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HCH-Contaminated Soils and Remediation Technologies

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and David Lorenzo Fernández*

Abstract

The production of lindane (gamma isomer of hexachlorocyclohexane, γ -HCH) in the second half of the twentieth century was an inefficient process that generated vast amounts of residues of other HCH isomers, without any pesticide activity. These residues were often dumped in an uncontrolled way or unsecured landfills in points near the production sites, causing hot spots of soil and groundwater contamination on all continents. Given the persistence and hydrophobicity of these pollutants, the problem generated decades ago is still a challenge to be solved. Several technologies, based on physical, chemical, and biological treatments, have been proposed for the remediation of HCH-contaminated soils. This chapter reviews the particularities of this kind of contamination and critically examines the bases and results of the technologies applied, paying special attention to the physicochemical remediation processes.

Keywords: lindane, HCHs, polluted soils, remediation technologies

1. Introduction

The intensive use of organochlorine pesticides (OCPs) during the last decades around the world and the inadequate management of the wastes generated during the production of these compounds represents a huge environmental problem. That is the case of lindane production, the gamma isomer of hexachlorocyclohexane (γ -HCH), whose production during the last century has generated large amounts of solid wastes, consisting of a mixture of other HCH isomers, that has caused hot points of soil and groundwater contamination [1].

Lindane was synthesized for the first time in 1825 by Michael Faraday [2] and deeply used as a broad-spectrum organochlorine insecticide since the 1940s [3, 4]. Among the eight isomers of HCH, lindane is the only one with insecticidal properties. Unfortunately, the lindane production, schematically summarized in **Figure 1**, is an inefficient process, generating large volumes of the other HCH isomers (mainly α -, β - and δ -HCH). The mixture of HCH isomers obtained in the chlorination of benzene is called technical-HCH, and it was usually subjected to a purification process to separate the γ -HCH isomer. After this step, about 10 kg of HCH wastes were obtained per kg of purified lindane. The solid HCH wastes (consisting of a white powder of HCH isomers) were inappropriately dumped during decades in the production sites nearby, resulting in environmental contamination with global dimension [5–14].

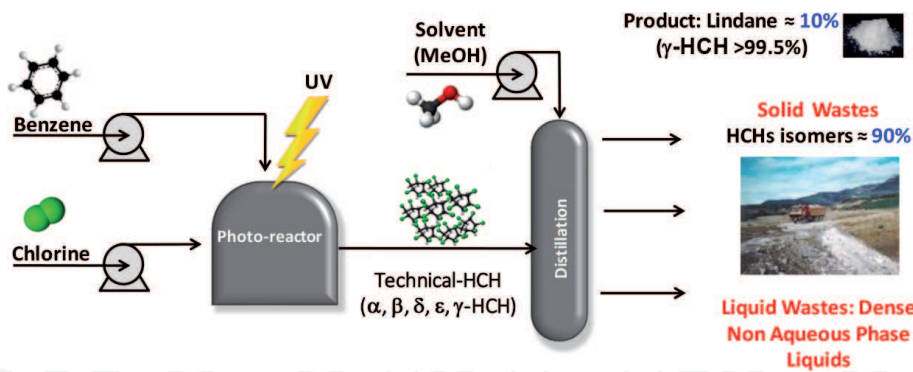


Figure 1.
Scheme of lindane production and purification processes.



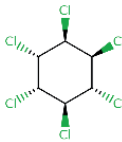
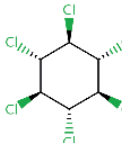
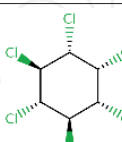
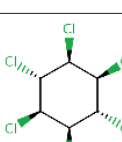
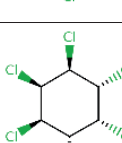
Figure 2.
Location of sites polluted with HCH wastes around the world, modified from [10].

It is estimated that approximately 450,000 tons of lindane were used worldwide between 1950 and 2000. Approximately 63% of the lindane produced was consumed in Europe, 17% in Asia, and about 4.2% in the United States, resulting in the ubiquitous presence of HCH wastes, as is shown in **Figure 2**.

Due to the high refractoriness and adverse effects of HCHs on the ecosystem and human beings [3, 15, 16], several HCH isomers are considered persistent organic pollutants (POPs) by the Stockholm Convention [10] and classified as neurotoxic, carcinogen, and teratogen by the Environmental Protection Agency (EPA) and the World Health Organization (WHO) [17, 18]. The structure and main chemical properties of HCH isomers are given in **Table 1**.

Due to its toxicity, the production and use of lindane have been banned in most countries, including Europe and the United States [24, 25], but many landfills and the surroundings of the lindane production sites remain polluted nowadays, with soil and groundwater contaminated by these compounds [5–14]. The low tolerance limits allowed for HCHs in water and soils have prompted a growing interest of the scientific community to develop simple, cost-effective, and fast methods for the degradation of these pollutants. Conventional methods commonly used include the excavation of polluted soil and its further containment in secure landfills. The traditional groundwater treatment consists of pump-and-treat, with adsorption in activated carbon as a common treatment. However, these options are very expensive and are not a definitive solution since the destruction of the pollutants is not achieved. Therefore, they are considered neither sustainable nor definitive remediation methods [1].

Some studies have focused on the remediation of HCHs in the aqueous phase, dealing with groundwater treatments applied in situ [26] or on-site [16, 27, 28].

Isomer	CAS	Solubility (mg/L)	MW (g/mol)	Structure
α -HCH [*]	319-84-6	1.2-2 [19–22]	290.83	
β -HCH [*]	319-85-7	0.15-0.7 [20–22]	290.83	
γ -HCH	319-86-8	8.6–31 [19, 21–23]	290.83	
δ -HCH [*]	58-89-9	2.1-15.3 [19–21]	290.83	
ϵ -HCH	6108-10-7	7.8 ^{**}	290.83	

^{*}HCH isomers included in the Stockholm Convention.

^{**}<https://comptox.epa.gov/dashboard/dsstoxdb/results?search=DTXSID0024135>.

Table 1.
Name, CAS, water-solubility, molecular weight (MW), and chemical structure of the main HCH isomers.

