Evidence for Anaerobic Microbial Dechlorination of Chlordecone in Microcosms and Soil from Guadeloupe

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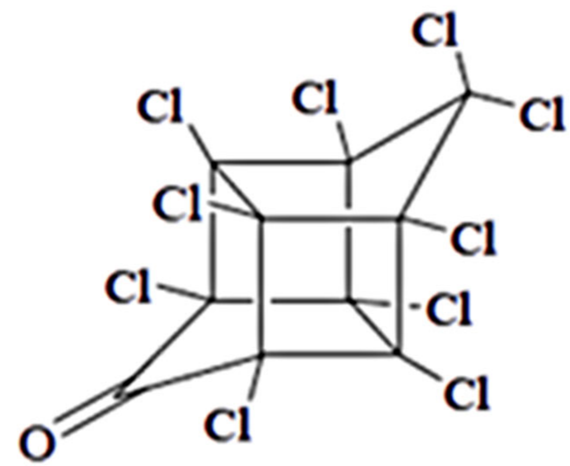
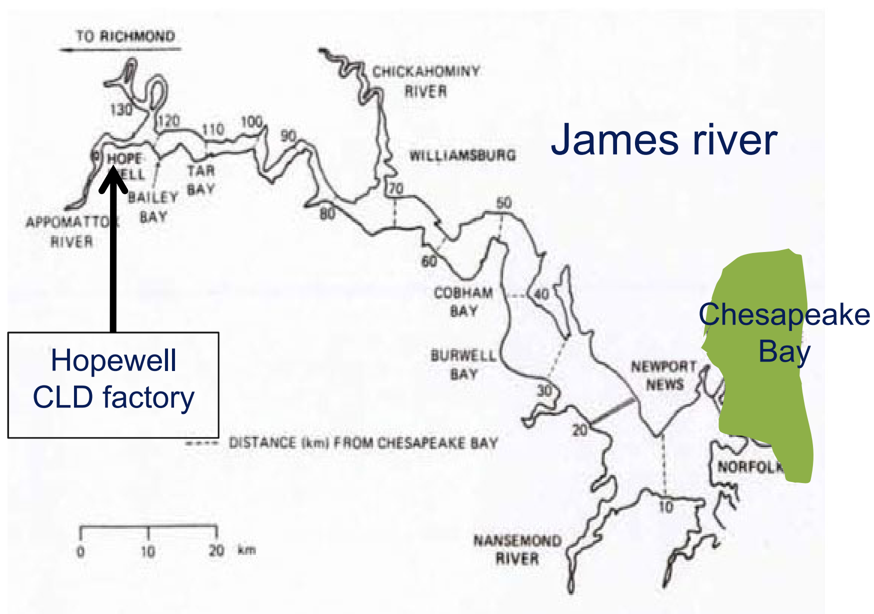
BioZone
Centre for Applied Bioscience and Bioengineering

History of Chlordecone



- 1951: First synthesis; 1952 US Patents
- 1958: First commercialized by Allied Chemical Company under the name Kepone® / produced in USA:

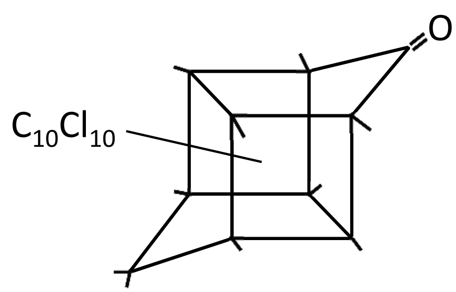
  Delaware, Pennsylvania, Virginia (Hopewell)



- **1966–1975** - The Allied Chemical Corporation dumps Kepone, a toxic, nonbiodegradable insecticide, into Virginia's James River. Its effect on the environment is eventually publicized, leading authorities to shut down the Allied Chemical Corporation plant that produced the chemical and to order fishing bans and advisories.

Chlordecone

- Pesticide that was extensively used in banana and sugar cane plantations in the Carribbean between 1972 and 1993
- Has led to the pollution of large agricultural areas
- Recalcitrant and adsorbs to soil
- Carcinogen



Chlordecone (kepone)
$C_{10}Cl_{10}O$

Chemistry suggests that anaerobic dechlorination is possible, but few studies have shown that biological dechlorination is happening in the environment


Jacksonville
New Orleans
Orlando
FLORIDA
Miami
Gulf of Mexico
The Bahamas
Havana
Turks and Caicos Islands
Cuba
Cancún
Cayman Islands
Haiti
Dominican Republic
British Virgin Islands
Jamaica
Port-au-Prince
Puerto Rico
Montserrat
Belize
Dominica
Honduras
St Lucia
Barbados
Salvador
Caribbean Sea
Nicaragua
Managua
Aruba
Curaçao
Grenada
Barranquilla
Maracaibo
Caracas
Trinidad and Tobago
Costa Rica
San José
Cartagena
Barquisimeto
Panama City
Panama
Bucaramanga
Venezuela
Georgetown
Medellín


Puerto Rico
Virgin Islands
Anguilla
Atlantic Ocean
St. Martin
St. Barts
Sint Maarten
Barbuda
Saba
St. Eustatius
Antigua
St. Kitts and Nevis
Montserrat
French West Indies
worldatlas.com
Guadeloupe
Dominica
Caribbean Sea
75 mi
75 km
Martinique
St. Lucia
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Objective: Investigate anaerobic biotransformation of chlordecone in microcosms

