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#### ▶ To cite this version:

Oriane Della-Negra, Delphine Muselet, Sébastien Chaussonnerie, Charles Mottes, Marion L. Chevallier, et al.. Dégradation naturelle de la chlordécone aux Antilles avec libération de nombreux produits chlorés. 4ème Rencontres nationales de la Recherche sur les sites et sols pollués, ADEME, Nov 2019, Montrouge, France. hal-04831952

#### HAL Id: hal-04831952 https://hal.science/hal-04831952v1

Submitted on 11 Dec 2024

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# Dégradation naturelle de la chlordécone aux Antilles avec libération de nombreux produits chlorés

Natural chlordecone degradation in the French West Indies with the release of numerous chlorinated products

Oriane Della-Negra, Delphine Muselet, Sébastien Chaussonnerie, Charles Mottes, Marion Chevallier, Luc Rangon, Agnès Barbance, Stéphanie Fouteau, Stéphane Vuilleumier, Gwenaël Imfeld, Thierry Woignier, Pierre-Loïc Saaidi, Denis Le Paslier



#### INTRODUCTION





**Chlordecone** = Used as insecticide or fire retardants in

- United States: 1958-1976
- French West Indies (FWI): 1972-1993 (used against the banana black weevil)

www.cirad.fr

- Mostly under its hydrate form
- 3 main impurities in its commercial formulations: Mirex, chlordecol & 8-monohydrochlordecone
- Persistant in the environment (soil, river water, mangrove...)
- Bioaccumulation in food chain (plants, animals, fishes...)
- Chronic toxicity (increase the risk of prostate cancer, neurobehavioral disorders in children)

POP

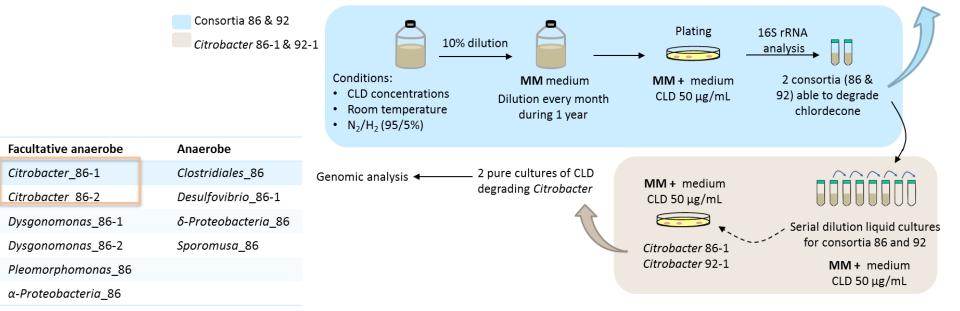
#### CHLORDECONE TRANSFORMATION IN LABORATORY



Identification and isolation of bacteria inducing chlordecone transformation



Metagenomic analysis

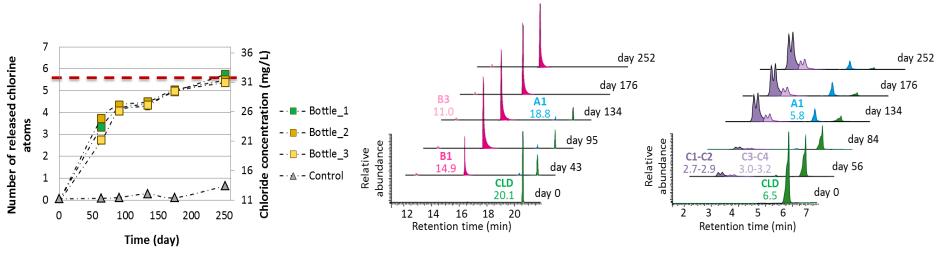


#### **CHLORDECONE TRANSFORMATION IN LABORATORY**





Detection & monitoring of chlordecone transformation products (TPs)



Chloride analysis

GC-MS analysis

LC-MS analysis

#### CHLORDECONE TRANSFORMATION IN LABORATORY

ADEME



Structurale diversity of chlordecone TPs

Family A Hydrochlordecone
Family B Polychloroindene
Family C Acid polychloroind

Family C Acid polychloroindenecarboxilic

Family D Methyl polychloroindenecarboxylate

Family E Ethyl polychloroindenecarboxylate



Family C

Identification of TPs in chlordecone bacterial transformation or microcosms by GC-MS and LC-MS

