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Fate of chlordecone (CLD) under methanogenic conditions



H. Macarie
Y. Labrousse
A. Amic



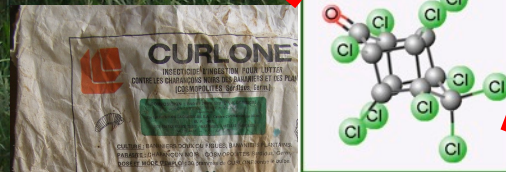
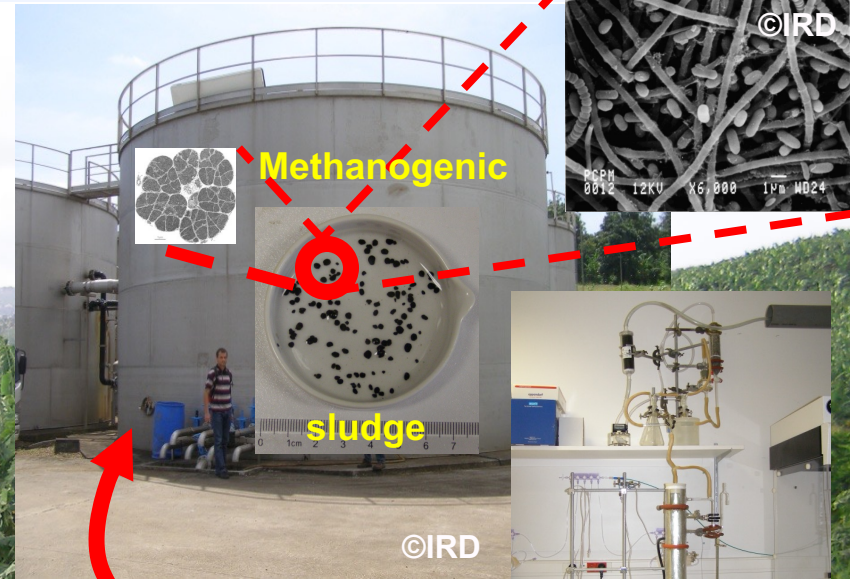
N. Cimetière



A. Soler



S. Bristeau
C. Mouvet



Background

CLD structure, manufacture and use

Organochlorine insecticide

Raw structure: $C_{10}Cl_{10}O$

Belongs to **bishomocubane** series of molecules

IUPAC name: perchloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-one

1951: 1st synthesis

1952: US Patents 2,616,825 & 2,616,928

1958: 1st commercialization by Allied Chemicals
as Kepone[®] in 3 locations in USA:

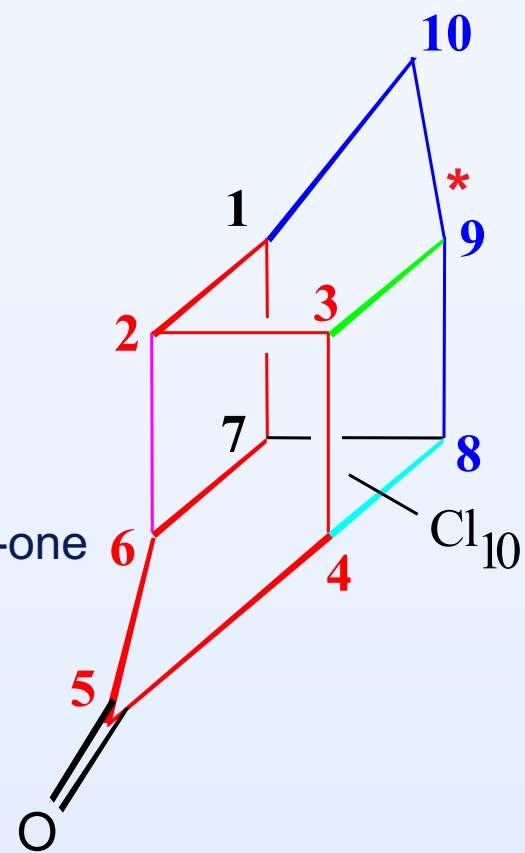
Main use against:

ants and cockroaches in traps

tobacco wireworm

potatoe colorado beetle

**banana weevil (5% dust)
(Charançon noir)**



Background

CLD structure, manufacture and use

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Raw structure: **C₁₀Cl₁₀O**

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IUPAC

5,10,3,9,10,4,8]decan-5-one

1951

1952

1958

Main



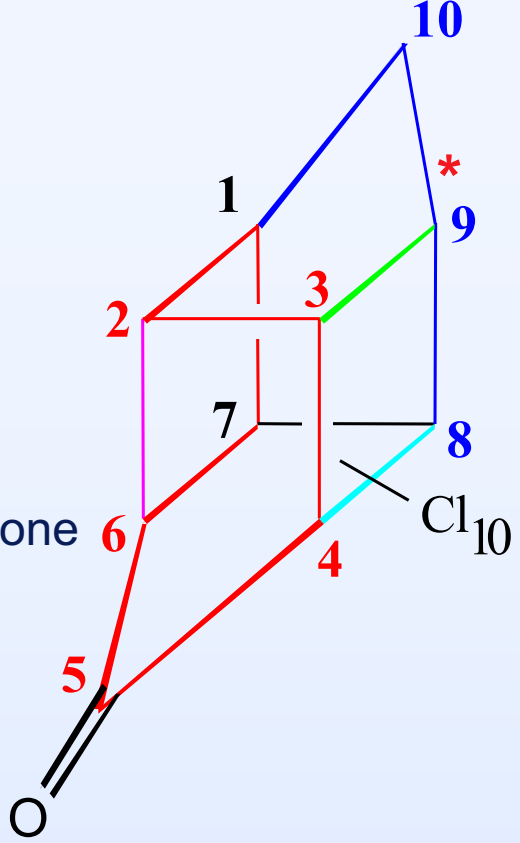
©CIRAD-Chabrier

ants and cockroaches in traps

tobacco wireworm

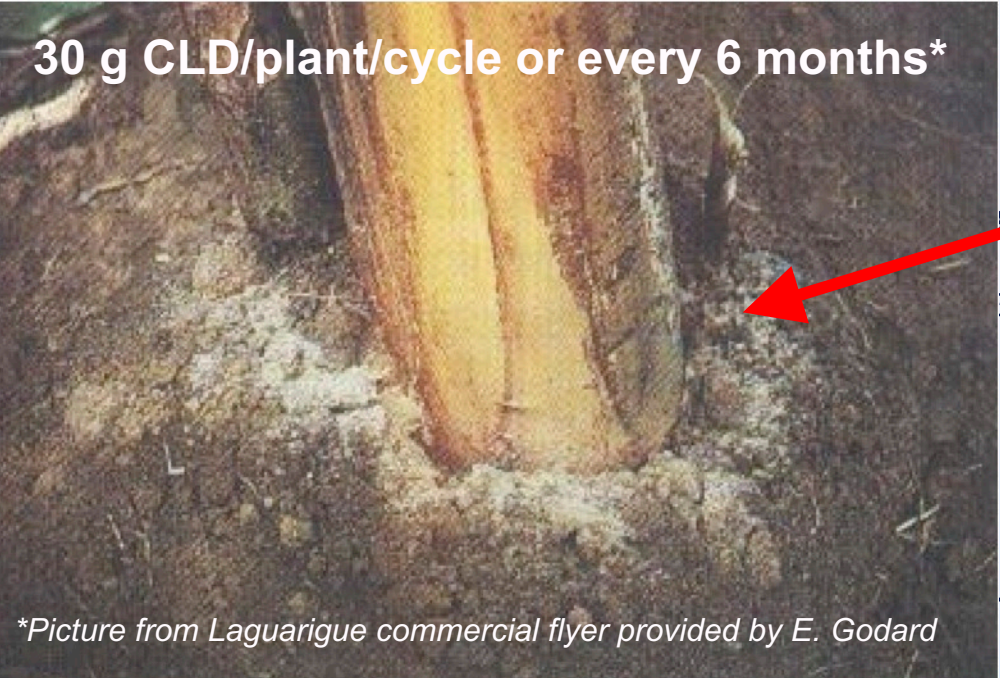
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Background

CLD structure, manufacture and use



Main

tobacco wireworm

potatoe colorado beetle

banana weevil (5% dust)
(Charançon noir)

SEPPIC

kepone 5%

lutte contre le charançon noir du bananier

- contrôle parfait du parasite
- efficacité de longue durée
- augmentation des rendements

