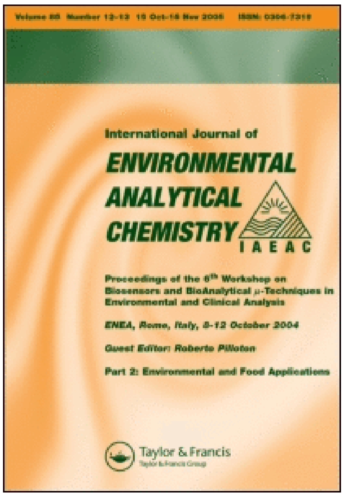

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Remediation of soils contaminated with pesticides: a review

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The aim of this work is to address the problem of soil contamination with pesticides and present a review of the existing techniques for remediation of these types of soils. First, a brief discussion of the soil structure and complexity is presented, and the impact of its contamination by pesticides is examined. Then, the main existing and emerging techniques for soil remediation, particularly for the elimination of pesticides, is discussed, and their relative advantages and disadvantages presented. In order to choose the best remediation technology, one must take into consideration the soil and site characteristics, the technique suitability, the costs and the environmental footprint. The comparison of existing technologies will be a helpful tool for a preliminary selection of the most promising techniques to use for a particular soil decontamination problem.

Keywords: pesticides; decontamination techniques; soil remediation; cost evaluation

1. Introduction

1.1 *The soil*

It is commonly believed that soil contamination is a relatively recent issue when, actually, it began a long time ago, particularly after the industrial revolution, even though only recently has mankind become aware of its dimension, persistence and harmful effects. In fact, in spite of the soil being the support of our ecosystem [1], man, by ignorance, and mainly for economical reasons, has been throwing all types of organic and inorganic matter into the soil, assuming that it possesses an infinite assimilation capability. Only in 1972 (in the European Soil Charter – Council of Europe) has it been recognised that appropriate protection measures should be implemented quickly whenever soil integrity is at risk. The soil must be considered as a non-renewable natural resource, as the

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estimated time for originating 1 cm of savage soil is situated between 200 and 400 years [2]. Hence, mankind has the obligation to itself and to the coming generations to take care of and preserve such a precious resource.

The soil has many functions, some of them being to sustain life and provide a 'habitat' for people, animals, plants and other living organisms; to be a part of the water and nutrients cycles; to provide some protection for the groundwater; to keep historical, natural and cultural footprints; to conserve mineral reserves and raw materials; to carry out food production; and to support social and economic activity.

The soil may be defined as the most superficial layer of the crust, containing mineral particles mixed with organic substances, water, air and microorganisms (ISO 11074:2005). As stated by de Jenny's fundamental soil equation [3], soil formation results from interactions of various factors, including: parent material, climate, topography, organisms and time. It is the numerous possible combinations of these five factors that will determine the precise properties of a soil, even though one or more of them may often exert a particularly strong influence at a given location. None of these five factors can be considered as being entirely independent from the others, each being influenced to some extent by the others. Extensive discussion of these soil-forming factors and the associated processes is provided by various authors [3–9].

Even though soil composition varies a great deal, four main layers can be identified. Figure 1 shows schematically a soil profile, which, as was already mentioned, may differ due to several factors [10–13]. The mother-rock (or parent material) is one of the predominant factors in determining the nature of the soil, limiting topography and soil thickness. The climate influences the erosion suffered by the mother-rock and the soil. The biological activity is extremely important from the agricultural point of view, and it is a preponderant factor in the formation of the organic substances. The age determines the formation or not of some of the layers evidenced in Figure 1, as these depend on the maturity of the soil. In Figure 1, the layers present in the soil profile are horizons O, A, B, C and R.

Horizon O is the top layer of the soil. It is composed mainly of plant litter at various levels of decomposition and humus. It is where most of the microbiological activity can be found, more than 500 years being necessary to form the existing organic substances therein.

Horizon A refers to the upper layer of the soil, nearest to the surface. It is the first layer and it is rich in humus and debris of organic origin. This layer is called fertile layer, as it provides plants with the nutrients that they need for life support. It is the best soil for plantation, and is in this layer that plants find some salts, minerals and water for their development. This layer is commonly known as *topsoil*.

The layer below horizon A is *horizon B*, which is poorer in humus. It is composed of small rocks, minerals and humus, also presenting some living activity (the majority of the roots exist in this zone). Horizon B does contain some elements from horizon A because of the leaching process. The leaching process may also take some minerals from horizon B down to horizon C. This layer is divided into three parts: the first part is calcareous rock, corresponding to 7–10% of the layer, the second part is made of clay, formed generally for kaolinite, kaolin and feldspat sediments, and corresponding to 20–30% of the layer, and the last part is composed of sand, which presents a high permeability, because of the spaces existing between the particles of sand, allowing an easier flux of air and water. This last portion corresponds to 60–70% of the layer, and is commonly known as *subsoil*. The horizon B has a lighter colour than the previous

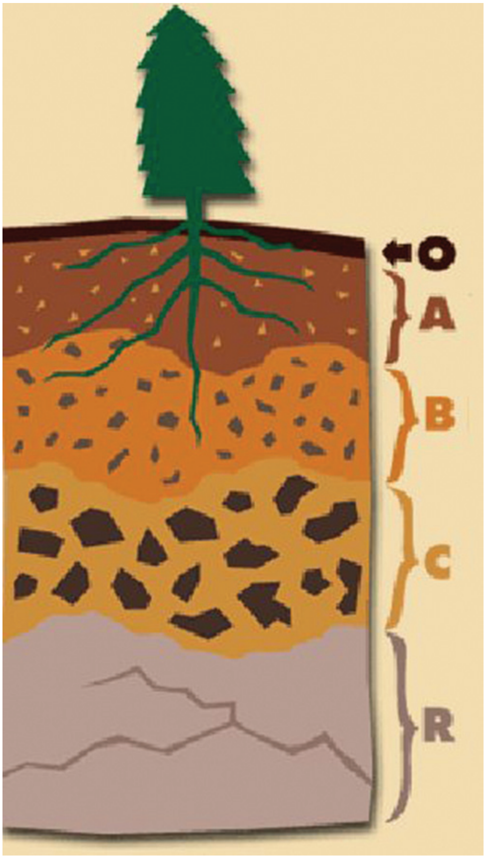

Figure 1. Schematic representation of a soil profile (from Turenne [10]).

horizon and is basically composed of clay, fragments of rocks, minerals and has much less humus and microorganisms than horizon A.

Horizon C consists mostly of weatherised big rocks, being composed of partially decomposed rocks. If the decomposition is total, due to the action of the erosion and geologic agents, these rocks can turn into sediments. Thus, this layer is composed basically of pieces of rocks and some leached material coming from the subsoil.

Horizon R is the consolidated rock. This fourth layer is made of rocks that are beginning to decompose, which are usually called mother-rocks. This solid rock is the one that gave rise to the horizons above it, and is therefore referred to as parental matter. It must not be forgotten that soil profiles look different in different areas of the world, and that they are influenced by climate among others factors [14,15].

The soil has different types of possible applications depending on its composition, localisation, profile and other characteristics. The soil behaviour depends heavily, among other factors, of the size of the particles composing it (i.e. its granulometry). In fact, according to the size of its mineral constituents, the soil may be classified in the following classes (with a decreasing size of grains): pebbles or gravel, sands (thick, average or fine), silts, and clays. Almost all soils are made of a combination of these last three types, and the relative amount of each type will influence the soil texture, aspect and thickness. For example, the texture of the soil depends on the percentage of sand, silt, and clay in its composition and this will influence the water infiltration rate, water storage, aeration, mechanisation easiness, and distribution of some particular nutrients (fertility of the soil). According to the relative percentage of sand, silt, and clay, the soil may be classified as: *erinaceous*, *argillaceous*, *silteous*, *humus* and *calcareous* [16].

