it;
- in **Biopile** air is circulated in the soil through pipes with extraction/injection techniques.

Let’s see both techniques in detail.

Landfarming
During a landfarming intervention, the soil, spread out in thin layers (between 0.5 and 1-2 meter thick), is frequently turned with disc grinding machines to promote a close contact between pollutant, biomass, oxygen, nutrients and humidity, thus optimizing the conditions that enhance the bacteria degrading activity. In addition, this type of remediation requires periodical soil irrigation, in order to keep the humidity level constant.

Generally, this intervention consists in the creation of a treatment basin enclosed by retaining walls implanted above the ground level or partially underground; in both cases, the bottom surface has a 1-2% sloping gradient.
Surface run-off water is collected and transported through a drainage tunnel at the bottom of the sandy bed, placed along the basin’s perimeter.
Figure 6-19 shows how the technology described above works.

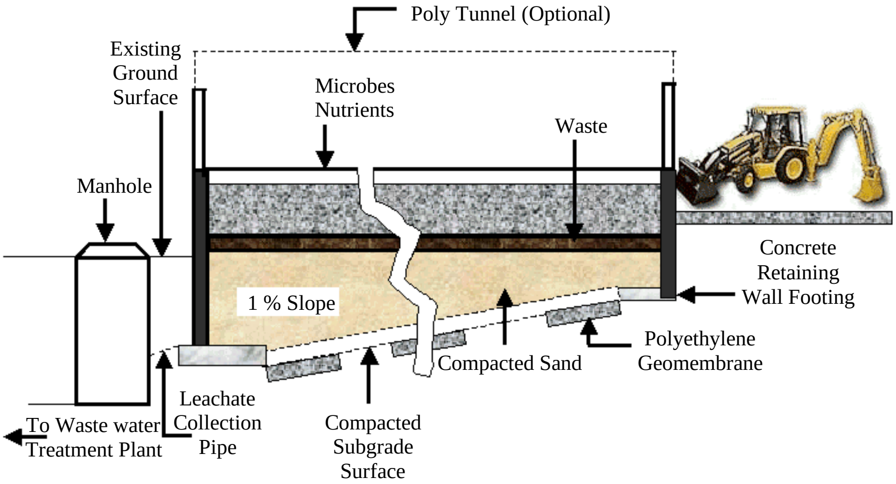


Figure 6-19 Landfarming operating diagram (source: FRTR, EPA)

Biopile

The "Biopile " technology - derived from the Landfarming and shown in **Figure 6-20** - entails the formation of biological reactors obtained by overlaying contaminated soil layers (up to 4-5 meters), interspersed by perforated pipes between one layer and the next, to distribute air and water/nutrient solutions (mostly nitrogen and phosphorous) into the contaminated material and air extraction pipes.
Inside these reactors, the optimal conditions to preserve nutrients, humidity and temperature are maintained artificially, while a ventilation system provides the oxygen necessary to the biodegradation processes.
In order to contain the emission of volatile substances, the Biopile is covered with plastic tarp and vapour is treated with activated charcoal.

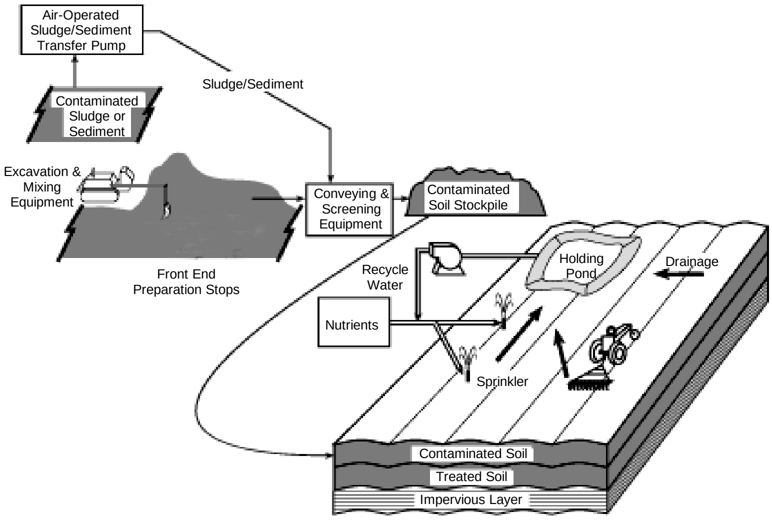


Figure 6-20 Biopile diagram (source: FRTR, EPA)

Conditions and application limits

The **Landfarming and Biopile techniques are particularly suitable** and applicable under the following conditions:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Contamination comprising organic compounds with less than 20 carbon atoms;
- Contamination with a low content of heavy metals;

CHARACTERISTICS OF THE SOIL TO BE TREATED

- Soil with medium-low permeability (sand and gravel);
- Soil with a microbial population density comprised between 10^4 and 10^7 $_{\text{CFU}}$ (Colony-forming units);
- Water content weight of about 12-30%;
- Variable temperature between 10°C and 45°C;
- Nutrients concentration C:A:F=100:10:1.

Conversely, **the Landfarming and Biopile techniques are not suitable or applicable** when the following conditions occur:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Soil contamination with inorganic compounds, Nitrobenzene and, in general, non-biodegradable contaminants;
- Soil with a high content of heavy metals (higher than 2500 mg/kg);
- High hydrocarbon concentrations ≥ 50,000 mg/kg

CHARACTERISTICS OF THE SOIL TO BE TREATED

- Soil with particle size greater than 60 mm;
- Presence of sandy-loamy soil, silt or loamy clay with medium-low permeability, even fairly.

Lastly, the treatment cells must be located in areas:

- With a minimum groundwater depth of 2 m (considering also seasonal changes) from the surface of the waterproof tarp at the bottom of the pile;
- Sufficient to spread the soil to be treated with good technical qualities to support the weight of the piles and the transit of vehicles heavier than 40 ton;
- Easily accessible, flat, located outside floodable areas (in compliance with the requirements set forth by national and regional regulations), in an enclosed area possibly near the excavation site, to minimize handling and transportation costs;
- Far from residential districts.

PARAMETER	VERY EFFECTIVE	MODERATELY EFFECTIVE	INEFFECTIVE
CONTAMINATION CHARACTERISTICS			
TYPE OF CONTAMINANT	Organic compounds with a quantity of carbon atoms < 20 (BTEX, phenols, light IPA, petrol-based hydrocarbons, certain pesticides). Contamination with a low content of heavy metals;	Moderately biodegradable compounds	Inorganic compounds, heavy metals, Nitrobenzene and non-biodegradable contaminants High hydrocarbon concentrations (≥ 50,000 mg/kg)
CONTAMINATION PHASE	Adsorbed and dissolved contaminant		Product in separated phase
CONTAMINATION DISTRIBUTION			
CONTAMINATION EXTENSION	Small	Medium	Large
POLLUTANT LOCATION	Unsaturated soil near the ground level	Unsaturated soil at limited depth	Deep unsaturated soil
CHARACTERISTICS OF THE SOIL TO BE TREATED			
LITHOSTRATIGRAPHY	Even soil with medium-coarse particle size, silt. Soil with a microbial population density comprised between 10^4 and 10^7_{CFU} (Colony-forming units) Water content weight of about 12-30% Variable temperature between 10°C and 45°C Nutrients concentration C:A:F=100:10:1	Fairly fine soil, sandy and gravelly silt, very fissured clay	Silt and clay, highly organic soil, fissured substrate, layered soil and confinement elements. Soil with particle size greater than 60 mm. Not applicable with a minimum groundwater depth of 2 m from the surface of the waterproof tarp at the bottom of the pile.
HYDRAULIC CONDUCTIVITY (K)	>10E-4 m/s	10E-5÷10E-4 m/s	<10E-5 m/s
OVERALL LEVEL OF HETEROGENEITY	Limited		Medium-High

Table 6-33 Land Farming and Biopile Effectiveness

Technology application pros and cons

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
DEGREE OF DEVELOPMENT, RELIABILITY AND DIFFUSION	🙂	Both technologies are easy to design and implement. Systems suitable to manage large volumes of material. Reliable and widespread techniques.
	😐	They require lab and on-site tests to determine the contaminants biodegradability and the nutrients' oxygenation and charge percentages.
APPLICABILITY BASED ON THE TYPE OF CONTAMINANT	🙂	Effective to treat organic contaminants with low biodegradation speed.
	😐	The LF treatment is not suitable to treat VOCs contaminated soil.
	🙁	Not effective on soil with high contamination levels or with inorganic contaminants. The presence of contaminated soil with a high concentration of heavy metals may inhibit microbial growth.
APPLICABILITY BASED ON THE SOIL CHARACTERISTICS	🙂	Soil with medium-coarse particle size, even silt, with medium-high permeability.
	🙁	Highly organic soil with fine particle size, fissured substrate, layered soil and confinement elements. Soil with particle size greater than 60 mm. Not applicable with a minimum groundwater depth of 2 m from the surface of the waterproof tarp at the bottom of the pile.
APPLICABILITY BASED ON THE SITE CHARACTERISTICS	😐	The treatment technologies require large spaces to spread the piles being treated and for the rainfall drainage and collection systems. They require trench stabilization interventions, in case of depths greater than 3 meters.

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
REMEDIATION TIMES	😐	Relatively short treatment times for Biopile s (between 6 months and 2 years) and medium-long term for Landfarming. Treatment times - especially for Landfarming - are significantly affected by climate conditions, so they are hard to establish.
INTERVENTION COSTS	🙂	Limited system construction and management costs.
	☹	They require a leachate collection and treatment system. High maintenance costs.
COMPATIBILITY WITH OTHER TECHNOLOGIES	-	-
ENVIRONMENTAL SUSTAINABILITY	☹	Being ex situ treatments, LF and Biopile technologies require the excavation, handling and transportation of contaminated soil; therefore, this may affect the environment and the workers' health. Volatile compounds tend to migrate into the atmosphere.

🙂 Good 😐 Medium ☹ Low

Table 6-34 Land Farming and Biopile pros and cons

Related technologies

There are no Landfarming/Biopile-related technologies.

6.14 Activate Sludge/Slurry Bioreactor Processes

Definition and general criteria

The **ex situ biological groundwater treatment** is a remediation technique applied to water contaminated by both organic and inorganic compounds.

Biological treatment exploits the technologies based on natural phenomena developed in controlled environments, in order to optimize them. These processes are based on communities of living (anaerobic or aerobic) organisms, which degrade the pollutants present in the water, forming a semi-solid material (sludge) which can then be separated from it by sedimentation.

The most common ex situ biological groundwater treatments are based on two **main configurations**:

- Free culture processes or activated sludge processes;
- Fixed culture processes or bioreactors.

Activated sludge

The activated sludge process is an aerobic biological treatment developed in tanks, where, following a forced ventilation, a series of physical and biological processes are triggered.

After a first chemical oxidation phase, the micro-organisms inside the tanks in the form of suspended colonies form a series of flakes that, through physical processes, incorporate any suspended solids and adsorb any colloidal solids. These substances, after being incorporated into the flake, are metabolised by the micro-organisms through biological processes.

Bioreactors

The bioreactors' operating principle is based on the proliferation of the bacteria responsible for the biological processes on physical media.

Bioreactors are mainly employed to treat volatile and semivolatile organic compounds, and are particularly effective in removing compounds with low molecular weight and highly soluble (e.g. aromatic compounds) with a total organic carbon concentration (TOC) lower than 5,000 mg/l.

This treatment consists in promoting the contact between micro-organisms and the stream to be treated, by making the water flow over a mass of material with a high specific surface, acting as support for the micro-organisms, which form a film of varying thickness. The type of filling material can comprise sandy volcanic rocks, metal coke, siliceous pebbles, compact and plastic materials.

Conditions and application limits

Biological water treatments are particularly suitable and applicable under the following conditions:

CONTAMINATION CHARACTERISTICS

- Presence of organic compounds (preferably treatable in an aerobic environment);

WATER STREAM CHARACTERISTICS

- Water stream with characteristics that do not change much over time.