SEPPIC 70, Champs-Élysées Paris 8^e

* Marque déposée Allied Chemical

photo IFAC

10

*

9

8

Cl₁₀

©IRD

ecules

3,9.04,8]dec

micals

Background

Chlordecone use in French West Indies (2756 km²)

Localization



Population ≈ 400 000 inh / island

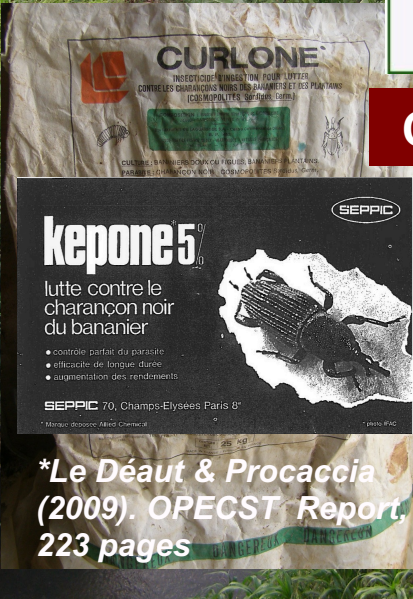
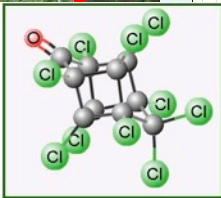
2nd European banana producer after Spain (≈ 250 000 tonnes/an; of which ¾ by Martinique)

Consequences of chlordecone use in French West Indies

Background

1972 – 1993

≈ 300 tonnes*
(1/6 of CLD world production)

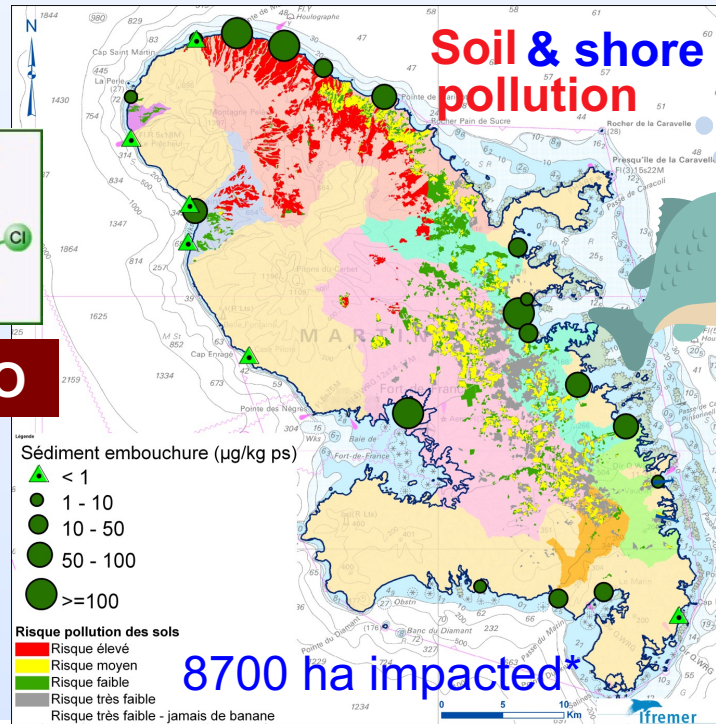


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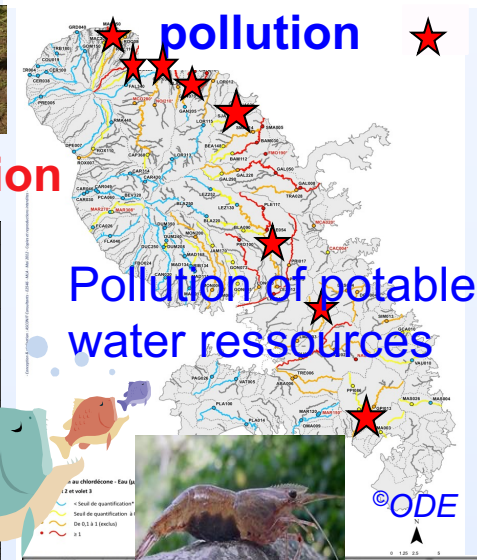
Nowadays (30 years later)



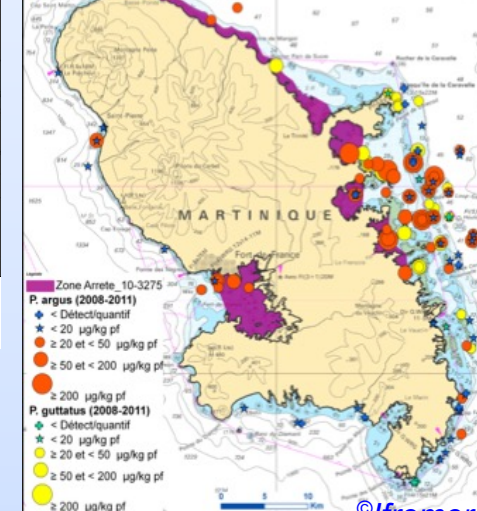
Food crops & livestock contamination



Rivers & aquifers pollution



Sea fish & lobsters contamination



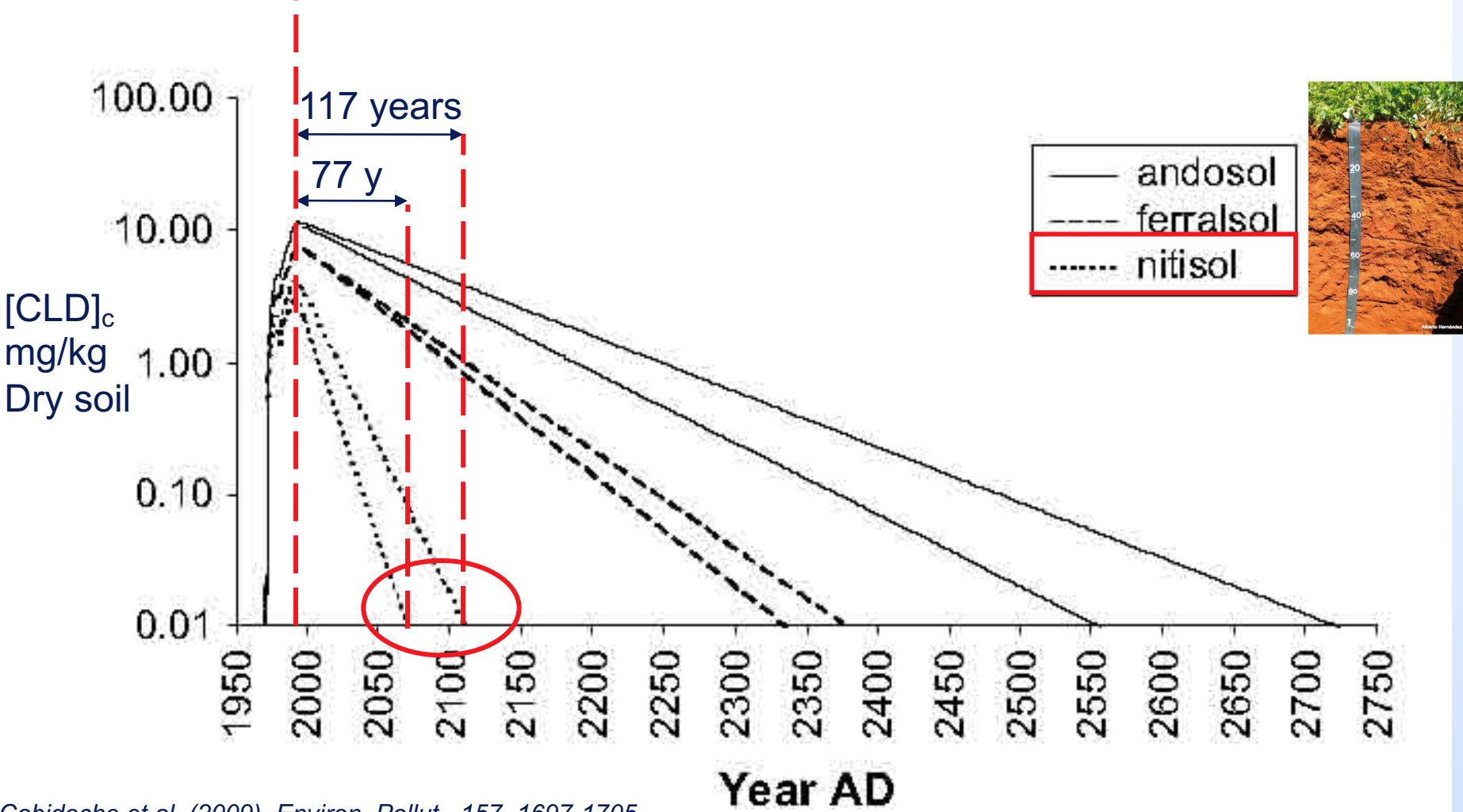
Human health consequences:

- ≥ 92% of people impregnated
- Prostate cancer
- Impairment of young cognitive & motor development

*Martinique & Guadeloupe (2756 km², 18970 ha with banana plantation)

Background

Behaviour of CLD in French West Indies soils if leaching due to rain is the only removal mechanism*

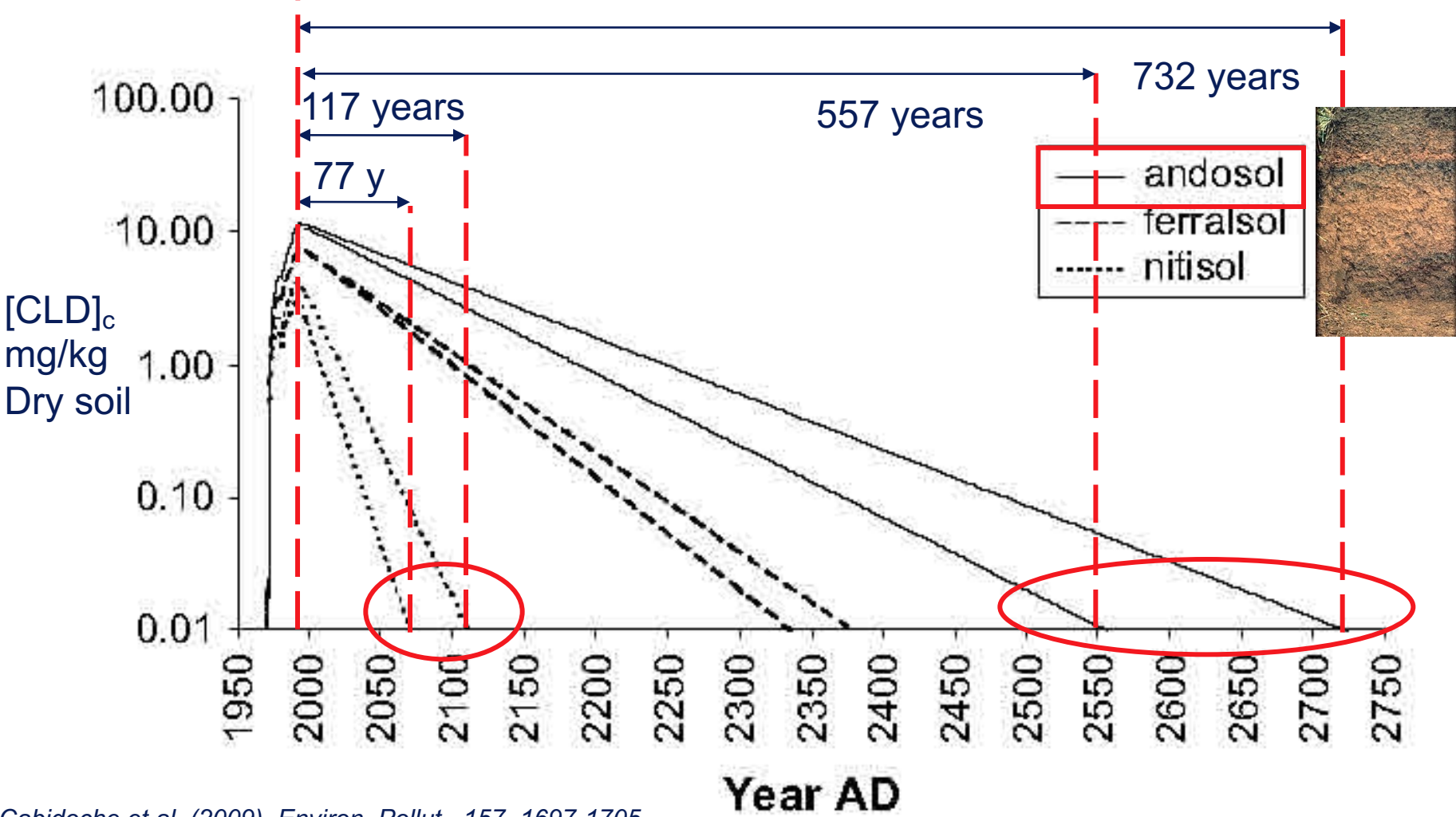


*Cabidoche et al. (2009). Environ. Pollut., 157, 1697-1705

Soil organic carbon content and annual rainfall considered are typical for each soils

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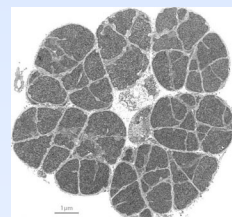


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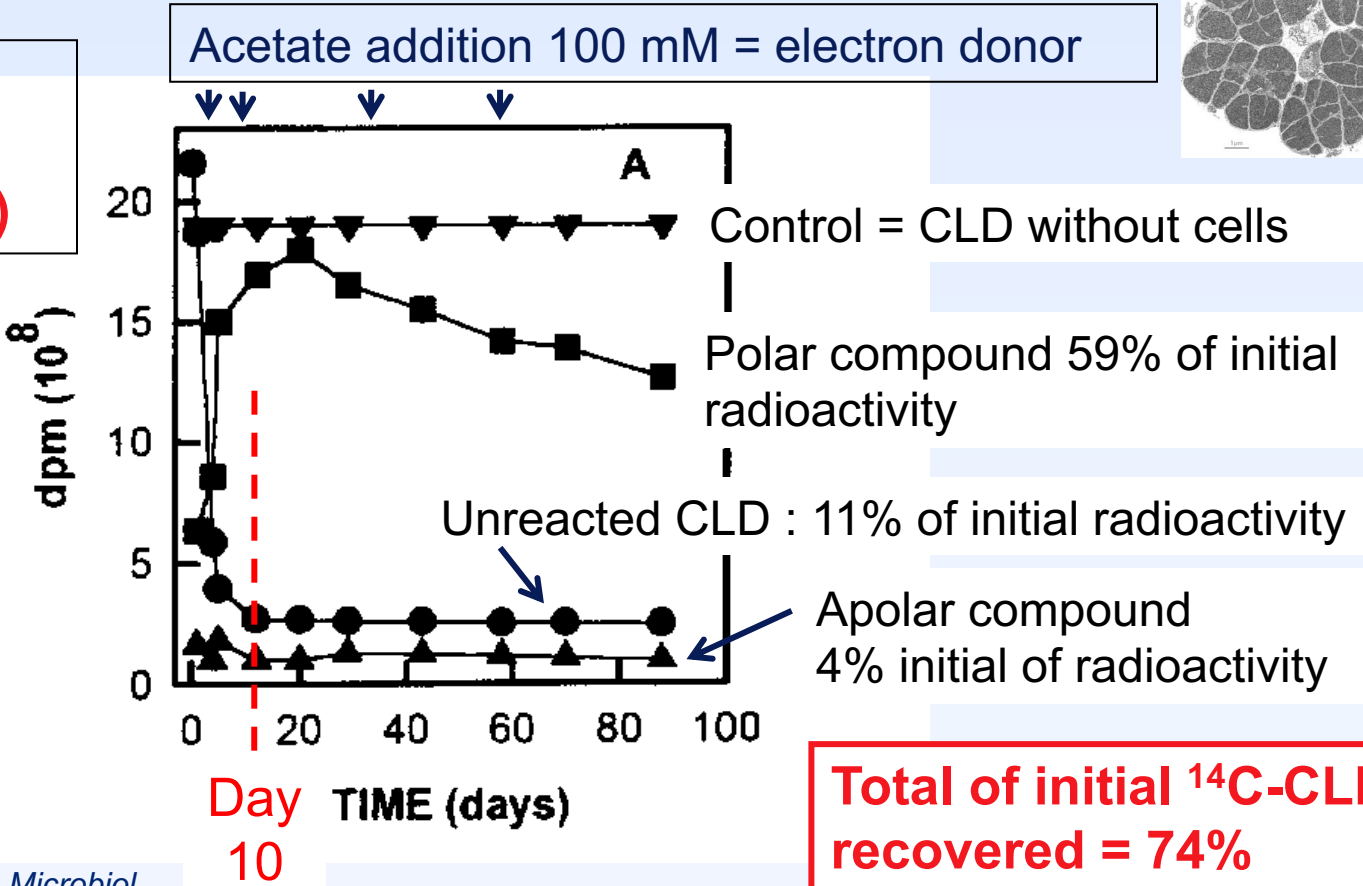
Soil organic carbon content and annual rainfall considered are typical for each soils

Background

1. No thermodynamic impediment to microbial degradation of CLD (Dolfing *et al.*, Environ Sci & Technol., 46, 8131-8139).
2. In 1996 Jablonski *et al.* Suggest that *Methanosarcina thermophila* has the capacity to degrade ^{14}C -CLD



Radioactivity
 = CH_4
 (< 1% ^{14}C -CLD)



*Jablonski *et al.* (1996). *FEMS Microbiol. Lett.*, 139, 169-173.