Erinaceous soil has good aeration, though plants and microorganisms live in it with some difficulty, due to its low humidity. This type of soil has more than 70% of sand in its texture. It also has clay in its composition and a lower percentage of other compounds. However, as it has good aeration, it does not hold back the water. *Argillaceous* soil is not aired, but it stores more water. It is less permeable; and therefore water has more difficulty in passing through. In this type of soil is possible to find water reservoirs. *Silteous* soil, which has a great amount of silt, is generally very erosive. *Humus* soil, which presents a higher amount of humus relatively to the other types of soil, is generally fertile, being the kind of soil where plants find better conditions to develop. It possesses about 10% of humus relative to the total solid particle content. In *calcareous* soil, the amount of calcareous rock is greater than in other types of soil. This type of soil has a white or yellowish dust that can be removed and then used in the fertilisation of soils used for agriculture and stockbreeding [17,18].

In nature, it is rarely possible to find a soil constituted of only one of ‘the pure’ types, one that is constituted in its totality of only a specific kind and size of particles. Therefore, soil usually presents certain percentages of sand, silt, clay, gravel, etc. Figure 2 shows a triangular diagram used to classify soil according to its texture [19]. The sides of the soil texture triangle are scaled for the percentages of sand, silt and clay. The intersections of the three coordinates on the triangle give the texture class. For instance, a soil with 20% clay, 60% silt and 20% sand falls in the ‘silt loam’ class.

When studying a soil, or even referring to it, it must be borne in mind that we are not concerned with a single environmental compartment but with three, corresponding to the three phases found in soil: solid, liquid and gas phases. The constitution of the solid phase is the local or transported ‘parental matter’ and organic material, originated by vegetal and animal decomposition; the liquid phase, on the other hand, is the water or the soil solution (organic and inorganic elements in solution); the gaseous phase presents

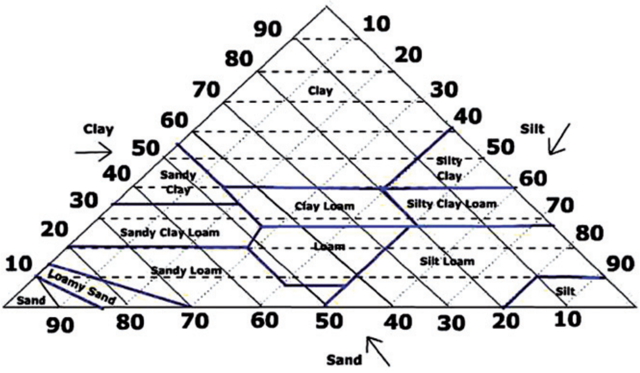

Figure 2. Diagram for soil classification with respect to texture (from Ritter [19]).

a changeable composition, in accordance with the gases produced and consumed by the roots of the plants and by the animals (CO_2 and O_2). Figure 3(a) shows a soil in its natural state and Figure 3(b) represents schematically the three phases that constitutes the soil.

The soil profile may be studied not only from the point of view of physical-chemical constitution or texture, but also having in consideration the transport zones. In this perspective, two main zones may be identified in the soil: one above the ground water level, which is designated by *non saturated zone* – a porous medium where the three phases coexist: a solid, constituted by non-consolidated materials of the subsoil, a liquid, constituted by water in movement or filling the pores, and a gaseous phase; and another zone below the groundwater level known as the *saturated zone*. The separation between these two zones is made by a *hair fringe* [20,21]. The permeability of the soil is essentially controlled by the pores of greater diameter, which can vary according to the nature of the soil [22]. The contaminants in their movement through this *porous medium* experience various phenomena like adsorption and diffusion [23–25], volatilisation, microbiological degradation, photo-decomposition, migration to plants, chemical degradation, solubilisation and leaching by underground waters. Thus, the contaminants can either be restrained superficially in the soil and enter quickly in the food chain or, if the soil is permeable, they may spread through the soil matrix contaminating also the underground water. The way contaminants suffer partition determines how they will get into the aqueous (moistness of the soil) and gaseous phases; their adsorption ability and non-mixability with the subsoil is also determinative for the migration process. Therefore, it is necessary to take in consideration all these concepts to evaluate the contamination and devise the most appropriate decontamination process for a particular soil. It is hence necessary, before proceeding to the decontamination of a soil, to carry out a preliminary study for the characterisation of the soil, of its contaminants and the climate conditions [26].

For choosing the most appropriate decontamination technique it is important to have knowledge of a set of parameters indicative of the nature of the contaminants and their tendency to be adsorbed by the soil; such parameters are: $\boldsymbol{K_{ow}}$ (octanol-water partition coefficient), $\boldsymbol{K_{oc}}$ (organic carbon partition coefficient), $\boldsymbol{K_{sw}}$ (soil-water partition coefficient) and $\boldsymbol{K_{oa}}$ (octanol-air partition coefficient) [27–29]. Values for these parameters are available in several databases [30]. For example, Arias-Estévez and co-workers reviewed the influence of the physical and chemical characteristics of the soil system, such as moisture content, organic matter and clay contents, and pH, on the sorption/desorption and degradation of pesticides and their access to groundwater and surface water [31–32];

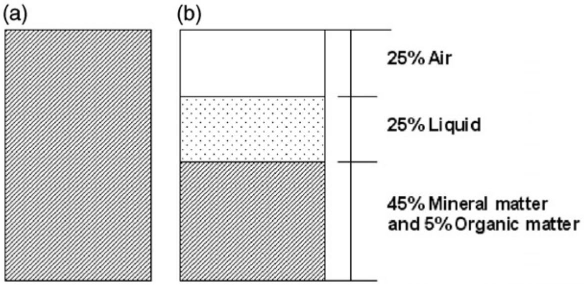

Figure 3. Volume percentage of solid, liquid and gaseous phases in the soil.

this knowledge is essential for deciding the best remediation technique for a specific contaminated site. From what has been said, it can be concluded that each case of contamination represents a very specific and complex situation, requiring a previous study of the soil and contaminant properties, in order to facilitate the choice of the most adequate technology to be used for the case under study. Soil decontamination is so complex that many authors have developed models to describe the different phenomena occurring during the process of soil remediation, allowing a faster and less expensive evaluation of the different techniques [27,32–38].

From the previous discussion it is clear that the soil is a complex and living structure that is difficult to study [39], requiring the mastery of different areas of knowledge, such as chemistry, physics, mathematics, biology, and health and safety. The complexity is even greater if remediation is made *in-situ*, because, most probably, situations will appear which were not taken into consideration during the laboratory study. This is the case, for example, for bioremediation [40].

1.2 *Pesticides*

The need of the modern industrial societies to increase agricultural production and to maintain the organoleptic characteristics of fresh foods for longer periods of time, has led to an increase in the use of pesticides and, more recently, transgenic products. A pesticide may be defined as any substance or mixture of substances that are used to destroy, eradicate, control or change the cycle of a certain plague. Pesticides may be natural or synthesised substances or even living organisms (NSW: National Registration Authority for Agricultural and Veterinary Chemicals) [41,42].