However, only a few works are found in the literature concerning the remediation of soils contaminated by HCH wastes. The objective of these treatments is the chemical or biological degradation of HCHs. They were carried out to the remediation of soils artificially spiked with HCH isomers and soils with real HCH contamination. The chemical technologies used for the remediation of soils polluted with high HCH concentration are analyzed and discussed in the following sections. Biological treatment of these highly contaminated soils requires long times [29, 30] and are not treated here. Moreover, to better understand the particularities and characteristics of the problem of HCH polluted soils, a description of the main sites contaminated by HCH wastes is also included.

2. Soils with historical HCH contamination

Soils contaminated by HCH isomers show a wide range of concentration values. In general, these soils come from areas where residues of the lindane manufacture or other chlorinated pesticides have been dumped and uncontrollably accumulated. The contamination is present in the form of particulate matter (white particles of HCH wastes in soil distinguishable with the naked eye) and/or adsorbed into the soil. When a particulate matter of HCH wastes is not reported, the concentration of β -HCH in the soil is usually higher than that of α -HCH [31], indicating that HCH isomers are adsorbed into the soil. Real soils polluted with adsorbed HCH isomers have been reported in the following works:

- Riparian area of the Mulde river (Germany). In this case, two highly contaminated sites were characterized by Keller (Kel) and Spittel (Spi) [32]. The concentration of β -HCH with the depth of the soil is shown in **Figure 3**. It can be seen that the HCH concentration decreases with this variable.
- Teltow Canal (Berlin) [33], where the concentrations of HCH isomers in the soils were analyzed. In general, the isomer with the highest concentration in the different sediments studied was β -HCH, as shown in **Table 2**. The lack of particulate matter of HCH wastes in these sediments could explain the higher concentration of β -HCH detected in the soil.
- A contaminated area in Bitterfield (Germany) was described by Wycisk et al. [13], including an old landfill used for the discharge of HCHs and other chlorinated pesticides. The concentration of β -HCH in the soil of the old landfill was higher than the concentration α -HCH, as shown in **Table 3**.
- A gravel pit located in the northeast of France [34], contaminated by HCH wastes dumped by the PCUK company. This company stopped the manufacture of lindane in 1974. In this place, the lindane wastes were encapsulated, but

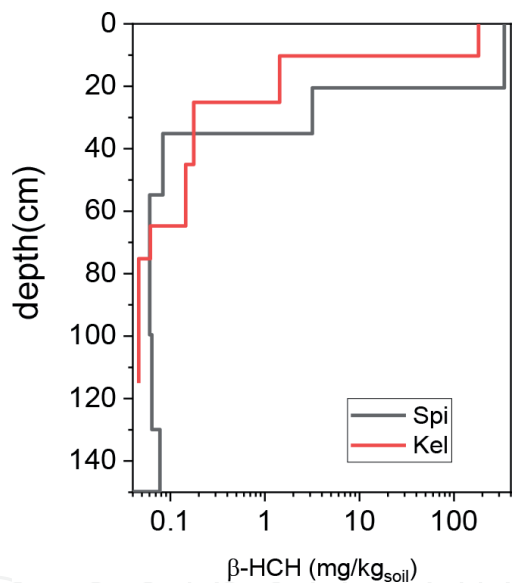


Figure 3.
Soil contamination by β -HCH as a function of depth [32].

Depth, cm	α -HCH	β -HCH	γ -HCH	δ -HCH	ϵ -HCH	Σ HCH
00–10	17	120	41	64	b.d.l.	242
10–15	48	110	29	44	b.d.l.	231
15–20	61	140	42	68	b.d.l.	311
25–30	79	170	50	97	b.d.l.	396
55–60	120	65	47	130	b.d.l.	362
60–65	28	20	12	40	b.d.l.	100
65–70	18	13	7.6	25	b.d.l.	64
95–100	0.3	0.3	0.2	2.1	b.d.l.	3

b.d.l. = below detection limit

Table 2.
Concentration ($\mu\text{g/kg}$) of HCH isomers in Teltow Canal sediments, Berlin [33].

β -HCH (45 mg/kg) and γ -HCH (25 mg/kg) isomers remained in the soil. The presence of α -HCH was not described in this case.

- Agricultural soils in India [29], where chlorinated pesticides were probably stored in the past. The concentration of HCH isomers in these agricultural soils varied from 4.9 to 7.4 mg/kg soil, with a concentration of α -HCH lower than that one of β -HCH.
- A contaminated industrial site in Beijing, China. In this case, Liang et al. [35] collected and analyzed soil samples from an old organochlorine pesticide plant located in Beijing. The soil, which was sieved (2 mm) and homogenized, was characterized, obtaining the following parameters: pH 7.8, total organic carbon 6.2 g/kg, total nitrogen 0.82 g/kg, and moisture 2.8%. The soil contained α -HCH, β -HCH, p,p'-DDT, or p'-DDT, p,p'-DDE, and p,p'-DDD with concentrations of 2.7, 10.8, 12.9, 3.1, 2.0, and 2.6 mg/kg, respectively.
- Farm soils in Kazakhstan, where obsolete pesticides were stored during decades [36]. As can be seen in **Table 4**, the concentration of β -HCH was higher than the concentration of α -HCH.

On the other hand, other works dealing with soils contaminated by HCH wastes reported the presence of white granules of particulate HCHs noticed with the naked eye. In these studies, the average concentration of α -HCH measured in the soil was higher than that of β -HCH, which agrees with the composition of technical-HCH. These studies are listed below:

- Contaminated soils in Galicia (Spain) affected by the industrial activity of lindane production [37]. The soils were analyzed at different points and depths, and the concentration values of HCH isomers found ranged from 5 to around 80,000 mg/kg, with very different concentrations depending on the depth analyzed. The highest values of HCHs (81,035 mg/kg) probably corresponds to the presence of HCH isomers in the form of particulate matter. Fragments and

Depth, cm	α -HCH	β -HCH	γ -HCH	δ -HCH
00–10	440.0	702.5	23.3	10.3
10–20	535.6	574.3	9.5	b.d.l.
20–30	109.0	60.1	0.4	b.d.l.
30–60	0.5	6.4	0.3	b.d.l.
60–80	0.4	2.4	0.1	b.d.l.
80–100	0.2	7.0	b.d.l.	b.d.l.

b.d.l = below detection limit

Table 3.
HCH content (mg/kg) in vertical floor profiles on Spittelwasser [13].

