



Mise en évidence d'une dégradation naturelle de la chlordécone avec libération dans l'environnement de produits de transformation chlorés

Della-Negra Oriane, Chaussonnerie Sébastien, Mottes Charles, Luc Rangon, Chevallier Marion, Vuilleumier Stéphane, Imfeld Gwenaël, Woignier Thierry, Saaïdi Pierre-Loïc, Le Paslier Denis

► To cite this version:

Della-Negra Oriane, Chaussonnerie Sébastien, Mottes Charles, Luc Rangon, Chevallier Marion, et al.. Mise en évidence d'une dégradation naturelle de la chlordécone avec libération dans l'environnement de produits de transformation chlorés. GFP 2019 Congrès du Groupe Français des Pesticides 2019, May 2019, Montpellier, France. hal-04409489

HAL Id: hal-04409489

<https://hal.science/hal-04409489>

Submitted on 22 Jan 2024

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MISE EN ÉVIDENCE D'UNE DÉGRADATION NATURELLE DE LA CHLORDÉCONE AVEC LIBÉRATION DANS L'ENVIRONNEMENT DE PRODUITS DE TRANSFORMATION CHLORÉS

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

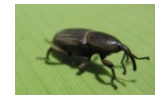


UMR GENOSCOPE
METABOLIC GENOMICS

RESEARCH UNIT METABOLIC GENOMIC UMR8030
CEA . DRF . INSTITUT DE BIOLOGIE FRANCOIS JACOB .
GENOSCOPE

Chlordecone characteristics

Pesticide used against the banana black weevil in the French West Indies (FWI, 1972-1993)



www.cirad.fr

- Mostly under its hydrate form
- 3 main impurities in its commercial formulation: Mirex, chlordecol & 8-monohydrochlordecone
- Persistent 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)
- ▢ Added to the POP list (Persistent Organic Pollutants)



Chlordecone biodegradability

Laboratory studies

1980 • **George & Claxton** ★

1988 • **Pseudomonas**, aerobiosis
CLD → CLD-Cl & CLD-2Cl (8-monohydrochlordecone)

★ **Orndorff & Colwell**

Pseudomonas, aerobiosis
CLD → CLD-Cl et CLD-2Cl (8-monohydrochlordecone)

1996

★ **Jablonski et al.**

Methanosarcina, anaerobiosis
CLD → polar & apolar transformation products

2011

★ **Sakakibara et al.**

Pseudonocardina spp., aerobiosis

2013

2015

★ **Merlin et al.**

Fungi,
aerobiosis
Biofixation

2016

★ **Chaussonnerie et al.**

Citrobacter sp.86, consortia
Anaerobiosis
CLD → hydrochlordecones & polychloroindenes

Aerobiosis
Chlordecone mineralisation
in andosol microcosm

Environmental studies

★ No degradation

★ Partial degradation

Complete degradation

2009

★ **Cabidoche et al.**

"the soil decontamination will take some decades for nitisol, several centuries for ferralsol, and more than half a millennium for andosol"