Conversely, **they are not suitable or applicable** when the following conditions occur:

CONTAMINATION CHARACTERISTICS

- Presence of organic pollutants that form precipitates;
- Plant protection products, dioxins and furans.

WATER STREAM CHARACTERISTICS

- Water stream with variable contaminant concentrations over time.
- Low temperatures.

Basic system components and main operating phases

The **basic system components** to implement a biological water treatment comprise:

ACTIVATED SLUDGE

- Contact unit:
- Air insufflators;
- Air insufflation compressor;
- Sedimentation unit:
- Sludge recirculation system;

BIOREACTORS

- Reactor with inert material support and air insufflators;
- air insufflation compressor,

The activated sludge processes, shown in **Figure 6-21,** is developed in several phases; in the first "contact" phase, by insufflating air into the tank, contact is promoted between the micro-organisms and the pollutants present in the air, in an aerobic environment; in the second step, the sludge is sedimented. During the sedimentation phase, there's also a stabilization phase, with the completion of the organic substance degradation processes, before the sludge is recirculated.

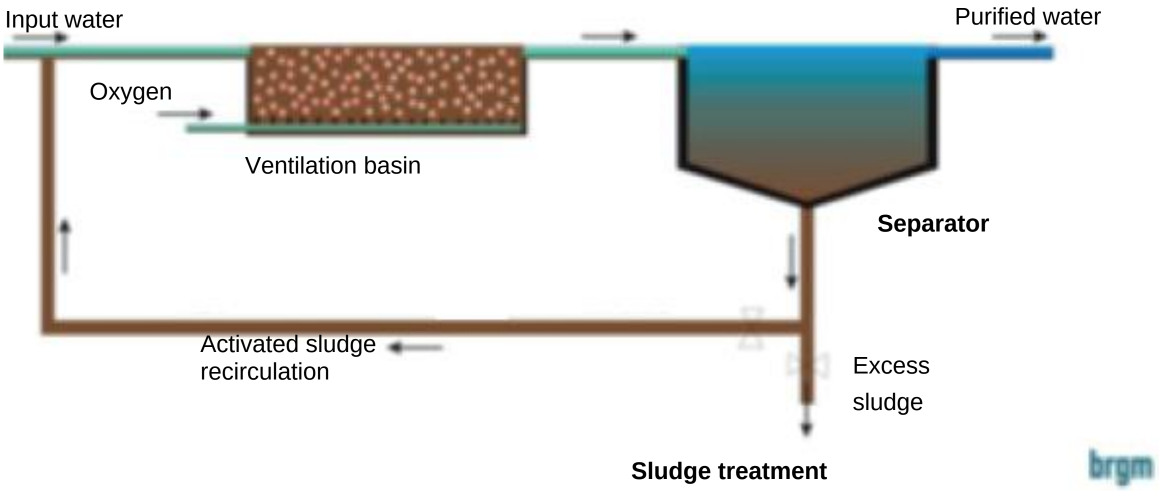


Figure 6-21 Activated sludge technology diagram (Source: Quelles techniques pour quels traitements - Analyse couts-benefices Rapport Final, BRGM, 2010 ©BRGM/RP-58609-FR - Edited)

Concerning bioreactors, shown in **Figure 6-22**, ventilation may be obtained through natural drafts or forced. Air insufflation from the bottom promotes a continuous mixing of the three phases in the reactor: solid phase (i.e. inert particles with the immobilized bacteria), gaseous section (given by the air bubbles) and a liquid phase, given by the solution to be treated. Differently from the activated sludge process, here there is no sludge recirculation and, in general, little sludge is generated.

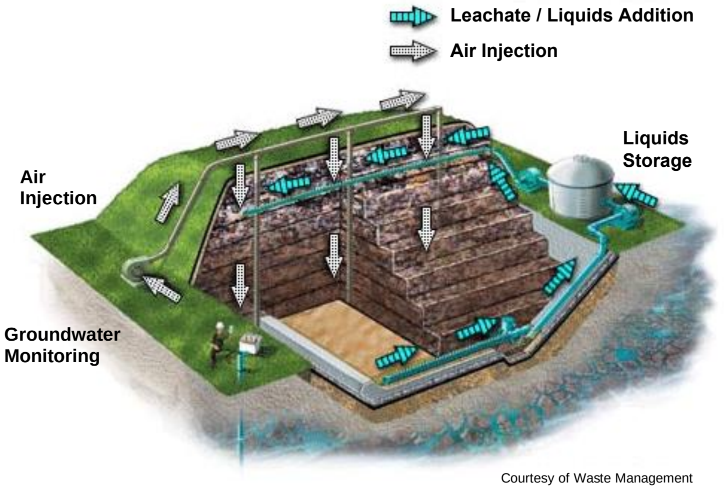


Figure 6-22 Bioreactor diagram (EPA-Waste Management)

Technology application pros and cons

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
DEGREE OF DEVELOPMENT, RELIABILITY AND DIFFUSION	🙂	Reliable and tested technique.
APPLICABILITY BASED ON THE TYPE OF CONTAMINANT	🙂	Possibility of configuring the system based on the contamination type and concentration, on the flow to be treated and on the type of effluent receptor.
APPLICABILITY BASED ON THE SUBSOIL CHARACTERISTICS	🙂	Not affected.
APPLICABILITY BASED ON THE SITE CHARACTERISTICS	😐	Plant solution may require even very large areas, based on the complexity of the plant layout identified, and on the flows to be treated.
REMEDIATION TIMES	🙁	Generally long .
INTERVENTION COSTS	😐	Generally lower costs, compared to chemical-physical processes, in connection with large volumes of treated water. Costs include also the maintenance and monitoring activities, and the management (treatment and disposal) of the sludge generated.
COMPATIBILITY WITH OTHER TECHNOLOGIES	🙂	Compatible with all the remediation methods that entail the draining of groundwater (the system layout may be more or less complex and articulated, based on the drain water volumes, contaminant's type and concentration, and final destination of the treated effluent).
ENVIRONMENTAL SUSTAINABILITY	🙁	This technology can lead to an impoverishment of the groundwater resources unless re-injection into the water table is provided for. The final treatment entails the production of sludge.

🙂 Good 😐 Medium 🙁 Low

Table 6-35 Pros and cons

Related technologies

A special kind of bioreactor is the so-called ***AFB Aerobic Fluidized Bed***, which entails the use of a reactor with a granular bed with biofilm distributed within it.

*Remediation Technologies Ex Situ - Chemical-Physical Processes**

(*) The *Soil Washing* technology is briefly described as related technique in the Soil Flushing datasheet (in-situ chemical-physical process).

6.15 Digging & Dumping

Definition and general criteria

This technology consists in mechanically removing the soil and disposing/treating it off-site, in a suitable authorized plant, after temporarily depositing it to suitably classify it through a Waste Characterization process.

The digging & dumping soil remediation technique is a good technology, from an effectiveness, time and cost standpoint, for those sites where the contamination is located at limited depth, or where excavations are performed within broader local redevelopment interventions.

Furthermore, it is a reliable and tested technique, whose effectiveness can be easily assessed by testing the trench bottom and walls, and it can be applied to any kind of soil (i.e. suitable to any particle size), regardless of the type of pollutant. Since it is a quick and simple technique, it could be considered a preliminary treatment phase, and is therefore compatible with following interventions.

From an environmental sustainability standpoint, however, it is strongly impactful and not very sustainable.

Figure 6-23 shows the layout of a digging site.

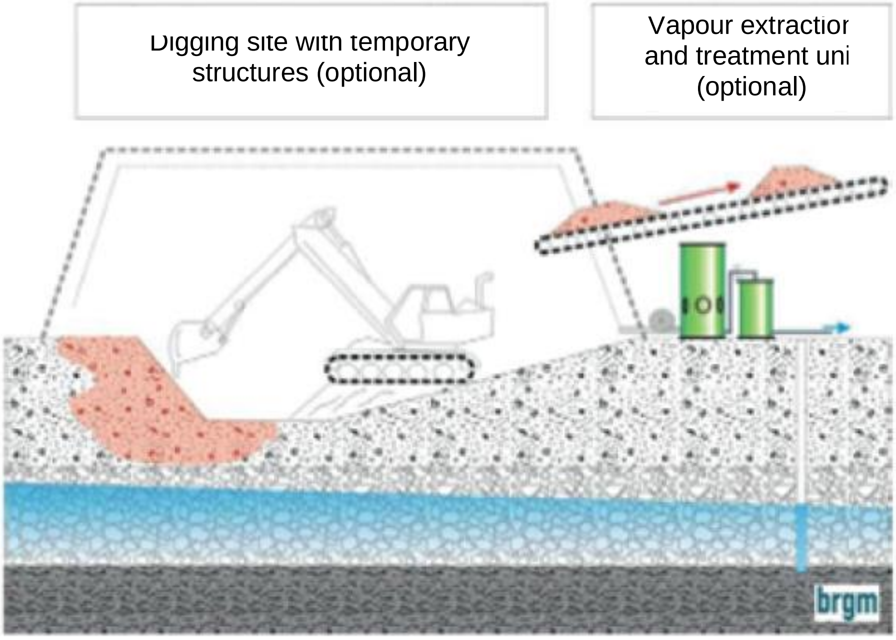


Figure 6-23 Digging & Dumping diagram (Source: Quelles techniques pour quels traitements - Analyse couts-benefices Rapport Final, BRGM, 2010©BRGM/RP-58609-FR - Edited)

Figure 6-24 Digging & Dumping application case (Source: Professor Petrangeli Papini)

Conditions and application limits

The **Digging & Dumping technique is particularly suitable** and applicable under the following conditions:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Contamination comprising both organic and inorganic compounds, also recalcitrant to the use of other remediation technologies and/or in large quantities;
- Presence of contamination hot-spots and/or in areas that are logistically difficult to treat with other remediation techniques;
- Presence of contamination in the unsaturated area, with possible deepening in the saturated portion. In this last case, suitable measures must be implemented to contain and monitor the groundwater;
- Depth of the unsaturated area to be treated comprised between 0 m and 3-5 m (or even deeper, thanks to the use of special excavation face supports).

SUBSOIL CHARACTERISTICS

- Presence of soil characterized by fine to coarse particle size.

Conversely, **the Digging & Dumping technique is not suitable or applicable** when the following conditions occur:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Widespread contamination on large areas;
- Contamination deeper than 3-5 from the ground level, unless suitable temporary structures are built.

SUBSOIL CHARACTERISTICS

- Mainly saturated soil;
- Presence of underground structures that may be damaged during digging and/or buildings near-by, if suitable supporting structures cannot be set in place.

Furthermore, it is unsuitable when the activities carried out on site cannot be stopped or limited due to the digging operations, or when disturbance to the surrounding areas (i.e. noise, dust, transportation vehicle traffic) should be absolutely avoided (after any mitigation actions have been applied).

Table 6-36 shows the degree of applicability of the Digging & Dumping technology, from a cost-effective standpoint.

PARAMETER	APPLICABLE	LIMITED APPLICABILITY	NOT APPLICABLE
CONTAMINATION CHARACTERISTICS			
TYPE OF CONTAMINANT	Any type of inorganic and organic contaminant	-	-
CONTAMINATION PHASE	Any contamination phase	-	-
CONTAMINATION DISTRIBUTION			
CONTAMINATION EXTENSION	Hot-spot	Medium	Large
POLLUTANT LOCATION	Near the ground level, at 3-5 m of depth	Between 3-5 m and 8-9 m of depth, with suitable temporary structures	Beyond 9 m of depth, with suitable temporary structures
SUBSOIL CHARACTERISTICS			
LITHOSTRATIGRAPHY	Fine to coarse soil	-	-
HYDRAULIC CONDUCTIVITY (K)	Impermeable to permeable soil	-	-
OVERALL LEVEL OF HETEROGENEITY	Even to uneven soil	-	-

Table 6-36 Digging & Dumping technique effectiveness

Main operating phases and equipment employed

The removal of contaminated soil is usually carried out according to the following operating phases:

- Construction of any temporary structure to support the excavation faces (e.g. sheet piling);
- Digging with mechanical excavator and preliminary selection, to allow a qualitative separation of manifestly contaminated fractions from seemingly inert ones;
- Storage in piles in temporary deposit areas identified on site;
- Waste characterization through sampling and lab testing;
- Loading of the contaminated soil on trucks, transportation and disposal to an authorized off-site structure;
- Following the test performed on the excavation walls and bottom, the digging site is restored with certified filling material and/or material coming from non-contaminated piles.