The use of pesticides has been generalised after the Second World War and is directly connected to the changes introduced in the production and growing of food species which allowed doubling the agricultural productivity when compared with other economical activities. Pesticides are by themselves responsible for 30% of this increase. Although no one can deny that their use has benefited agricultural production and the fighting of diseases like malaria, yellow fever and dengue, and in the elimination of external and internal parasites, their continuous and reckless use have determined the appearance of health problems for mankind and endanger the survival of many living species. It is known nowadays that the lack of specificity of these compounds (interacting with other organisms present in the soil), and their long persistence in the environment enhances their menace to the health of mankind and to the equilibrium of the ecosystems.

In fact, pesticides represent a two-edged sword, being a solution for fighting starvation and human diseases, having helped to save millions of human lives, but by their continuous use leading to the contamination of food and natural resources with substances dangerous for mankind, many of which are carcinogenic. As pointed out above, pesticides can be natural or synthetic chemical compounds used to control insects, mites, harmful grass, fungus and other forms of animal or vegetal life, that may be dangerous for farming, cattle and other products. The inadequate use of these substances (disrespect for the appropriate concentrations to be used, testing periods and security measures) may provoke not only the contamination of soil, but also the contamination of groundwater, rivers, lakes and man.

The classification of pesticides is variable according to the desired goals, and can be made according to: the nature of the enemy to be fought, its use, way of acting, way of penetration, chemical composition and toxicity, among others. Table 1 shows a possible classification of the pesticides according to the nature of the enemy to be fought.

Another possible classification of the pesticides has in consideration their chemical nature (see Table 1). The main classes of pesticides, according to their chemical nature, are: organophosphorus pesticides (OPPs) [43–49], organochlorine pesticides (OCPs) [1,43,48], carbamats and pyrethroids. The organochlorides (e.g., aldrin, endosulfan and DDT) [33,43,50] are considered the most dangerous, because after their application in the soil, they can remain in the environment for more than three decades [51], contaminating water reservoirs, superficial and groundwater, biota and consequently ending up contaminating man [52,53]. The chemical analysis of soil, water and food samples are used as an indication of the degree and sources of environmental pollution, providing in addition important information regarding the risks of these resources for the population.

2. Remediation techniques

A polluted soil can be defined as a soil with a concentration of a contaminant that exceeds the level defined by the applicable regulations. Environmental regulations concerning water and air pollution are common practice in most of the developed countries; however, very few countries have regulations for soil contamination.

In the last decade the most common solution for dealing with contaminated soil was to excavate and put it in a landfill, or isolate it with one of the different types of barriers that are available and capable of preventing the flow of the contaminant away from the site, thus avoiding the contamination of neighbouring sites [54]. This was good practice in terms of risk management, because it controlled the dangers for the surrounding environment, but it was not capable of treating the source of the contamination. Recently, the remediation of contaminated soils [55], in part due to regulatory changes (e.g. Landfill Directive 199/31/EC), has improved, mainly in connection with the allowed treatment processes and the types of soils to be treated (it is not restricted to polluted soils). In some countries, the *in situ* containment is now viewed as a type of waste disposal, and therefore has to obey more stringent regulations [56]. Due to this change of paradigm, we have been witnessing a much higher effort to treat contaminated soil, which has led to the development of new and more effective technologies for soil remediation. These techniques may be applied in the contaminated area (*in situ*), or by removing the soil from the contaminated area, treating it in a specific treatment complex, and restoring the treated soil to its original place (*ex situ*). These techniques are usually preferable to the solution of confinement/isolation of the contaminated area, as this latter process does not provide a true solution for the problem in hand, constituting instead only a provisional solution. The decontamination techniques can be classified, based on the nature of the treatment, as: physical-chemical, biological, thermal or other techniques [57]. In some situations, it may be necessary to combine two or more of these techniques in order to arrive at a more economical and effective treatment [58]. It is important to understand that the success of a decontamination process relays on the proper selection, design and operation of the remediation technology, which should be selected based on the contaminant and soil characteristics. Although not constituting a technique that may be placed under the umbrella of the above cited groups of techniques, due to its lack of or insufficiently high treatment efficiency, the confinement/isolation of the contaminated area is of great applicability, especially when a quick confinement/isolation of the site is required to avoid

Table 1. Classification and characteristics of pesticides [120–123].

Class	Activity	Chemical classification	Examples	K_{oc}*	Half-life** (days)
Acaricides	Destroy and eradicate all these types of mites	Organophosphorus	Malathion	1800 μg mL^{-1}	1
		Amidines	Amitraz	163 mL kg^{-1}	1
		Pyrethroids	Fluvalinate	1000 g mL^{-1}	30
Algicides	Control algae in water, including swimming pools	Natural	Bacillamide	n.a.	n.a.
		Synthetic	Nostocarboline	n.a.	n.a.
		Dicarboxylic acid	Endothal	85 mL g^{-1}	7–21
Bactericides	Destroy, eradicate or prevent the appearance of bacteria	Alcohol/Ether	Broponol	5.0 mL g^{-1}	>1880
		Aldehydes	Formaldehyde	1.567	1600
Fungicides	Control, destroy and regulate fungus effects	Tetranortriterpenoids	Azadirachtin	7 mL g^{-1}	26
		Organochlorine	Pentachlorophenol	1000 mL g^{-1}	45
		Organomercurials	Copper Sulfate	1000–18000 mL g^{-1}	26
Herbicides	Used to destroy evil weed or any kind of unwanted vegetation	Chlorophenoxys	Bentazon	34 mL g^{-1}	7–94
		Ureias	Diuron	480 g mL^{-1}	14–24
		Triazines	Atrazine (Aatrex)	100 g mL^{-1}	60
			Simazine	130 g mL^{-1}	60
Insecticides	Destroy, eradicate or stun, inhibiting the feeding or preventing infection and the attack of insects	Organochlorines	DDTs	238,000	4300
		Organophosphorus	Acephate/Orthene	2–8 mL g^{-1}	3–4
		Carbamate esters	Carbaryl/Sevin	100,00	22
		Pyrethroids	Permethrin	8600 g mL^{-1}	30
Molluscides	Used against molluscs	Organophosphates	Fenamiphos	400 mg L^{-1}	50
		Carbamates	Thiodicarb	418 mL g^{-1}	<2
Nematocides	Used against nematodes	Carbanilate pesticides	Oxamyl/Vydate	25 μg g^{-1}	1–2
		Carbamates	Carbofuran/Furadan	22 μg g^{-1}	30–120
			Adicarb/Temik	20 μg g^{-1}	7–10
Rodenticides	Used specifically in the control of rodents	Organobromines	Brodifacoum	5000 mL g^{-1}	157

*The larger the $\boldsymbol{K_{oc}}$, the more strongly the pesticide is held to the soil organic matter and the less likely will it leach.

**Half-life is the period of time it takes for one-half of the amount of pesticide in the soil to degrade. Non-persistent pesticides have a half-life of less then 30 days, moderately persistent pesticides have a half-life of 31 to 99 days, and persistent pesticides have a half-life greater than 100 days.

further expansion of the contamination. Therefore, this technique will be considered in the following analysis.

2.1 *Primary action techniques*

2.1.1 *Confinement/isolation techniques*

The confinement technique consists of the use of barriers that can be passive or reactive. The function of these barriers is to prevent the migration of the contaminants to neighbouring sites, and to inhibit the flow of clean water into the contaminated area. The usual configuration is the total enclosure of the contaminated area. These barriers are constructed in order to have a low hydraulic conductivity (constant of proportionality between the debit and the pressure drop) [57], of the order of 7–10 cm/s. Reactive permeate barriers (RPBs) [59,60] are barriers constructed to act directly on the contaminants. They have in their constitution reactive materials, which are placed in the subsoil, through which water passes, promoting the decomposition of the existing contaminants. The construction of this type of barrier is usually made in two different configurations: funnel or straight, both requiring the drilling of a well with a depth of 15 to 20 metres. The material used for this type of barrier can vary, iron being the most commonly used. Besides the chemical treatment, it is also possible to apply a biological treatment, using for that purpose the organic carbon content of the water stream to be treated (e.g. sawdust).