Université des Antilles
Pôle Guadeloupe
COVACHIM-M2E

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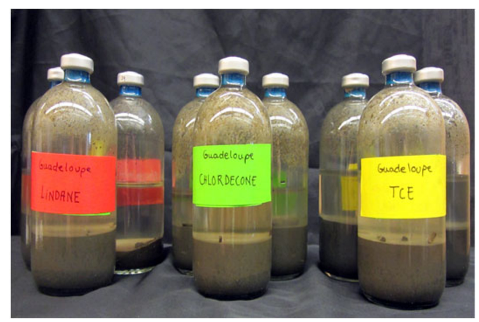
Microcosm setup December 2010

Development of analytical procedures

2018: Analysis of new field samples from Guadeloupe

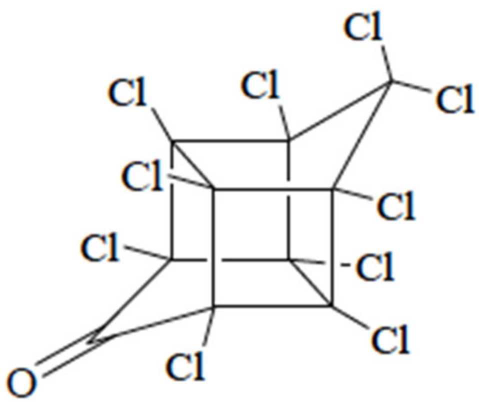
Field sampling

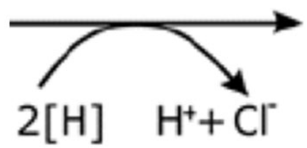
Microcosm setup
(Laurent Laquitaine)