2013

2016

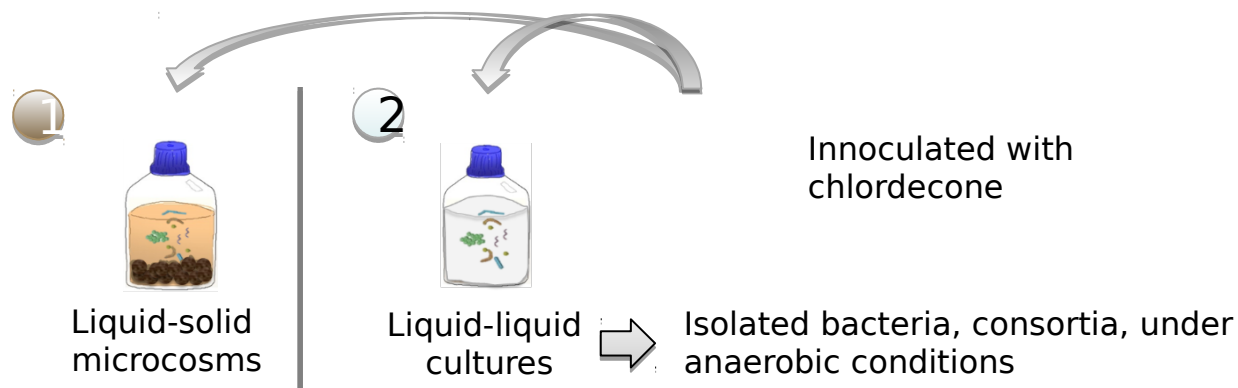
★ **Devault et al.**

Marginal transformation of CLD into 8-monohydrochlordecone (CLD-Cl) in FWI



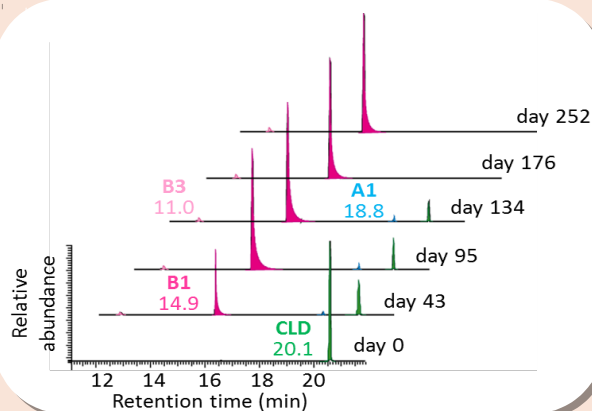
Strategy

Design of microbiological experiments: a dual approach



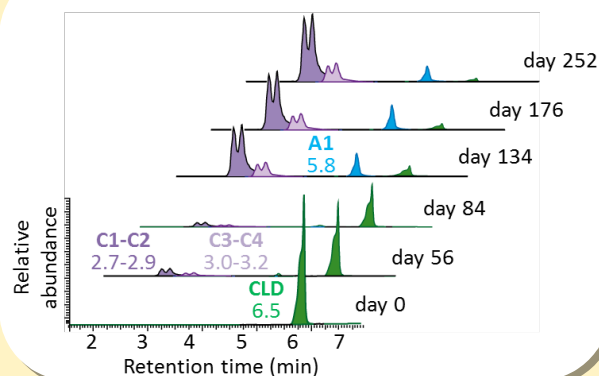
➤ Dual analytical monitoring

GC-MS analysis



+

LC-MS analysis



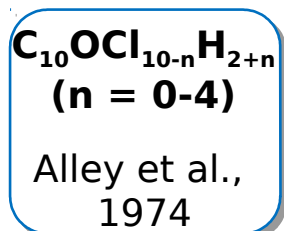
Detection of chlorinated transformation products over time

Mass spectrometry analysis of the newly identified chlordane transformation products

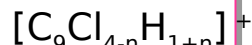
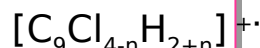
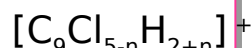
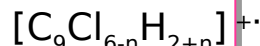
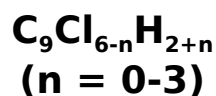


- In-source mass fragmentation signature enables to cluster chlorinated compounds into 5 families

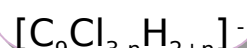
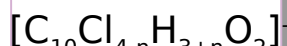
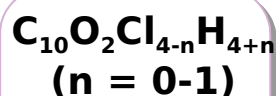
A



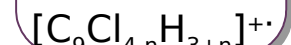
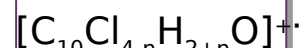
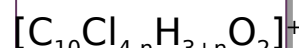
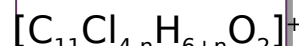
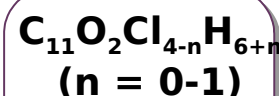
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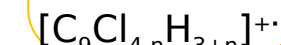
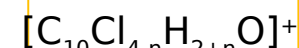
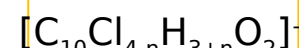
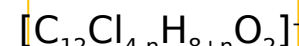
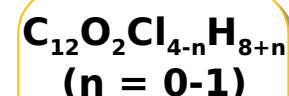
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D

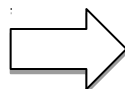


E



 Detected using GC-EI-MS analysis

 Detected using LC-ESI-MS analysis



Chemical synthesis of these compounds to obtain a significant quantity of them and allow their complete structural elucidation