Technology application pros and cons

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
DEGREE OF DEVELOPMENT, RELIABILITY AND DIFFUSION	🙂	Reliable and tested technique. Easy to apply (within limited intervention depths).
APPLICABILITY BASED ON THE TYPE OF CONTAMINANT	🙂	Applicable to any type of pollutant. Suitable to hot-sport contaminations in unsaturated soil within 5-6 m from the ground level.
	😐	Its applicability, from a cost-effectiveness standpoint, decreases as the contamination depth increases, due to the need to install excavation face supporting structures. Unsuitable for very widespread contaminations.
APPLICABILITY BASED ON THE SUBSOIL CHARACTERISTICS	🙂	Suitable to soil with any type of particle size and permeability level, mainly in the unsaturated area, with possible deepening in the saturated portion.

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
APPLICABILITY BASED ON THE SITE CHARACTERISTICS	😐	This technique is often affected by site-specific logistic conditions, and it may be incompatible with on-site activities. The existence of underground and/or above-ground structures near the digging site should be thoroughly assessed.
REMEDIATION TIMES	🙂	Significantly faster than other remediation techniques.
INTERVENTION COSTS	😐	Costs are proportional to the volume of soil to be removed (they are also higher in case of temporary and/or risk mitigation structures and measures). The realization of geotechnical tests to correctly size any temporary structures should also be taken into account.
COMPATIBILITY WITH OTHER TECHNOLOGIES	🙂	Compatible with other remediation methods. It often replaces the preliminary treatment phase.
ENVIRONMENTAL SUSTAINABILITY	🙁	It is very impactful (soil handling, noise, dust) and not very sustainable, since the soil is removed and taken off-site to be treated and disposed of. In addition, this technology generally entails the procurement of additional certified material to fill the digging site.

🙂 Good 😐 Medium 🙁 Low

Table 6-37 Digging & Dumping technique pros and cons

Related technologies

A possible replacement technique is the ***Continuous Flight Auger (CFA).*** This solution allows digging to remove contamination hot-spots located at great depth, and is based on the use of a continuous propeller, soldered to a hollow rod which, by penetrating into the soil and breaking it up with a special tool, collects the excavation material on the propeller faces and transports it above ground, further compacting it toward the excavation walls. The main characteristic of the injectors obtained with the CFA technique is the absence of stabilizing sludge or lining pipes, and the drastic reduction of the quantity of soil extracted, which rises along the propeller and outside of the dig. The dig does not require any consolidation and ensures a higher level of safety for workers.

6.16 Ex Situ Chemical-Physical Water Treatment Methods

Definition and general criteria

The ex situ chemical-physical groundwater treatment is a remediation technique applied to water contaminated by both organic and inorganic compounds.

In case of water contaminated by inorganic compounds, the process consists in the following treatment phases combined:

- precipitation - coagulation - flocculation (also called clariflocculation);
- oxidation;
- ionic exchange;
- membrane processes (e.g. reverse osmosis);
- adsorption.

In case of water contaminated by organic compounds, the following technologies may be also be applied:

- forced oxidation (e.g. UV oxidation);
- stripping.

Clariflocculation

Clariflocculation is a treatment process that entails the combination of three phases to remove non-sedimentable suspended solids.

Precipitation is a chemical-physical process where, through a precipitating additive, soluble metals and inorganic compounds are transformed into insoluble metals and inorganic compounds.

The precipitating additives usually employed include:

- Hydroxides, such as caustic soda, hydrated lime, magnesium hydroxide;
- Sulphurs, such as nitrogen sulphur, acid sodium sulphide, iron sulphur or calcium sulphur;
- Carbonates, such as calcium carbonate and sodium carbonate;
- Xanthans (sulfonated organic compounds).

Precipitates are then subjected to a coagulation and flocculation process, whose purpose is promoting the development of colloidal particle flakes, which will then be removed from the water current in the following phases.

The process in question is developed through the following steps:

- Flocculant addition (trivalent iron and/or aluminium salt or polymers);
- Quick mixing;
- Coagulation adjuvants addition (e.g. aluminium or iron derivatives, or lime or polyelectrolytes);
- Slow mixing;

- Sedimentation;
- Filtration;

Oxidation

Oxidation is used to remove metal ions and inorganic constituents. This process is regulated through the use of chemical products that ensure an adequate oxidation. The most used chemical products - specially to remove iron and manganese - are:

- Chlorine;
- Chlorine dioxide;
- Oxygen;
- Ozone;
- Potassium permanganate.

Redox reactions are effective in removing Arsenic and Cyanide, and in reducing metals such as Chromium, Chromium VI and Lead. In this case, the most commonly adopted reagents are:

- Ferrous sulphate;
- Sodium bisulphite.

Adsorption

Adsorption is a process to remove the organic compounds in water, and is particularly effective against poorly soluble compounds, and all those found at high concentrations. Adsorption is a chemical-physical process that exploits the capacity of certain substances (called adsorbents) to trap the aforementioned compounds on their surface.

In general, adsorption mechanisms may be classified in different groups: physical, chemical or electrostatic adsorption.

The most used adsorbing supports are activated charcoal (granular, GAC, or powder, PAC), but even activated alumina, clay, zeolites and synthetic resins may be used.

Stripping

Stripping is a deabsorption process in which the mass is transferred from the liquid phase to the gaseous one. This process can occur in two different ways:

- Diffused aeration: this process involves the insufflation of compressed air, through a perforated or porous support (tube or plate) in the water contained in a tank.
- Stripping tower: the water flow enters the tower from the top and, flowing through it downward, it is intercepted by an air flow exiting the nozzles at the tower's base. To optimize the exchange, stripping towers are usually equipped with inert filling materials (ceramic glass or plastic).

Reverse osmosis

Reverse osmosis is a process that allows the separation of elements such as salts, organic substances, viruses and bacteria, by making a concentrated saline solution pass through a membrane with a pressure higher than the osmotic pressure.

UV oxidation

The UV oxidation process is an advanced oxidation process characterized by the formation of hydroxyl radicals - with a strongly oxidizing nature - in water. This treatment involves the combined action of an oxidizer (ozone or hydrogen peroxide) and UV light.

The process includes one or more reaction chambers (photoreactor) with UV lamps and an oxidizer injection system. The system also includes a unit that destroys any ozone accumulated in the reaction chamber.

Conditions and application limits

CLARIFLOCCULATION

This process, as summarized above, **is particularly suitable** and applicable under the following conditions:

CONTAMINATION CHARACTERISTICS

- Presence of suspended solids, heavy metals and certain pathogens;

CHARACTERISTICS OF THE FLOW TO BE TREATED

- High water volumes to be treated and continuous flow.

Conversely, **Clariflocculation is not suitable or applicable** when the following conditions occur:

CONTAMINATION CHARACTERISTICS

- Presence of organic contaminants;

CHARACTERISTICS OF THE FLOW TO BE TREATED

- Presence of small or intermittent flows.

OXIDATION

The oxidation process **is particularly suitable** and applicable under the following conditions:

CONTAMINATION CHARACTERISTICS

- Presence of metal ions, and Iron and Manganese in particular;

CHARACTERISTICS OF THE FLOW TO BE TREATED

- N/A.

Conversely, **chemical oxidation is not suitable or applicable** when the following conditions occur:

CONTAMINATION CHARACTERISTICS

- Chromium, Chromium VI and Lead, for which reducing compounds should be used;

CHARACTERISTICS OF THE FLOW TO BE TREATED

- N/A.

ADSORPTION

The adsorption process **is particularly suitable** and applicable under the following conditions:

CONTAMINATION CHARACTERISTICS

- Presence of organic compounds characterized by low solubility and high molecular weight, neutral or slightly basic pH;
- In general, they are particularly effective to remove organic solvents (benzene, toluene, nitrobenzene), chlorinated aromatic compounds (PCBS, chlorobenzene, chloronaphthalene), phenols and chlorophenols. Aromatic polycyclic compounds (acetonaphtalene, benzopyrene), hydrocarbons with high molecular weight (diesel, amines, humic substances), volatile and non-volatile chlorinated aliphatic compounds, pesticides and herbicides, trihalomethane and their precursors;
- Generally effective also to remove metals such as Arsenic, Chromium and Mercury.

CHARACTERISTICS OF THE FLOW TO BE TREATED

- Continuous flow.

Conversely, **Adsorption is not suitable or applicable** when the following conditions occur:

CONTAMINATION CHARACTERISTICS

- Presence of organic compounds characterized by high solubility and low molecular weight, strongly acid or low pH, high temperatures;
- In general, they are not very effective to remove ketones, acids and aldehydes, aliphatic hydrocarbons with low molecular weight, starches and sugars, contaminants with a very high molecular weight, organic colloids and compounds with low specific attraction;
- Generally ineffective to remove metals/metalloids, except for Arsenic, Chromium and Mercury.

CHARACTERISTICS OF THE FLOW TO BE TREATED

- Discontinuous flow (in case of prolonged stagnation, there is a risk of bacteria proliferation and nitrite formation) or with pollutant concentration very variable over time or full of suspended o precipitated solids.

STRIPPING

The stripping process **is particularly suitable** and applicable under the following conditions:

CONTAMINATION CHARACTERISTICS

- Presence of volatile compounds (e.g. BTEX, chlorinated solvents).

CHARACTERISTICS OF THE FLOW TO BE TREATED

- N/A.

Conversely, **Stripping is not suitable or applicable** when the following conditions occur:

CONTAMINATION CHARACTERISTICS

- Presence of poorly volatile compounds.

CHARACTERISTICS OF THE FLOW TO BE TREATED

- Flow with suspended solids or with high calcium or magnesium concentrations, that tend to form precipitates.

REVERSE OSMOSIS

The **reverse osmosis process is particularly suitable** and applicable under the following conditions:

CONTAMINATION CHARACTERISTICS

- Presence of dissolved volatile hydrocarbons at low concentrations;

CHARACTERISTICS OF THE FLOW TO BE TREATED

- The treatment is configured as a tertiary technique that requires pre-treatments.

Conversely, **Reverse osmosis suitable or applicable** when the following conditions occur:

CONTAMINATION CHARACTERISTICS

- Very hard water can lead to the formation of encrustations and reduce the system's effectiveness.

CHARACTERISTICS OF THE FLOW TO BE TREATED

- Not sufficiently treated water flows, with presence of biological material, oil and grease;
- Very variable contaminant concentration.

UV OXIDATION

The **UV light oxidation process is particularly suitable** and applicable under the following conditions:

CONTAMINATION CHARACTERISTICS

- Presence of organic compounds.

CHARACTERISTICS OF THE FLOW TO BE TREATED

- The treatment is configured as a tertiary technique that requires pre-treatments.

Conversely, **UV light oxidation is not suitable or applicable** when the following conditions occur:

CONTAMINATION CHARACTERISTICS

- Non-negligible concentrations of heavy metals.

CHARACTERISTICS OF THE FLOW TO BE TREATED

- Not sufficiently treated water flows, with presence of oil and grease.

Basic system components and main development parameters

Clariflocculation

Basic system components for the clariflocculation treatment are the following:

- Equalizing tank;
- Relaunch pump:
- pH monitoring system (binding parameter for the precipitation process);
- Precipitating agents feed system;
- Flocculating agents and adjuvants feed system;
- Clarifier (where the sedimentation process takes place);

The metal removal effectiveness in the solution is strongly affected by a suitable pH monitoring; therefore, the use of specific quantities of reagents is required.

The Clariflocculation operating diagram is shown in **Figure 6-25**.