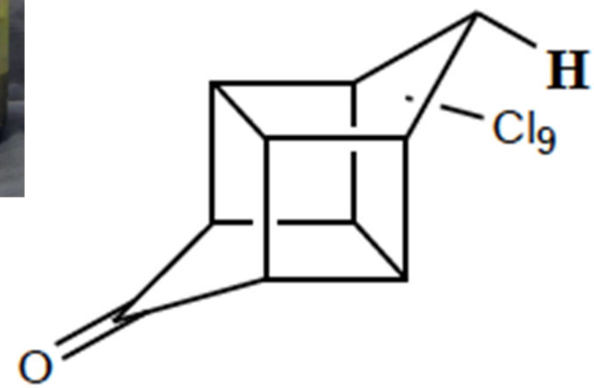
Chlordecone Microcosms

Chlordecone: $C_{10}Cl_{10}O$



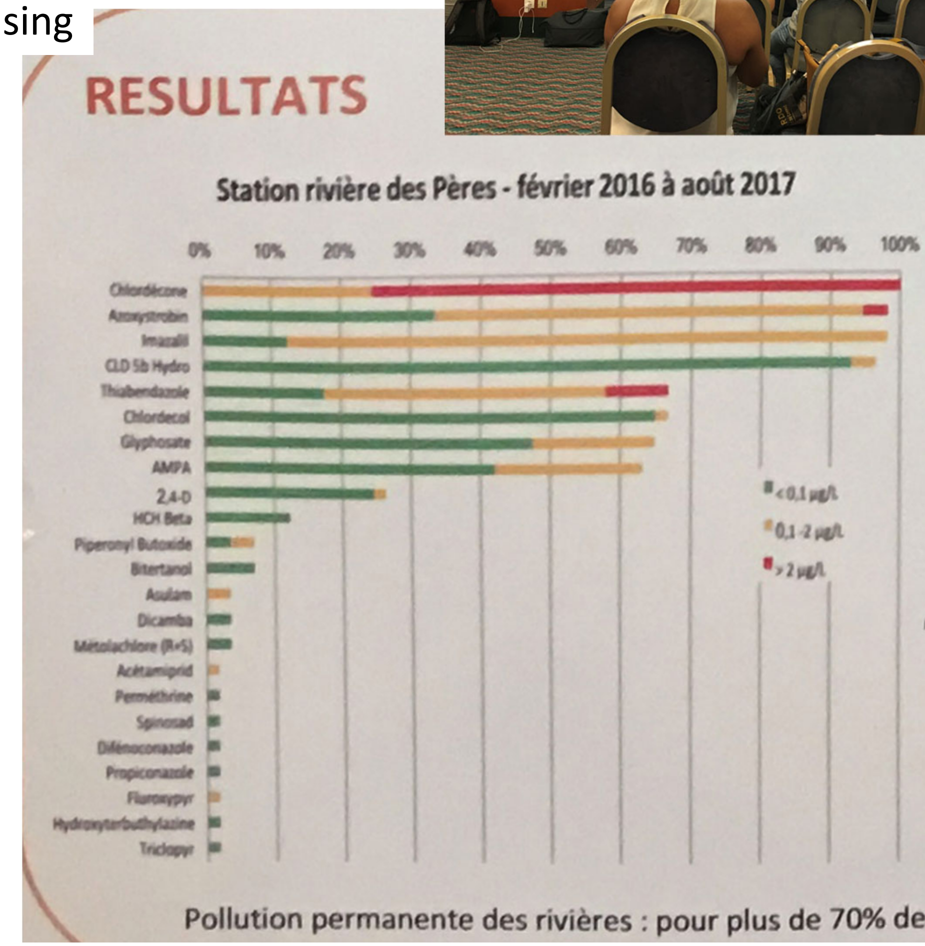


Hydrogenolysis



Monohydrochlordecone: $C_{10}HCl_9O$

