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Test of chlordecone dechlorination by chemical reduction using Fe(II)/Fe(III)-oxides coupling

Jean-Pascal ANDRAUD[1]*, Stéven CRIQUET[1], Benjamin OURSEL[2], Stéphane GREFF[1], Thierry WOIGNIER[1,3], Hervé MACARIE[1]

[1] Aix Marseille Univ, Univ Avignon, CNRS, IRD, IMBE, Marseille, France.
[2] Aix Marseille Univ, Université de Toulon, CNRS, IRD, MIO, Marseille, France.
[3] IRD, IMBE, Campus Agro-environnemental Caraïbe, Le Lamentin, Martinique, France.
* Corresponding author: jean-pascal.andraud@imbe.fr

Background & Challenges

Today, chlordecone (CLD), an organochlorine pesticide spread on the soil to control the populations of the banana weevil, is responsible for an unprecedented health, environmental, social and political crisis in the French West Indies (FWI). Despite the health management measures implemented by the authorities to prevent CLD from reaching the consumer's plate, the population continues to be exposed. A definitive solution to the problem would be to destroy the CLD stock in the soil.



Figure 1: *Fe(III)-oxides powders (Goethite, Ferrihydrite, Hematite)*

FWI soils are very rich in iron, which accounts for 7 to 11% of their dry weigh. As these soils are oxic, iron is found mainly in the form of Fe(III)-oxides, and more precisely in the form of goethite, hematite and ferrihydrite whose proportions vary according to the type of soil (Fig. 1).

The potential ($E^{0'}$) of the redox couples formed by Fe(III)-oxides/Fe(II) and Fe(II)/Fe^0 ($E^{0'}$ ≈ -470 mV) are similar (Fig. 2 : Redox scale). This indicates that the Fe(II) resulting from the Fe(III)-oxides microbial reduction could be an electron donor as effective as Fe^0 for attacking CLD.

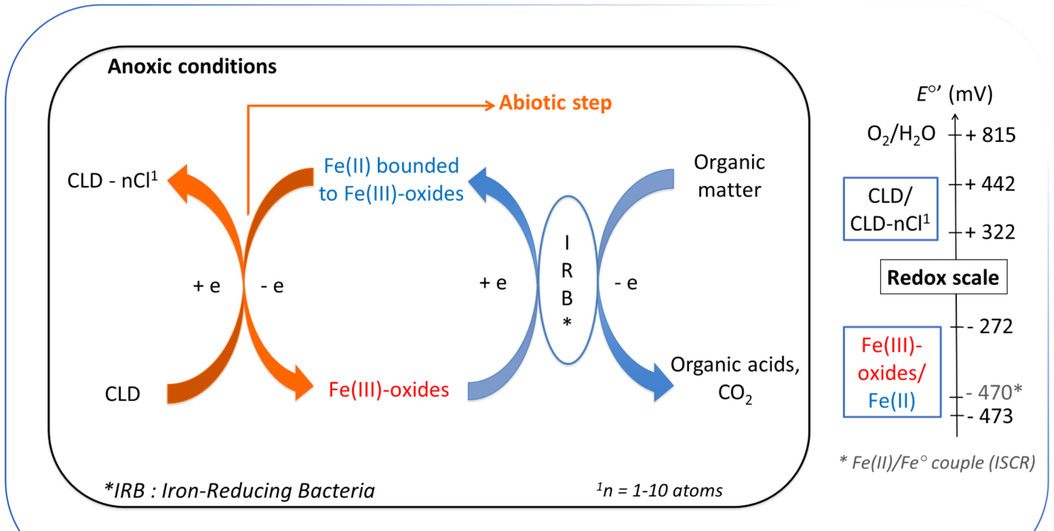


Figure 2: *Abiotic dechlorination of CLD and iron-reduction coupling*

Objectives

Degrade the chlordecone stock of FWI soils by using Fe(III)-oxides present *in situ* via biological iron-reduction.

1. Show that chlordecone can be dechlorinated by chemical reduction using Fe(II)/Fe(III)-oxides coupling (Fig.2 : "Abiotic step")
2. Couple biological iron reduction with chemical reduction of chlordecone, using Iron-Reducing Bacteria (IRB)
3. Test chemical and biological steps on FWI soils incubated under anoxic conditions at lab-scale.

Material & Methods

- Anoxic incubation under agitation at 25°C (room temperature)
- 25 mL of buffer to maintain a pH of the reaction mixture at 7.5-8:
  - Organic buffer: MOPS (25 mM)
  - Inorganic buffer: $NaHCO_3$ (11.9 mM)
- Fe(III)-oxides: hematite, goethite, ferrihydrite, magnetite
- 1 mM $FeSO_4$, 7 H_20
- Redox potentials and pH measurements under anoxic conditions



Results & Conclusions

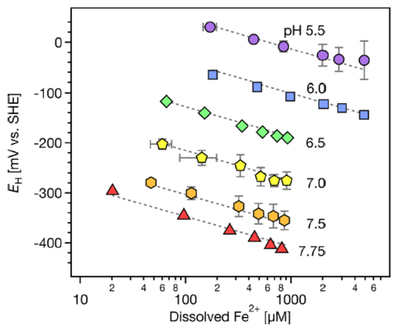


Figure 3: *Reduction potential (Eh) values of goethite suspensions as a function of aqueous Fe^{2+} concentration and pH. Error bars represent the standard deviation from triplicate reactors. No error bars are present for the pH 6.0 and 6.5 reactors because only one reactor was measured for each point. The dashed gray lines represent the model fit. Experimental details: 1 g/L goethite, 25 mM KCl, 50 mM buffer, and 10 µM mediator.*

From Gorski et *al.* Thermodynamic characterization of Iron Oxide-aqueous Fe^{2+} redox couples. *Environ. Sci. Technol.*, 50, 8538-8547, 2016.

Table 1: *Redox potentials and pH measurements at 72h of Fe(III)-oxides suspensions in the absence or presence of aqueous Fe^{2+}*

	$NaHCO_3$ buffer		MOPS buffer	
	pH	**E_h* (mV)**	**pH**	**E_h* (mV)**
Magnetite control	8.1	293	7.7	314
Magnetite + Fe^{2+}	7.5	-113	7.5	231
Hematite control	8.1	338	7.7	356
Hematite + Fe^{2+}	7.7	-113	7.6	-49
Goethite control	8.3	343	7.7	316
Goethite + Fe^{2+}	7.6	-168	7.6	-125
Ferrihydrite control	7.9	319	7.5	317
Ferrihydrite + Fe^{2+}	7.3	-79	7.5	-4

**versus Standard Hydrogen electrode (SHE)*

- Dechlorination test at acid pH: no degradation showed by measuring chlorides with ionic chromatography.
- Negative redox potentials are required for dechlorination, and these are mostly conditioned by the pH as derived from the literature (Fig. 3).
- With $NaHCO_3$ buffer, the formation of a $FeCO_3$ precipitate appears. The Eh measured therefore correspond to the Fe(III)-oxides/$FeCO_3$ couple which are theoretically less negative than the Fe(III)-oxides/Fe(II) couples (Table 1).

$$E_h\,(NaHCO_3) > E_h\,(MOPS)$$

- Coming soon: dechlorination test in both types of buffer with goethite and then the other Fe(III)-oxides.