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SOIL DEPOLLUTION METHODS USED IN REMEDYING THE SITES CONTAMINATED WITH HEXACHLOROCYCLOHEXANE

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ABSTRACT. Hexachlorocyclohexane it's been used almost fifty years as a pesticide. 50's studies about its consequences to the environment revealed the serious damage it can create. The storage, disposal and utilization of Hexachlorocyclohexane as a pesticide generated environmental contamination with HCH.

This is an overview of the methods used by different countries for the remediation of contaminated sites with hexachlorocyclohexane. The method used depends by soil's type, soil utilization, level of pollution, cost. The optimal results require experimental research, time, money and knowledge from a wide scientific area such us: chemistry, physics, engineering, etc.

Key words: *hexachlorocyclohexane, remediation, contaminated site, pesticide*

INTRODUCTION

The history of hexachlorocyclohexane began in the year 1825, when the physicist Michael Faraday artificially synthesized it in the laboratory, and in 1912 the Belgian chemist Van Linden discovered the properties of the isomer γ-HCH. The technical HCH was produced and used all over the world: USA, the former Soviet Union, Spain, France, the Netherlands, Romania, China, and India are only a few countries where it was produced and used as pesticide (www.ihpa.info). Li (1999) estimated that, at world level, between 1948-1997 were used approximately ten million tons of technical HCH, more than any other pesticide. Initially, technical HCH was used, but, because of its unpleasant smell that also infiltrated the cultures, it was gradually replaced with lindane (Vijgen and Egenhofer, 2009). One ton of lindane was obtained from approximately 8-10 tons of technical HCH.

The subsequent studies on this substance reveal the toxic character both on the environment, and on the live bodies. The information and awareness campaigns concerning the effects of this pesticide have led to the limitation of its use, and later to the prohibition of HCH.

The contamination of the environment with HCH happened following its use as a pesticide, following the storage of the manufacturing residues, following the storage of the unused pesticides. In time, countries such as the Netherlands, Brazil, Spain,

India, Germany, where there have been factories manufacturing technical HCH and lindane, have been facing and are still facing the issue of the depollution of the sites polluted with HCH. The methods are various (cremation, washing, vitrification, isolation in situ, thermal desorption), depending on the pollution degree, type of ground, costs.

The purpose of this paper is to take a look at the methods used to depollute the sites contaminated with HCH in order to choose the suitable technology considering the output of the process, the costs, the impact on the environment.

METHODS OF DECONTAMINATION

The methods of decontamination may be classified according to the technological procedure used (physical, chemical, thermal, biological) or to the application site (in situ, ex situ). Considering these two classifications, the methods used in the decontamination of the grounds polluted with HCH may be synthesized in the following table:

Table 1. *Methods used in the remediation of soils contaminated with HCH*

Application place / Technique	In-situ remediation	Ex situ remediation
Physical methods	Washing	Isolation (Spain - Sabinanigo; France - Gouenhams, site Ecospace) Washing(1990-1998, Holand - Rosmalen)
Thermal methods	Thermal desorption	Incineration (1986, France - Voreppe; 1998, France - Château-Arnoux, Saint-Auban) Thermal desorption (Germany-Rotterdam)
Biological methods	Biodegradation (SUA, Daramend technique) Landfarming (Spain - O Porrino, Pontevedra)	

Isolation has been used in Spain, in Sabinanigo, on the location of the former Inquinosa factory. Open in 1970, it produced lindane between 1975-1988, and lindane-based products until 1992 (Fernandez et al., 2013).

The abandoned wastes also contaminated the ground from the area neighboring the former factory. The most accessible measure was to isolate the solid wastes. The insulating wall consists in two sets of HDPE geo-membranes (high density polyethylene) (1.5 mm), bentonite (5.500 g/m^2), and HDPE (1.5 mm). The membranes are separated to control any leaks by a layer of gravel in which are inserted draining tubes collecting the levigate. It is oriented towards a tank connected to the waste water treatment plant. When it was applied, this method was not deemed to be a final solution, but only an intermediate one, until more financially accessible funds or solutions were found.

Fig. 1. *Isolation, used in former factory Inquinosa*
(*photo source:* Fernández et al., 2013, *POP-contaminated sites from HCH production in Sabiñánigo, Spain, Springer*)

Incineration is a high-output method and it may be applied in a relatively short interval of time. The method was used in France in 1986 in Voreppe, on the location of the former Sico factory, and in 1998, in Château-Arnoux, Saint-Auban, to decontaminate the wastes resulting from the production of HCH. The output of the method depends on the properties of the ground (type of soil, quantity of organic matter, concentration of the pollutant, humidity). The procedure leaves the soil sterile, unfavorable to agriculture.