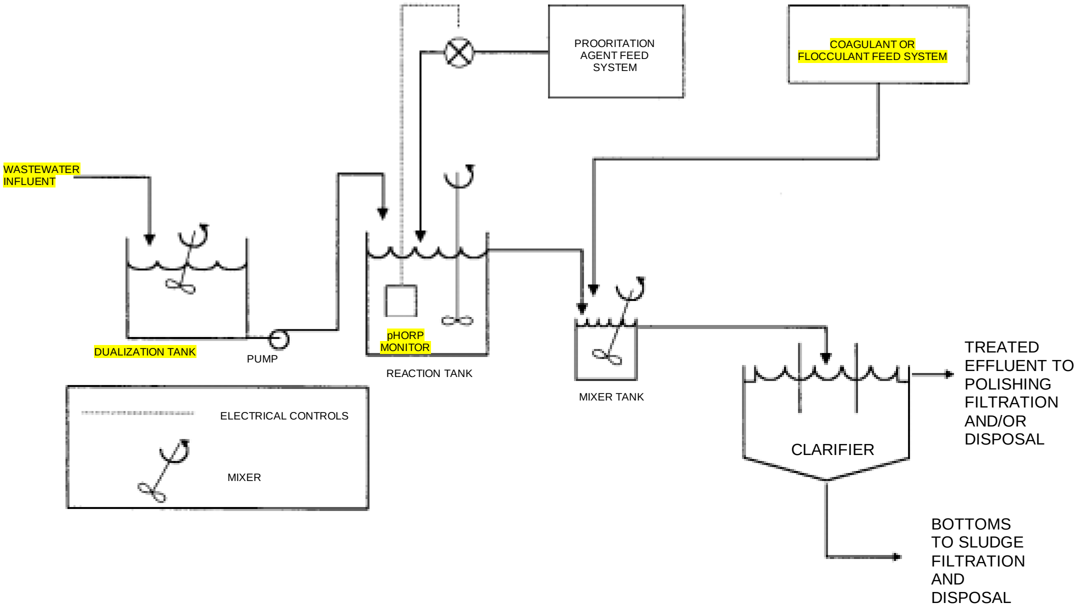


Figure 6-25 Clariflocculation Diagram (Source: FRTR, EPA)

Oxidation

The **basic system components** for the oxidation process shown in **Figure 6-26** are the following:

- Oxidizer (or reducer) preparation system;
- Water mixing system (batch, flash mixer);
- Reaction conditions monitoring equipment (RedOx, pH);
- Reaction tank (reaction duration: 5-10 minutes);
- Precipitate separation structure.

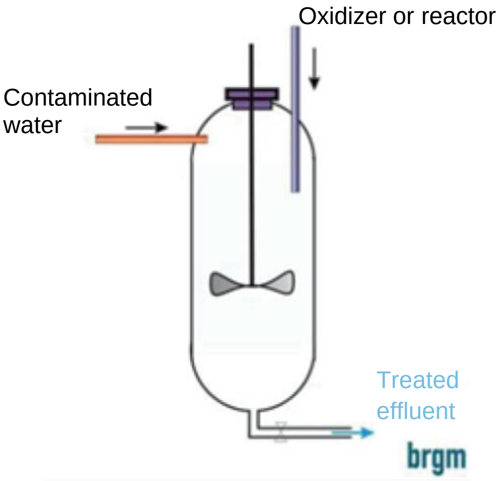


Figure 6-26 Oxidation Diagram (Source: Quelles techniques pour quels traitements - Analyse couts-benefices Rapport Final, BRGM, ©BRGM/RP-58609-FR– Edited)

Adsorption

The adsorption treatment requires the installation of column devices where the adsorbent material is stored. If more than one filtering column needs to be installed, the favourite choice is planning their installation in sets, to have more flexibility during the charcoal change phase.

The **basic components** for the adsorption process shown in **Figure 6-27** are the following:

- Grit separator filter (pre-treatment);
- Injection line on the filter head and output line on the filter bottom;
- Counter-washing lines with related valves;
- Flow meter;
- Filtering column.

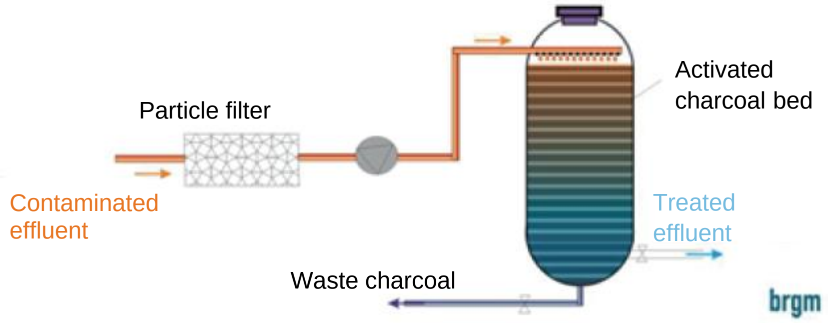


Figure 6-27 Adsorption diagram (source: Quelles techniques pour quels traitements - Analyse couts-benefices Rapport Final, BRGM, 2010©BRGM/RP-58609-FR - Edited)

Stripping

The **basic components** for the stripping process shown in **Figure 6-28** are the following:

- Relaunch pump to lift the water to the stripping column head;
- Stripping column;
- Compressed air insufflation compressor;
- Treated effluent relaunch pump;
- Treatment unit for the gaseous effluent exiting the tower.

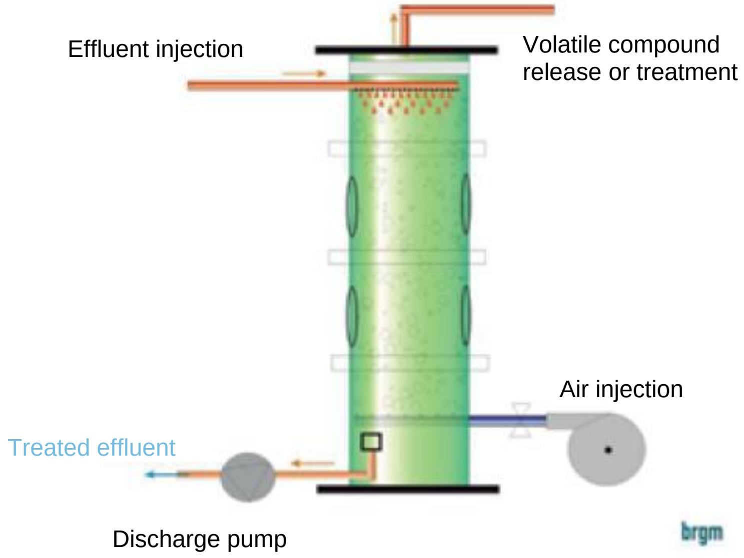


Figure 6-28 Stripping diagram (source: Quelles techniques pour quels traitements - Analyse couts-benefices Rapport Final, BRGM, 2010 ©BRGM/RP-58609-FR - Edited)

Reverse osmosis

Osmotic membranes are formed by polyamide or polytetrafluoroethylene compounds and can be configured with a coil structure or with a cylinder tube-shaped layout.

The **basic components** for the reverse osmosis process shown in **Figure 6-29** are the following:

- Pumping system (pressure higher than the osmotic pressure);
- Membrane system

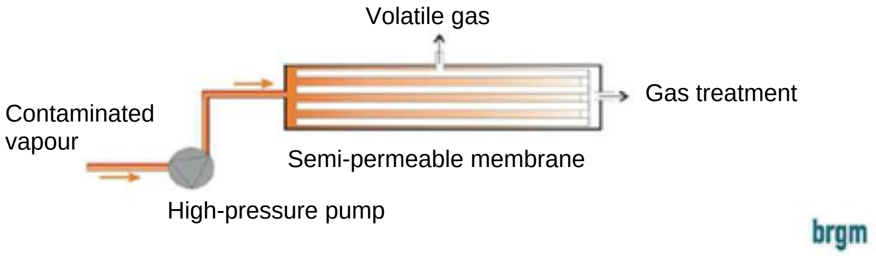


Figure 6-29 Reverse osmosis (Source: Quelles techniques pour quels traitements - Analyse couts-benefices Rapport Final, BRGM, 2010 ©BRGM/RP-58609-FR - Edited)

UV oxidation

The **basic components** for the UV light oxidation process shown in **Figure** 6-30 are the following:

- Ozone generator;
- UV reactor;
- Ozone destroyer;
- Dissolved ozone monitoring device.

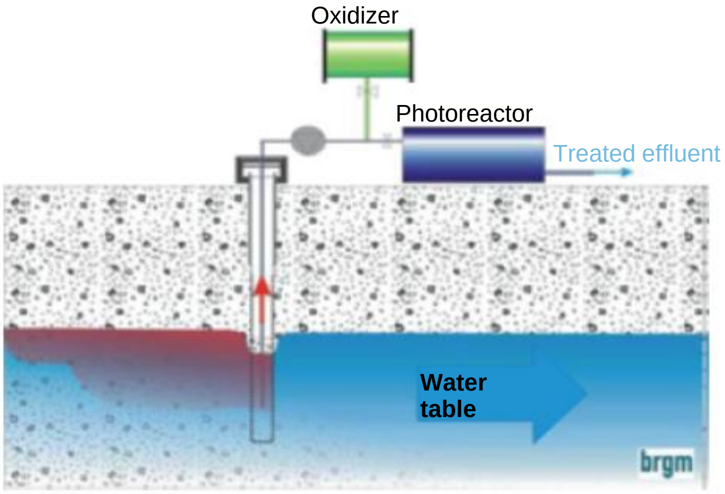


Figure 6-30 UV oxidation diagram (Source: Quelles techniques pour quels traitements - Analyse couts-benefices Rapport Final, BRGM, 2010 ©BRGM/RP-58609-FR - Edited)

Technology application pros and cons

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
DEGREE OF DEVELOPMENT, RELIABILITY AND DIFFUSION	🙂	Reliable and tested techniques, compatible with automatic monitoring.
APPLICABILITY BASED ON THE TYPE OF CONTAMINANT	🙂	Possibility of configuring the system based on the contamination type and concentration, on the flow to be treated and on the type of effluent receptor.
APPLICABILITY BASED ON THE SUBSOIL CHARACTERISTICS	🙂	Not affected.

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
APPLICABILITY BASED ON THE SITE CHARACTERISTICS	😐	Plant solution may require even very large areas, based on the complexity of the plant layout identified, and on the flows to be treated.
REMEDIATION TIMES	☹	Generally long
	🙂	The adsorption technology is generally quick
INTERVENTION COSTS	😐	Generally limited costs, in connection with large volumes of treated water; however, they are strongly affected by the system configuration implemented. Costs include also the maintenance and monitoring activities, and the management (treatment and disposal) of the sludge generated.
COMPATIBILITY WITH OTHER TECHNOLOGIES	🙂	Compatible with all the remediation methods that entail the draining of groundwater (the system layout may be more or less complex and articulated, based on the drain water volumes, contaminant's type and concentration, and final destination of the treated effluent).
ENVIRONMENTAL SUSTAINABILITY	☹	These technologies can lead to an impoverishment of the groundwater resources unless re-injection into the water table is provided for. The final treatment entails the production of sludge.

🙂 Good 😐 Medium ☹ Low

Table 6-38 Pros and cons

Related technologies

No related technologies.

Remediation Technologies in Situ/ex Situ - Heat Processes

6.17 Heat Treatment

Definition and general criteria

Heat treatment (or Thermal Desorption) is an in situ remediation technology for unsaturated soil, aimed at promoting the volatilization of volatile and semi-volatile contaminants (aromatic hydrocarbons, IPA, chlorinated aliphatic hydrocarbons, PCB, chlorobenzene, phenols, aromatic amines, plant protection products, dioxins and furans) through an increase of the soil temperature, followed by their extraction and destruction.

Effective on even soil with medium-coarse particle size and medium-high permeability.

Thermal desorption, diagram in Figure **6-31**, can be applied also ex situ. Differently from incineration, the polluted soil is not destroyed as ash; it preserves a good portion of its physical properties and can be incorporated with other materials or buried.