Hot points	α -HCH	β -HCH	γ -HCH
MAC	0	100	100
Point 1	67.1 ± 9.1	176.0 ± 23.3	22.2 ± 3.2
Point 2	15.3 ± 7.3	83.2 ± 5.5	13.0 ± 4.2
Point 3	b.d.l.	b.d.l.	b.d.l.

b.d.l = below detection limit

Table 4.
Concentration values of HCH isomers (µg/kg) in various soils analyzed [36].

dust of this white substance were present in the studied area. This material was also analyzed to determine the presence of technical-HCH wastes. The technical HCH produced in that fabric presented the following composition: 77% of α -HCH, 16% of β -HCH, 5% of γ -HCH, and 2% of δ -HCH. The composition of some soil samples analyzed in this work is shown in **Figure 4**. It was noticed that samples with the highest proportion of β -HCH correspond to those with the lowest total concentration of HCHs, whereas samples with the highest percentage of α -HCH correspond to soils with higher total HCH concentration (probably as grains of technical-HCH wastes). The presence of HCH in the form of particulate matter could add difficulties in the remediation of these sites.

- Sabiñánigo (Huesca, Spain), with two landfills contaminated with HCH wastes dumped by INQUINOSA, a lindane factory which operated from 1975 to 1988 [11]. High concentrations of HCHs in the soil were measured (**Table 5**), and a higher concentration of α -HCH isomer than that of β -HCH was reported, which is in agreement with the presence of HCHs as particulate matter detected in that soil.
- City of Meninos, Brazil, where contaminated soils were found near to a former lindane factory, which operated between 1950 and 1962 [12]. Although the distribution of HCH isomers in the soil was not reported, the high concentration of these pollutants measured (several thousand mg/kg), indicates the presence of HCH-wastes as particulate matter.
- Santo André, Sao Paulo (Brazil) with HCH-contaminated land [38]. In this study, there is no explicit indication of the presence of HCH particulate matter, but the high proportion of α -HCH, shown in **Figure 5**, seems to confirm this hypothesis.
- Soil contaminated by HCH wastes in the Midwest (USA). Phillips et al. [30] studied three areas (A, B, and C) with a high concentration of HCHs, mainly due to the presence of HCHs granules. The total concentration of HCHs along

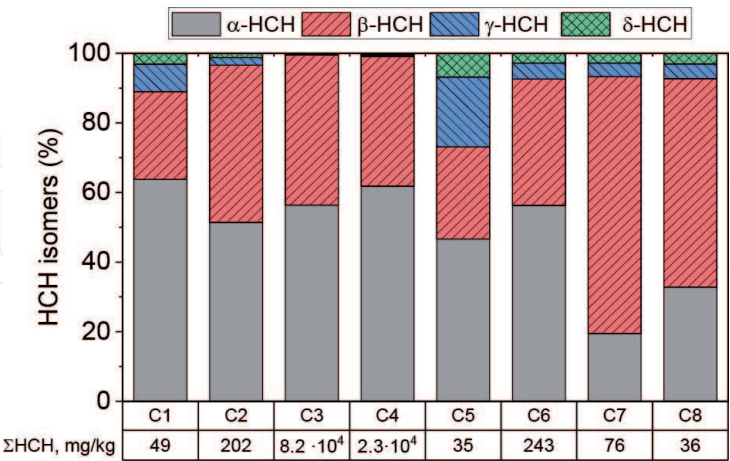


Figure 4.
Percentages of HCH isomers found in soil samples [37].

	α -HCH	β -HCH	γ -HCH	δ -HCH	ϵ -HCH	Σ HCH
Maximum	57,000	5600	9700	2200	2700	74,730
Mean	2303.2	245.5	406.8	105.7	138.9	3200.2

Table 5.
HCH concentration (mg/kg) in soils located at Sabiñánigo landfills [11].

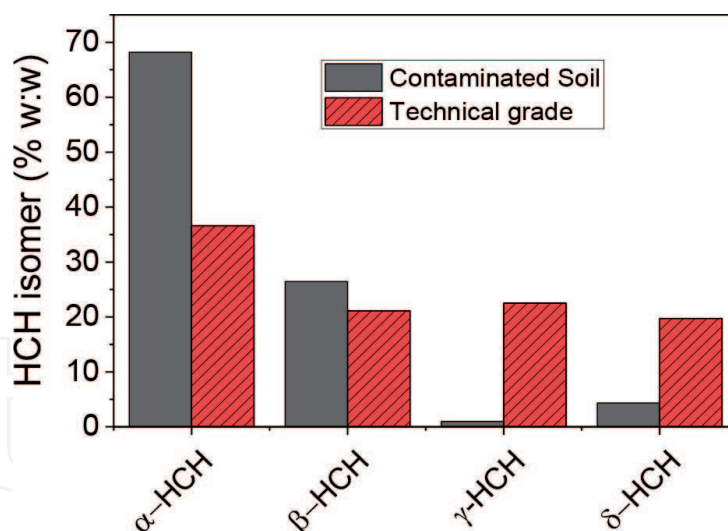


Figure 5.
 Distribution of HCH isomers in soils located at Santo André and Sao Paulo (Brazil) [38] and in technical HCH.

a west to east gradient ranged from 22,430 to 1069 mg/kg in the A zone and from 21,100 to 730 mg/kg in the B zone, whereas in zone C, the concentration ranged from 52 to 1427 mg/kg. The composition of HCH wastes was rich in the isomer α (α -HCH 20,000 mg/kg and β -HCH 2000 mg/kg).

3. Physicochemical remediation of HCH-contaminated soils

Physicochemical treatments have been studied in the literature applied to real or spiked contaminated soils. The last ones obtained by contacting the soil with concentrated solutions of HCHs solved in different organic solvents and the subsequent evaporation of the solvents. In the first case (real soils), the contaminants can be absorbed into the soil (a higher concentration of the isomer β -HCH is noticed) or present as HCH granules (with a higher concentration of the isomer α -HCH). The proportion of HCH isomers found also depends on the composition of the dumped HCH wastes or the spiking procedure (in the case of spiked soils).

In general, β -HCH is always the most recalcitrant isomer regardless of the treatment tested (biological or chemical oxidation and biological or chemical reduction). The following sections summarize the works found in the bibliography related to physicochemical remediation treatments.