2.2 *Biological techniques*

Biological techniques are based on the bioremediation principle [62], where microorganisms are used for the removal of the contaminants of the soil and for the treatment of sludge and underground water. It is necessary to point out that other biological techniques exist, which will not be detailed in this work, as we have restricted ourselves to the presentation of techniques that currently present a greater potential of application [63].

2.2.1 *Biopiles and landfarming*

Two examples of biological techniques are the agrarian technique ('landfarming') [64] and biopiles, which consist of the excavation of the contaminated soil and stimulation of the activity of microorganisms by the addition of air and nutrients, and a control of the humidity. In the biopiles, airing is done by pipes placed in the bottom part of the biopile with the help of a compressor, while in the agrarian techniques airing is made by a tractor that digs the soil [57,65]. Synonyms for biopiles include biocells, bioheaps, biomounds and compost cells [66,67]. The treatment areas are often covered with an impermeable liner to prevent the release of contaminants and/or contaminated soil to the environment, and to protect the soil from wind and precipitation.

The thickness of the soil layer spread in the agrarian techniques is small (no more than 1.5 m) as compared with the one used in biopiles [68]. These techniques are used for the treatment of contamination with hydrocarbons of high molecular weight, which are not easily volatilised, contrary to what happens with the volatile organic compounds (VOCs) [66,67,69,70]. Mid-range products, like diesel or kerosene, contain lower amounts of volatile components, and their biodegradation is more effective. This treatment technology may be applied for site remediation in surface soils and unsaturated soils [71].

Table 2. Applicability of soil remediation techniques (type of contaminant and soil).

Technology	Category	Type of contaminants	Type of soil
Confinement/isolation	*Primary action*	Passive treatment walls: VOCs, SVOCs and inorganics.	The PRB technologies were mainly designed to passively capture and treat contaminated groundwater.
		Reactive treatment walls: chlorinated organic compounds and heavy metals.	
Biopiles and landfarming	*Biological*	Non-halogenated volatiles and semi-volatiles, fuel hydrocarbons. Some other compounds that have been treated successfully include: PCV, residues of coke and some pesticides.	Surface soils and unsaturated soils.
			Soils with a low permeability are difficult to aerate but retain water better than soils with a high permeability.
Natural attenuation	*Biological*	Hydrocarbons, BTEX (Benzene, Toluene, Ethylbenzene and Xylenes), PAHs (Polycyclic Aromatic Hydrocarbons).	Efficiently carried in aired soils and easily permeable ones. It is difficult to apply in saturated soils and clayey soils with low permeability.
Composting	*Biological*	PAHs and explosives (TNT, RDX and HMX), when using thermophilic aerobic composting.	Surface soils, unsaturated soils and sediments.
Bio-airsparging	*Biological*	Various fuels (such as gasoline, diesel and jet fuel), oils and greases, BTEX compounds and chlorinated solvents (e.g. perchloroethylene, tetrachloroethylene, dichloroethylene).	Saturated and unsaturated zone.
Bioventing	*Biological*	Petroleum products including gasoline, jet fuels, kerosene, and diesel fuel. Some other compounds that have been treated successfully include: non-halogenated solvents, some pesticides and wood preservers, among other organics compounds.	Low levels of humidity may limit bioventing efficiency.
Bio-rehabilitation	*Biological*	Non-halogenated volatiles and semi-volatiles compounds, fuels.	
Phytoremediation	*Biological*	Radio-nuclides, hydrophobic organic compounds, BTEX, PAHs, heavy metals and pesticides	Soils, groundwater and surface water.

(*Continued*)

Table 2. Continued.

Technology	Category	Type of contaminants	Type of soil
Soil vapour extraction	*Physical-chemical*	VOCs and some fuels.	Compact soils or with high humid ($>50\%$) present a lower permeability to the air, therefore requiring a more powerful pump which turns the process more expensive and some times very difficult to applied. Soils with organic matter or very low humidity are capable of adsorbing the VOCs, resulting in a low removing rate.
Airsparging	*Physical-chemical*	VOCs, BTEX, MBTE. Airsparging is less applicable to diesel fuel and kerosene.	Fine-grained, low permeability soils, limit the migration of air to the subsurface, thereby limiting the effectiveness of air delivery and vapour recovery.
Dechlorination	*Physical-chemical*	Halogenated SVOCs and pesticides. It is also applicable to VOCs, but with lower efficiency. The APEG process is one of the few available processes, besides incineration, that has been tested successfully in the treatment of PCBs.	High values of humidity and clay fraction increase operation costs.
Soil flushing	*Physical-chemical*	Inorganic compounds, including radioactive contaminants. It can also be used to treat heavy metals, PCBs, VOCs, SVOCs, fuels and pesticides, but it may be less cost-effective.	If the soil has a high percentage of silt or clay the flushing solution cannot easily move through the soil, and therefore it cannot easily make contact with the contaminants. This limits the overall effectiveness of the soil flushing process.

Solvent extraction	*Physical-chemical*	Sediments, sludge and soils containing mainly organic contaminants such as PCBs, VOCs, halogenated solids, petroleum wastes and also some inorganic compounds (e.g., acids, bases, salts or heavy metals).	Soils, sludge and sediments.
Solidification/stabilization	*Physical-chemical*	Inorganic compounds, including radio-nuclides.	Soil, sand and/or building materials.
Thermal incineration	*Thermal*	Explosives and residues, particularly chlorinated hydrocarbons, PCBs and dioxins, semi-volatiles, and pesticides.	Surface soils and unsaturated soils.
Thermal desorption	*Thermal*	All types of organic contaminants. The target contaminants for HTTD are SVOCs, PAHs, PCBs, volatile metals and pesticides.	Soil with high fractions of clay and humus need large treatment periods.
Vitrification	*Thermal*	SVOCs, pesticides, PCBs, dioxins, PAHs and many other organic and inorganic compounds. Volatile metals can be removed if the temperature is sufficiently raised, but they are not destroyed.	Soil, sludge, and sediments must be dried to decrease the gas stream to be treated.
Electrokinetic	*Special*	Heavy metals, anions, and polar organic compounds in soil, sludge and marine sediments.	Low permeability soils (totally or partially saturated with clays and silt-clay mixtures).
Plasma	*Special*	Toxic or hazardous organic compounds from different materials, particularly petroleum and oil contaminated soils.	Soil and stored waste.
Supercritical extraction	*Special*	PBCs, PAHs,TPH, pesticides and radio-nuclides.	Soil and stored waste.

2.2.2 *Natural attenuation*

Another biological process is natural attenuation, which is a controversial process, being considered by many as the 'do-nothing' solution. This technique, in which the biodegradation occurs by natural causes, without human intervention, requires a specific and constant monitoring, possessing very slow degradation kinetics and, therefore, having the risk of not attaining the desired decontamination in the estimated time of degradation [57,62,65].

2.2.3 *Composting*

Composting is a controlled biological process through which organic biodegradable contaminants are converted into innocuous and stabilised by-products, due to the activity of microorganisms (in aerobic or anaerobic conditions). Generally, thermophilic conditions are kept (54–65°C) so that the composting of soils contaminated with dangerous organic contaminants may be carried out adequately. The contaminated soil is excavated and mixed with organic dispersants and corrective agents, such as vegetal and animal wastes, sawdust and residues, in order to increase the porosity of the material to be treated. The maximum degradation efficiency is reached by keeping constant the humidity, pH, oxygen concentration, temperature and carbon/nitrogen ratio.

