Bioremediation of French-West-Indies soils polluted by the insecticide chlordecone (CLD) using iron-reducing bacteria

PhD thesis promoters: Hervé Macarie (Research Officer, IRD)
Steven Croquet (Lecturer with HDR, Aix Marseille University)

Doctoral school: Environmental Sciences (ED251)

Context & objective of the project
Since 2009 IMBE (http://www.imbe.fr/) develops research on CLD, the organochlorine insecticide of raw formula C_{10}Cl_{14}O, which was used from 1972 to 1993 in French-West-Indies (FWI) for the control of the black weevil populations in banana plantations and which is still present, 23 years after the ban of its use, in the soils where it was spread. Under the action of rain, this molecule has diffused in most of the FWI environmental compartments (surface & ground water, shore areas). As a consequence, CLD is nowadays responsible of an unprecedented sanitary and social crisis in the FWI islands of Guadeloupe and Martinique whose importance has justified the set up of 3 national Action plans by the French Government since 2008.

Despite of the sanitary measures taken by the authorities to avoid that CLD reaches the plate of consumers, the last survey of population impregnation has shown that CLD is still detected in the tissues of the people although at a lower concentration than previously observed. This suggests that despite of all the efforts done, contaminated food is still being distributed. In these conditions, a final solution to the problem would be to destroy (eliminate) the stock of CLD still present in the FWI soils.

At this stage, only the ISCR (In Situ Chemical Reduction) process which consists to add zero valent iron (Fe°) to soil has shown the capacity to reduce CLD concentration by 70% in 2 of the 3 main FWI soil types allowing afterwards to grow on them food plants whose contamination levels remain below the authorized MLR (Maximum Limit of Residues) (20 µg/kg fresh weight) (Mouvet et al., 2016; BRGM RP-65462-FR, 2016). The ultimate fate of CLD achieved with this process remains incompletely known but the dechlorination products that it generates have been found to be less toxic than CLD itself (Legay et al., 2017). The only problem is that the cost of this treatment which is due for 89% to the Fe° that must be imported to FWI, is extremely high (19 €/m³) (BRGM RP-65462-FR, 2016), making by the way its application unrealistic at a large scale.

FWI soils are very rich in iron that may represent 7 to 11 % of their dry weight (Mouvet et al., 2016). These soils being oxic, iron is present mainly in the form of ferric iron oxides (Devault et al., 2016). The redox potential of the redox couples formed by these “iron oxides” and ferrous iron (FeII) being of the same order than those of the FeII/Fe° couple this indicates that the FeII resulting from their reduction should be an electron donor as efficient as Fe° for the attack of CLD (Devault et al., 2016; Dolfing et al. 2012; Macarie et al., 2016).

The coupling of the biological reduction of iron oxides to the dehalogenation of organochlorine compounds (tetrachloromethane; DDT; 2,4-D; chloroform, pentachlorophenol) other than CLD has been already described in the literature (Li et al. 2008, 2009, 2010). In this process, the phase of dechlorination caused by the biogenic FeII formed is a purely abiotic process. Despite of their oxic character, the FWI soils contain important populations of iron-reducing bacteria. This is not surprising since a lot of iron-reducers are known to be anaerobic facultative. In these conditions, it should be possible to stimulate their activity by favouring the formation of anoxic conditions.

The main objective of the PhD thesis will be to study the feasibility to couple the biological reduction of iron oxides to CLD dechlorination.

Methodology.
The thesis will be divided in 4 steps. The 2 first steps will have the objective to check the concept under controlled conditions, the 3rd step to apply it to soils historically contaminated by CLD and the 4th to check the harmlessness of the transformation products generated:

Step 1. In vitro abiotic experiments of CLD dechlorination in aqueous media in presence of a FeII salt and iron oxides. At this stage, only the concentration of chloride will be followed. If a dechlorination is obtained, then the presence of dechlorination intermediates and the identification of their structures will be searched through GC-MS or any other appropriate tools.

Step 2. Confirmation in microcosm of the capacity of FeII generated by the action of a model iron-reducing bacteria to dechlorinate CLD. As in the 1st step, the monitoring of chloride concentration will be the main indicator used to detect an
eventual dechlorination. It will be possible to complement this monitoring by the measurement of FeII concentration and of course the formation of possible dechlorination intermediates.

**Step 3.** Test under microcosms of the feasibility to apply the iron-reducing concept to the degradation of CLD in historically contaminated FWI soils. Due to the high chloride concentration in these soils, this time the only way to demonstrate dechlorination will be to follow the concentration of CLD and of its possible dechlorination products. Test with ^13^C-CLD could be also considered and would allow to show or not a full mineralization of the product.

**Step 4.** The expertise of IMBE will be mobilized to perform a comparative study of the toxicity of CLD and of its dechlorination products available commercially for different biological targets. The results obtained will bring indications about the toxicity evolution trend versus the degree of chlorination of the CLD bishomocubane cage. This is key information since a remediation process should not generate products more toxic than the parent ones.

As a whole, the results obtained during this thesis will produce factual information about the feasibility of an assisted bioremediation of FWI soils contaminated by CLD.

**References**