3.1 Thermal treatments

Thermal treatments have been traditionally applied to the remediation of soils contaminated with persistent organic pollutants, as HCH wastes. However, the use of high temperatures has major drawbacks, such as the low-cost effectivity of the process and the generation of compounds even more toxic than the starting ones when chlorine is in the structure of the organic pollutant, such as dioxins and furans. The main thermal treatments found in the literature for the remediation of HCH-polluted soils are described below:

3.1.1 Thermal desorption

This thermal process was applied to the remediation of real soils located in Sao Paulo (the distribution of HCH isomers suggests the presence of HCHs in the form

of particulate matter) [38]. The excavated soils were subjected to high temperatures (up to 450°C), as is indicated in the scheme of the heat treatment plant shown in **Figure 6**. The results obtained for the abatement of the different HCH isomers are shown in **Figure 7**, as a function of the reaction time and the temperature of the treatment. An important degradation of HCHs is achieved in only a few hours of reaction, although temperatures above 250°C are required. It should be noted that β -HCH is also the most recalcitrant isomer.

3.1.2 Deep oxidation by using basic catalysts

Rozdyalovskaya and Chekryshkin [39] studied the destruction of pure lindane at high temperature by using basic catalysts. The deep oxidation of lindane on a catalyst can be represented by the following reaction (Eq. (1)):

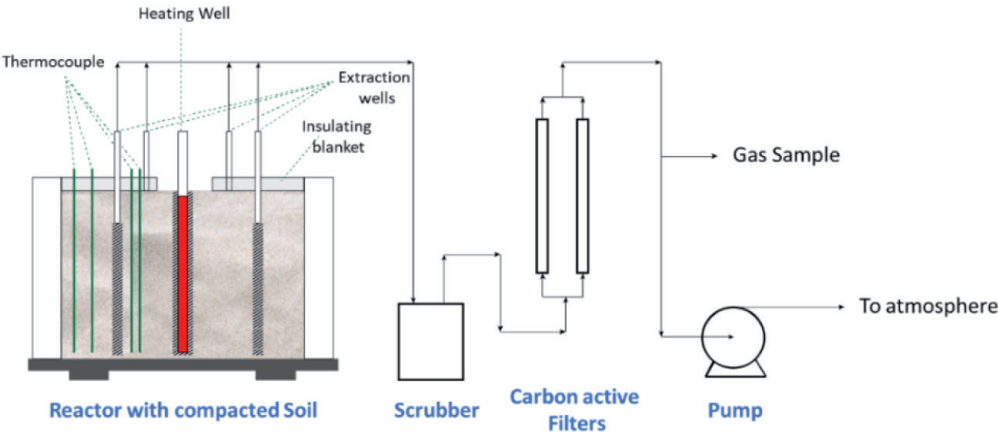


Figure 6.
Heat treatment plant for HCH-contaminated soils [38].

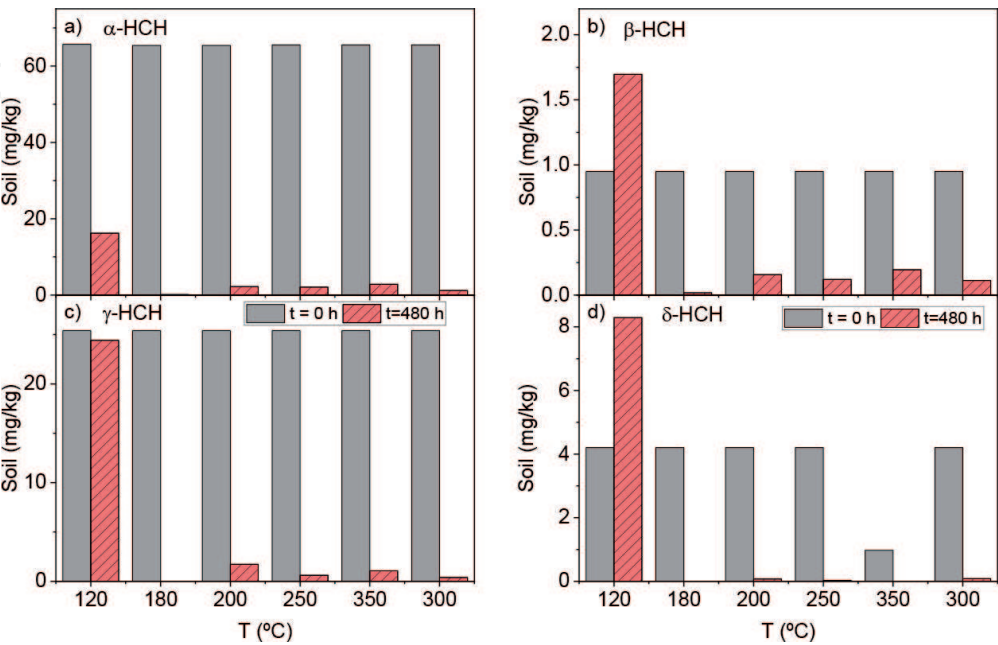


Figure 7.
Removal of HCHs from the soil under different heat treatment conditions [38].

The oxidation was performed in the temperature range of 400–750°C in the presence of some fused catalysts. The catalyst samples were prepared by dehydration, weighing, and mixing of the components and liquid phase synthesis (melting).

The highest activity in the reaction of deep oxidation of lindane was obtained using a molten catalyst based on a eutectic mixture of carbonates of alkali metals with 10 wt % of V_2O_5 and CuO. Moreover, simultaneously with the reaction of deep oxidation of lindane, its dehydrochlorination in a melt of sodium and potassium hydroxides was also noticed. The temperature required for lindane destruction in this process was higher than 450°C. Although there is no mention about dioxins and furans in the work, when working at these temperatures, these compounds are usually generated.

3.1.3 Dehalogenation

This treatment consists of the addition of specific reagents to the soil contaminated with halogenated organic compounds under strong temperature conditions. The process of dehalogenation is achieved by replacing halogen atoms or by the decomposition and partial volatilization of the contaminants [40]. Among dehalogenation processes, base-catalyzed decomposition (BCD) and alkali glycol/polyethylene glycol (APEG) processes [41–43] can be considered. These treatments have been successfully applied to remediate soils and sediments contaminated with chlorinated organic compounds, especially PCBs, dioxins, and furans, but high temperatures are required (150–330°C).

3.2 Chemical oxidation

Different oxidants and activators have been tested in the treatment of soils with real or simulated HCH contamination. However, no studies have been found to date on soils contaminated with HCHs in the form of particulate matter. The presence of this kind of pollution (particulate matter) could pose an additional limitation since the prior solubilization of these granules would be necessary. This phenomenon would be controlled by the interfacial surface between water and the solid phase. The contact between the two phases will increase (i) as the particle size of the HCH granules decreases and (ii) the agitation of the slurry soil-aqueous phase increases.