2.2.4 *Bio-airsparging*

When the goal is to reduce the concentration of volatile compounds adsorbed in the soil, in the saturated zone, or dissolved in the underground water, the technique of bio-airsparging may be applied, which is also a biological technique [57,62,65] that consists in injecting, from time to time, oxygen and nutrients into the saturated zone in order to increase the activity of microorganisms. Although the bio-airsparging technique may be used for the decontamination of the unsaturated zone, bio-ventilation is more recommended for these situations. Heavier compounds like heating and lubricating oils do not evaporate easily, and therefore biodegradation is more appropriate for their elimination [72]. This *in situ* technology generally uses microorganisms that are indigenous to the area [73,74], and is ineffective in the case of non-strippable and non-biodegradable contaminants [75,76].

2.2.5 *Bioventing*

In this technology, the air is injected into the contaminated media at a rate optimised to maximise *in situ* biodegradation and minimise or eliminate the off-gassing of volatilised contaminants to the atmosphere. Contrary to bio-airsparging, which involves pumping air and nutrients into the saturated zone, bioventing pumps the air only into the unsaturated or vadose zone [77,78].

2.2.6 *Bio-rehabilitation*

Another biological technique that is frequently used is bio-rehabilitation, which is based on the water removal from the subsoil, prior to its entrance into the contaminated zone, by pumping it to the surface where oxygen and nutrients are added, being then re-injected downstream from the contaminated area [57].

2.2.7 *Phytoremediation*

A promising biological technology is phytoremediation, which is an *in situ* and clean technique based on the use of some species of plants with the ability to degrade specific organic pollutants [79–82]. Its cost is 20–50% inferior to the cost of alternative chemical, physical and thermal *in situ* processes. The main disadvantages of this technique are its seasonal characteristic and the possibility of provoking bio-accumulation of the contaminants in animals. The main categories of this remediation technique are: *extensive biodegradation* in the rizosfera (one of the regions immediately adjacent to the roots of the plants, where the nutrients and microorganisms can be found); *phytoaccumulation* (a process used in the removal of heavy metals from the soil, leading to their accumulation in the plant, which is later dried or incinerated); *phytodegradation* (that consists of the metabolisation of the contaminants by the plants); and *phytostabilisation* (where immobilisation of contaminants occurs using compounds produced by the plants) [62,83].

2.3 ***Physical-chemical techniques***

Physical-chemical techniques are based on physical and/or chemical phenomena. In this section the most important techniques based on the application of physical-chemical methods for soil decontamination will be reviewed in some detail.

2.3.1 *Soil vapour extraction*

Within the physical-chemical techniques, one of the most used is soil vapour extraction (SVE), which is a non-biological technology for the treatment of volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), polychlorinated biphenyls (PCBs) and existing dioxins in the non-saturated zone of the soil (i.e. infiltration zone), where a source of vacuum is applied to the soil matrix creating a pressure gradient that originates the movement of the air present in the wells of extraction [84–86]. Bio-venting is a technology similar to SVE. While in SVE the main mechanism of removal is volatilisation, in bio-venting the biodegradation is promoted, thus presenting lower rates of volatilisation in the wells. From the application of this process usually results a gaseous phase that needs further treatment before being launched into the atmosphere (by using, for example, adsorption in activated coal) [87,88].

2.3.2 *Airsparging*

This technology, which is also known as '*in situ* air stripping' or '*in situ* volatilisation', involves the injection of contaminant-free air into the subsurface of the saturated zone, enabling a phase transfer of the hydrocarbons from a dissolved state to a vapour phase. The air is then vented through the unsaturated zone [62,89,90].

2.3.3 *Dechlorination*

Dechlorination, also known as dehalogenation, is a chemical technique [91,92] that is based on the loss of halogen atoms (i.e. atoms of chlorine, fluorine, bromine and iodine) from the halogenated organic molecules, converting toxic compounds into less toxic substances, that are frequently soluble in water, facilitating, therefore, their separation from the soil [93]. This technique applies the nucleophylic substitution reaction of atoms of chlorine (or other halogens) for other less dangerous ones, using as agents of dehalogenation, sodium and potassium hydroxides and polyethylene glycol, among others [57,94,95].

Basically, this technology is presented in two variants: base catalysed decomposition (BCD) and glycolate/alkaline polyethylene glycol (APEG). The first of these uses as a reactive reagent the hydrogencarbonate of sodium and has been applied in the treatment of ground and sediments contaminated with chlorinated organic compounds, mostly PCBs, dioxins and furans. In the alternative process, the reacting chemical used is a polyethylene alkaline glycol generating residual water that needs further treatment.

2.3.4 *Soil flushing*

Soil decontamination is also possible through the *in situ* washing of the soil ('soil flushing') [96,97], which consists of the extraction of contaminants from the soil by dissolution, suspension in watery solutions, or through the chemical reaction with the liquid that passes through the contaminated soil layers [57,93,98,99]. The washing of the soil may be also carried out *ex situ*, going in this case through the following stages: excavation, fragmentation, separation in different grain sizes, washing of the different fractions and disposal. This technique allows the removal of organic and inorganic compounds, metals and radioactive substances. Its efficiency may be increased by using appropriate additives. The sludge resulting from this process can be reused if mixed with soil or, depending on the contaminant, may be submitted to a specific treatment, as for example: solvent extraction, solidification or vitrification. This technique is often considered as a pre-treatment [53] for the reduction of the amount of material (contaminated soil) to be treated by another decontamination technology.

2.3.5 *Solvent extraction*

While soil flushing generally uses water or water with wash-improving additives, this technology uses an organic chemical as a solvent. Commercial-scale units are already in operation, and they vary in regard to the type of soil, type of equipment used and mode of operation. They usually consist of a preliminary soil preparation stage (after its removal and transport) followed by its insertion into an extractive unit together with a stream of solvent; two flow streams exit from the extractor: one containing the treated soil which usually requires further treatment, and another that is sent to a separator for recovery of the solvent and concentration of the removed contaminants. These are then eliminated by a chemical or biological treatment. The technique of solvent extraction does not achieve the elimination of the contaminants, but only their separation from the soil, being, therefore, considered as a technique for pre-treatment, similarly to soil flushing [100,101]. The success of this technique depends on the choice of the solvent, which must be chosen having in consideration the type of pollutant to be extracted [57,93]. As pointed out above, this technique is habitually used in association with other remediation technologies.

2.3.6 *Solidification/stabilisation*

Soil remediation is also possible through the solidification/stabilisation technique which consists in mixing a reactive material (e.g. cement or concrete) with solids, semisolids and sludge for immobilisation of the contaminants. The solidification produces blocks with a great physical stability through the addition of stabilising agents (e.g. leached ashes and wastes from the furnaces) in order to limit the mobility and solubility of the constituents of the residues. Some variants of this technique exist, namely: cement-based solidification (direct addition of the cement to the soil); silicate-based solidification (where material, as leached ashes, is added to the cement and to the stabilising agents to be later mixed with the soil); and micro-encapsulation [57,93].