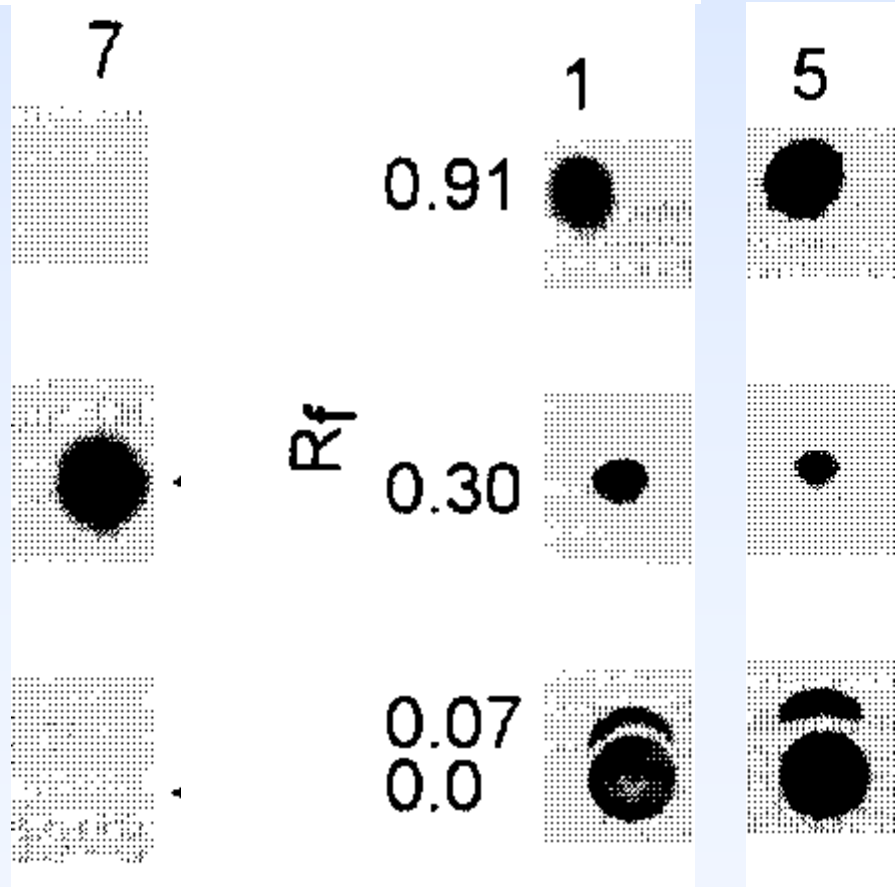
Background: enzymes & cofactors implicated in CLD attack by *M. thermophila* using TLC (Thin layer Chromatography)*

Without cells or enzymes

Supernatant after 90 days of culture

Vit B12 Sigma

Ti III-citrate + N₂



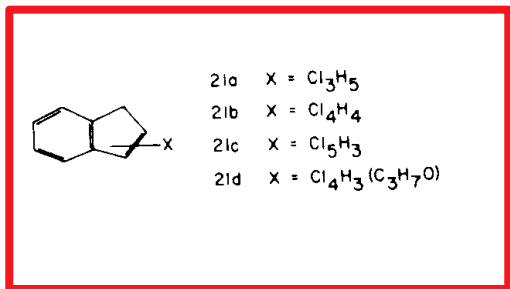
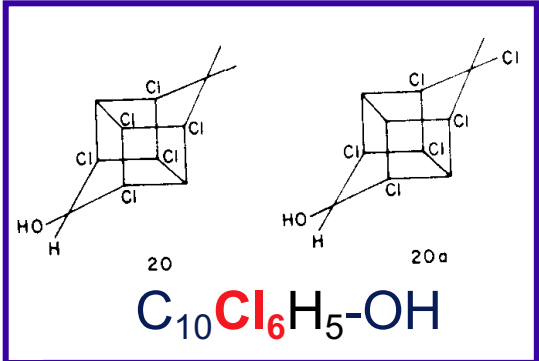
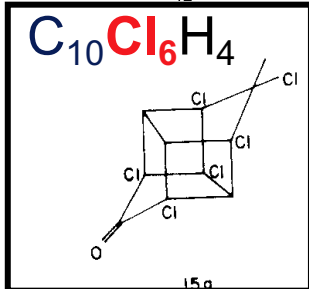
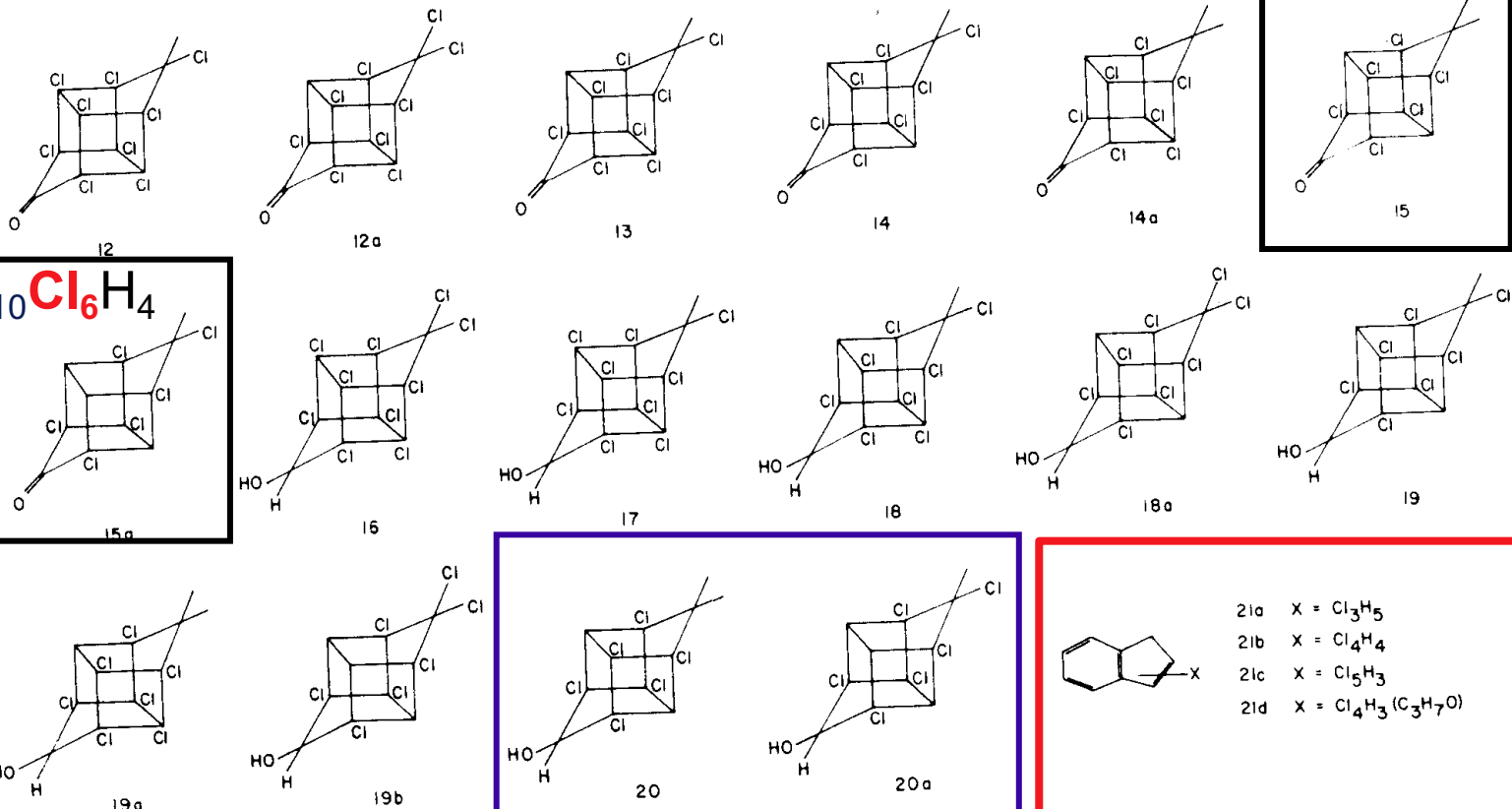
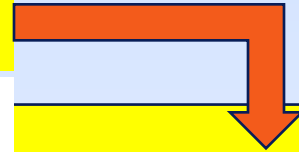
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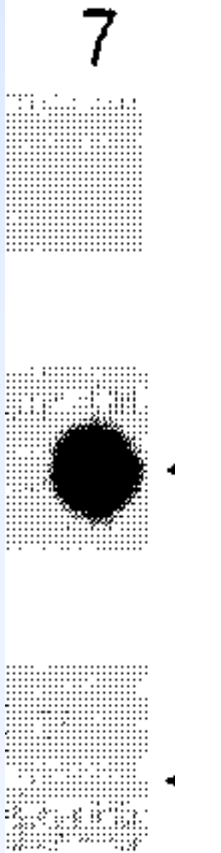