Chemical synthesis, purification & structural elucidation

Screening of chemical degradations
21 tested conditions



A1

Vitamin B₁₂,
Na₂S, H₂O

B

Vitamin B₁₂,
TiCl₄, H₂O

C

Vitamin B₁₂,
Fe(0), H₂O,
acetone

D

Vitamin B₁₂,
TiCl₄, H₂O,
methanol

E

Vitamin B₁₂,
TiCl₄, H₂O,
ethanol

Quantity on a mg scale after a purification step

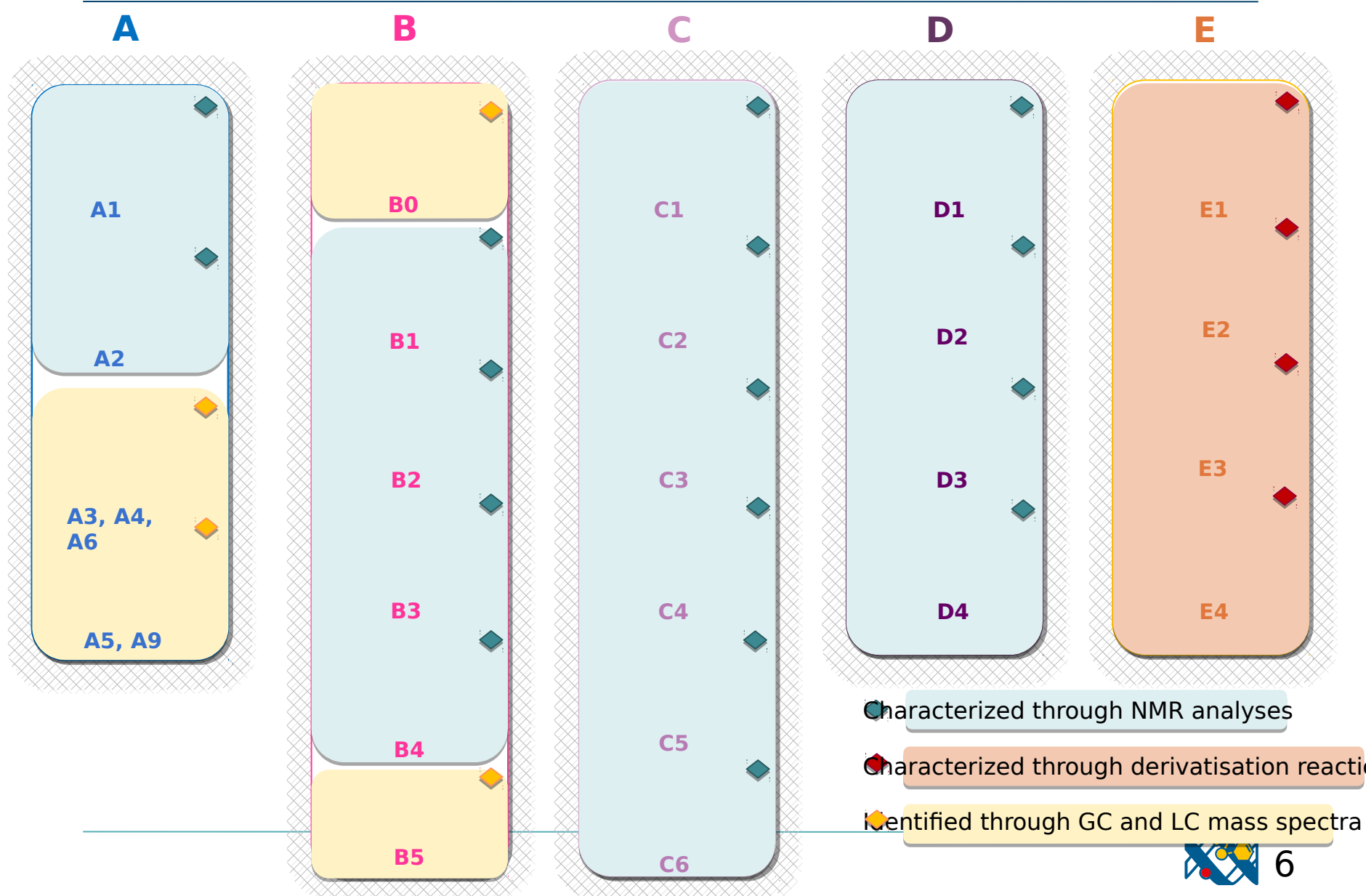
Nuclear Magnetic Resonance (NMR) analysis to completely elucidate the structure of 17 chlordane