Thermal desorption was used in Rotterdam by the enterprise Ecotechniek (Roth et al., 2005), which, by treating 1200 tons of soil contaminated with α-HCH isomers (2300 mg/kg), β-HCH (550 mg/kg), γ-HCH (2mg/kg), δ-HCH (15 mg/kg), managed to decrease the ground concentration to less than 0.1 mg/kg for each isomer.

As regards the application of the thermal treatment of correction, an emission over the allowed threshold of PCDD/PCDF has been noticed.

Biodegradation is a non-invasive procedure which, in the case of the ground polluted with HCH, has a long period of action and a relatively low output. Studies have shown that the zerovalent iron ion (Fe^0) accelerates the degradation of β-HCH, but has much weaker effects on the other isomers (Yang et al., 2010; Mao et al., 2013). To have the same reducing effect on the γ-HCH isomer as well, Fe nanoparticles have been combined with a small quantity of another metal, and the experiments showed a favorable effect in combination with Pb (Singha et al., 2012).

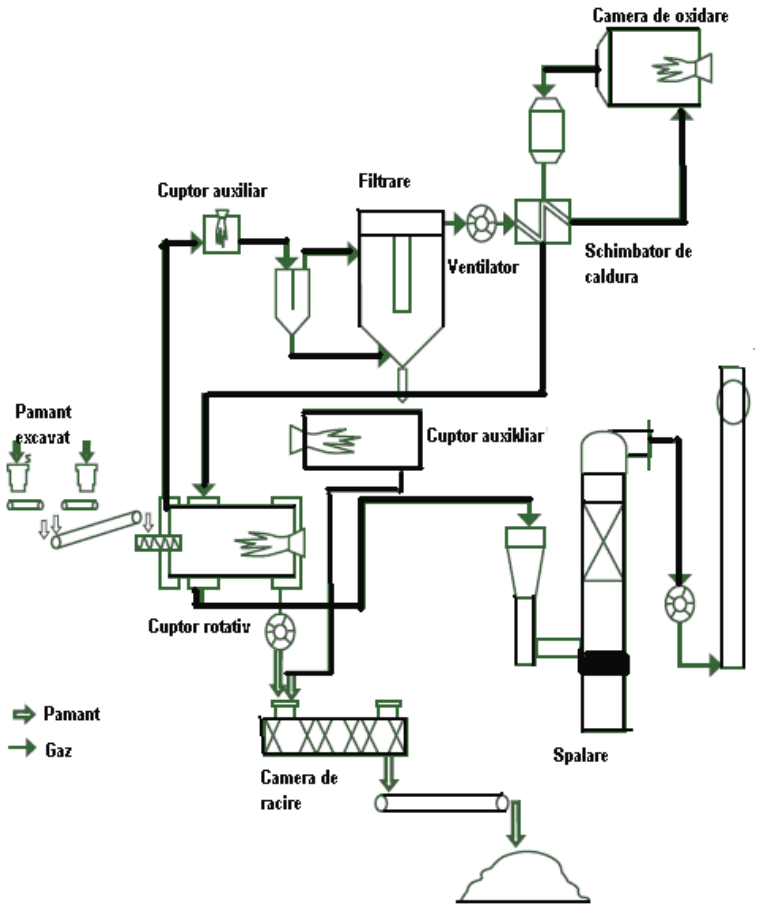

Fig. 2. *Mobile thermal desorption plant METTS (Ecotechniek). (Source: Fabre et al., Les isomeres de hexachlorocyclohexane, Rapport bibliographique élaboré dans le cadre d'une collaboration UHA - ADEME – 2005, pag 79)*

In U.S.A., the Daramend technology is successfully used, which is a bio-correction technique using Fe^0 ion to speed up the process. The experimental studies that have used this procedure (Philips et al.) in a contaminated site from Kentucky (USA) showed a decrease of the HCH isomer concentration, in the ground, of approximately 92%.

At present, lab tests are made, concerning the capacity of certain bacteria to speed up the degradation of the hexachlorocyclohexane isomers (Raiana et al., 2007).

Studies on the use of *landfarming* as bio-correction method of the HCH-contaminated sites have been performed in N-W of Spain, on the grounds of a former lindane factory from O Porrino, Pontevedra (Rubinos et al., 2007). The ground acidity

has been corrected by means of $CaCO_3$. Fertilizers have been added (urea – 100 kg/ha, P_2O_5 - 100kg/ha), the ground has been irrigated to maintain the soil moisture constant. Also, it was ploughed every week in the first month, and in the following 2 months, it was ploughed twice a month. Best results have been noticed for α and γ-HCH, with production of pentachlorocyclohexane (PCCH) and tetrachlorocyclohexane (TCCH). β-HCH does not react to this type of depollution.