**Schrauzer and Katz (1978). *Bioinorg. Chem.*, 9, 123-143.

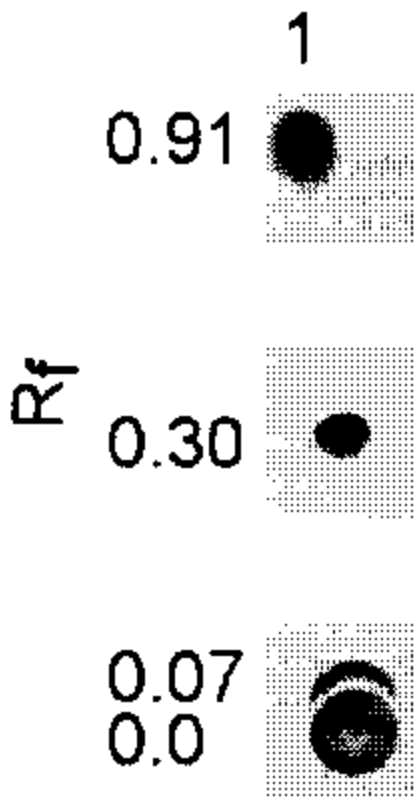
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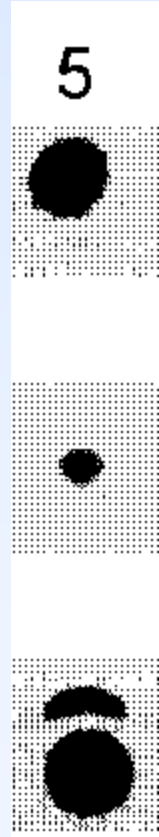


Supernatant after 90 days of culture



Vit B12 Sigma

Ti III-citrate + N₂



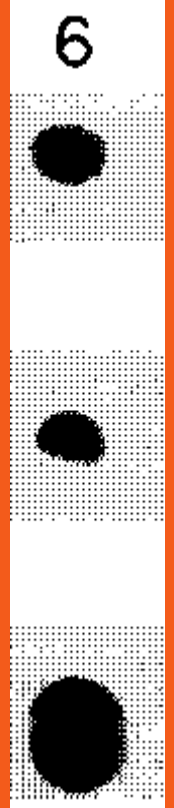
Factor III of CO-dehydrogenase complex



Ti III-citrate + N₂

Factor III = Co/Fe-S coenzyme = analog Vit. B12

F₄₃₀ factor (Ni)
Ti III-citrate + N₂



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Background

- 1. No the *et al.*, E
- 2. In 19 the cap
- 3. Coba consequ
- 4. Sludge digesters
- 5. Bioaugmentation of soils + CLD with anaerobic
- 6. Following of [CLD] in industrial digesters treating rum vinasses



**53-91% CLD removal between in / out
CLD-5b-hydro – exit < LQ
[CLD] & CLD-5b-H sludge <<< [expected]**

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thermophila has
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*UASB: Upflow Anaerobic Sludge Blanket; DAF: Downflow Anaerobic Filter.

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et al., E...
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of [CLD] in industrial digesters treating rum vinasses



53-91% CLD removal between in / out
CLD-5b-hydro – exit < LQ
[CLD] & CLD-5b-H sludge <<< [expected]

Weak results:

- Quantification of biomass difficult at this scale
- very low [CLD] & huge background for GC-MS & IC

*UASB: Upflow Anaerobic Sludge Blanket; DAF: Downflow Anaerobic Filter.

Objectives & methodology

Confirmation of the capacity of CLD degradation under methanogenic conditions in liquid medium.

- Operation of a lab scale anaerobic reactor (1,975 L) fed continuously under the following conditions :

**Inoculum*

= Granular sludge¹ of the studied UASB reactor treating rum vinasses at full scale

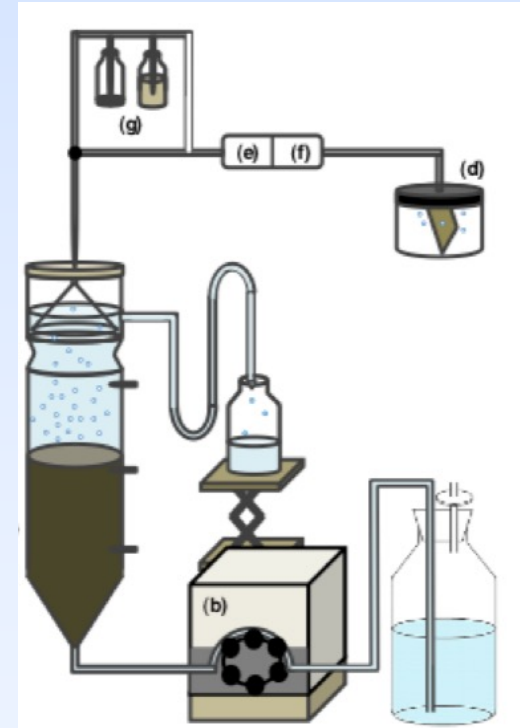
* *Feeding solution containing :*

- CLD* ([CLD] = 2 mg/L \approx solubility limit)
- Carbon & electron source = ethanol/acetate/glucose
- Source of N, P, S & Fe, Ni, Co **without Cl⁻ and SO₄²⁻**

* *HRT² & constant volumetric loading rate*

¹Sludge having been in contact with CLD

²HRT = Hydraulic Retention time



*Source Dr Ehrenstorfer

Objectives & methodology (following)

- **Parameters monitored during the operation of the reactor:**

- * **Parameters confirming that the system is working fine :**

- COD in, out (colorimetry)
- pH & TSS* (gravimetry) in, out, sludge
- Sludge redox potential (confirmation of anaerobic conditions)
- CH₄ flow rate (confirmation of methanogenic conditions)

- * **Parameters to follow CLD biodegradability**

- [CLD] in, out, sludge (precise mass balance, % of removal)
- [CLD-5b-hydro]**, [CLD-OH]**, [CLD-1Cl_{ISCR}]** in, out, sludge.
- Presence of unknown degradation products (tentative of identification from mass spectra)
- [Cl⁻] (Ionic chromatography, proof of dechlorination balance Cl-organic, Cl-inorganic)