Soil **heating** can be done by:

- Vapour injections at variable temperatures between 150 and 230°C;
- Microwave irradiation into the soil (temperature up to 560°C);
- Energisation with electromagnetic waves within the radio waves frequency range (temperature between 100 and 300°C);
- Heating with electric resistors and burners (temperature up to 560°C).

Starting from the injection point, the heat spreads in the entire area to be treated, progressively generating the water vaporisation and volatilization of the contaminants contained in the soil, which are then retrieved through extraction points and treated on the surfaced. This process is shown in **Figure 6-31**.

The intervention area must be isolated on the surface with special covers (e.g. capping with HDPE tarps), in order to:

- Minimize heat loss;
- Optimize the extraction of contaminants through retrieval systems;
- Prevent rainwater infiltration that would affect the heat propagation.

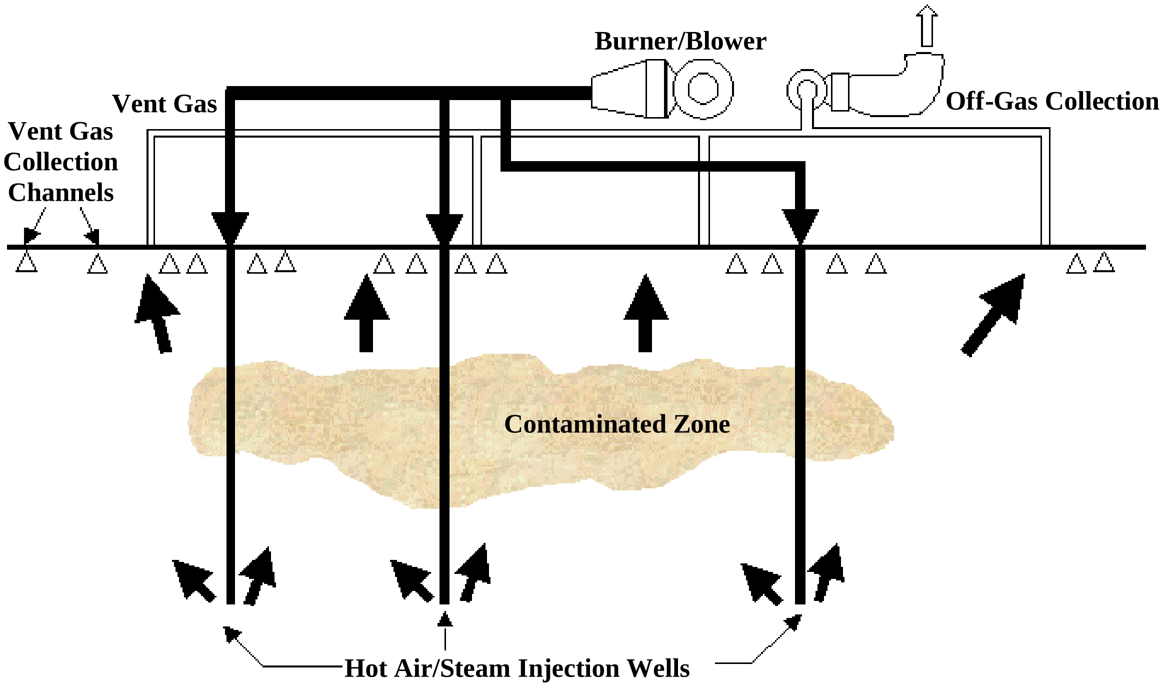


Figure 6-31 In situ heat treatment diagram (source: FRTR, EPA)

Conditions and application limits

Heat treatment is particularly suitable and applicable under the following conditions:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Presence of waste, and carbonaceous-matrix solid substances (plastic, rubber, paper, organic substances, etc.) in particular;
- Presence of volatile and semi-volatile organic contaminants and volatile heavy metals;
- Reduced concentrations of organic phosphorous compounds (limited mg/kg);
- Moderate concentrations of alkaline metals (hundreds of mg/kg);
- Saturated area depth between the ground level and 8-9m.

SUBSOIL CHARACTERISTICS

- Presence of even soil with coarse particle size (sand), or clayey and fairly uneven soil.
- Soil with a low humidity level.

Conversely, **thermal treatment in situ is not suitable or applicable** when the following conditions occur:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Presence only of inorganic contaminants and/or metals;
- High concentrations of organic phosphorous compounds;
- High concentrations of alkaline metals;

SUBSOIL CHARACTERISTICS

- Highly uneven soil with a high content of organic matter;
- Presence of high levels of soil humidity.

Adverse and potential effects

The application of the Heat Treatment technique can cause the following adverse effects in the treated area and immediately near-by, which relevancy depends on the site-specific characteristics:

- Negative effects on the biological communities present in the subsoil, and significant reduction of mesophilic and thermophilic microbial species;
- Soil "withdrawal" effect due to drying and dewatering;
- Alteration of the groundwater geochemical characteristics due to the temperature change;
- Possible damages to underground utilities and infrastructures and/or any structure in the treatment area or near it.

Table 6-39 shows the effectiveness of the heat technologies.

PARAMETER	VERY EFFECTIVE	MODERATELY EFFECTIVE	INEFFECTIVE
CONTAMINATION CHARACTERISTICS			
TYPE OF CONTAMINANT	Presence of waste, and carbonaceous-matrix solid substances (plastic, rubber, paper, organic substances) in particular Volatile and semi-volatile: halogenated and non-halogenated solvents, hydrocarbons and mineral oil, IPA, pentachlorophenol, PCB, pesticides and herbicides, BTEX, chlorinated phenols, petrol, diesel, kerosene, heating and lubricant oil, volatile heavy metals		High concentrations of alkaline metals High concentrations of organic phosphorous compounds
CONTAMINATION PHASE	Dissolved, adsorbed or gaseous contaminant		Free product
CONTAMINATION DISTRIBUTION			
CONTAMINATION EXTENSION	Small	Medium	Large
POLLUTANT LOCATION	Near the ground level	Medium deep soil	Deep soil (>8/9 m)

PARAMETER	**VERY EFFECTIVE**	**MODERATELY EFFECTIVE**	**INEFFECTIVE**
SUBSOIL CHARACTERISTICS			
LITHOSTRATIGRAPHY	Even soil with big particle size (sand), even silt	Sandy and gravelly silt, very fissured clay	Soil with a high content of organic matter and a high level of humidity
HYDRAULIC CONDUCTIVITY (K)	>10E-5 m/s		<10E-5 m/s
OVERALL LEVEL OF HETEROGENEITY	Limited or isotropic	Moderate	High

Table 6-39 Heat treatment technology effectiveness

Basic system components and main development parameters

The **basic system components** to implement an in-situ heat treatment intervention comprise:

- Electrodes or one or more heating wells and related power supply system (vapour generator, microwave generator, radiofrequency generator, electricity generator);
- One or more vertical or horizontal air/vapour extraction wells or trenches;
- One fan or vacuum pump;
- The related *interconnecting* networks;
- A condenser and a water separator;
- Extracted vapour treatment unit;
- One treatment or storage unit for water resulting from the water separator;
- One storage unit for oily compounds resulting from the water separator.

The **basic system components** to implement an in-situ Thermal Desorption intervention comprise:

- Pre-treatment unit:
- Crushing or separation unit;
- Drying unit;
- Crumbling unit;
- Mixing unit (with additives such as calcium, gypsum, etc.);
- Homogenization unit;
- One over: rotary kiln or screw unit or belt unit;
- Material for flow creation and thermal parameters adjustment;
- Gas treatment unit:
- Heat exchanger;
- Dust, humid powder or powder collector filters;

- Post-combustion chamber, burner, catalytic oxidation;
- Condenser, adsorption on activated charcoal;
- Solid and liquid waste (resulting from the treatment) storage.

Technology application pros and cons

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
DEGREE OF DEVELOPMENT, RELIABILITY AND DIFFUSION	☺	Reliable and tested technique. In the "in situ" version, it also reduces the SVE technology application times. Possibility of reaching abatement rates up to 99%.
APPLICABILITY BASED ON THE TYPE OF CONTAMINANT	☺	Applicable to volatile, semi-volatile or even slightly volatile organic compounds (petrol-based hydrocarbons, heavier hydrocarbon fractions, chlorinated solvents, oil, PCB, pesticides, dioxins/furans, IPA).
	☹	Unsuitable to treat non-volatile inorganic pollutants and non-volatile metals.
APPLICABILITY BASED ON THE SUBSOIL CHARACTERISTICS	☺	Suitable to even and uneven soil and/or with low permeability. Applicable also to treat contaminations located within 8-9 m from the ground level.
	☹	Not suitable in case of high quantities of organic matter or soil humidity.
APPLICABILITY BASED ON THE SITE CHARACTERISTICS	☺	In situ, it can be used to treat even the soil under existing buildings, provided that vapour generation is constantly monitored.
	😐	Possible damage to underground utilities and infrastructures and/or structures inside or near the treatment area.
	☹	Ex situ, the process requires soil excavation (it can be done on-site too, but it requires a very large area).

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
REMEDIATION TIMES	🙂	Relatively fast in optimal conditions. In situ, between 3 and 6 months.
INTERVENTION COSTS	☹	Mid-high, depending on the site geological characteristics, and on the contaminant's type and concentration. Extracted vapour treatment costs can be considerable. Costs may increase in case of soil transportation off-site.
COMPATIBILITY WITH OTHER TECHNOLOGIES	🙂	In situ, compatible with other remediation methods (e.g. SVE, MPE).
ENVIRONMENTAL SUSTAINABILITY (IN SITU)	☹	It eliminates the risks and costs related to transporting large quantities of polluted soil. Extracted vapour treatment system required Negative effects on the biological communities present in the soil and subsoil, plant destruction in the treatment area, and significant reduction of mesophilic and thermophilic microbial species Soil "withdrawal" effect due to drying and dewatering Alteration of the groundwater geochemical characteristics due to the temperature change
ENVIRONMENTAL SUSTAINABILITY (EX SITU)	☹	Risks related to transporting large quantities of polluted soil. Extracted vapour treatment system required Process-related CO2 emissions can be significant.

🙂 Good 😐 Medium ☹ Low

Table 6-40 Heat technologies pros and cons

Related technologies

The **main variant** to in-situ heat treatment techniques is in-situ ***Vitrification***.

This technique consists in heating the soil so as to melt it (1200°C - 2000°C) and then quickly cool it down, in order to trigger the vitrification of its constituting elements. This process destroys organic contaminants and immobilizes inorganic contaminants. This technique can be used also for asbestos and radionuclides.

7.0 INNOVATIVE REMEDIATION TECHNIQUES

In these Guidelines, we present some innovative remediation techniques.

It should be noted that the technologies included have reached an on-field application stage, and for which the market or institutions have expressed interest. It does not include those technologies that are still in their early development stage, on which only single academic research results are available.

Micro and Nanotechnologies

Concerning the remediation of contaminated aquifers, ***Nanoremediation*** is emerging as an effective and competitive approach to generate reactive areas. This technique consists in injecting reactive micro- and nanoparticle water suspensions into the subsoil, in order to induce the pollutants in-situ degradation, transformation and/or immobilization.

Currently, the most interesting nanomaterials are iron-based ones: microscopic (MZVI) or nanoscopic (NZVI zero-valent iron particles are known for their effective reductive dehalogenation of many organic pollutants (mainly halogenated organic compounds, but also pesticides) and heavy metal immobilization; on the other hand, iron oxides are employed to remove heavy metals or as electronic acceptors during organic compounds biodegradation processes (e.g. BTEX).

Figure 7-1: SEM image of nanometric zero-valent iron particles.

Two essential aspects for a successful intervention are the colloidal stability of the nano- and micro reagents, and their mobility underground. To this end, innovative approaches to stabilize iron suspensions have been developed, with the use of eco-compatible biodegradable polymers.

The reagents distribution in the aquifer can be obtained through:

- Injection techniques via permeation inside wells, piezometers or multiple injection stations;
- Fracking with direct push systems or multiple injection stations.