2.4 *Thermal techniques*

2.4.1 *Thermal incineration*

One of the most used technologies is thermal incineration, which consists of the combustion of the organic contaminants at high temperature in the presence of enough oxygen to convert them into carbon dioxide (CO_2) and water (H_2O), thus promoting their destruction [102]. This technique allows effective treatment of soils contaminated with halogenated and non-halogenated compounds, pesticides, PCBs and dioxins/furans, and there are many incineration units operating at an industrial scale. The incinerators can be divided into two types: recuperative (pipe and shell exchanging system) and regenerative (ceramic exchanging system), depending on the type of energy recovery system adopted. The regenerative systems are capable of supporting high temperatures and allowing the recovery of around 90% of the combustion energy [103], presenting, however, higher capital costs, compared to the recuperative systems, which are counterbalanced by the lower costs of operation. The design of these incinerators is influenced by three parameters (the so-called 'three T**s**'): temperature, turbulence and residence time. A correct combination of these parameters allows attaining efficiencies as high as 95%. The operating temperature depends on the type of contaminants, the turbulence influences the degree of oxygenation of the mixture and the residence time must be enough to allow the complete combustion of the contaminants [102]. The incineration process produces, however, three different types of residues: solids coming from the incinerator, fuel gases (combustion gases), and when applied to the treatment of soils containing acid gases, the water of the washing system. There are also catalytic incinerators that operate in a similar form, having the same objectives, but using a catalyst that allows the temperature of activation of the combustion reaction to be between 320 and 800°C; i.e. half of the operating temperature of the thermal incinerators. The catalytic incinerators are safer than the thermal incinerators, having lower energy costs and less pollutant gaseous emissions [103]; however, they have the disadvantages of higher capital costs, the need for periodic regeneration/substitution of the catalyst, and the requirement for a larger area of implementation in the soil [93,104–107]. Although it is not frequently used in the removal of inorganic compounds, it can be used for removing volatile metals by operating at high temperatures [108]. The treatment consists of heating the soil matrix at a high temperature (300–550°C) to provoke the water and contaminants desorption from the soil and their vaporisation. The temperature of this process is inferior to the temperature of combustion, and it is able to decompose the simplest substances [57,107]. The organic vapours resulting from this process are collected and treated in secondary treatment units (catalytic oxidation chambers, condensing or adsorption units) before being discharged into the atmosphere. Finally, the treated soil is cooled, stabilised, the humidity adjusted, and later returned to its original place.

2.4.2 *Thermal desorption*

Thermal desorption is a thermal separation process that does not aim at the destruction of the contaminants. The soil is heated in order to volatilise the water and the contaminants. A gaseous stream or a vacuum system transports to a gas treatment unit the previously volatilised compounds. The temperatures reached and the time of residence are determined in such a way as to promote the volatilisation of the selected contaminants but without allowing them to oxidise. Depending on the operating temperature, the processes may be classified into two different categories: high temperature thermal desorption (HTTD) and low temperature thermal desorption (LTTD). The thermal desorption systems may be applied in the treatment of soils contaminated with different types of organic contaminants, but with different degrees of efficiency. The LTTD processes are usually applied to the treatment of non-halogenated and combustible VOCs. They can also be used to treat SVOCs, but with smaller efficiencies. The contaminant target groups for the HTTD processes are the SVOCs, PAHs, PCBs and pesticides. HTTD systems can also remove volatile metals. The process is applicable in the separation of organic residues proceeding from the wood industry, and in the treatment of synthetic rubber, inks, soils contaminated with creosote or hydrocarbons.

2.4.3 *Vitrification*

Another thermal technique for soil decontamination is vitrification, where the soil contaminated is converted into a vitreous product and therefore stabilised. This technique can be applied *ex situ* or *in situ*. The *in situ* vitrification consists in the insertion of graphite electrodes into the soil creating a high electric current, such that the released heat provokes the fusion of the soil matrix [93]. As the vitrified zone grows, it incorporates inorganic contaminants. The pyrolised organic components migrate to the vitrification zone where they are burned in the presence of oxygen, being necessary to provide a treatment area for the gases before they are released into the atmosphere. The *ex situ* vitrification is based on a similar treatment, with the difference that the soil is excavated and introduced into a vitrification system that functions in an identical way to the described process of *in situ* vitrification [57].

2.5 ***Special techniques***

Some techniques can be considered as special, as they are in a development stage and have been shown to deserve a more careful study for better analysing their efficiency and implementation. Some of these techniques, those that probably will have more impact in the general public, will be discussed in the following paragraphs. They can be applied to specific locations without the need for excavation. However, they are less effective in organic and carbon-rich media and a control of the soil pH is a key management factor in the application of these techniques as it determines the pollutants' solubility and thus, treatment rates.

2.5.1 *Electro-kinetic*

In this technique, the movement of the contaminants in the soil is induced by an electric current of low voltage, in the order of mA/cm^2, which is created by two electrodes placed in the soil. This technique is sufficiently effective in the removal of heavy metals and polar organic compounds from soil of low permeability, sludge or marine sediments [109,110]. When an electric current is applied, the first phenomenon that occurs is the electrolysis of the water, the solution near the anode becoming acid due to hydrogen production and release of oxygen. This 'acid front' of the anode displaces by migration to the cathode leading to desorption of the contaminants of the soil. This migration involves different types of phenomena, as the electro-osmosis (movement of the soil mixture to the cathode), electro-migration (ionic transport of ions and complexes into the opposite sign electrodes) and electrophoreses (charged and colloid particle transport under the influence of the electric field) [111]. The contaminants that arrive to the electrode can be removed by precipitation/co-precipitation, complexation with ions, or pumping. The possibility of precipitation of species, as heavy metals, next to the cathode, has been one of the main drawbacks to the use of this process. However, recent studies have improved this technique by reducing the problem of precipitation of species next to the cathode [112].

2.5.2 *Plasma*

One technique that is increasingly becoming the focus of research studies and applied in a growing number of areas, namely in soil decontamination, is the plasma technique. This technology has been shown to be more efficient, from the energy point of view, than the alterative thermal technologies [113]. In the plasma system, a gas is heated at extreme temperatures to create the plasma. When the contaminated soil is placed next to the plasma it is heated to very high temperatures, under these conditions there is an absence of oxygen molecules. Organic compounds are partially degraded, as they usually are not totally broken, and the inorganic compounds (metals, reactive radicals) suffer a process of vitrification. Products of the incomplete combustion, as dioxins and furans, can appear in this step leading to the need for extra treatment. This technology can be used to deal with mixtures of residues, sludge and solids, not being recommended when the contaminants are salts, as these are hardly immobilised in the glass state. The plasma units can be made mobile, treating *in situ* the contaminated area, avoiding therefore the risks and costs of transportation of toxic materials. Economical evaluation indicates that the process is very competitive with existing technologies, without presenting some of the environmental and technical limitations of those processes [114,115].

2.5.3 *Supercritical extraction*

Another technique that has recently been suggested for soil decontamination is supercritical extraction, which is a technology that is based on the application of a supercritical fluid as the separating agent [93,116–118]. A supercritical fluid is any substance at a temperature and pressure above its critical point. This technique has the advantage of using as extracting solvents compounds such as CO_2 and H_2O, which are not toxic. Another advantage in the use of supercritical fluids is the possibility of controlling its characteristics (e.g. its power of dissolution) through small changes in the operating pressure and temperature, making these solvents adequate for the extraction of a large spectrum of contaminants. One of the main reasons for the application of supercritical extraction for the removal of pesticides from contaminated soils is the possibility of carrying out the extraction of the contaminants without significantly modifying the structure of the soil and without leaving solvent residues [1,35,49,108,119].