SPME
ou ASE
GC/MS***
& LC-MS
for sludge

**Total Suspended Solids*

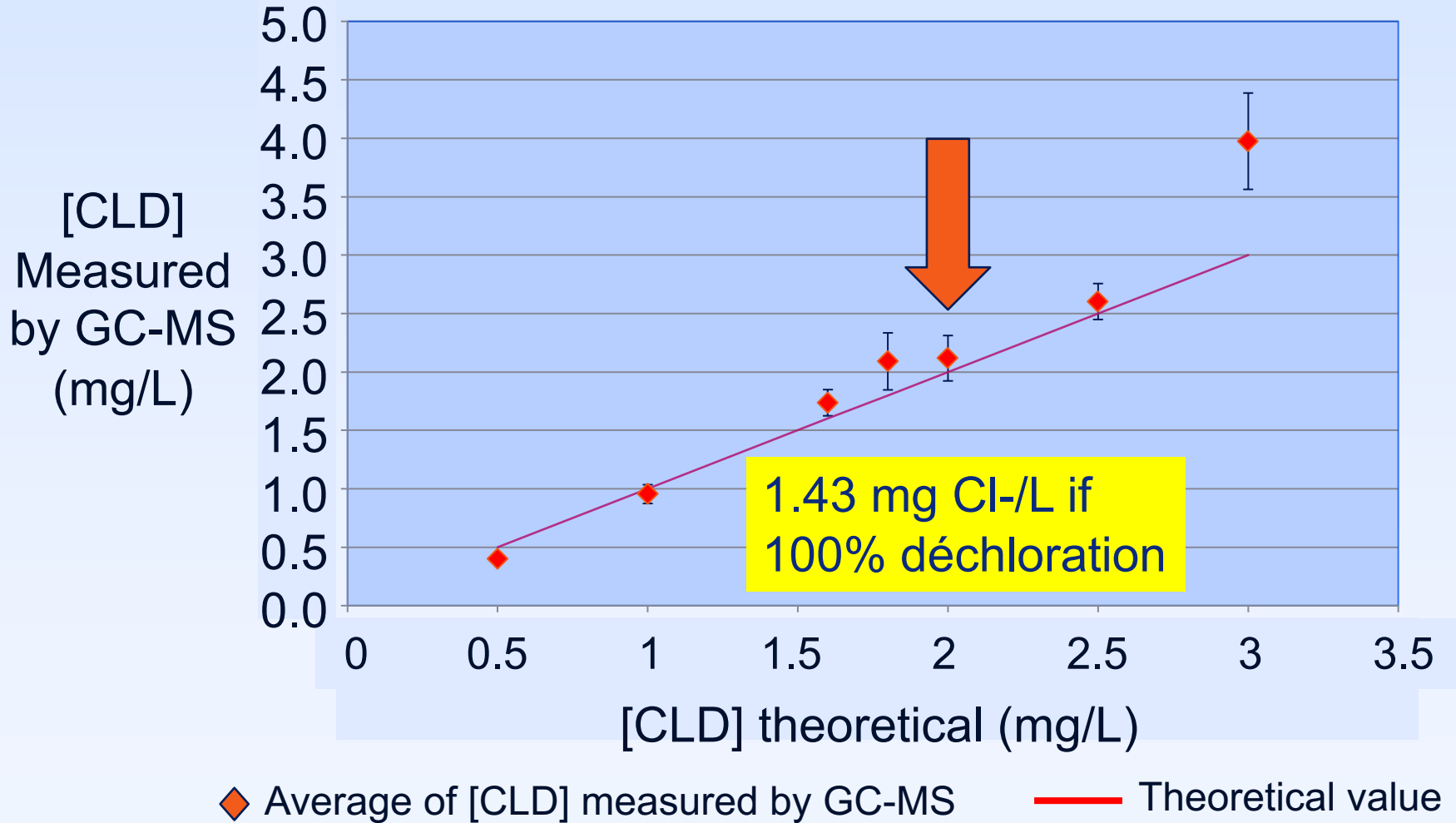
***Analytical standards available*

****SPME: Solid Phase Micro-Extraction*

ASE: Accelerated Solvent Extraction

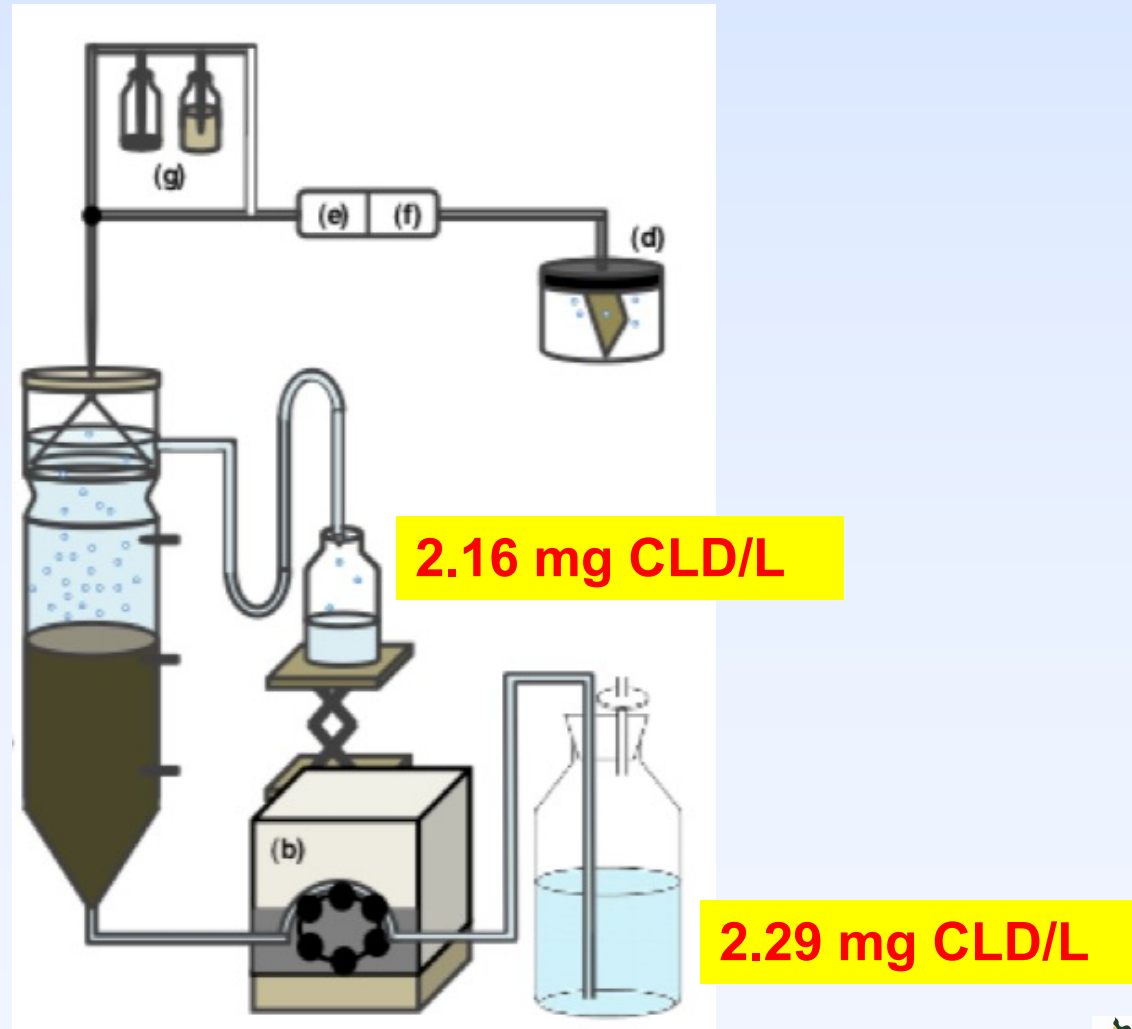
Results

- Solubility of CLD in the feeding solution



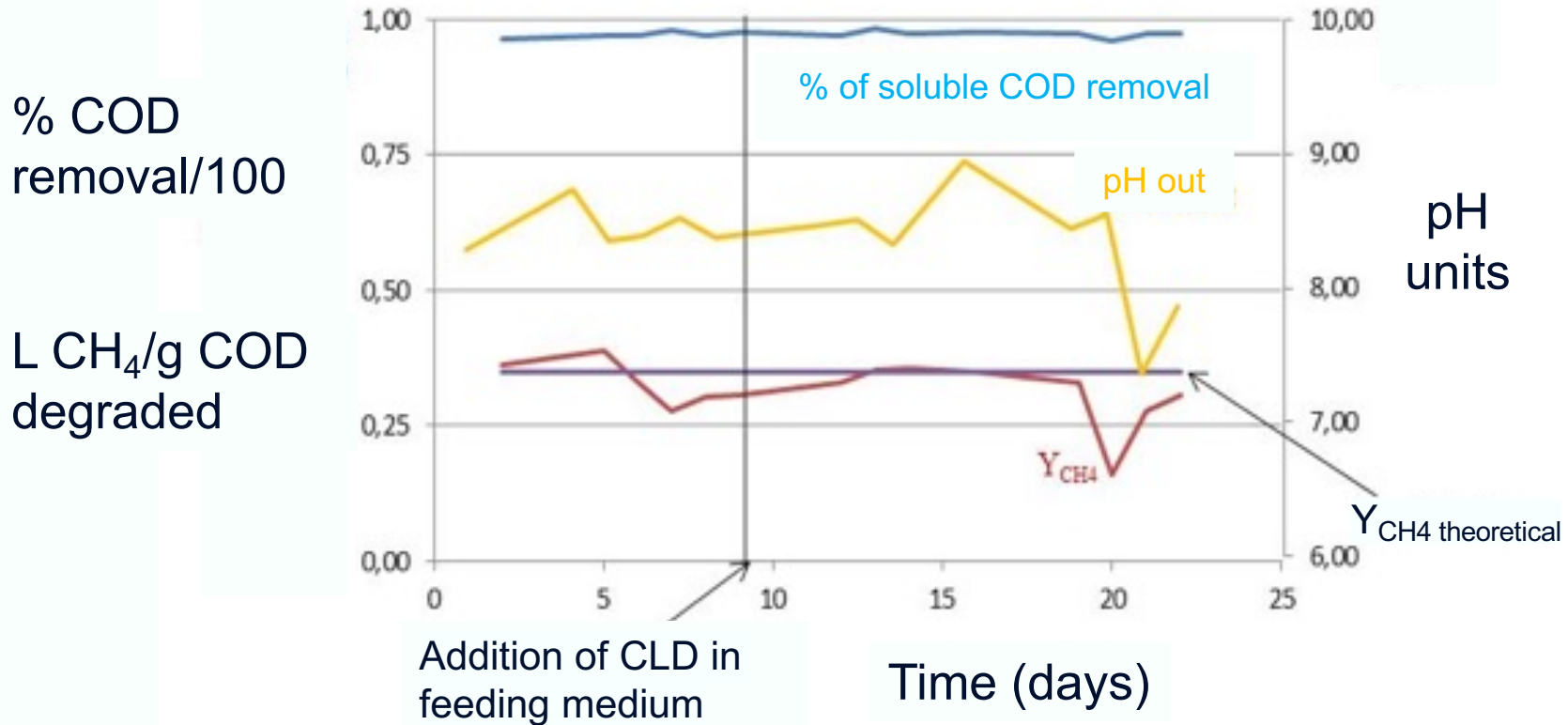
Results

- Adsorption of CLD on the feeding tubes (teflon) and reactor walls (glass) while operated empty (without biomass)



Results

● Methanogenic behaviour of the reactor