Interpretation of GC and LC mass spectra

Obtention of exact mass and raw formulae by LC-HRMS

Chemical synthesis and purification of each TP

Structural elucidation by NMR experiments



Structural elucidation by NMK experiments

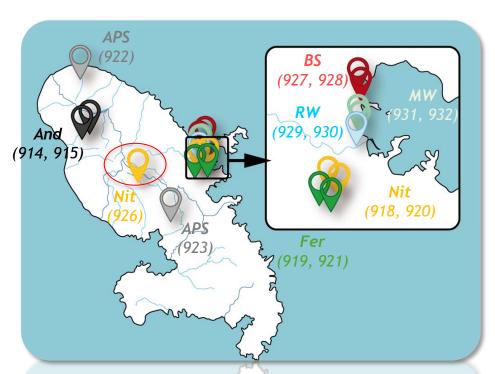
Constitution of a chlordecone TPs database

#### **SEARCH FOR CHLORDECONE TPS IN THE ENVIRONMENT**





#### Sampling and extraction strategy



- 14 samples historically contaminated by chlordecone
  - $\rightarrow$  6 soils
  - → 2 ashes & pumice stones
  - $\rightarrow$  2 sediments
  - $\rightarrow$  2 river water
  - $\rightarrow$  2 mangrove water
- 1 negative control

#### SEARCH FOR CHLORDECONE TPS IN THE ENVIRONMENT





#### Sampling and extraction strategy

4 g of crude soil + 15 mL H<sub>2</sub>O



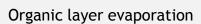
750 mL of water

 12 extraction for river water (6L/L of river water)

6-12 extractions for soils
 & sediments

Aqueous layer extraction with dichloromethane

Acidification vortex & sonication



GC-MS analysis

H<sub>3</sub>COOC

CI<sub>4.n</sub>H<sub>3+n</sub>

CI<sub>4.n</sub>H<sub>3+n</sub>

CI<sub>4.n</sub>H<sub>3+n</sub>

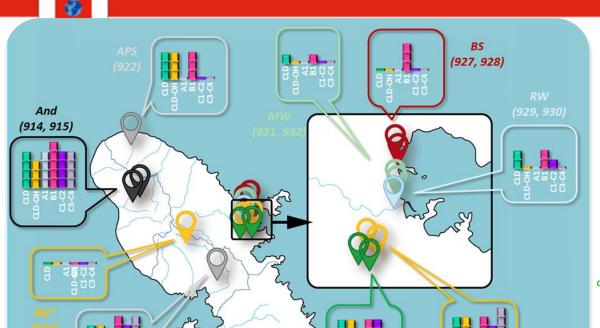


No grinding No drying steps

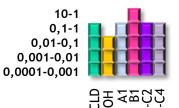
#### SEARCH FOR CHLORDECONE TPS IN THE ENVIRONMENT

ADEME





Order of magnitude of chlordecone and TPs concentration (mg/kg wet soil or mg/L)



Under the detection threshold

**CLD-OH** 

Fer (919, 921)

#### THE OBSERVED CONTAMINATION TPS PROFILE





#### Observations and questions



- Chlodecone found in every sample excepted negative control & bed sediments
  - -> Extraction protocol may not be appropriate for chlordeone in bed sediments



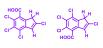
- > A1 only found in andosol
  - -> Such soils could have a specificity allowing A1 formation or retention (bacteria? physico-chemical properties?)



- Chlordecol found in every soil samples
  - -> Does it come from chlordecone initial formulation (impurity) or from degradation/metabolisation?

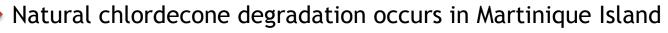


> B1 found in every sample (soil, water, sediments) with sometimes a concentration range similar to chlordecone



- C1-2-3-4 presence is more variable compared to the others
  - -> It could be due to the carboxylic acid function generating a higher mobility in the environment





#### THE OBSERVED CONTAMINATION TPS PROFILE

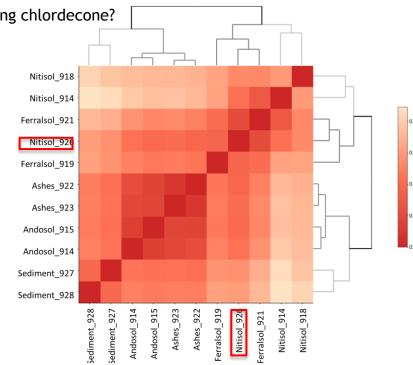




#### Biodiversity of the environmental samples

Do we find the previously identified bacteria degrading chlordecone? Are there any differences with negative control?

