In Situ Chemical Reduction (ISCR) for Removal of Persistent Pesticides; Focus on Kepone in Tropical Soils

Site: **Impacted Banana Fields, French West Indies**

Key Contractor: **BRGM**

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Solid Technology, Superior Value, Proven Results

PROJECT CASE STUDY SERIES

Background/Objectives

The global use of organochlorine pesticides (OCPs) such as Kepone, Lindane, DDT, Dieldrin, Chlordane, and Toxaphene has resulted in long-term soil impacts at many sites. Given the potential risks to human health and the environment, some OCP-impacted sites require treatment. In certain cases, the "dig-and-dump" approach is not practical due to magnitude of the problem, access issues, and/or resource constraints.

Here, "bioremediation" can be used to treat the soil on site, often at lower costs, and certainly with lower generation of greenhouse gases. Unfortunately, most OCPs are not amenable to conventional bioremediation technologies, hence they persist over time.

Use of the insecticide Kepone on banana plantations until the mid-1990's in the French West Indies islands has led to major environmental impacts. These include damage to drinking water supplies, bans on vegetables, fish and sea food consumption and commercialization, and increased occurrence of prostate cancer in Guadeloupe. Kepone is widely considered as an extremely persistent neurotoxic organochlorine insecticide, with no evidence of environmental attenuation. Natural, very slow leaching from the impacted soils to the water compartment will take centuries to significantly reduce current Kepone soil concentrations.

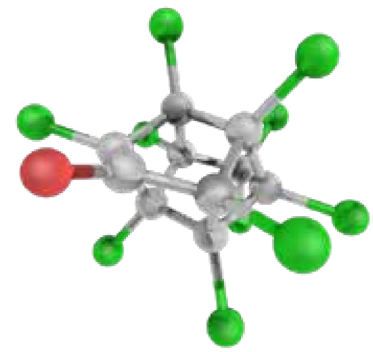
The study presented here was financed by the French Ministry of Environment.

Left to right: A typical Guadeloupe landscape; Typical row of banana plants; Targeted plant pest—the common weevil, one of the numerous beetles of the family *Curculionidae*.

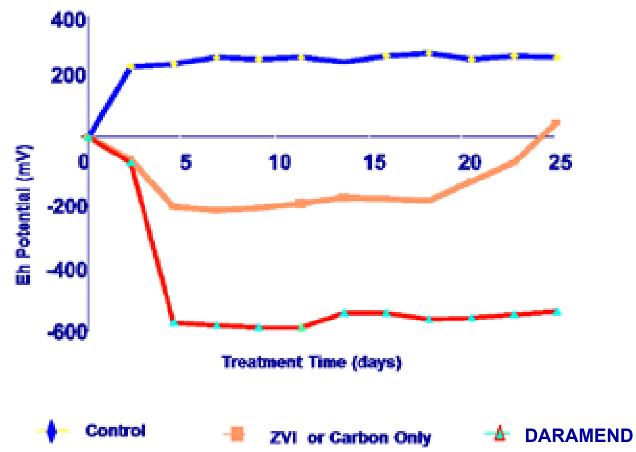
DARAMEND®
The Original ISCR Reagent for Surface Applications

Approach/Activities

DARAMEND® *in situ* chemical reduction (ISCR) technology uniquely combines controlled-release carbon with a reduced metal—such as zero valent iron (ZVI) or zinc—to yield a highly effective material for stimulating the complete degradation (no accumulation of catabolic intermediates) of persistent organic compounds present in soil, sediment and groundwater. The term ISCR is used to define the combined effects of stimulated biological oxygen consumption (via "fermentation" of complex organic carbon sources), direct chemical reduction with reduced metals, and the corresponding enhanced decomposition reactions that are realized at the lowered redox (Eh) conditions. In brief, the ZVI oxidizes to form ferrous iron and releases electrons in the process. The organic carbon is consumed by microorganisms that are indigenous to the soil, resulting in release of additional free electrons. These electrons transferred to the OCPs result in the removal of chlorine from the compound's structure (reductive dechlorination); ultimately, complete destruction of the pesticides can occur. Most soils can be effectively treated in a reasonable time frame (e.g., from 4 to 8 weeks) using standard agricultural machinery at a price typically less than €15 per tonne of soil treated.

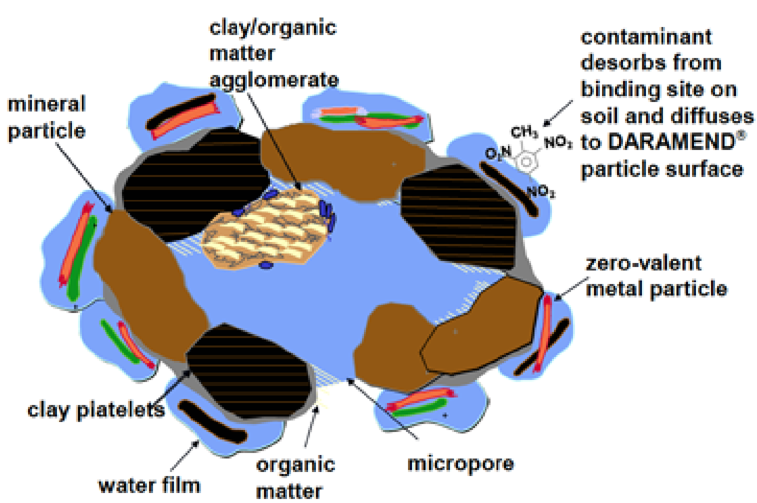


Kepone structure
$C_{10}Cl_{10}O$



Significantly Lowered Eh Potential (ISCR™)