$$E_{Ag/AgCl} t_0 = -345 \text{ mV}$$

$$E_{Ag/AgCl} t_f = -434 \text{ mV}$$

No noticeable toxic effect after the addition of 2 mg/L to the feed of the reactor

Results

- Mean removal of CLD & other products detected in the liquid phase at the entrance of the reactor over the range of reactor operation

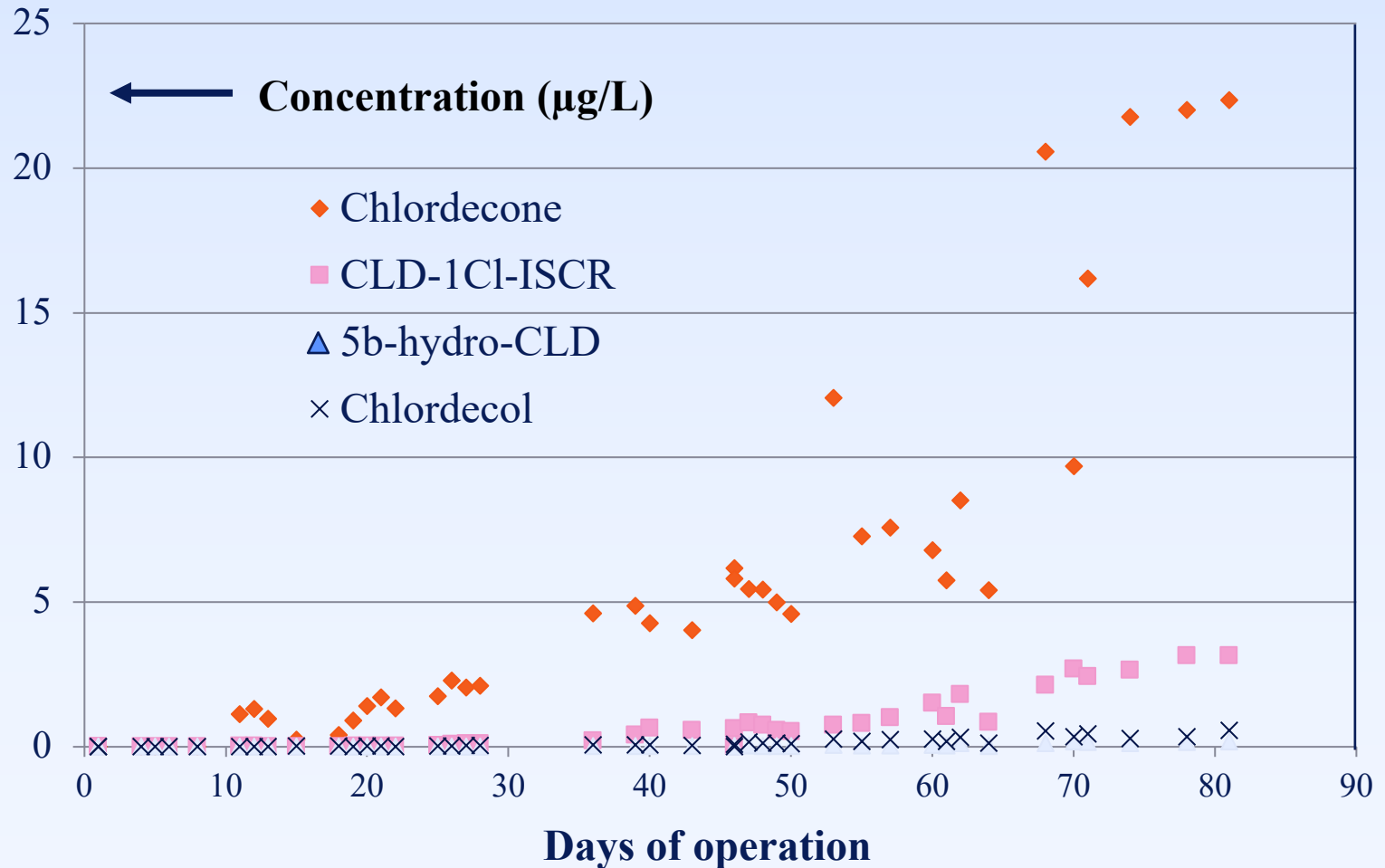
	CLD	CLD-5b-hydro	CLD-1Cl _{ISCR}	CLD-OH
Entrance µg/L	2210±394	1.47±0.1	≤ 0.0999	17.2±3.9
Exit µg/L	6.45±6,5	0.0653±0.058	0.85±0.975*	0.15±0.16
Removal (%)	99.71	95.58	NA	99.12