and / or

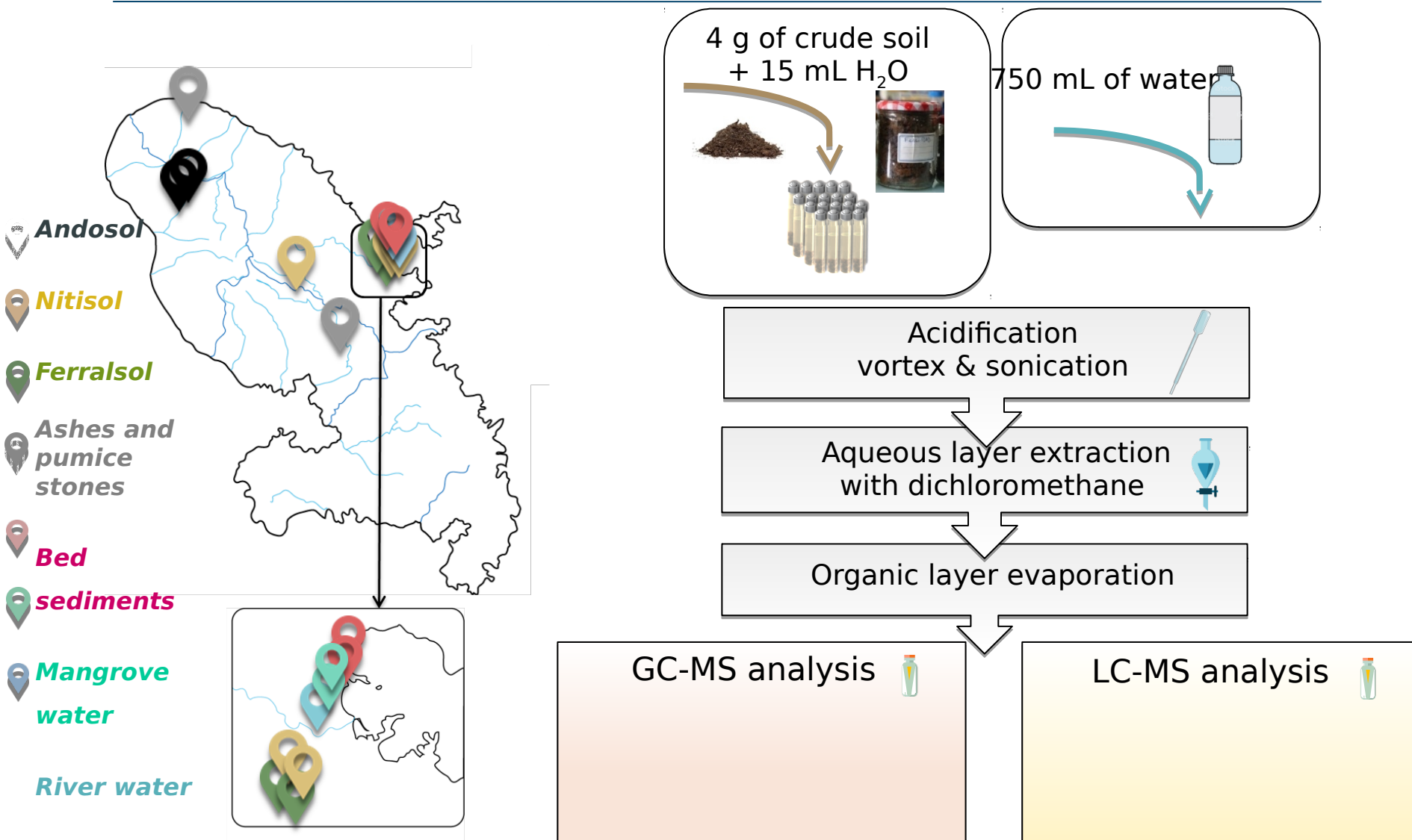
Chemical derivatisation reactions



Chlordecone TPs database



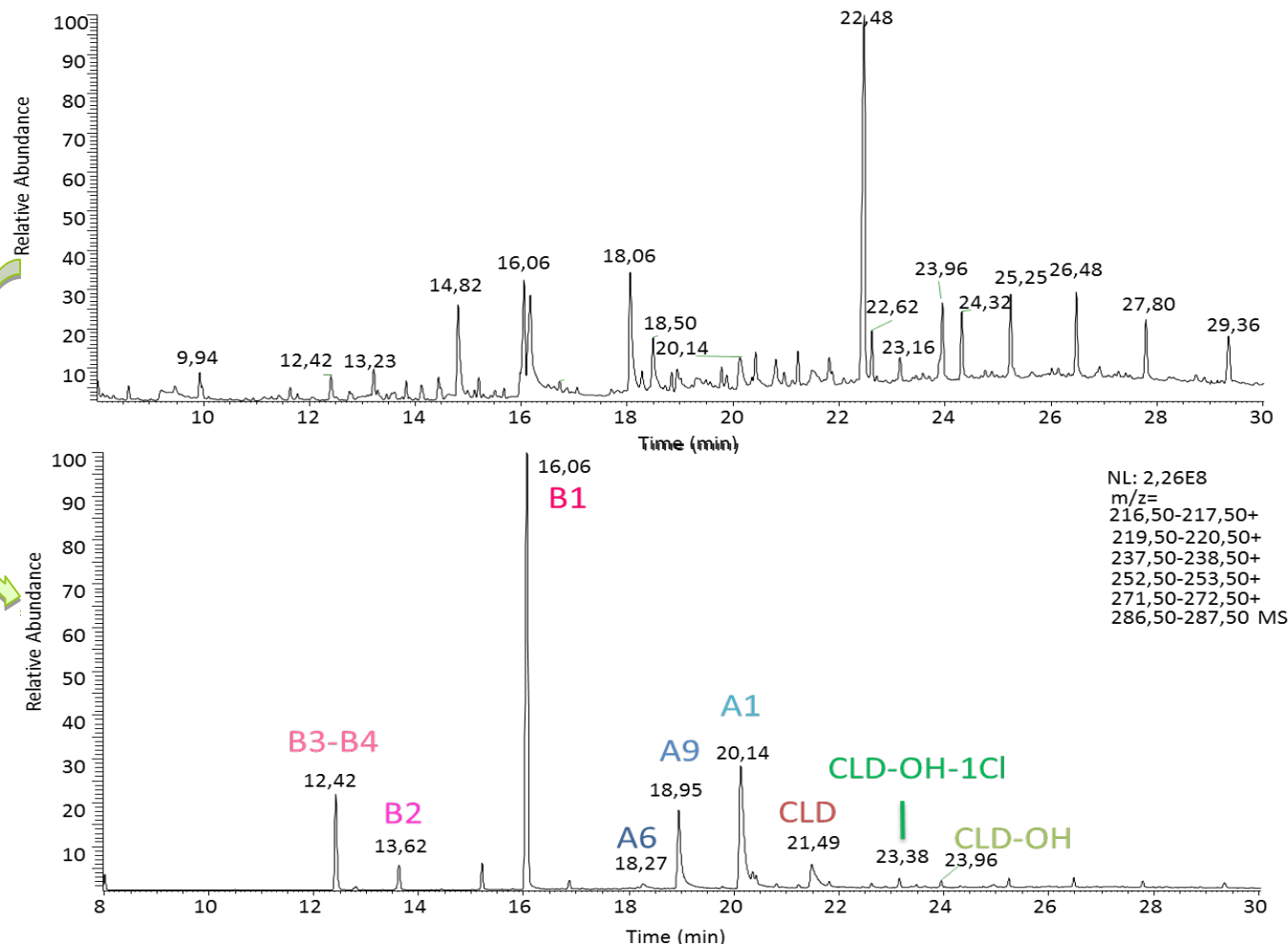
Sampling and extraction strategy



GC & LC MS dual analysis

Example of a GC-MS analysis

Extract ion chromatogram established from chlordane TP data base



SEARCH FOR CHLORDEcone TP_s IN SAMPLES FROM MARTINIQUE ISLAND