The main results obtained in the remediation of HCH-contaminated soils with oxidation technologies are described below:

3.2.1 Oxidation with activated persulfate, Fenton reagent, and permanganate

Peng et al. [44] tested the thermal activation of persulfate (PS), at 20 and 40°C, in the treatment of soils artificially contaminated with 800 mg/kg of lindane (γ -HCH was the only HCH isomer studied in this work). The water/soil mass ratio selected was 4:1, and the concentration of PS in the aqueous phase was 0, 5 and 50 g/L. At 20°C, there was no reaction noticed, whereas at 40°C, lindane was eliminated with 50 g/L of PS in 15 days reaction time. When a lower concentration of PS was used (5 g/L) at the same temperature (40°C), the reaction extent was small, as shown in **Figure 8**.

These authors also used the alkaline activation of PS. When this treatment was applied, it was observed that lindane was converted into trichlorobenzenes [44]. Regrettably, there is no information about how these compounds (trichlorobenzenes, TCBs), or other reaction by-products, disappear once formed. The authors did not study the abatement of other HCH isomers than γ -HCH. Recently, Dominguez et al. [45] studied the oxidation of real soils polluted with α -HCH

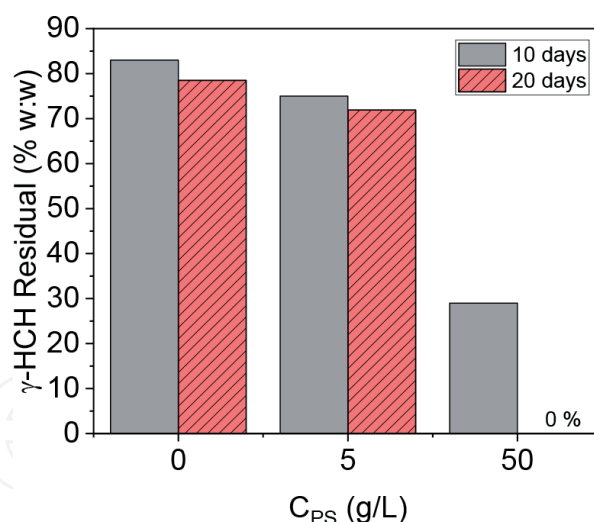


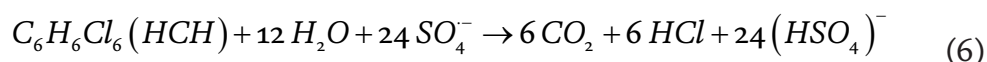
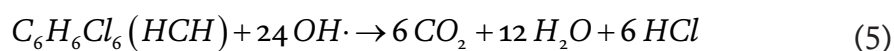
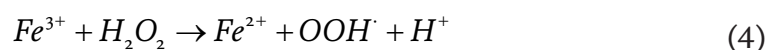
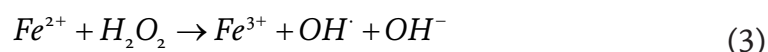
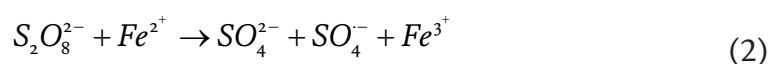
Figure 8.

Removal of lindane from soil after 10 and 20 days with temperature-activated PS at 40°C and using different concentrations of PS [44].

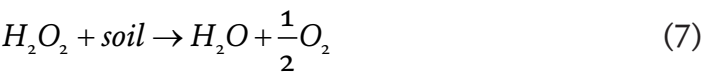
(120 mg/kg) and β -HCH (35 mg/kg) isomers by persulfate activated by alkali finding that the hydrolysis of the β -HCH was the limiting step and that the oxidation rate of TCBs increases notably when the reaction temperature rises from 20 to 40°C.

Usman et al. [34] used artificially contaminated soils (100 mg/kg of each HCH isomer: α , β , γ , δ in sand) and real contaminated soils (concentration of β -HCH = 45 mg/kg and γ -HCH = 25 mg/kg). The high concentration values of β -HCH in the real soil indicate that no particulate matter was present in that soil. The oxidation treatments tested by the authors were persulfate activated by temperature, Fenton reagent ($H_2O_2 + Fe$), and permanganate. The carbonate content in the real soil was relatively high (195 g CO_3Ca /kg soil), which is relevant for the potential application of H_2O_2 as an oxidant, since it would lead to high unproductive consumption of the oxidant. Moreover, the pH of the soil was slightly alkaline (8.05), which also hinders the application of iron as an activator due to its precipitation at this pH.

A water/soil mass ratio = 20:1 and a large excess of oxidant (17 g/L H_2O_2 and 71 g/L PS) were used, with molar ratios of $Fe/H_2O_2 = 1/10$ and $Fe/PS = 1:2$. The higher proportion of Fe used in the activation of PS than in the Fenton process is due to the fact that in the first case, iron is a reagent that is consumed with the progress of the reaction (Eq. (2)), whereas in the case of Fenton reagent, iron is a catalyst, which is continuously regenerated during the radical species production. Fe(II) reacts with hydrogen peroxide to give hydroxyl radicals and Fe(III) (Eq. (3)), which is after regenerated to Fe(II) reacting with another molecule of hydrogen peroxide (Eq. (4)). The reaction of HCHs with the radical species generated by both processes, $OH\cdot$ or $SO_4^{\cdot-}$, yields oxidized by-products or the complete mineralization of the pollutant (oxidation to carbon dioxide, water and salts) (Eq. (6) and Eq. (7)).



In the aforementioned work, the authors compare the results obtained with the following treatments: H_2O_2 only, Fenton reagent ($H_2O_2 + Fe(II)$), PS only, PS activated with $Fe(II)$ and potassium permanganate after 24 hours [34]. When iron is used, it is necessary to carry out the reaction at acid pH to avoid iron precipitation, which results unaffordable in the case of soils with high carbonate content. The results and specific conditions obtained in each treatment for both spiked (a) and real contaminated (b) soils are shown in **Figure 9**. The most recalcitrant HCH isomer was β -HCH regardless of the treatment tested, and the best results were obtained with Fe -activated PS (it should be noted that it was necessary to bring the pH to the acidic zone 2–3). Data about the consumption of the different oxidants are not supplied in the article, but it is expected that H_2O_2 reacted unproductively when this oxidant is applied to the remediation of the real polluted soils (Eq. (7)), being the reason for the cause of the lower HCH conversion obtained with this treatment.