Traces of 2 dihydro-CLD_{ISCR} ≠ dihydro-CLD_{NIST-USEPA}

***Represents only 0.17% in mole of the removed CLD**

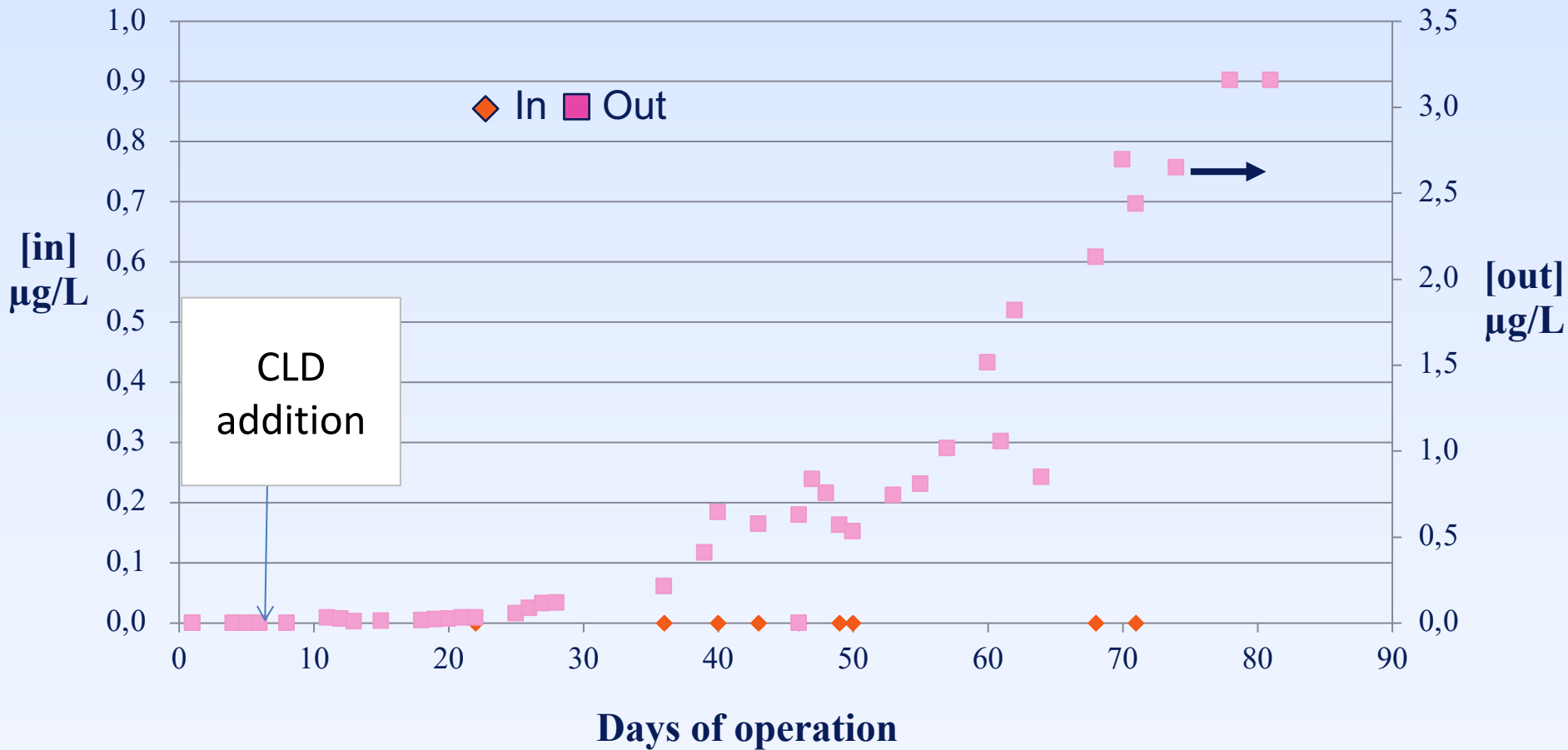
Results

- Evolution of the concentration of CLD, CLD-5b-Hydro, CLD-OH & CLD-1Cl_{ISCR} at the exit of the reactor over time



Results

- Evolution of $[CLD-1Cl]_{ISCR}$ at the entrance and exit of the reactor over time



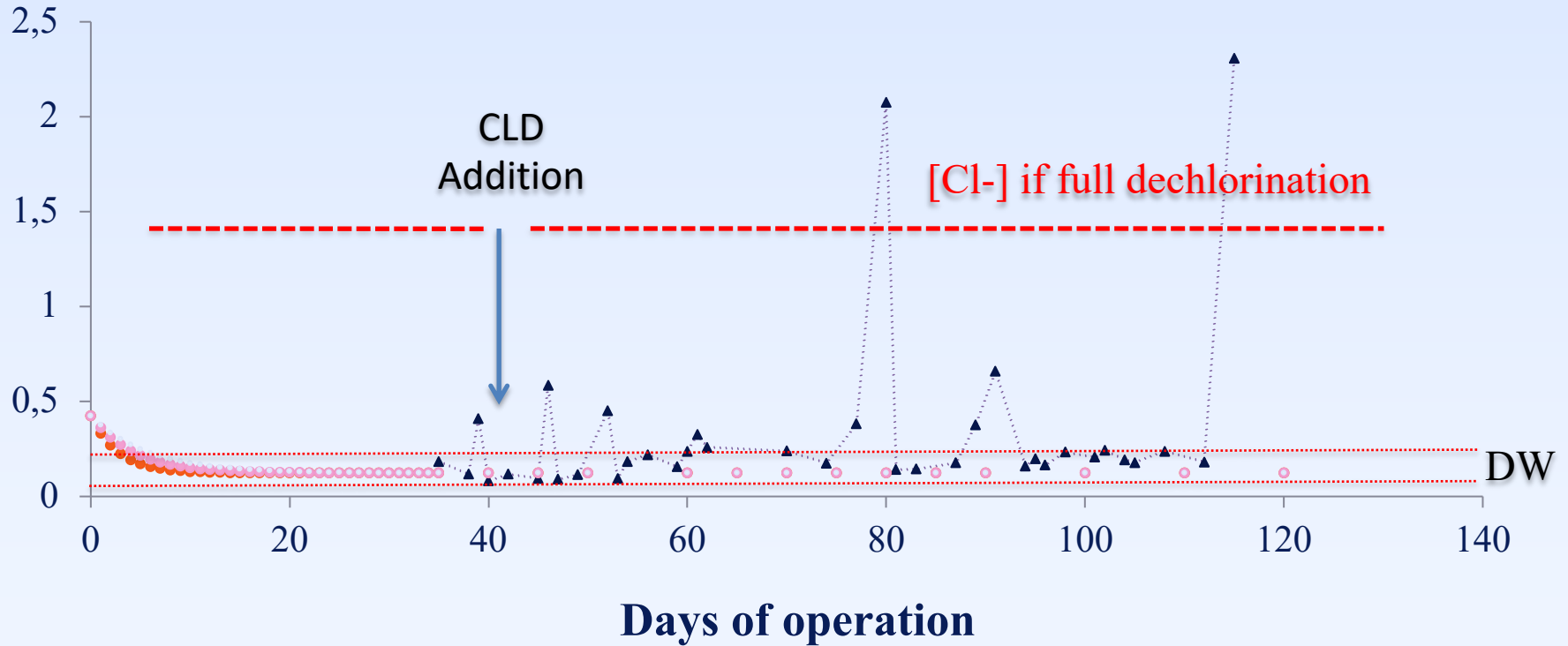
Results [CLD], [CLD-5b-hydro], [CLD-1Cl_{ISCR}], [CLD-OH] in reactor sludge

	Drying	Method extraction/ analysis	CLD	CLD-5b-hydro	CLD-1Cl _{ISCR}	CLD-OH
[T0] mg/kg MS	40°C	ASE/ GS-MSMS	< 0.2	< 0.2	< 0.2	0.39±0,24
[Tfinal] mg/kg MS	40°C		77±1.5 (11% CLD expected)	< 0.2	0.91±0.08 (0.14% CLD expected)	1.6±0.17
[Expected] mg/kg MS			708	0.472	≤ 0.032	5.512
[Tfinal] mg/kg MS	40°C	SPME/ GC-MSMS	190 (27% CLD expected)	<< 18	27.5 (4,2% CLD expected)	<< 15
[Tfinal] mg/kg MS	Fresh sludge	dosed addition	490 (69% CLD expected)	<< 32	28.4 (4,33% CLD expected)	<< 25
[Tfinal] mg/kg MS	Fresh sludge	Acetonitrile/ LC-MSMS	251.8 (35% CLD expected)	ND	8.76 (1,3% CLD expected)	ND

Results

● Evolution of Cl⁻ concentration at the reactor exit

[Cl⁻] mg/L



- ▲●● [Cl⁻] reactor out
- [Cl⁻] To 0.425 mg/L, TRH 3.37 jour
- [Cl⁻] To 0.425 mg/l, TRH 4.74 jours
- [Cl⁻] To 0.425 mg/l, TRH 6.21 jours

Conclusions & perspectives

1. Although the CLD mass balance did not close the previous results show that the **main mechanism of CLD removal** in the reactor **was due to adsorption on the biomass**.
2. The presence of CLD-1Cl and CLD-2Cl not detected at the entrance of the system confirms however that **the methanogenic biomass used had the capacity to dechlorinate CLD**, **but that this capacity was very low** despite massive inoculation of the reactor.
3. **The microbial group capable of dechlorinating CLD was probably not methanogenic** and represented a very tiny proportion of the microbial consortium.
4. Although the results suggest a slow capacity for enrichment of this population over time they also show that **the possibility of using digester sludge for bioaugmentation in a soil remediation process to achieve CLD degradation would not be viable**.

IRD-CNRS-IMBE microbiology & pedology team



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Herve Macarie

Thierry Woignier

Luc Rangon

Yoan Labrousse



Sébastien Bristeau



Christophe Mouvet



Nicolas Cimetière



Alain Soler



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INRAE

With
funds



Plan
chlordécone



UNION EUROPÉENNE
Fonds européen de
développement régional



Collectivité
Territoriale
de **Martinique**

Martinique (FWI) views



Thanks for your attention