Concerning micro-reagents there are also products that help destroy organic contaminants on the market, and they are commonly used to treat chlorinated solvents.

Lastly, there are also patented technologies that entail the possibility of configuring more than one remediation process, through different micro- and nanotechnologies, based on the type of contaminants to be treated and on the environmental context.

As of today, there are hundreds of micro and nanoremediation interventions worldwide, based on the use of iron-based or other micrometric or nanometric particles.

Electrokinetic Bioremediation

This technology consists in the continuous generation of oxidizing compounds inside the aquifer to treat the contamination, making this technique effectively applicable also in case of complex lithologies and in PRB configuration (reactive permeable barriers), or in situations that cannot be tackled with traditional ISCO technologies based on the injection of oxidizing reagents.

This category includes underground electrokinetic systems tested on field, that effectively integrate ISCO, microbiological and geophysical mechanisms into contaminated aquifers.

Contaminants, such as chlorinated solvents (PCE, TCE, DCE, VC), BTEX, and MTBE are removed through multiple oxidation reactions and accelerated biodegradation, using oxygen and iron as the favourite electron accelerators.

Surfactant Enhanced Recovery (SER)

In recent years, the remediation technology through biodegradable non-ionic surfactant compounds has been used to selectively desorb the contaminants from the solid matrix and make the NAPL miscible in the liquid phase.

This technology can be employed to treat a wide range of LNAPL (petrol-based hydrocarbons) and DNAPL (i.e. chlorinated solvents) contaminants, especially when traditional system (skimmers and pumps) are no longer effective, due to a reduced product thickness in the free phase, or when extended contaminations in the capillary fringe need to be treated, before any other treatments (such as ISCO, bioremediation, MPE, etc.).

The surfactants' mode of action entails lower costs and a reduced environmental impact compared to traditional surfactants. In addition, in can be used even in poorly permeable lithology.

In Italy, there are several commercial products used for this type of remediation.

Combined absorption and biodegradation treatment

Some innovative remediation technologies for source and highly contaminated areas entail a combined treatment with two operating mechanisms: absorption and biodegradation.

For instance, some products promote an accelerated bio-destruction of the adsorbed mass to reach very low concentrations. Other products are capable or removing hydrocarbons from the dissolved phase quickly, by adsorbing them and stimulating in-situ anaerobic biodegradation. The contaminants treated are mainly BTEX, petrol-based hydrocarbons, MTBE, IPA, chlorinated solvents, pesticides and phenols.

These products are applied through low pressure injection (direct push, wells) or excavation application.

Self-feeding heat treatment in situ

Among the innovative technologies present on the Italian market, there's also a highly sustainable patented remediation technology based on flameless combustion, where the contaminants to be degraded fuel the heat treatment. The main contaminants treated are heavy and light hydrocarbons, especially in pure form (LNAPL).

The process is supported by an air flow input through an injection well into the target treatment area and triggered by a short low-energy "ignition event". Once the process is started, the energy of the reagent contaminants is used to preheat and start the contaminant combustion in the adjacent areas, spreading a self-sufficient flare through the contaminated area (without external energy or added fuel, after the ignition), provided that there is a sufficient air flow. The active flare control is maintained by the air input. This efficient energy recirculation is made possible by the porousness of the contaminated soil, which is therefore reclaimed.

The equipment used to implement this technology are similar to those employed in Air Sparging (AS) / Soil Vapour Extraction (SVE) systems, and comprise compressors to insufflate air into the subsoil, fans to extract the interstitial vapour connected to a gas treatment system, and specific equipment used to start the flame-less combustion.

ENI INNOVATIVE TECHNOLOGIES AND METHODS

e-hyrec® technology

Definition and general criteria

The e-hyrec® technology can be applied in case of groundwater contamination by non-soluble organic compounds - usually hydrocarbons - with a low density, present as supernatant products (Light Non Aqueous Phase Liquids, LNAPLs).

The e-hyrec® device is based on the selective permeation principle, thanks to the use of an hydrophobic and oleophilic filter, capable of recovering only the organic phase. Due to the material's chemical-physical characteristics, when it is immersed in the interface between the supernatant hydrocarbon status and the groundwater, the LNAPL permeates through the filter pores, and water is rejected from the surface. An iridescence status can be reached, following the contaminant removal process.

The filter is coupled to a relaunch pump to collect and send the supernatant to the tank or line. An automatic water/oil interface positioning system optimizes the performance and allows to follow the water table oscillations without loss of selectivity, differently from traditional equipment.

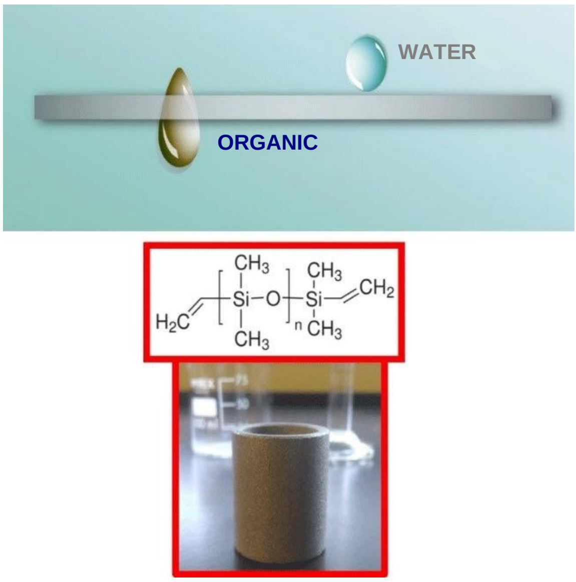


Figure 8-1: PDMS (central fig.) makes sintered steel hydrophobic (bottom fig.)

Basic system components

The device comprises two parts interconnected by electric and pneumatic connections: one part lowered into the piezometric well, and the other management and control part, located above ground.

The main well unit components are:

- Hydrophobic filter: sintered steel filter with a surface polydimethylsiloxane (PDMS) surface coating, which makes it hydrophobic and oleophilic;
- Total Fluid pneumatic pump connected to the filter;
- Phase sensor for automatic positioning, which distinguishes the water, oil and air phases.

The main surface unit components are:

- Well unit supporting cable winding/unwinding drum;
- Automatic positioning motor;
- Encoder to measure the filter depth in the water table;
- Flow meter connected to the pneumatic pump that measures the number of pump cycles, and therefore the volume of liquid retrieved;
- Electric panel containing the PLC control unit and the HMI operator interface;
- Skids and steel covers;
- Photovoltaic panel option: motor and sensors/electronic components power supply.

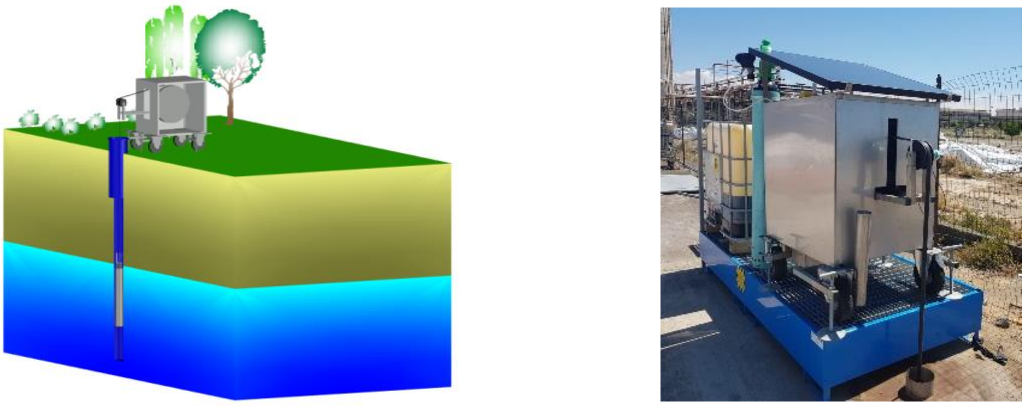


Figure 8-2: The e-hyrec® device positioned in the water table. It comprises the part lowered into the well and the handling, management and control system located on the well's mouth.

Conditions and application limits

Contamination characteristics

- Presence of water-insoluble organic compounds, in supernatant phase (LNAPL);
- Optimal performance with supernatant viscosity ≤ 5 cSt (40°C) and water table refilling ≤ 20 litres/day;
- Removal of LNAPL in the water table, up to very low thickness, even 5 mm;
- Not applicable to water-dissolved organic compounds.

Water table characteristics

- Aquifer depth between 0.5 and 30 m;
- Minimum distance of 2 m between the water table level and the well bottom.

Area characteristics

- Availability of air or compressed nitrogen (network or cans);
- Well area free from hindrances (area dimensions: 2x1m);
- ATEX Directive: external area: zone 2, well area: zone 0. In case of external area classified as 0 or 1, a special return must be used;
- Not applicable with well diameter < 4''.

Technology application pros and cons

The e-hyrec® technology - included in the innovative technologies - is in the first on-field large-scale use stage. Some items are related to possible implementation processes.

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
SELECTIVITY	☺	The product retrieved does not contain any aqueous
LNAPL REMOVAL EFFICIENCY	☺	Final supernatant thickness in the water table of just a few cm, up to the ceiling, based on the groundwater refilling Removal of LNAPL in the water table, up to very low thickness, even 5 mm

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
AUTOMATION	🙂	This characteristic helps optimize the performance
	😐	This characteristic should help reduce technical staff's interventions Further optimizations will be assessed, following on-field application
APPLICABILITY BASED ON THE TYPE OF CONTAMINANT	🙂	Optimal performance with supernatant viscosity ≤ 5 cSt (40°C) and water table refilling ≤ 20 litres/
	😐	Possible performance reduction with high viscosity and refilling (greater final thickness)
INTERVENTION COSTS	🙂	Reduction of aqueous fraction disposal costs Reduction of technical staff intervention costs (currently being optimized)
FLEXIBILITY OF USE	🙂	Mobile device, possible use on rotation on different wells Wide range of application in terms of aquifer depth
	☹	Not applicable on carriageable wells (compact model required) Not applicable with well diameter < 4"
ENVIRONMENTAL SUSTAINABILITY	🙂	The photovoltaic power supply model is more advantageous compared to the skimmers (no water disposal, lower operating interventions)

🙂 Good 😐 Medium ☹ Low

Table 8-1 e-hyrec® technology pros and cons

E-limina® (Eni-Linking Isotopic and Microbial Investigations to aid Natural Attenuation) method

Definition and general criteria

The e-limina® (Eni-Linking Isotopic and Microbial Investigations to aid Natural Attenuation) technology consists in the combination of different monitoring methods, applied to biologic or BIOREMEDIATION techniques (for these remediation technologies, see the relevant datasheet).

The monitoring methods applied to the remediation in a coordinated and synergistic way are:

- Microbiological method (microcosm culture set-up);
- Molecular method (quantification of the key-genes that make up species-specific and/or functional markers);
- Isotopic method (assessment of the isotopic ratio through CSIA, Compound Specific Isotopic Analysis).

This technology can be applied both to polluted sites in a preliminary characterization phase, and to monitor the remediation process.

Characterization: e-limina® allows assessing the existing site biodegradation and suggesting remediation methods based on local microbiology, to accelerate the natural attenuation phenomena in progress;

Monitoring: e-limina® allows assessing the contaminants biodegradation status in real time, during the bioremediation intervention (see **Figure 8-3**).

The e-limina® method can be applied on any type of matrix (aquifer or soil) to obtain information on the level of contaminants biodegradation and assess the suitability of a biological treatment.

The selection and monitoring instruments applied are highly selective and accurate, to reduce the risk margins common to many remediation techniques.

Figure 8-3: Field set-up for a biological remediation process

Conditions and application limits

An essential prerequisite to apply the e-limina® technology is the presence of microbiological activities on the remediation molecules - pollutants - in the site in question. Theoretically, all pollutant molecules can be attacked by micro-organisms, as described in the Bioremediation datasheet, as long as the concentration is not too high and the site conditions in terms of temperature, humidity and pH allow it.