García-Cervilla et al. have recently studied the remediation of a soil located at 14 m below the ground level in an alluvial of an old landfill contaminated with liquid wastes of lindane production [46] at Sabiñanigo (Spain). A high carbonate concentration was also found in this soil (>45%), and the alkaline activation of PS was selected as a remediation technology. The organic and inorganic composition of the soil sieved at two particle sizes: F ($dp < 0.25\text{ mm}$) and G (0.25–2 mm) is summarized in **Table 6**. This soil presented high HCH concentration in some points (up to 9000 mg/kg) due to the adsorption of DNAPL (dense non aqueous phase liquid) that percolated through the soil and reached the alluvial. The absence of the isomer β -HCH in the DNAPL is the reason of the lack of this HCH isomer in the soil studied.

As previously commented, persulfate activated by alkali was applied for the remediation of this soil. This method follows a free radical mechanism [47–49], summarized in Eqs. (8) and (9).

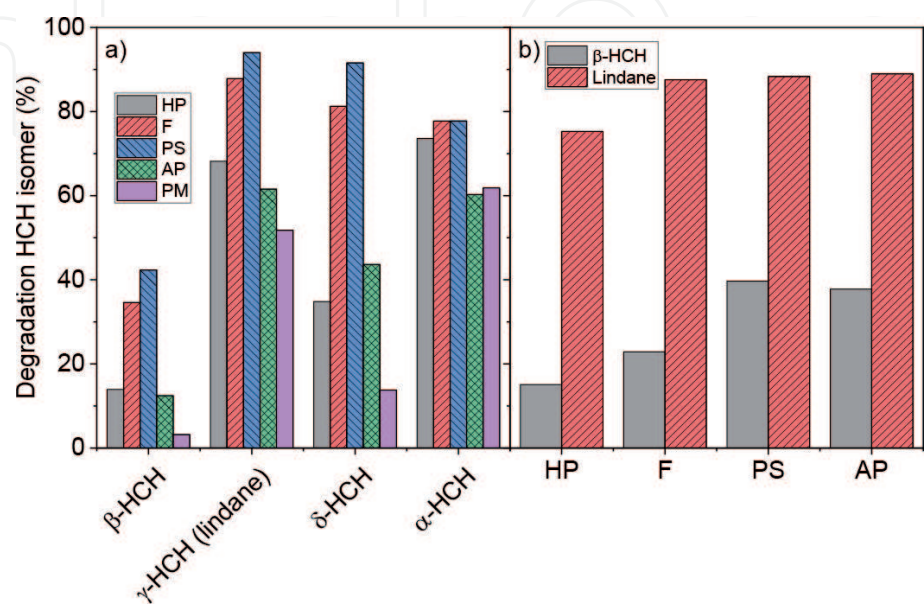
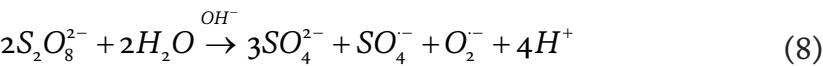


Figure 9.
Degradation of HCH isomers in (a) spiked sand with HCHs and (b) real contaminated soil [34].

	F, dp < 0.25 mm	G 0.25 < dp < 2 mm
TOC, mg/kg	2820	840
TC, mg/kg	54,660	54,840
Carbonates (as CaCO ₃) (%w)	43.2	45.0
Fe, mg/kg	33,078	31,662
ΣHCH, mg/kg	6597.3	1735.5
ΣHeptachlorocyclohexanes, mg/kg	1997.0	690.7
Total mg/kg	10,109	3346

Table 6.
Inorganic and organic composition of polluted soil (14 mg g l) [46].



The addition of an alkali provoked that HCH and heptachlorocyclohexane isomers adsorbed into the soil as a residual phase were converted to trichlorobenzenes and tetrachlorobenzenes, respectively, in less than 48 h. The dehydrochlorination reactions at alkaline conditions, shown in **Figure 10**, were previously described elsewhere [50–52].

At pH above 12, it has been noted that hydroxyl radicals ($OH\cdot$, $E^0 = 2.7\text{ V}$) are predominant against sulfate radicals ($SO_4^{\cdot-}$, $E^0 = 2.6\text{ V}$) [53]. In addition to hydroxyl radical, superoxide radical is also produced in the alkaline activation of persulfate, as can be seen in Eq. (8). These species are capable of producing a nucleophilic substitution when reacting with halides, as described in **Figures 11** and **12**, where trichlorobenzene is mineralized by the attack of both superoxide [54] and hydroxyl [44] radicals.

The main results obtained in this work are shown in **Figure 13** [46]. The molar ratio NaOH/PS ratio was 2:1, the mass ratio water/soil was 10:1, and the concentration of PS varied between 25 and 100 g/L. As can be seen, more than 1 month was required for the remediation of the soil with a particle size <0.25 mm, due to the high pollutant concentration and the strong adsorption of the pollutants to the soil (higher presence of clays than the other fraction) found in the fraction “F”.

3.2.2 Electrochemical oxidation of HCHs in washing solutions

Muñoz Morales et al. [55] studied the remediation of a soil artificially contaminated with lindane (100 mg/kg). An anionic surfactant, SDS, was used to extract the pollutant from the soil (0.1 g SDS per g soil) using a liquid to solid phase mass ratio of 10. Subsequently, lindane extracted from the soil and solved in the aqueous phase was removed by electrooxidation. Therefore, this was a treatment train consisting, firstly, in the solubilization of the pollutant and secondly, in the selective oxidation of the pollutant, in aqueous emulsion. A diamond electrode was used to in-situ generate hydrogen peroxide by injecting air. Remediation times of 400 min were needed, and the surfactant was recycled for further washing cycles.