The above discussion on remediation techniques is not focused on the removal of pesticides, not only because this type of information is very scarce in the literature, but also because it can be expected that pesticides will behave similarly to other analogous organic compounds, where decontamination is concerned. However, Table 5 tries to summarise some of the techniques that are potentially capable of treating soils contaminated with pesticides, but, of course, it must be kept in mind that their feasibility relies on many variables, including: pesticide concentration, type of soil and present status of development of the technique, among others. The techniques that had already been proved to be adequate for the treatment of soils contaminated with pesticides include: solvent extraction, thermal desorption at high temperatures and dechlorination. Other techniques show a high potential for the remediation of this type of soils. Some of these are: biopiles, landfarming, bioventing (only for some types of pesticides), phytoremediation, thermal incineration, vitrification and supercritical extraction.

The type of soil affects the efficiency and applicability of a particular remediation technique, as is pointed out in Table 2.

3. Economic analysis

For many reasons, it is very difficult, and sometimes even impossible, to accurately compare the costs associated with the different remediation technologies. One of the main problems in obtaining comparable cost information is that the available information is from reports concerning the application of the technique under some specific *in situ* conditions, and therefore difficult to extrapolate to other conditions with different contaminants, contaminant concentration and type of soil. That is, the site conditions and type of contaminants influence not only the performance of the technique, but also the associated costs. Another problem is that the reports made by the vendors are frequently done using different measuring parameters, making it difficult to compare them. That is, the costs can be reported per volume of treated soil, reduction in contaminant concentration, reduction of contaminant mobility, mass of removed contaminant or surface area treated. These variations in the cost reports make it very difficult to compare costs of competing technologies. Another problem that makes the economical study so difficult is the fact that in most of the cases technology providers do not report the variable costs (set-up of the equipment in the contaminated site, treatability studies to prove the technology, modification of site conditions and others); just the ‘up and running’ costs are given. This can be acceptable to compare the costs of installed operations, but it is usually necessary to know the overall project costs in order to evaluate the economic feasibility of remediation techniques. For example, certain remediation technologies that have large and variable initial costs may not be competitive, although the ‘up and running’ costs appear competitive. And finally, another problem is related to the fact that for *in situ* technologies, cost information is often developed by geotechnical consultants rather than technology providers, and is rarely compiled for general reference by the general public. Even when cost information reaches the general public, it is given in general terms and no cost breakdowns are detailed, hence private users are not able to judge the realism of the cost elements. Although some governments are compiling cost data and creating guidelines for cost computation and reporting these results (e.g. the US Federal Remediation Technologies Roundtable, 1995), these guidelines have not been adopted by the private sector.

Table 3. Costs associated with some soil remediation technologies.

Technology	Total cost (US$)	Contaminants	Execution time (Months)	Development state
Off-site incineration.(1) (11500 m^3 of contaminated soil)		PCBs		Full(6,7)
ENSCO (type of incinerator)	32,772,259		2–3	
APTUS (type of incinerator)	20,810,416		5	
Infrared incineration.(1) (11500 m^3 of contaminated soil)				Full(6,7)
EP toxicity soil	7,188,849		3	
Non-EP toxicity soil	4,905,269		3	
Incineration.(3)	86–839/tonne (O/M costs)	PCBs		Full(6,7)
Off site RCRA/TSCA Landfill.(1) (cost of shipment and disposal of the 11500 m^3 of soil)	13,835,407		2	Full(6,7)
Solvent extraction.(1) (11500 m^3 of soil are treated with an average PCB concentration of 1000 ppm)		PCBs		Full(6,7)
EP toxicity soil	5,282,409		17	
Non-EP toxicity soil	3,065,365		17	
Solvent extraction(3)	46–214/tonne (O/M costs)	PCBs		Full(6,7)
Glycolate dechlorination (APEG).(1)		PCBs		
EP toxicity soil	6,743,200		6–12	
Non-EP toxicity soil	6,243,407		6–12	
Critical fluids extraction.(1) (11500 m^3 of contaminated soil)		PCBs		
EP toxicity soil	6,859,900		24	
Non-EP toxicity soil	3,662,888		24	
Dehalogenation.(3)	>229/tonne (design, installation, excavation, O/M costs)			Full(6,7)
In situ vitrification.(1)	5,461,446	PCBs	6	Pilot(6,7)
Soil flushing(4)		High level radioactive material		Full(6,7)

(*Continued*)

Table 3. Continued.

Technology	Total cost (US$)	Contaminants	Execution time (Months)	Development state
Small site/easy	42 per cubic metre			
Large site/easy	24 per cubic metre			
Bioventing(8)	30–90 per tonne		6–24	Full
Bioventing(4)				
Small site/easy	928 per cubic metre			
Large site/easy(4)	104 per cubic metre			
Soil vapour extraction (SVE)(7)	20 to 50 per tonne	NA		Full(6,7)
Soil vapour extraction (SVE)(4)		SVOCs		
Small site/easy(4)	1,275 cost per cubic metre			
Large site/easy(4)	5533 per cubic metre			
Airsparging (8)	26–66 per cubic metre (8)	Petroleum contaminated soil/ groundwater		Full(6,7)
Temperature desorption(7)	50 to 330 per tonne, and 20–35 for operating costs.	Petroleum contaminated soil/ groundwater		Full
High temperature desorption	107–312 per tonne (design, installation, excavation, O/M costs).(2)			Full(6,7)
Thermal treatment(4)		SVOC's/VOCs		
Small site/easy(4)	67 per cubic metre			
Large site/easy(4)	38 per cubic metre	SVOC's/VOCs		
Vitrification *in situ* (7)	>80 per cubic metre			
Vitrification *ex situ* (7)	<110 per tonne including excavation			
Vitrification	550 tonne (design, installation, excavation, O/M costs).(2)			Full(6,7)
Phytoremediation(5)	105 per cubic metre(5)	Metals(5)		
	70,000 (5)	Petroleum hydrocarbons (site size not disclosed)(5)		
	850,000(5)	Radionuclides in surface water(5)		Pilot(6,7)

Phytoremediation(7) (one acre of soil contaminated with lead to a depth of 50 cm)	60,000 to 100,000	NA		
Biopiles(7)	130 to 260 per cubic metre	NA		Full
Excavation and disposal	50/tonne municipal landfill disposal. 390/tonne hazardous waste disposal.(3)			
Passive-reactive treatment walls		VOCs	24	Pilot(6,7)
Small site/easy(4)	1,267 per cubic metre (of treatment wall)			
Large site/easy(4)	1,563 per cubic metre (of treatment wall)			

(1) An engineering evaluation and cost analysis (EE/C A) to investigate and evaluate treatment technologies of soils contaminated with polychlorinated biphenyls (PCBs) at Fell Iron and Metal Inc. (Fell) site in Bloomington, Indiana, was made. Costs are changing and in many cases have decreased in the past few years.

(2) US Environmental Protection Agency (USEPA), *Remediation Technologies Screening Matrix and Reference Guide*, Version I. Cincinnati, 1991.

(3) Canadian Petroleum Products Institute, *Manual of Petroleum Contaminated Soil Treatment Technologies*, CPPI Report No. 91-9 (1991).

(4) Detailed Cost Estimate – Available at http://frtr.gov/matrix2/section4/4-41.html

(5) Jonathan Chappell, *Phytoremediation of TCE in Groundwater using Populus* (Technology Innovation Office, USEPA, Washington, DC) (http://clu-in.org).

(6) P.J. Marks, W.J. Wujcik and A.F. Loncar, DOD Environmental Technology Transfer Committee, *Remediation Technologies, Screening Matrix and Reference Guide*, 2nd ed. (Report No. 02281-012-009, 1994).

(7) Faisal I. Khan, Tahir Husain, Ramzi Hejazi1, *An Overview and Analysis of Site Remediation Technologies*, Journal of Environmental Management 71 (2004): 95–122.