The initial assessment is made by setting up microcosm cultures of the groundwater and/or polluted soil in aerobic and anaerobic conditions. The pollutant molecules degradation is monitored through gas-chromatographic analysis, according to standard methods (e.g. EPA), if available.

Once the presence of microbial activities toward the pollutants (Natural Attenuation) has been assessed, with the same experimental method, it is possible to test the conditions that can promote the biodegradation phenomena (Enhanced Biodegradation).

Microcosm cultures are also essential to fine tune the isotopic analysis method: kinetic testing is carried out, in which the cultures in triplicate are subjected to close sampling to build an accurate degradation curve. The isotopic ratio is calculated on the residual contaminant, as described in the following paragraph.

At the same time, within the degradation metabolic path known or recreated based on the degradation and/or intermediate products, the metabolic chain key-enzymes and, if known, the bacterial species responsible for biodegradation need to be identified. Based on the nucleotidic sequences identified, general (primers), species-specific and functional probes are designed, to represent the markers for that specific metabolic path (see the following paragraph for more details). The more the preliminary study is accurate, the more the probes will be efficient in monitoring the degradation bacteria activity.

Required lab instruments and method development

In order to apply e-limina® technologies, apart from basic chemical -biological lab equipment, special instruments to quantify molecular markers (Thermal Cycler for quantitative PCR or qPCR) are needed, along with an isotopic mass gas spectrometry-chromatography. **Figure 8-4** shows the method application on groundwater.

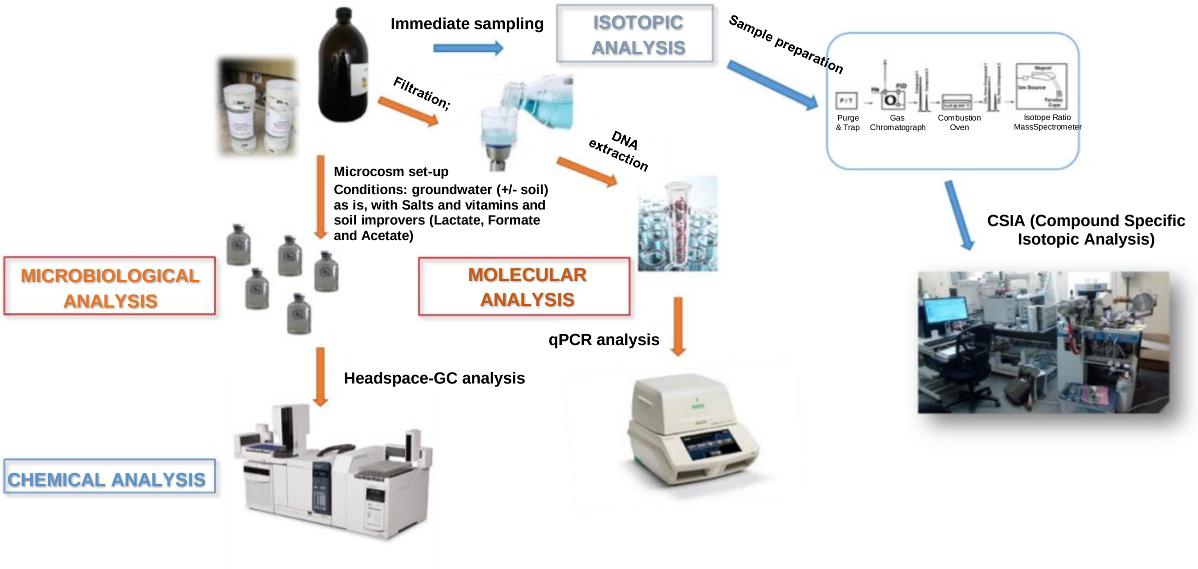


Figure 8-4: Diagram of the e-limina® method technologies

MICROBIOLOGICAL ANALYSIS

Starting from the contaminated matrices (water or soil), microcosm cultures are set up in the following conditions:

a) AEROBIC: minimal saline plate to promote the bacterial metabolism and provide the oligoelements required for growth and activity, enhanced aeration (for liquid cultures, shaking with an orbital shaker is sufficient; for soil microcosms, periodical shaking is required, to promote air exposure); no other carbon sources are usually necessary, since the pollutant must be the only source of energy.

b) ANAEROBIC: degassed minimal saline plate with oxygen scavengers addition (e.g. cysteine), bottle filling to minimize the headspace, stationary cultures; in this case, soil improvers tested on different cultures should be added, to trigger and accelerate biodegradation.

Cultures are useful during the site characterization phase because they allow the study of biodegradation mechanisms, metabolic pathways and bacterial species present; furthermore, they allow testing different biodegradation acceleration conditions.

In addition, culture set-up even during the remediation intervention allows to monitor in the lab under controlled conditions what is happening on field.

MOLECULAR ANALYSIS

As mentioned above, preliminary studies on degradation metabolic pathways are key to identify the key-enzymes (and the related genes) and the bacterial species for biodegradation. Based on this, specific DNA sequences (probes or PRIMERS) can be designed: if the Primer identifies the bacteria species, it is called TAXONOMIC MARKER, while if it identifies a metabolic gene, it is called FUNCTIONAL MARKER.

The approach selected to characterize a site, and follow the remediation progress, employs the PCR (Polymerase Chain Reaction) technology, in its quantitative version (qPCR). This technology is used to amplify the genes related to the biodegradation species or enzymes in a quantitative way, within the DNA extracted from the environmental samples. The principle of this quantification lies in the possibility of determining the quantity of the specific marker within a sample, by amplifying it and measuring the quantity generated at every reaction cycle (see **Figure 8-5**). By comparing the data with a calibration curve created within the same experiment, with a known target, it is possible to estimate the quantity of taxonomic sequences of the desired species, or the functional genes within a complex community. If used during a characterization process, this provides information on the site's biodegradation potential (presence and quantity of degradation species and specific enzymes), while when used during a remediation process, it monitors the effectiveness of the treatment.

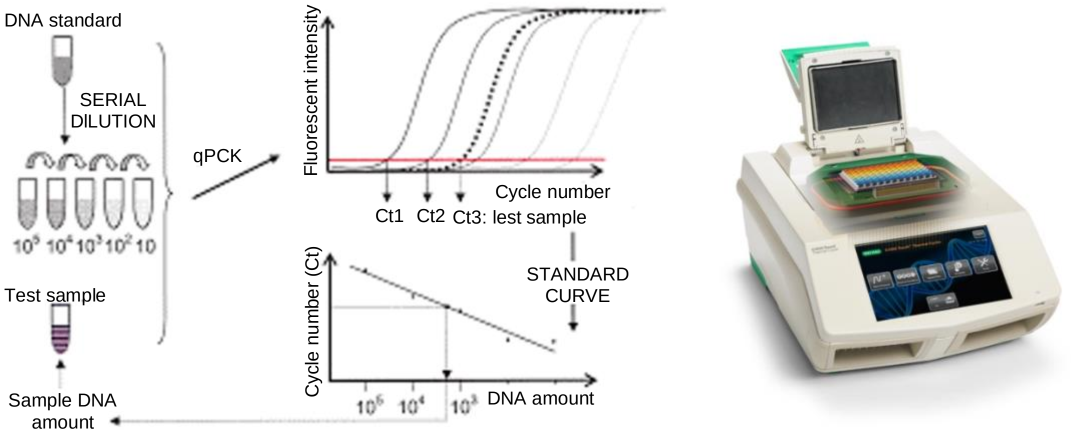


Figure 8-5: qPCR reaction and dedicated instrument

ISOTOPIC ANALYSIS

The isotopic analysis, or Compound Specific Isotopic Analysis (CSIA) is based on the use of gas chromatography paired with isotopic mass spectrometry (GC-IRMS). This technology is used to identify the contamination source between several plausible sources (used for forensic investigation purposes), and to determine the contaminant degradation and related degradation pathways; in this second case, it is used in the environmental field.

The results of this analysis are represented by the isotopic ratio value between the atoms stable isotopes, that comprise the majority of the contaminants, such as Carbon (13C/12C), Hydrogen (2H/1H) and Chlorine (37Cl/35Cl). This ratio is unique for each contaminant, and is based on different factors, such as the manufacturing origin (based on the raw materials and production processes), and it varies following biodegradation processes, since micro-organisms prefer to attack and degrade those molecules that contain the lighter isotope, causing an accumulation of molecules containing heavier isotopes in the environment.

In data, this translates in a shift of the isotopic ratio - through a special equation - from more negative values to values that are gradually less negative, as the degradation process progresses. The entity of this change is calculated with a site-specific enrichment factor, linked to the contaminant and to the degradation pathway it is subject to. For instance, as shown in Figure 4, in case of chlorinated solvent dehalogenation processes, this shift is very significant. The Figure shows a sample diagram obtained from the values of the samples collected while monitoring a remediation process, along with the chemical analysis of the contaminant in question (1,2-dicholoroethane or 1,2-DCA).

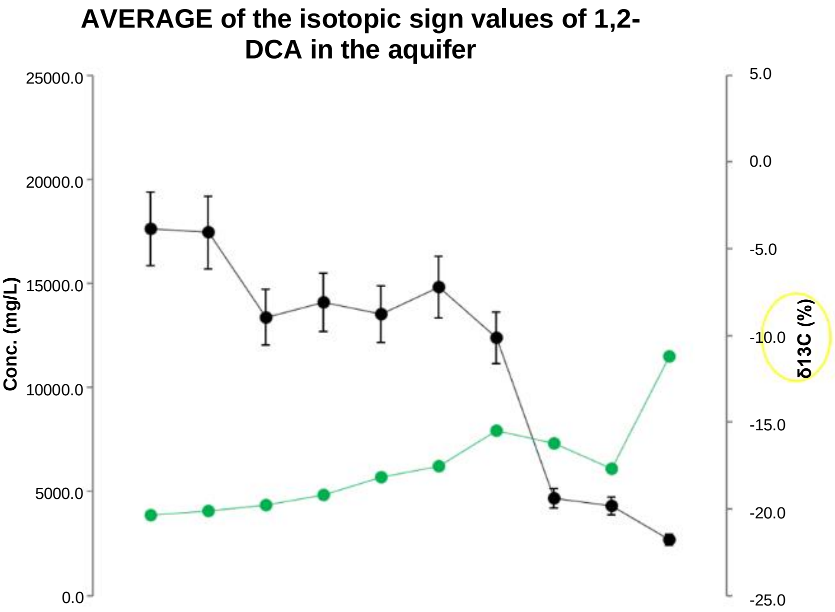


Figure 8-6: Diagram representing the variation of the Carbon isotopic sign (□13C, green curve) along with the reduction of the concentration of 1,2-DCA (black curve during a remediation intervention.

Technology application pros and cons

The combined techniques included in the e-limina® method help characterize the contamination more accurately, by identifying at the same time the source and assessing the alteration processes occurred in the environment (degradation speed and choice of the most suitable remediation technology).

The integration of CSIA analysis protocols with microbiological and molecular methods is proving to be a powerful tool to determine the contaminants origin and any related degradation processes in the environment, whereas single analyses may not be as effective.

Given the complexity of the majority of contaminated sites that undergo a remediation process, where concurrent contaminant transformation and division mechanisms exist in ‘natural’ conditions, it is certainly effective to support the site’s CSIA measures with lab testing on native matrices and supporting techniques to identify the molecule fractioning data in a well characterized environment at microbial community level.

During a remediation intervention on a site entailing the characterization, planning and implementation of an Operating Remediation Project, consolidating the knowledge available during the characterization phase determines time and cost savings at process level and reduces the risk of adopting non-effective technologies.