Washing soil is meant to detach and isolate the pollutant from the fine particles to the highest percentage possible. This procedure may precede other soil correction procedures, significantly reducing the quantity of treated soil/mud.

The techniques that may be used for washing are: wet sifting, scrubbing, centrifuging, decanting, flotation.

Because HCH isomers do not have high solubility (β-HCH is the least soluble), the water needs washing reactives. As regards solvents, an important part is played by temperature, activation time and concentration. For this reason, it is necessary to make a detailed study of the contaminated area, a rigorous analysis of the soil composition, of the type of pollutant.

Studies made on an excavated soil from a former HCH factory (Cuyten, 2000) show the efficiency of solvents depending on the percentage used in combination with water:

Table 2. *The efficiency in terms of percentage of solvent of water (Cuyten, 2000)*

H_2O (%)	Efficiency using methanol (%)	Efficiency using izopropanol (%)	Efficiency using acetone (%)
0	96±0,4	96±0.05	93±0.04
20%	94±0.05	89±0.08	102±0.02
40%	42±0.06	66±0.02	74±0.04

The enterprise Heijmans Enviroment Technology successfully applied the ground washing technique in the Netherlands (Cuyten, 2000). Laboratory tests began in 1990. In the beginning, they passed the ground through a wet sieve with the diameter of 2 mm. Then, the mud particles that were smaller than 63 μm were separated from the sand. The sand was cleaned by separating the organic matter from the sand, and afterwards it was washed by scrubbing with a solvent.

Table 3. *The results of laboratory tests performed in 1990 (Cuyten, 2000)*

Initial concentration (μg HCH/kg dry soil)	Final concentration
1020	<30
9000	<100
19000	<200

Having these laboratory results, they tested a washing prototype on the Rosmalen platform.

Table 4. *Results using soil washing platform Rosmalen 1990 (Cuyten, 2000*)

Initial concentration (µg HCH/kg dry soil	After first washing (µg HCH/kg dry soil)	After second washing (µg HCH/kg dry soil)
1020	-	50
9000	700	90
19000	1200	240

The purpose was to obtain 10 µg HCH/kg of dry soil (according to the norms in force). In order to improve the efficiency of the scrubbing, tests have been initially performed with various chemical substances. Because the chemical substances would have decreased the feasibility, other techniques have been searched. Various techniques have been tested, to separate coal and organic matter, because they contain the biggest quantity of HCH, and the foam flotation was chosen.

Between 1992-1994, improvements have been operated on the technique used on the Rosmalen platform, succeeding, in 1994, to obtain a concentration complying with the standards (<10 µgHCH/kg dry soil).

Table 5. *Results from the application of the washing procedure in 1995, 1997, 1998 (Cuyten, 2000)*

Year	Initial concentration (µgHCH/kg dry soil)	Final		Standard	Efficiency (%)
		First washing	Second washing		
	HCH	HCH	HCH	HCH	HCH
1995	18000	80	<10	<10	99,8
1997	11000	<35	-	<35	99.7
1998	12000	<35	-	<35	99.7

The wastes stored in an uncontrolled manner, resulting from the production of lindane at the Chemical Plants in Turda, have contaminated the area with various pollutants, including hexachlorcyclohexane. The methods proposed for decontamination have been: the thermal desorbtion per site (Simule and Dobrin, 2010), bio-correction in-situ, cremation, isolation (Proorocu et al., 2009). The methods depend on the targeted area, on the pollution degree, on the type of pollutant, but also on the allocated funds.

CONCLUSIONS

The described methods show us that it is not possible to transfer a technology from one site to the other. Each site has unique features, which are not obvious during a simple analysis. Among these features, we mention the type of ground, its utility, mineralogy, physical, chemical properties, the type of contaminant, the concentration, the period from overflowing/storage, etc.

The Dutch experience shows without any doubt that an optimal method requires time, research and funds. If a method with immediate effects is necessary, cremation or isolation may apply. Bio-correction is a non-invasive, but long-term method. If the pollutant is the hexachlorocyclohexane, the output is low. The washing is efficient as previous method, but also as basic method, if adjacent technologies are applied.

A decisive budget is the budget allocated for the depollution process. There are many polluted sites, kept under observation, on which no actions are taken because there are no funds. In the areas where the pollution degree is way above the allowed limit, temporary measures are taken.

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