October 2018; Guadeloupe/Martinique

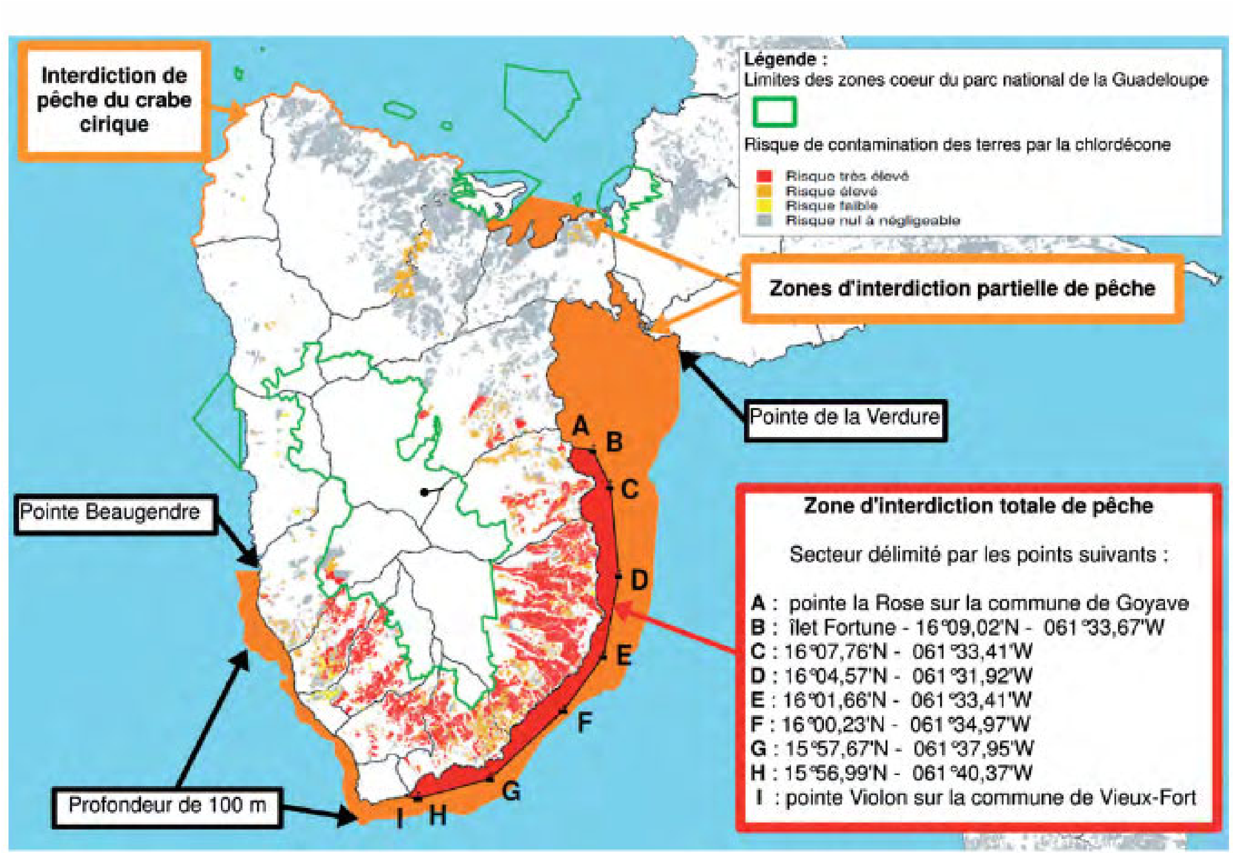


Impact on the Economy

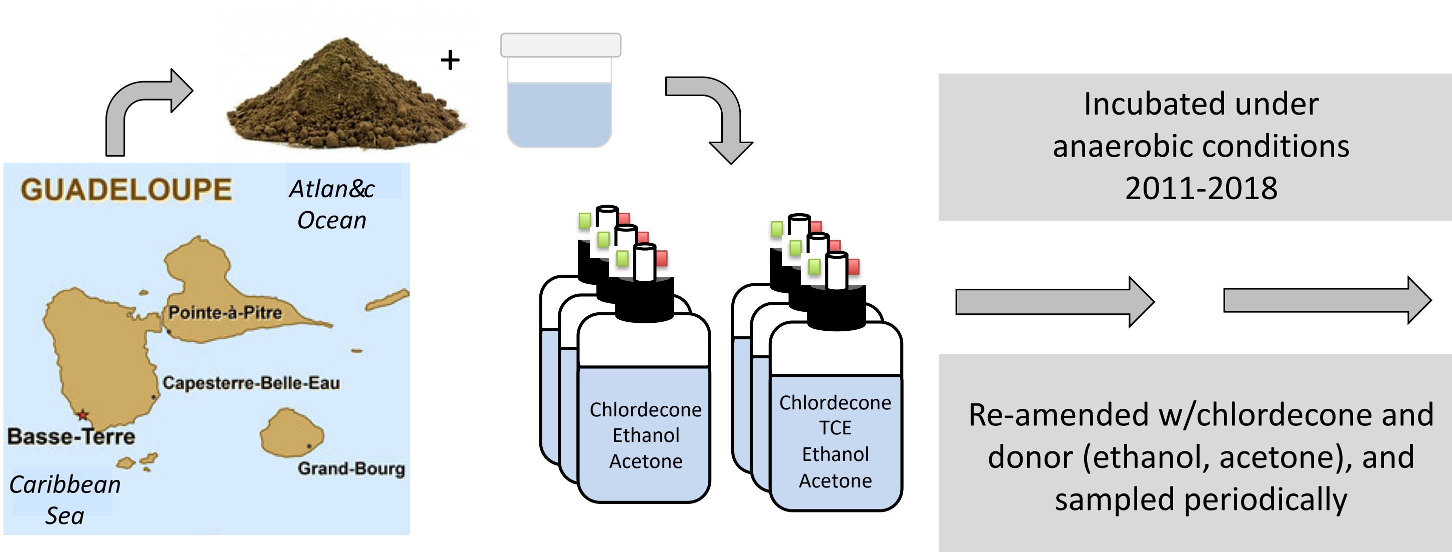
Restriction of use of contaminated soils