Idealized soil aggregate showing mechanism of DARAMEND bioremediation



Results/Lessons Learned

This case study summarizes implementation of the ISCR theory, followed by results on technology validation tests for remediation of Kepone impacted soils (banana fields) from the French West Indies (Caribbean). Bench-scale studies with spiked sand demonstrated rapid (< 2 weeks) and extensive degradation of Kepone: catabolites with up to 7 Cl removed were identified by GC/MS/MS.

Extensive validation of an analytical procedure involving the use of Kepone-13C as internal standard was conducted for the three soil types. Mesocosm (scale-up) studies with tropical soils determined that treatment duration of 6 months resulted in 90% decrease in Kepone concentration for two of the major soil types, and 45% for the third soil type.

Significant effect of the treatment was observed on microbial biomass and activity, and genetic structure of the bacterial community.

Ecotoxicity tests and bioaccumulation studies will also be considered in the evaluation of the process. Recognized technology development needs include insight into catabolite environmental fate/affect. Significant advances in the biogeochemistry of OCP degradation are anticipated from basic research on microbiology and genetics of ISCR processes.

Properties of the French West Indies soil studied

Soil	CEC meq/100 g	pH KCI	Org matter %	clay %	kepone mg/kg	5b-hydro mg/kg
Andosol						
mean (n=3)	37.5	4.8	13.4	23.6	15.9	0.17
std dev	2.2	0.0	0.2	0.52	1.0	0.02
CV (%)	*5.8*	*0.0*	*1.5*	*2.1*	6.4	10.4
Ferralsol						
mean (n=3)	17.2	4.9	3.9	59.1	1.7	<0.05
std dev	0.4	0.1	0.1	2.3	0.1	
CV (%)	*2.0*	*1.2*	*3.0*	*4.0*	3.9	
Nitisol						
mean (n=3)	26.9	5.2	3.7	37.8	1.0	<0.05
std dev	0.2	0.0	0.0	1.3	0.1	
CV (%)	0.9	0.0	0.0	3.6	6.6	

Kepone concentrations after 6 months treatment

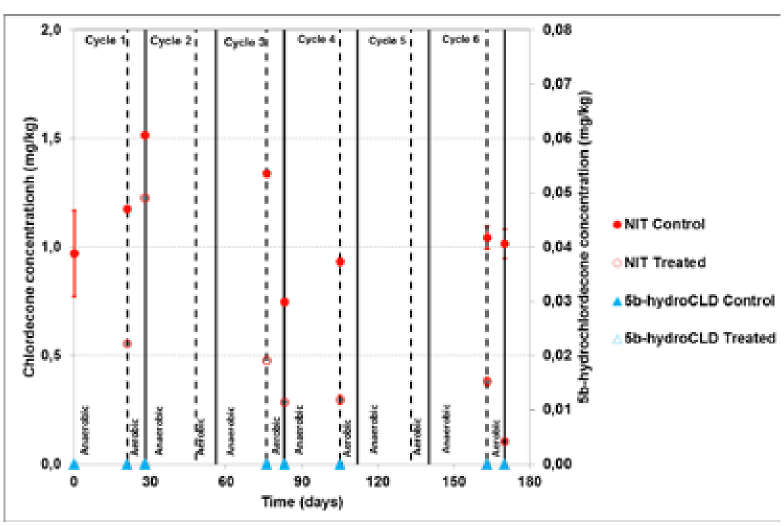
Kepone (mg/kg)	Ferralsol control	Ferralsol treated	Andosol control	Andosol treated	Nitisol control	Nitisol treated
mean	**1.7**	**.20**	**15.9**	**8.7**	**1.0**	**0.10**
std. Dev.	**0.1**	**0.01**	**1.0**	**0.9**	**0.1**	**0.10**
C.V. (%)	**3.9**	**4**	**6.4**	**10.9**	**6.6**	**5.5**
% decrease		**88%**		**45%**		**88-90%**

Relative intesity of the MS peaks of kepone transformation products after 6 month treatment in the 3 soils