3.3 Chemical reduction

Zero-valent iron (ZVI) has attracted the interest of the scientific community over the past decade for its potential to remediate a wide variety of environmental contaminants both in superficial and groundwater [56]. The use of ZVI

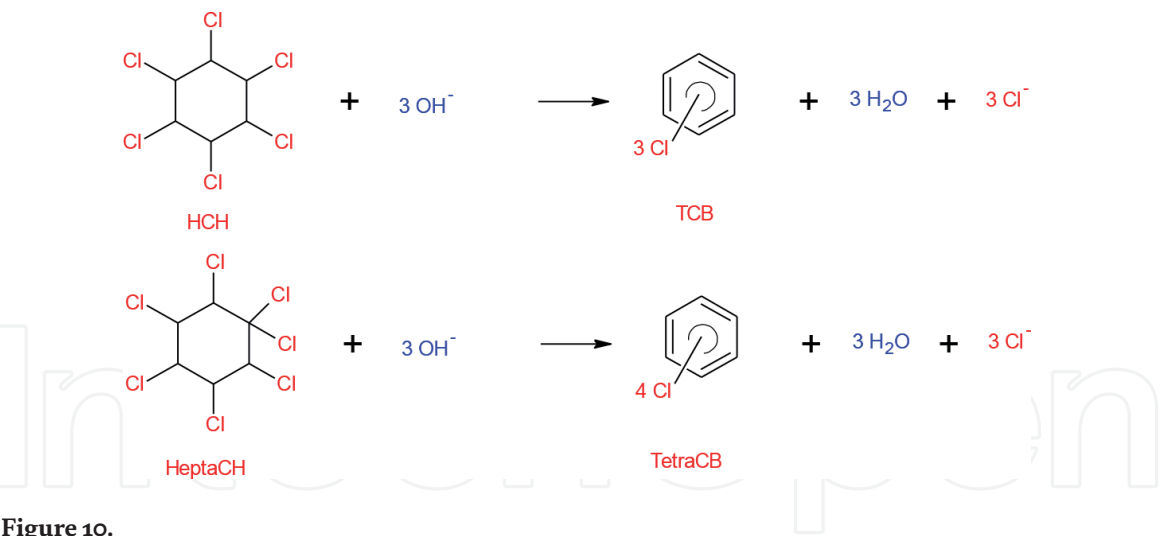


Figure 10.
Dehydrochlorination reactions at alkaline pH [52].

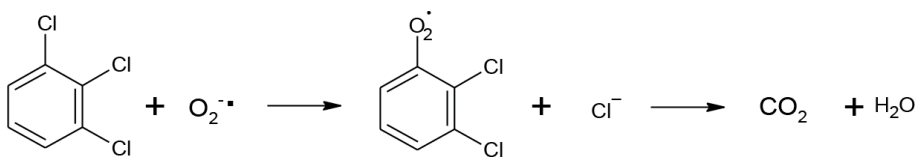


Figure 11.
Nucleophilic substitution of the superoxide radical in the reaction with trichlorobenzene as an example of oxidation reaction. Tetrachlorobenzene isomers follow the same reaction mechanism [54].

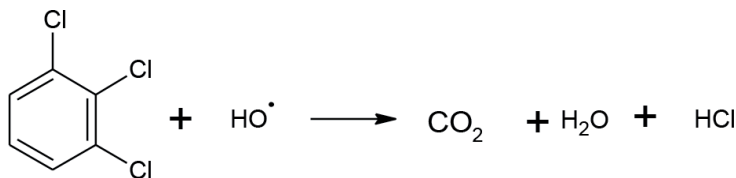


Figure 12.
Attack of hydroxyl radicals on trichlorobenzene as an example of oxidation reaction. Tetrachlorobenzene isomers follow the same reaction mechanism [44].

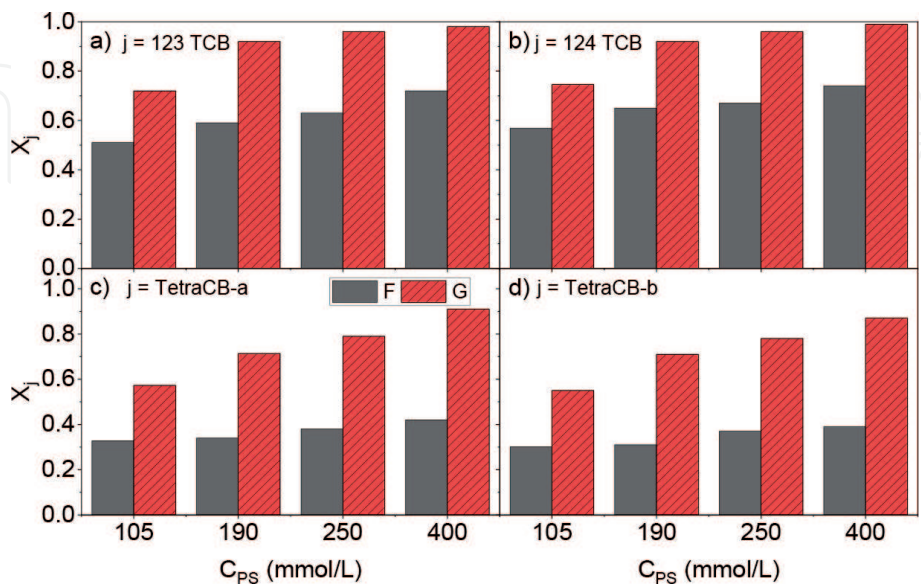


Figure 13.
Conversion of isomers: (a) 1,2,3 TCB, (b) 1,2,4 TCB, (c) TetraCBs-a in soil F, and (d) TetraCBs-b in soil F and G after 509 h. $C_{PS} / C_{NaOH} = 1$. Soil F: Diameter lower than 0.25 mm, soil G: Diameter between 0.25 and 2 mm [46].

over other metals is a preferred choice due to its high abundance, low cost, and benign environmental impact [25, 56, 57]. Among other pollutants, ZVI showed high efficiency in the treatment of chlorinated organic compounds such as HCH isomers [2, 4, 17, 25, 26, 57–65].

Most of the reported works are focused on the degradation of lindane and the use of ZVI nanoparticles [2–4, 17, 25, 58, 60–63] or the combination of ZVI with other metals, Pd being the most studied [17, 25, 60]. In the presence of ZVI nanoparticles, lindane can be eliminated in 24 hours reaction time when this pollutant is dissolved in water [2] or present in spiked soils [4]. In the case of using bimetallic Pd-Fe nanoparticles [17, 25, 60] or more complex systems, like carbon-supported Cu-ZVI nanoparticles [3] or carboxymethylcellulose Fe/Ni nanoparticles [63], the reaction times for lindane dichlorination can be even decreased. It has been reported that anaerobic conditions favor lindane degradation in the presence of stabilized iron nanoparticles [17], and the temperature has a beneficial effect on the pollutant degradation rate [60], whereas lindane degradation decreases with pH increasing, initial lindane concentration, and in the presence of cations [60]. Several degradation pathways for lindane degradation have been proposed based on the detection of certain reaction intermediates during lindane dichlorination reactions in the presence of ZVI nanoparticles [3, 25, 62, 63].