Fishing Restrictions

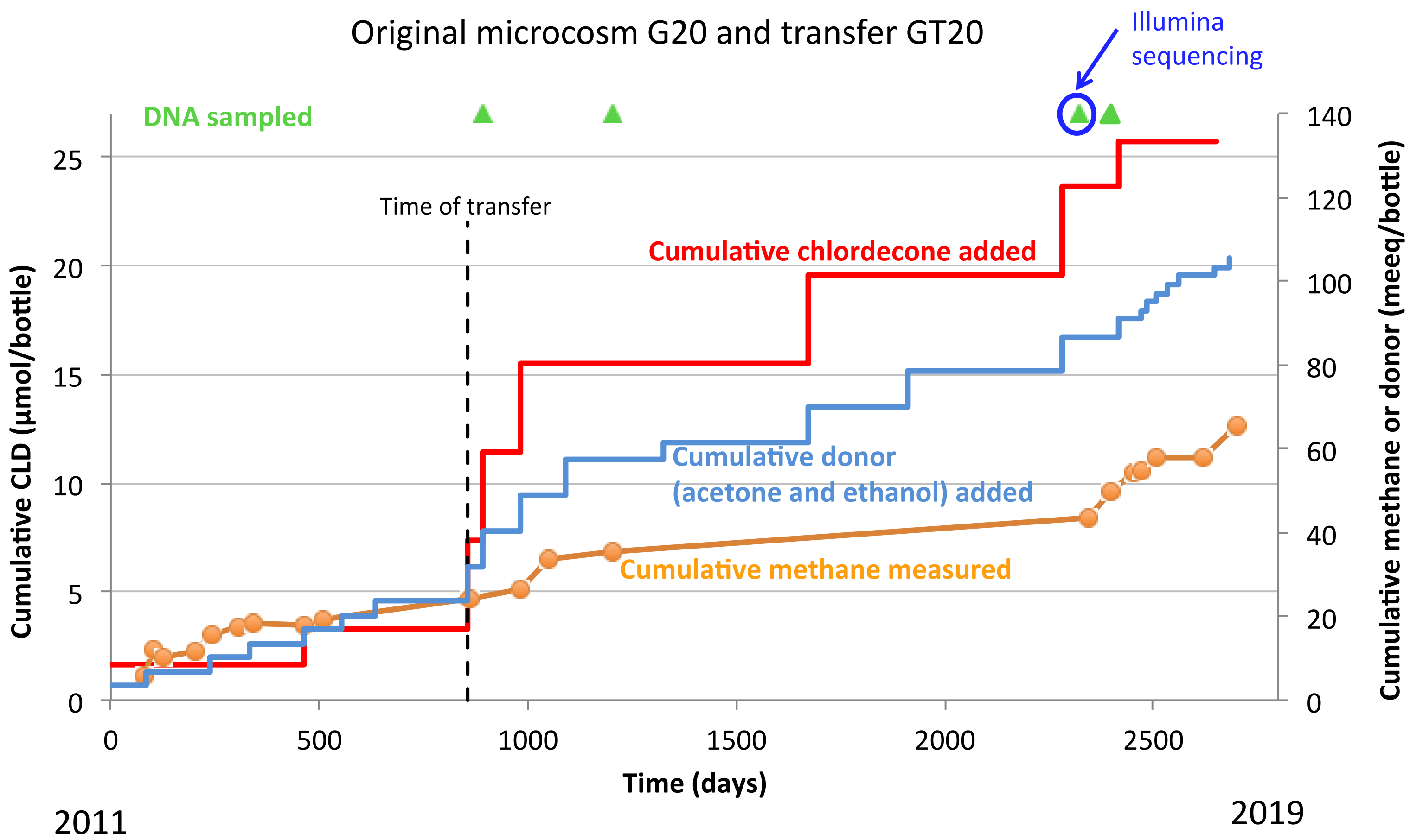
Restrictions on fish farming

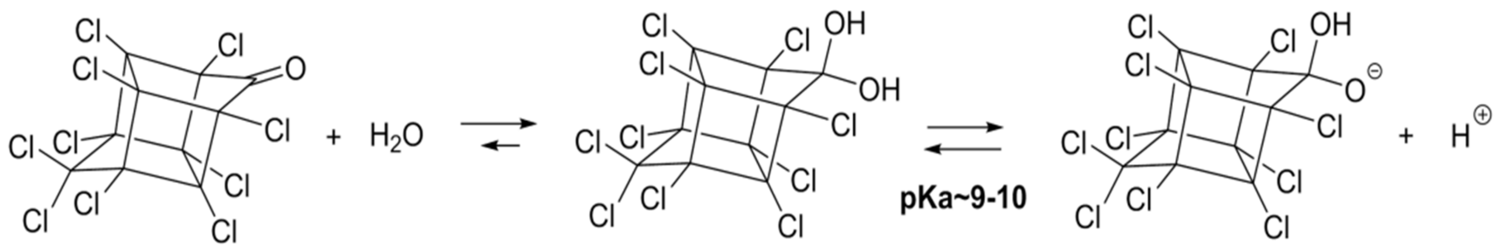


Construction of anaerobic microcosm from Guadeloupe soil



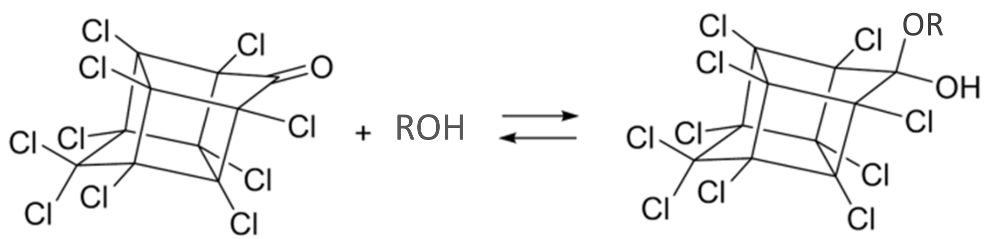
Overview of Microcosms





Chlordecone Chlordecone hydrate

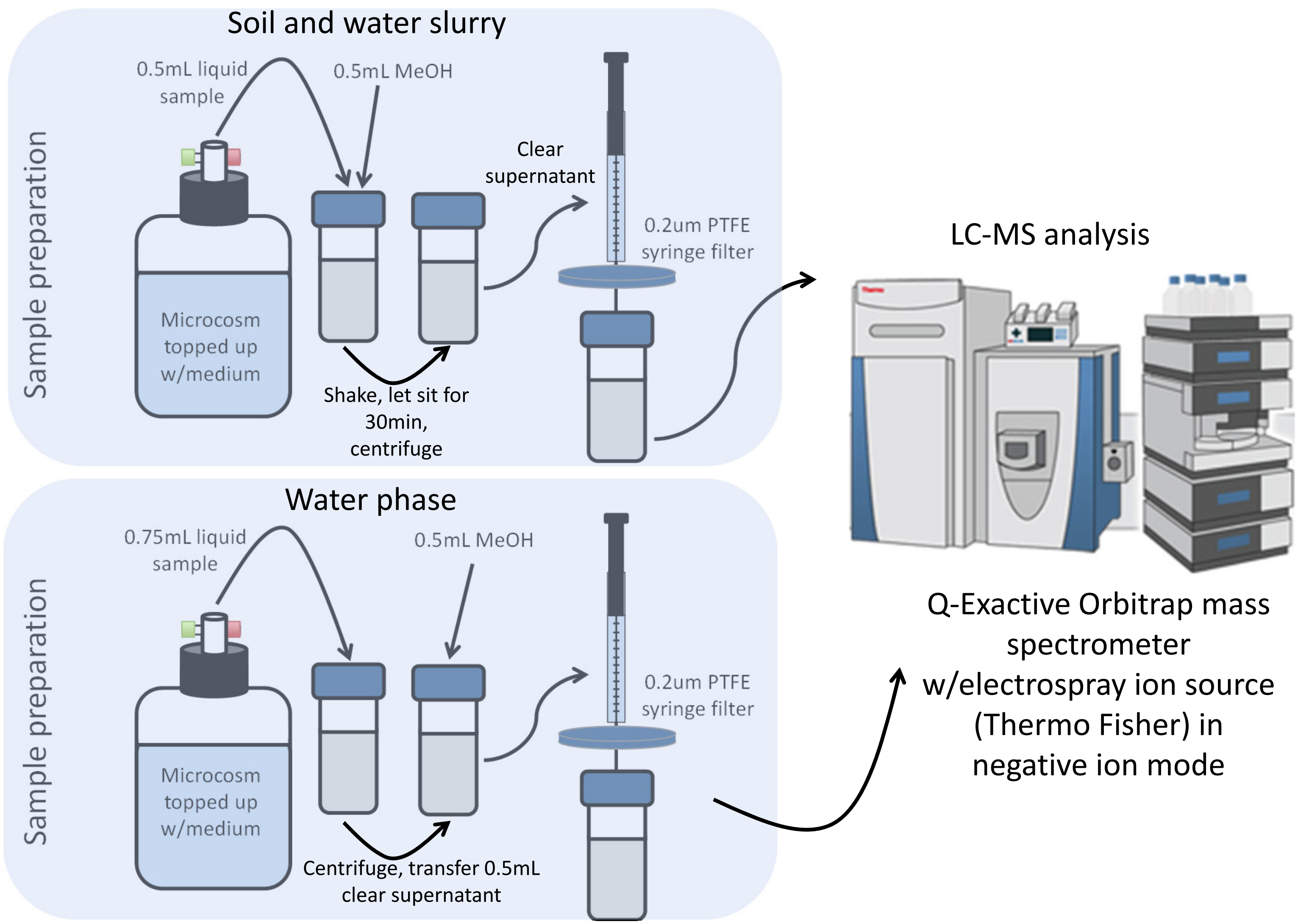
The carbonyl or keto group (C=O) can combine with water to form a geminal diol