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
ACCURACY	🙂	The combination of different monitoring technologies leads to a more accurate characterization
SELECTING THE REMEDIATION TECHNOLOGY	🙂	Combined monitoring technologies allow to select the most effective remediation technique
ANALYSIS COMPLEXITY	😐	It requires the involvement of complex equipment and trained personnel to execute and interpret the analyses.
GENERAL APPLICABILITY	😐	Method applicable only to biological remediation interventions
APPLICABILITY BASED ON THE TYPE OF CONTAMINANT	🙂	Applicable to all biodegradable contaminants
APPLICABILITY BASED ON THE TYPE OF CONTAMINATION	😐	Knowledge of the biodegradation pathways required. Permissive on-field conditions for the micro-organisms (T, pH, redox, saltiness...) required
INTERVENTION COSTS	🙂	Reduced infrastructural and staff costs
INTERVENTION TIMES	🙂	The coordinated application of monitoring techniques helps reduce biological remediation times
ENVIRONMENTAL SUSTAINABILITY	🙂	Reduced environmental impact in terms of hazardous chemical substances, high temperatures and landscape alteration.

🙂 Good 😐 Medium ☹ Low

Table 8-2 e-limina® technology pros and cons

Passive samplers in LDPE

Definition and general criteria

Method to determine organic contaminants and their distribution profile in sediments and soils, through passive sampling systems operating in balanced conditions, and based on low-density polyethylene film (LDPE) and developed by Eni's central research, in partnership with Eni Rewind, the University of Roma Tor Vergata and the Massachusetts Institute of Technology.

These passive sampling systems exploit the physical pollutant molecular diffusion process based on the concentration gradient between the environmental matrix to be monitored (e.g. water, interstitial gas, etc.) and an adsorbent system (LDPE film) present in the sampler. The contaminant division entails their accumulation on the sampler film, until balance is reached, allowing to determine the concentration of pollutant compounds available and their distribution, also along the vertical profile.

Samplers are exposed in the environmental matrix for a time sufficient to ensure the onset of the balance conditions between the matrix and the adsorbent system. At this point, after measuring the contaminants concentration in the polyethylene film through lab analysis, the mobile and available contaminant concentration in the matrix can be determining knowing the partition coefficients between the adsorbing system and the sampled matrix.

In the initial sampling phase (see **Figure 8-7**), pollutants are adsorbed by polyethylene at a rate directly proportional to their concentration in the environmental matrix (linear capturing area). As the exposure time progresses, the contaminant gradually reaches its balance concentration in the sampler. LDPE-based passive sampler can be used to sample the saturated and unsaturated area, since the contaminant concentration absorbed in the LDPE will be related to the concentration in the aqueous phase and/or interstitial gas - if present - based on the corresponding polyethylene-water (Kpew) and polyethylene-air (Kpea) partition coefficients. These partition coefficients depend on several factors, such as the contaminant's chemical-physical properties and the polymer's characteristics. In balance conditions, based on the analytes concentration measured in the polyethylene at the end of the exposure, it is possible to estimate the contaminant concentrations in aqueous or soil-gas phase, based on the partition coefficients estimated for each substance. The data provided by passive samplers can be applied to estimate the actual contaminants mobility, to integrate technical characterization techniques, and better define the conceptual site's model, with specific reference to the contaminants' volatilization and leaching pathways and groundwater transportation.

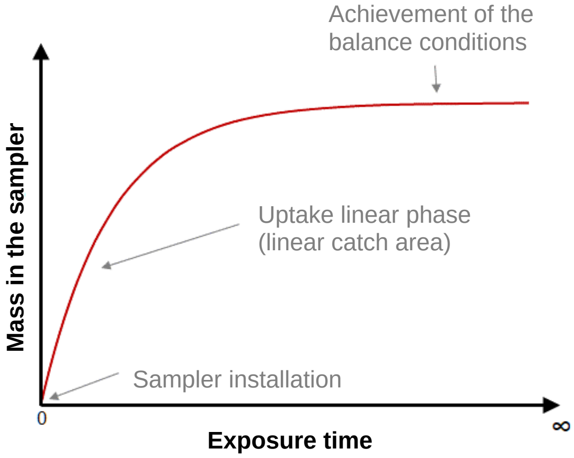


Figure 8-7: Mass of contaminant adsorbed in the passive sampler, based on the exposure time.

Figure 8-8: Low-density polyethylene (LDPE) that can be used for passive monitoring.

The concentration of a contaminant dissolved in water (CV) or in soil gas (CSOIL GAS) can be obtained by analysing the concentration of the contaminants adsorbed on the PE at the end of the exposure, and considering the related partition coefficient PE-water (KPE-W) or the partition coefficient PE-air (KPE-A):

$$C_W = \frac{C_{PE}}{K_{PE-W}} \qquad C_{SOIL\ GAS} = \frac{C_{PE}}{K_{PE-A}}$$

Where:

- CW = concentration dissolved in water;
- CPE = concentration adsorbed on the PE;
- KPE-W = PE-water partition coefficient;
- CSOIL GAS = concentration in the soil gas;
- KPE-A = PE-air partition coefficient.

Technology development

Passive sampling technologies are already consolidated and applied for monitoring contaminants in dissolved phase in groundwater and sediments. To monitor substances in aeriform phase, the first passive sampling systems were already applied in the 1970s, and in the first years of the 1980s, they were broadly employed for industrial hygiene purposes. In the last years, soil gas monitoring systems based on passive sampling are being implemented at national and international level.

Conditions and application limits

Passive samplers are applicable in the following conditions:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Presence of organic compounds;
- Contamination in two or more phases, including supernatant product;

SUBSOIL CHARACTERISTICS

- Sediments;
- Saturated and unsaturated, permeable or slightly permeable soil, also uneven;
- Presence of groundwater, even superficial (unsaturated and saturated soil);

Conversely, **passive samplers are not applicable** when the following conditions occur:

CONTAMINATION CHARACTERISTICS AND DISTRIBUTION

- Metal or inorganic compounds contamination;

The following table shows the level of effectiveness of passive samplers in relation to the environmental conditions listed above.

PARAMETER	VERY EFFECTIVE	MODERATELY EFFECTIVE	INEFFECTIVE
CONTAMINATION CHARACTERISTICS			
TYPE OF CONTAMINANT	Volatile compounds* and petrol-based hydrocarbons in particular. Recent contamination.	Semi-volatile compounds	Non-volatile compounds. "Old" contamination
CONTAMINATION PHASE	Dissolved or gaseous contaminant	Adsorbed contaminant	DNAPL

PARAMETER	VERY EFFECTIVE	MODERATELY EFFECTIVE	INEFFECTIVE
CONTAMINATION CHARACTERISTICS			
	LNAPL		NAPL thickness < 1 cm and density very close to 1
(*)The pollutant volatility is determined by the vapour pressure, Henry's Law Coefficient, its composition and its boiling point.			

Table 8-3 Passive sampler technology effectiveness

Basic system components and main development parameters

To apply this type of samplers, stainless steel windowed rods placed at the right depth (**Figure 8-9**) are used, with polyethylene film a few cm long and with a few mg of weight inserted.

Figure 8-9: Stainless steel probe with the polyethylene film inside for field installation through direct push techniques

These devices are inserted in the soil manually at different depths, starting from the top soil up to max 1 m to retrace the contamination profiles and migration pathways. Sampling is carried out by placing a sampler at each depth level chosen.

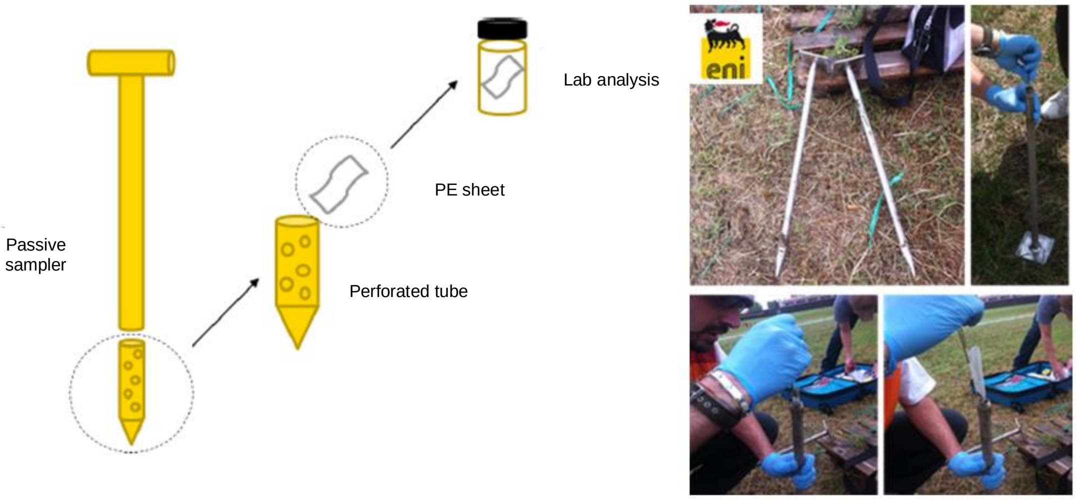


Figure 8-10: Passive sampler for surface monitoring - manual application

In order to reach greater depths and study also the contaminants lathing pathways from the top-soil to the groundwater on the vertical sampling pathway, samplers that could be inserted using a geoprobe have been designed.

These samplers are equipped with:

- Coating system (Dual Tube) to be applied on the interstitial gas sampling system currently being used, to ensure exposure exactly at the sampling depth selected;
- A metal grid to protect the polyethylene film, to prevent the soil from containing the film during its positioning, especially at great depths, but also if it's not used in combination with the outer sleeve, e.g. in case of manual sampling at low depth.

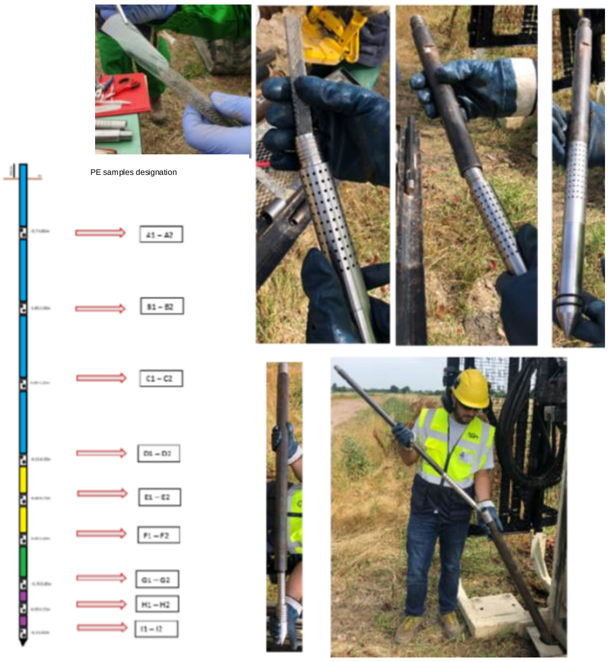


Figure 8-11: Passive sampler for in-depth monitoring - coating system and application via PEO probe

Technology application pros and cons

- High sampling density;
- Measure of the only actually mobile/available fraction;
- Good representation of the contamination level;
- Simple and cost-effective system;
- Applicable also in case of humidity;
- It does not affect the exiting balance in environmental matrices;
- Prevents environmental matrix sampling;
- Possibility to obtain vertical profiles.

PARAMETER	ASSESSMENT IN TERMS OF PROS/CONS	NOTES
DEGREE OF DEVELOPMENT, RELIABILITY AND DIFFUSION	🙂	Reliable and proven technique for sediments and volatile compounds in the soil-gas. Relatively fast sampling. Determines the mobile/available fraction, responsible for the environmental risk. It does not affect the environmental matrix. Possibility to obtain a detailed contaminant and vertical profile distribution
	😐	Need to optimize the lathing pathway analysis
APPLICABILITY BASED ON THE TYPE OF CONTAMINANT	🙂	Applicable to volatile and semivolatile pollutants, and to petrol-based hydrocarbons, in particular. Applicable to pesticides monitoring in water and sediments
	😐	Method to be validated for volatilizing and lathing pathway analysis
APPLICABILITY BASED ON THE SUBSOIL CHARACTERISTICS	🙂	Applicable in several environmental contexts (unsaturated area, capillary fringe and saturated area). Applicable in soil of different nature

🙂 Good 😐 Medium ☹ Low

Table 8-4 Passive samplers in LDPE technology pros and cons

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