Results of the study

➤ Contamination levels of the main chlordane TP_s

CLD CLD-OH

A1

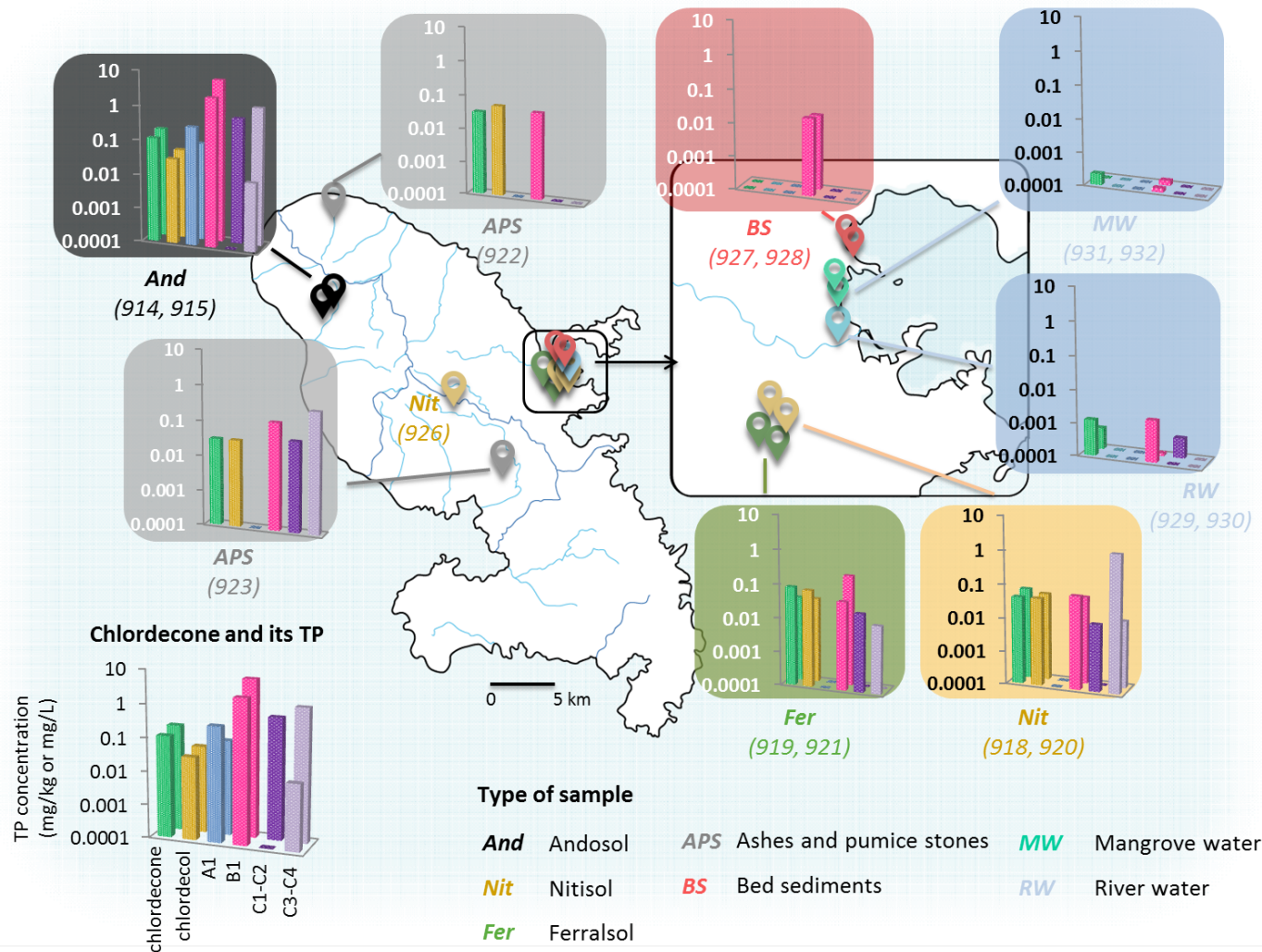
B1

C1

C2

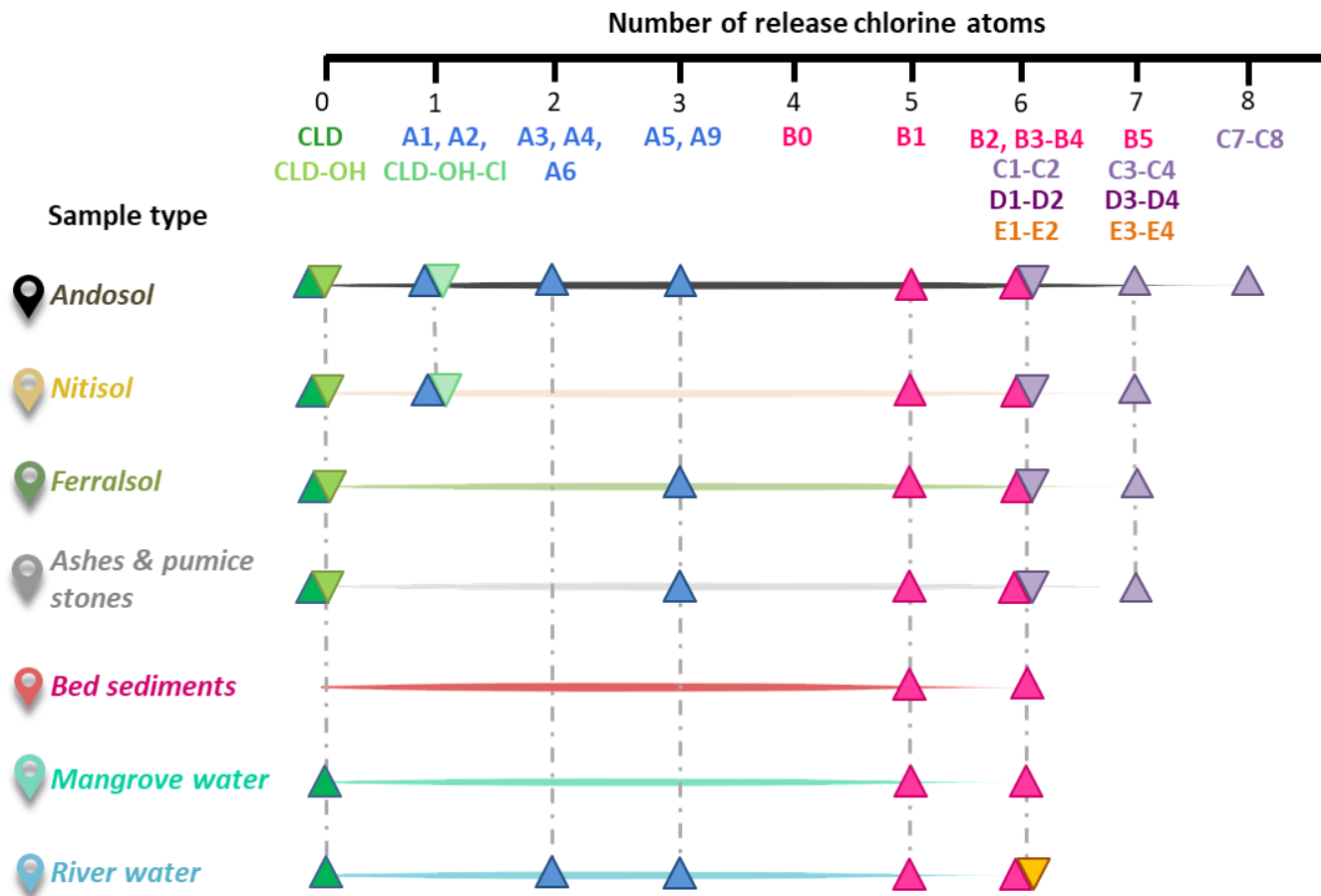
C3

C4



Results of the study

- Detection of many chlordecone TP_s



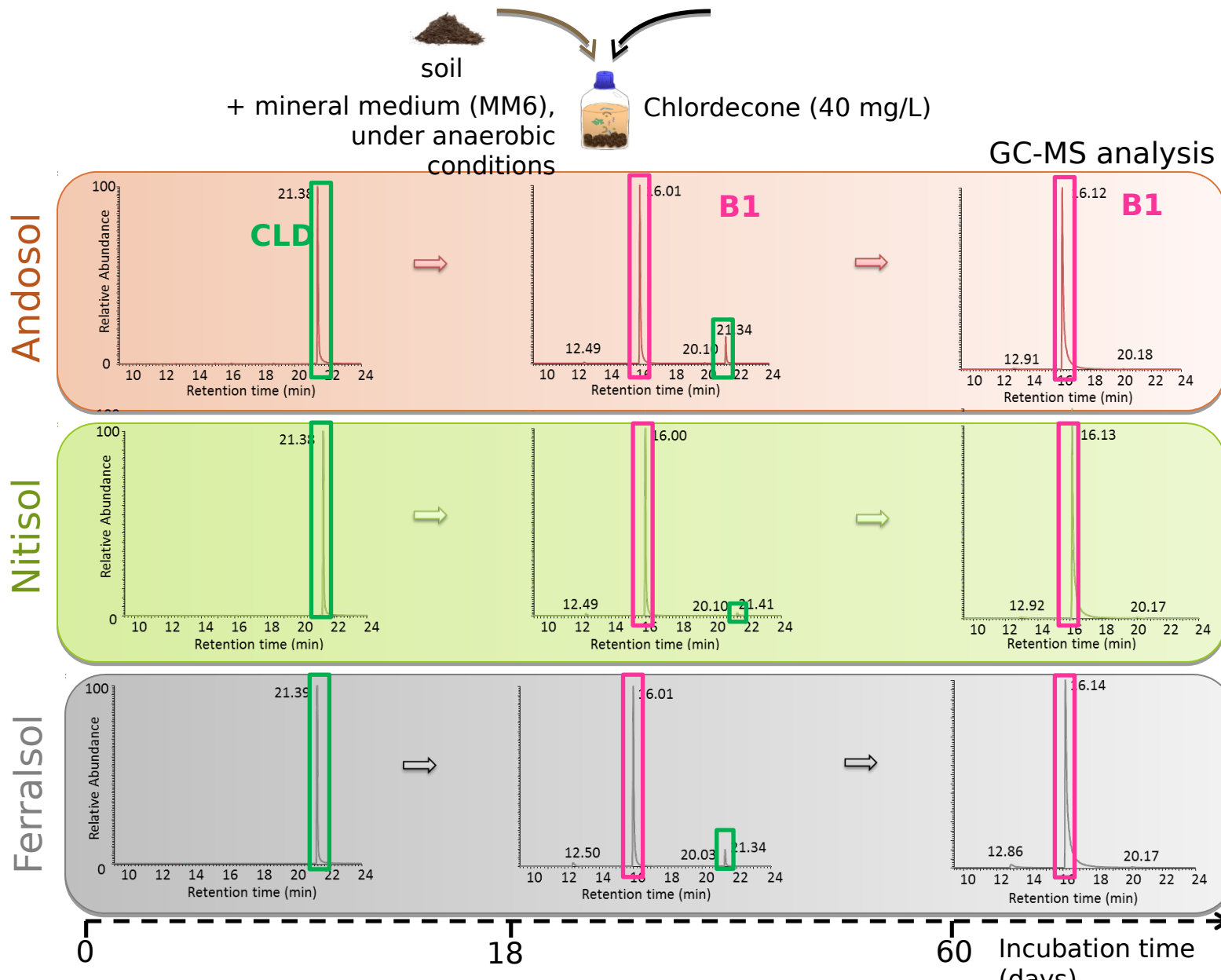
Detection of numerous chlordecone TP_s in samples from Martinique

-> Natural degradation of chlordecone

CONFIRMATION OF MARTINIQUE MICROFLORA CAPABILITY TO TRANSFORM CHLORDECONE



Strategy & results



1) Structural elucidation of 19 TPs & discovery of 3 new families of chlordecone TPs

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



Hydrochlordecones
(n = 1, 2, 3)



Polychloroindenes
(n = 0, 1)



Polychloroindene
carboxylic acids
(n = 0, 1, 2)



Ethylpolychloroindene
carboxylates
(n = 0, 1)



3) Identification of TPs contamination levels of the same order of magnitude as chlordecone

4) 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

Improve our knowledge about transformation products

- Toxicity
- Stability
- Biodegradability

Quantification of these TP_s in environmental compartments

What about human exposure to these TP_s?

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





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 Stéphane Vuilleumier



Article

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Natural Chlordecone Degradation Revealed by Numerous Transformation Products Characterized in Key French West Indies Environmental Compartments

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