(8) USEPA, *How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites* (Office of Solid Waste and Emergency Response, US Environmental Protection Agency. Publication # EPA 510-B-95-007 (Washington, DC, 1995).

(9) The cost of biopiles is dependent on the contaminant, the procedure used, pre- or post-treatment, or the need for emission control equipment. It requires few personnel for operation and maintenance.

Table 4. Advantages and disadvantages of the main remediation techniques.

Remediation technique	Advantages	Disadvantages
Passive walls	Provisional solution for the contamination problem (in some cases is enough).	Some physical properties may change with time.
		Depth limitations.
		Non-perfect mixture of the constituents.
Reactive permeable walls	Conversion of the contaminants in non-toxic species or barely soluble.	The permeability of the reactive zone must be equal or higher than the permeability of the aquifer.
Agricultural techniques	Easy to implement and design.	It requires a large area.
	Short treatment times, between 6 months and 2 years, under optimum conditions.	Reduction above 95% in concentration and concentrations below 0.1 ppm are hard to achieve.
		It is not possible to apply when the concentration of heavy metals are higher than 2500 ppm or the total concentration of hydrocarbons of oily origin are higher than 50 000 ppm.
Bio-rehabilitation	Degradation of the material adsorbed or dissolved in the infiltrated and saturated zones.	The pit may be clogged by biomass or precipitates.
	Easy to use and availability of equipment.	The total concentration of hydrocarbons of oily origin must be below 50 000 ppm.
	Does not create any residues.	Rehabilitation may occur only in the most permeable zone.
Fito-remediation	The costs are much less than for other conventional options.	It is a seasonal technique.
	The set-up costs are similar to the ones for farming equipments.	May originate bioaccumulation in animals.
		Is applicable only at low depths.
		May not be able to achieve the intended levels of decontamination.
Soil vapour extraction	Proven performance, easily available equipment and simple set-up.	Reductions above 90% in concentrations are hard to achieve.
	Minimal disturbance at the operation site.	Low efficiency when applied at sites of low permeability.
	Small treatment times (from 6 months to 2 years under optimal conditions).	May require treatment of the extracted vapour.
	May be combined with other technologies.	Only the non-saturated area is treated and may force the use of other methods to treat the saturated areas and the underground water.
Solidification/ stabilisation	This technique, either *in situ* or *ex situ*, is available at large scale for non-volatile heavy metals.	An increase in the treated volume implies an increase in the quantity of reagents.

	It is a relatively simple technology.	Environmental conditions may have to be taken in consideration when considering large periods of immobilisation.
	It is a technique applicable with success to inorganic compounds and metals.	Some preliminary studies may be needed to determine the adequate stabilising agents.
		Permeability and compressibility tests are needed to calculate product integrity.
		The toxicity of the contaminant is not reduced.
Solvent extraction	The quantity of the contaminated material is reduced.	Does not reduce the toxicity of the contaminant, only promotes its concentration.
	The recovery and treatment of the contaminant may be achieved.	Generally, this technique is less efficient for molecules of high molecular weigh.
		Is not efficient in non-organic compounds.
Supercritical extraction	Is an accepted method for the analysis of contaminated soils.	The recovery depends on the type of contaminant, and the use of co-solvents may be needed to attain higher recoveries.
	Supercritical extraction may also be allied with other technologies to reduce or eliminate the extracted contaminant.	It is a technique still under development for soil treatment.
		This technique presents higher equipment costs as compared with traditional techniques, presenting however smaller operation costs.
Electro-kinetics	It is an *in situ* technique.	It is a process limited by the solubility of the contaminants and by soil adsorption.
	The energy needs are low when compared with other decontamination processes.	Electrolyte reactions in the electrodes neighbourhood may cause variations of medium pH, and cause changes in the solubility of the contaminant.
	Recovers ionic contaminants that are hard to remove by other techniques, as they usually stay adsorbed in soil particles.	Heterogeneity or anomalies at the site, such as the presence of iron and iron oxides, may cause a decrease in the removal efficiency.
	Techniques such as SVE are not very efficient for soils of low permeability, allowing this process the ovecome of this problem.	Sometimes migration may be slow, making decontamination insufficient.
Incineration	The operation and maintenance is simple and overcomes the capital costs.	High energy costs.
	Light equipment easy to adapt to the existing facilities.	Heavy metals such as arsenic, mercury, cadmium and chromium are not destroyed by the combustion, thus being some of them present in the ashes or released in the gases.
		Soils containing rocks may need to be fragmented.

Table 5. Techniques suitable to treat soils contaminated with pesticides.

Name	Suitability	Name	Suitability	Name	Suitability
Landfarming, biopiles	✋	Vitrification	✋	SVE	----
Ex situ soil washing	✋	Thermal desorption at low temperatures	✋	Dechlorination	👍
In situ soil washing	✋	Thermal desorption at high temperatures	👍	Bio-rehabilitation	*
Solvent extraction	👍	Incineration	✋		

👍 – Demonstrated efficiency; ✋ – Potential efficiency.
*Depends on many conditions, among which is the concentration of contaminants.

Table 3 presents associated costs and execution times for some of the described remediation techniques.

4. The choice of the best technique for soil remediation

The above discussion shows clearly that many techniques may be applied for specific situations, and that some can be more effective or cheaper than others in a particular situation. Table 4 summarises the main advantages and disadvantages of some of the technologies previously discussed. An important step in determining the best technology to apply in a particular situation is the evaluation of the suitability of the chosen technique for the type of contaminant to be removed.

SVE is the most frequently used technology as it provides good results in a short time, and is also cost-effective, presenting in some cases, costs of remediation estimated at just above US$2 per cubic yard ($0.76\,m^3$). Landfarming, a traditional technology, may still be used at effective costs to treat some contaminants like total petroleum hydrocarbons (TPH). Bioventing has been successfully tested in some sites, and nowadays can be almost considered a full scale working technology, although with the limitations already detailed. Although efficient and fast, soil washing presents the problem of being only effectively applicable for limited soil quantities. Thermal desorption is a technique very efficient and cost-effective to treat a wide range of contaminants present in harsh soil environments (clay and silty soil). US$200 per tonne of treated soil is the operational cost usually associated with this technology. Another technology that is able to treat a wide range of contaminants is *in situ* vitrification, which, however, is usually only effective in complex hydrogeologic settings. Biopiles and phytoremediation are technologies still under pilot testing.

Selection of the best technique to apply to a certain situation is often difficult, as most of the remediation technologies are site and contaminant specific.

5. Conclusions

Soil contamination is a complex problem due to the number of variables involved, such as soil structure, climatic conditions and the huge number of potential contaminants.

In this work we started by analysing the soil composition and structure, emphasising its complexity. This is an important factor to be taken into account when determining the best remediation technology for a certain kind of contaminant. Then, the main classes of pesticides, which constitute one of the most important and difficult soil contamination problems, were reviewed. Details of their classification were given. Nowadays, there are many techniques for remediation of soils contaminated with pesticides, all of them having specific advantages and disadvantages. In this work, the main decontamination techniques were reviewed, and their advantages, disadvantages, suitability and efficiency discussed (Table 4). It is almost impossible to clearly elect a technique as being the most suitable for the remediation of soils contaminated with pesticides, as this depends on many factors, such as contaminant concentration and characteristics, partition coefficients, etc. However, some hints were given concerning the choice of an appropriate technique to solve one particular contamination problem (Tables 4 and 5). Economic and social factors must also be taken into account; therefore, an analysis of costs associated with the implementation of the most important soil remediation technologies was presented (Table 3). Regulatory regimes are very important to determine economic viability and the principles of sustainability and the importance of restoring the ecological function to soils should always be taken into consideration.

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