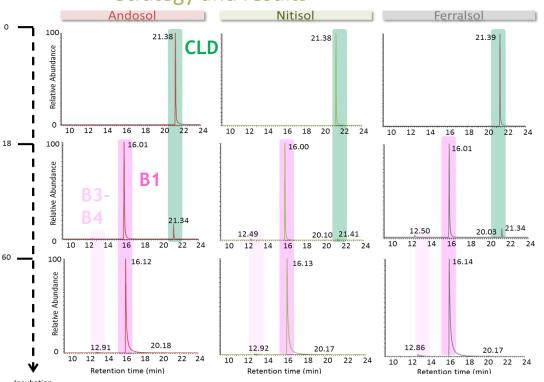
- ❖ A few Desulfovibrio & Citrobacter bacteria genus < 1% diversity found in 918, 919, 920</p>
- Similar soil type can be clustered according to their biodiversity
- No difference was observed between the negative control and other nitisols
  - Other bacteria probably induce chlordecone degradation
  - Chlordecone TPs diversity may depend on soil physico-chemical properties
  - Chlordecone concentration does not seem to be high enough to disturb bacterial community



## CONFIRMATION OF MARTINIQUE MICROFLORA CAPABILITY TO TRANSFORM CHLORDECONE







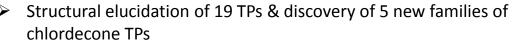


- 3 soils contain bacterial consortia able to transform chlordecone
- Indigenous bacteria are able to transform chlordecone in anaerobiosis

#### CONCLUSION



Guadeloupe

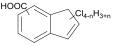




Detection of 17 TPs including in several environmental compartments (soils, river, mangrove, sediment)



CI<sub>5-n</sub>H<sub>3+n</sub>



13CH<sub>2</sub>COOC CI<sub>4-n</sub>H<sub>3+</sub>

Hydrochlordecones (n = 1, 2, 3)

Polychloroindene caboxylic acids (n = 0, 1, 2) Ethylpolychloroindene carboxylates (n = 0, 1)









- Identification of TPs contamination levels of the same order of magnitude as chlordecone
- Highlighting the intrinsic capacity of Martinique soils to degrade chlordecone

**Paradigm shift**: **natural degradation of chlordecone** into soils and presence of an unsuspected pollution by its transformation products



#### **PERSPECTUVES**

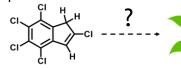


Guadeloupe

Improve our knowledge about transformation products

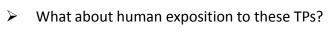
- Toxicity
- Stability
- Biodegradability







Quantification of these TPs in environmental compartments





Understand degradation mechanisms (microbiological?) and find methods to improve this degradation (soil types, physicochemical parameters, microbiota ...)



#### SEARCH FOR CHLORDECONE & TPS IN JAMES RIVER

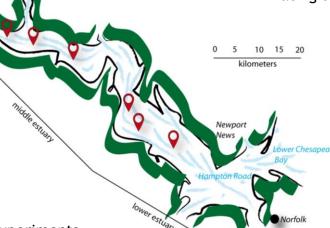




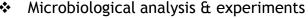
recherche

sites&sols pollués

- Dating of sediment stratum using <sup>137</sup>Cs & <sup>210</sup>Pb



- Chemical analysis of cores
  - $\rightarrow$  Is there still any chlordecone?
  - → Do we find the previously described chlordecone TPs?
  - $\rightarrow$  Do we find some others?





 $\rightarrow$  Is there any bacteria able to fully

biomineralize chlordecone (loss of the 10 chlorine atoms)?

 $\rightarrow$  Is there any bacteria able to degrade B1?



#### **AKNOWLEDGMENTS**

























### THANK YOU FOR YOUR ATTENTION