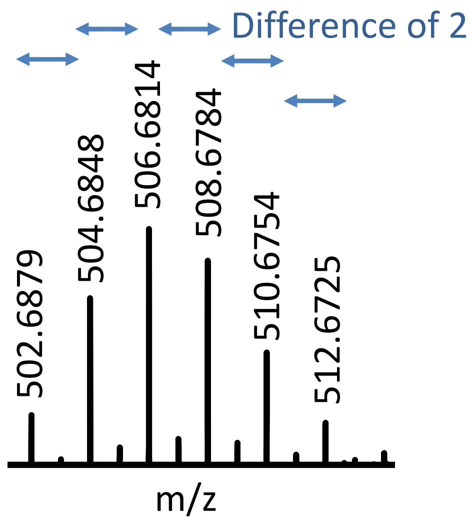


Chlordecone Chlordecone hemiacetal

Chlordecone in the presence of alcohol (R = methanol or ethanol)
The alcohol is added to the ketone to form the hemiacetal (or hemiketal)

Analysis of chlordecone and degradation products



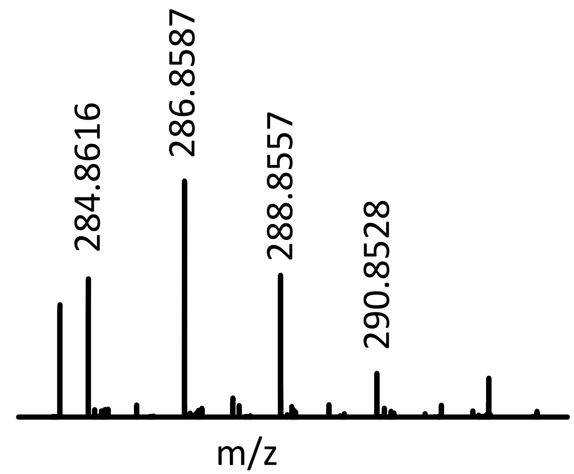


Chlordecone

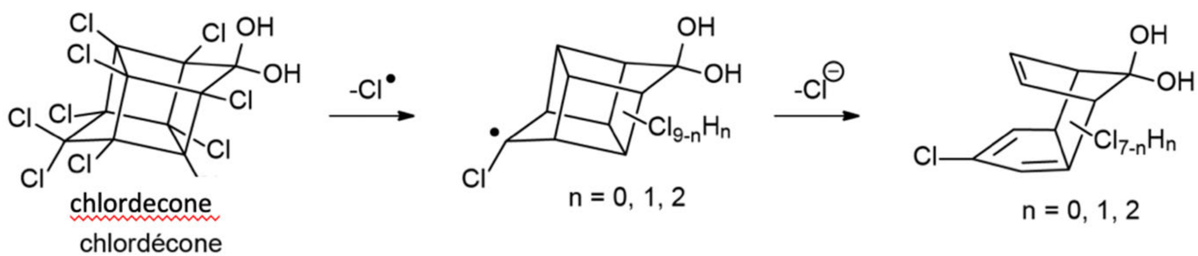
$C_{10}Cl_{10}O$

Cl-35 - 75.8%

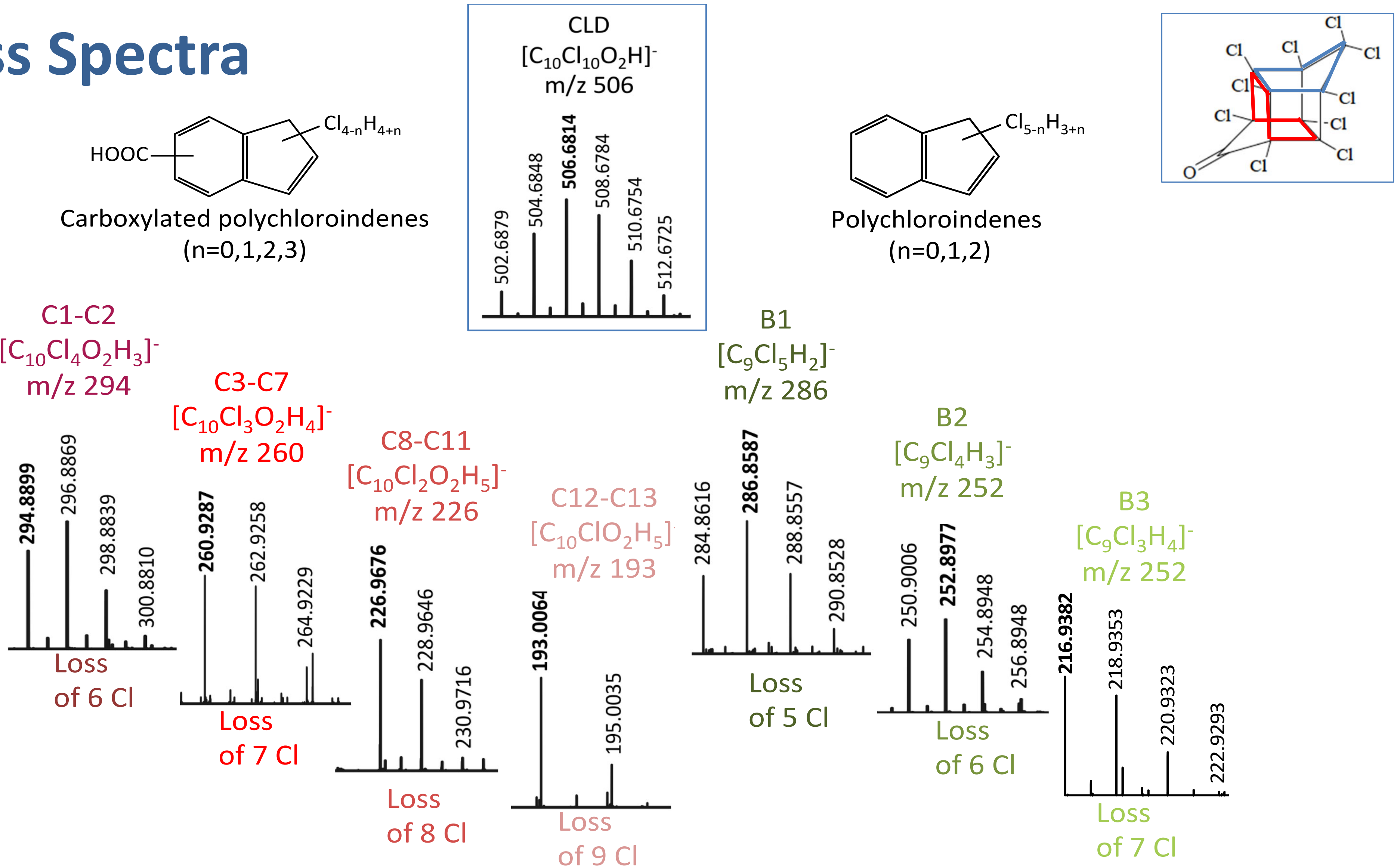