Although encouraging results in HCH treatment in the presence of these materials have been achieved, the low stability of iron nanoparticles due to aggregation [3, 17, 25, 62] and the unaffordable cost of noble metals like Pd [57] has encouraged the use of ZVI in the form of microparticles during the last years, with lower cost and higher stability [26, 64, 65].

The predominant mechanism for the degradation of lindane using ZVI is the reductive dehalogenation of the pollutant, owing to the electron exchange between the HCH molecule and zero-valent iron [3, 58, 60, 62, 65]. Benzene is obtained as the final product of lindane reduction (along with chlorides), as is shown in **Figure 14**.

As occurred with chemical oxidation, β -HCH presents high recalcitrance towards chemical reduction, in both aqueous and soil phases [2, 65, 66] due to the chlorine's position and the low water solubility of this HCH isomer.

Even though promising results have been obtained with ZVI in the degradation of HCHs in the aqueous phase, the use of this material for soil remediation entails additional problems. The application of ZVI in the form of microparticles on contaminated soils would yield low HCH conversion due to the hindered contact between the solid phases (soil and ZVI microparticles). Using ZVI nanoparticles for soil remediation is limited by problems of agglomeration and the high cost associated. Furthermore, if HCH granules are present in the soil, a remarkable decrease in the efficiency of the dechlorination treatment is expected, due to the expected poor contact between the two solid phases.

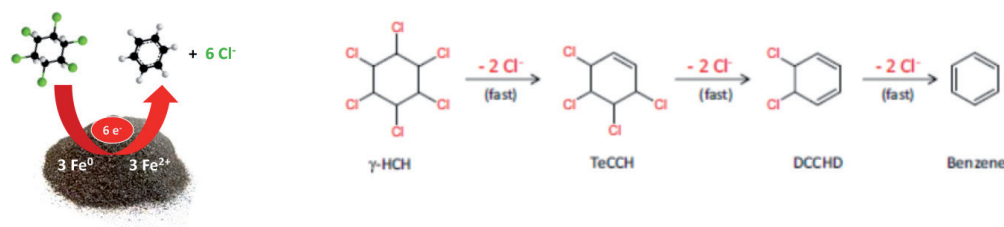


Figure 14. Dechlorination pathway of lindane over zero-valent iron microparticles [65].

3.4 Soil washing

In this technology, surfactants are used to solubilize the contaminants absorbed into the soil in the aqueous phase. The resulting solution requires a second stage in which the objective is the selective oxidation of the contaminant from the emulsion and the surfactant recover for a next use [67, 68]. However, the solubilization of pollutants from solid phases is hindered by the pollutant transport from the soil to the aqueous phase.

There are few papers in the literature using this technology for the treatment of HCH-contaminated soils, none dealing with the presence of particulate matter, and only spiked soils with HCHs or DNAPL were used.

Muñoz-Morales et al. [55] used soil washing as a first stage to remediate a soil spiked with lindane. For that purpose, the authors used an anionic surfactant, SDS. This surfactant was selected because the next step of the remediation treatment was the electrochemical oxidation of the pollutant in the emulsion, and high conductivity of the solution is required in this oxidation treatment. Using a surfactant concentration of 10 g/L in the aqueous phase, the concentration of lindane found in the aqueous emulsion was 10 mg/L, which was further oxidized by the electrochemical treatment.

Dominguez et al. combined soil flushing (with a nonionic surfactant) and Fenton oxidation [67]. A nonionic commercial surfactant (E-Mulse 3[®]) was used to extract most of the residual DNAPL in the soil at column conditions. The resulting surfactant flushing solution showed a high concentration of chlorinated organic compounds (COCs = 3693 mg/L, 40% of this amount corresponded to HCH isomers, although β -HCH was not in the mixture). This emulsion was treated by the Fenton process using different concentrations of hydrogen peroxide (200%, 100%, and 50% of the theoretical stoichiometric amount for the complete mineralization of the COCs) and a molar ratio of $\text{H}_2\text{O}_2:\text{Fe} = 32$. A degradation of COCs >80% was obtained using a concentration of $\text{H}_2\text{O}_2 \geq 100\%$ of the stoichiometric amount. HCHs (and other nonaromatic COCs) were less prone to oxidation by hydroxyl radicals than chlorobenzenes. The surfactant was recovered at the end of the treatment for further flushing steps.

Regrettably, there are no studies in the literature dealing with soil washing of soils polluted with β -HCH, the least soluble and the most stable HCH isomer against oxidation and reduction. Moreover, if the contamination of the soil by HCHs involves also the presence of particulate matter, transport resistances will be more limiting, and the step of soil washing will slow down. In this case, a good agitation or ultrasound application will be required to improve the contact between the phases and, therefore, to improve the efficiency of the process.

4. Conclusions

Soil contamination by the solid residues generated from the manufacture of lindane, a chlorinated organic pesticide whose use and production has been prohibited, is a great environmental problem, ubiquitous and persistent, given the high toxicity and low biodegradability of these residues in the environment. These soils contain a mixture of HCH isomers, mainly α and β , isomer β being the most recalcitrant to both chemical and biological treatments, due to its lower water solubility and higher chemical stability. This kind of contamination appears as solid HCH particles mixed with soil (usually with a higher concentration of the isomer

α -HCH) or adsorbed onto the soil (with a higher concentration of the isomer β -HCH) reaching values up to several hundreds of mg HCH/kg soil. It represents a serious problem due to the large volume of wastes to be treated. Among the physicochemical treatments used, thermal processes are the traditional ones but the less sustainable because the requirement of high temperatures and, therefore, the associated costs are prohibitive for treating large amounts of wastes. In the last decade, chemical treatments have shown promising results. Among them, oxidation with Fenton reagent or activated persulfate seems to be more suitable than reduction using zero-valent iron particles, because of the greater limitations for the contact between phases in the last one treatment. The selection of the most suitable oxidation method will depend on the type of soil (presence of carbonates and pH). On the other side, the time and method of contact will also be strongly influenced by how the contamination is present (in the form of particulate or adsorbed matter).

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