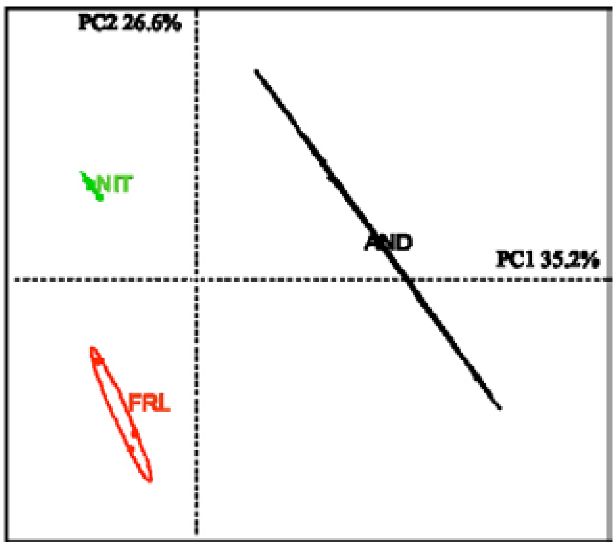
Experimental condition	?	5bhydro	dihydro	?	?	-3 Cl	?	-4 Cl	-5 Cl (1)	-5Cl (2)	-6 Cl	-7 Cl
Andosol control	31	195	0	0	0	0	0	0	0	0	0	0
Andosol Dara	3523	83	218	70	18	140	8	10	14	24	0	3
Nitisol control	1	17	0	0	0	0	0	0	0	0	0	0
Nitisol Dara	59	4	30	4	0	12	0	0	3	0	0	8
Ferralsol control	0	23	0	0	0	0	0	0	0	0	0	0
Ferralsol Dara	77	4	24	4	0	19	0	0	2	0	0	10

NOTES: the data presented here are preliminary and qualitative/indicative only; the question marks, indicated in the above table, relate to compounds in which level of dechlorination is unknown.

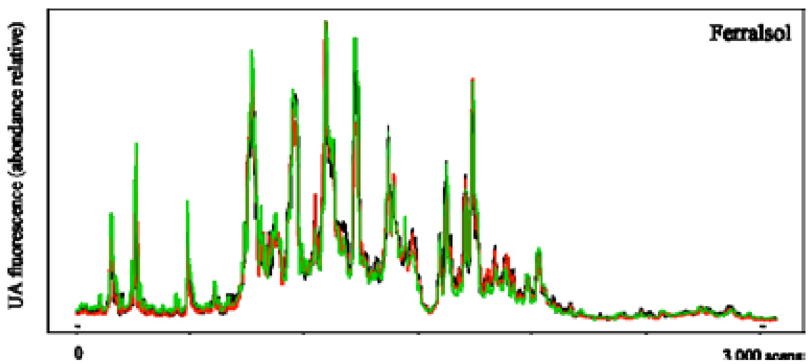
Evolution of kepone concentrations during the treatment of the nitisol



Experimental set-ups (left to right): 28°C thermostated unit; Addition of DARAMEND to the soil; 60 L laboratory experiment mesocosms and data loggers



PCA of t-RFLP DNAr 16S (triplicates) of the 3 soil types at the start of the treatment



t-RFLP DNAr 16S (triplicates) of the ferralsol at the start of the treatment

Results presented here do not constitute an official endorsement or recommendation for use of ISCR – DARAMEND® by Brgm

Géosciences pour une Terre durable brgm

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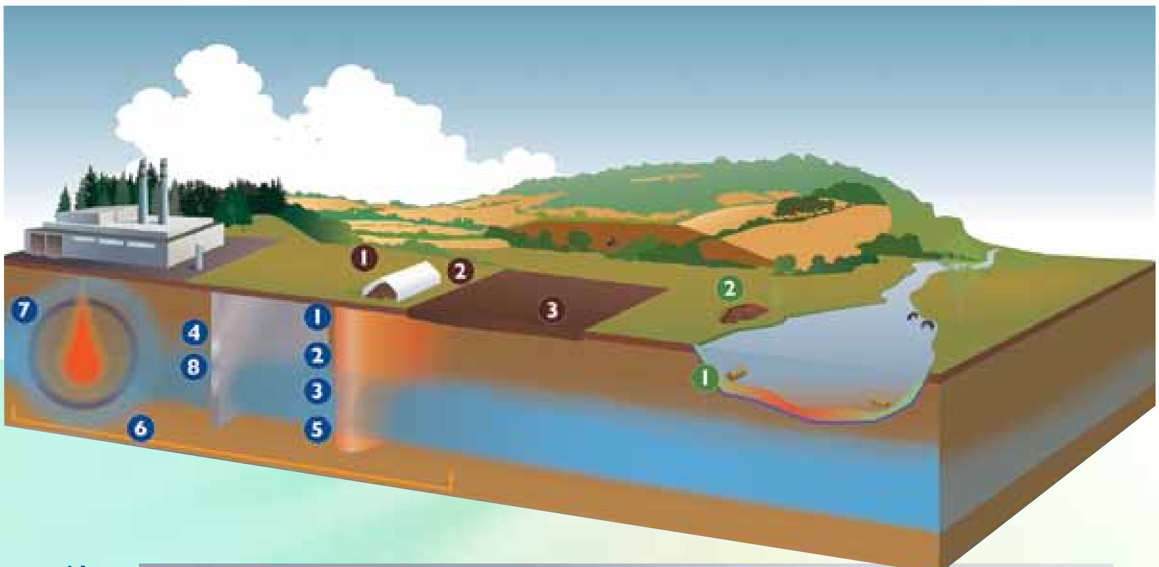

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3. **EHC®-M** injectable immobilization of heavy metals
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