Cl-37 - 24.2%



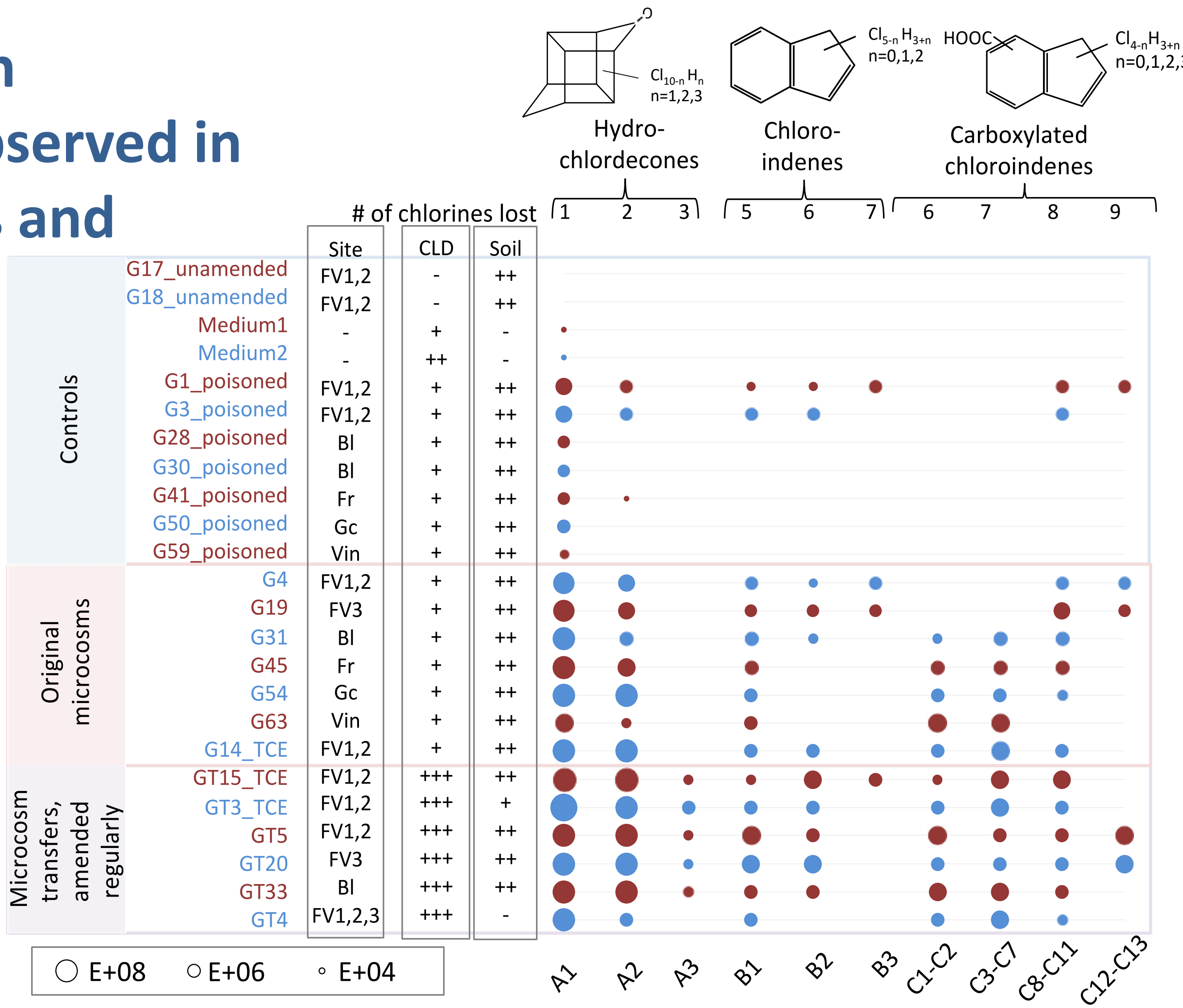
Must be a metabolite



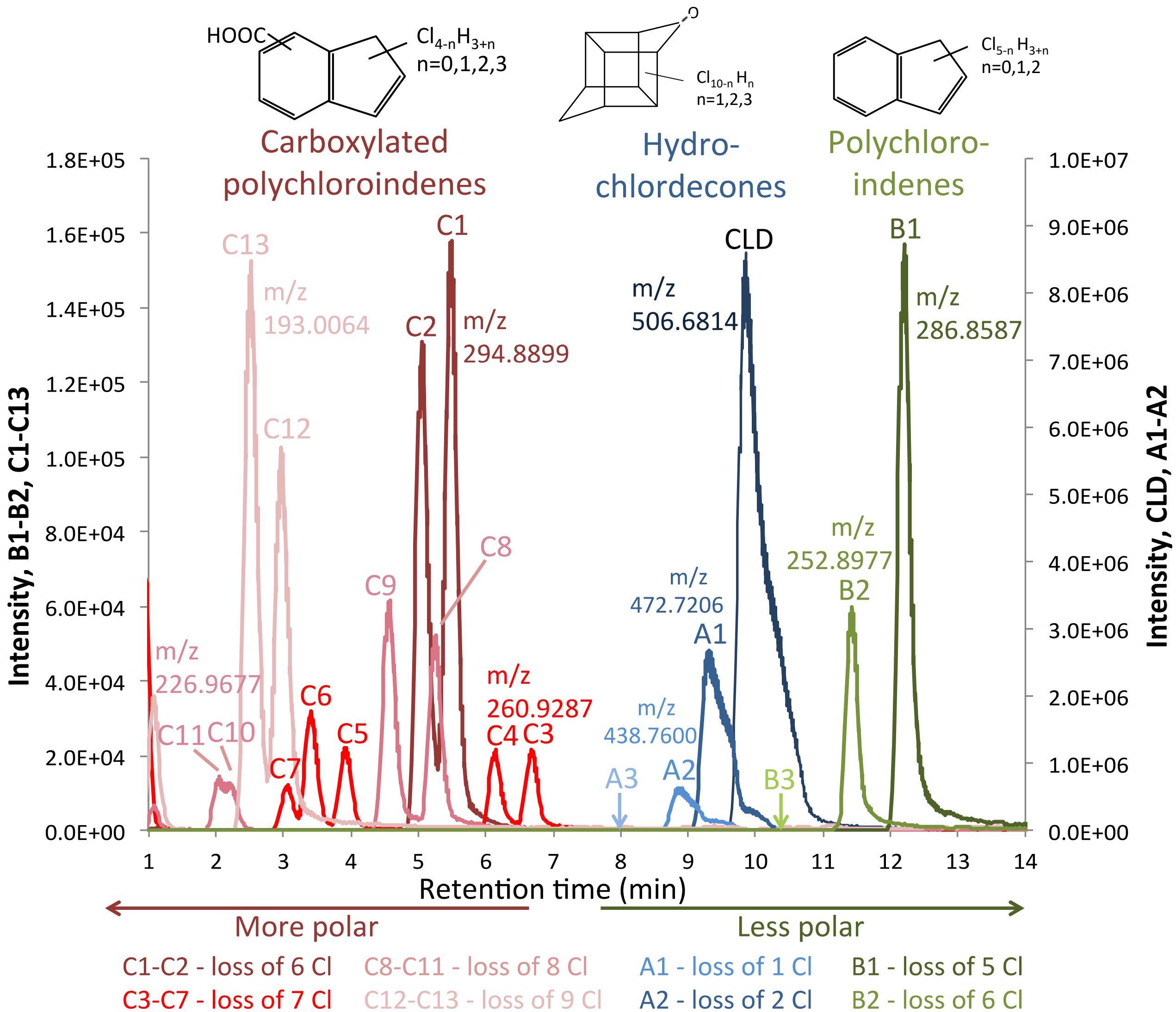
Mass Spectra



Degradation products observed in microcosms and controls



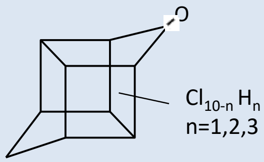
Chromatogram of chlordecone and its dechlorination products



Sample G20_soil from June 29th 2018

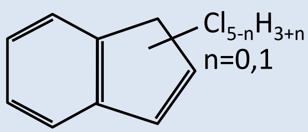
Structure and formula of dechlorination products observed in the anaerobic microcosms

Reductive dechlorination products (loss of 1-3 chlorines)



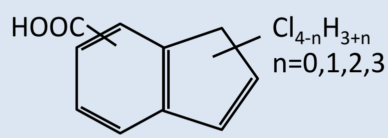
$C_{10}Cl_9OH$ Monohydrochlordecone (**A1**)
$C_{10}Cl_8OH_2$ Dihydrochlordecone (**A2**)
$C_{10}Cl_7OH_3$ Trihydrochlordecone (**A3**)

"Open Cage" structures (loss of 5-9 chlorines)



$C_9Cl_5H_3$ (**B1**)
$C_9Cl_4H_4$ (**B2**)
$C_9Cl_3H_5$ (**B3**)

Chloroindenes

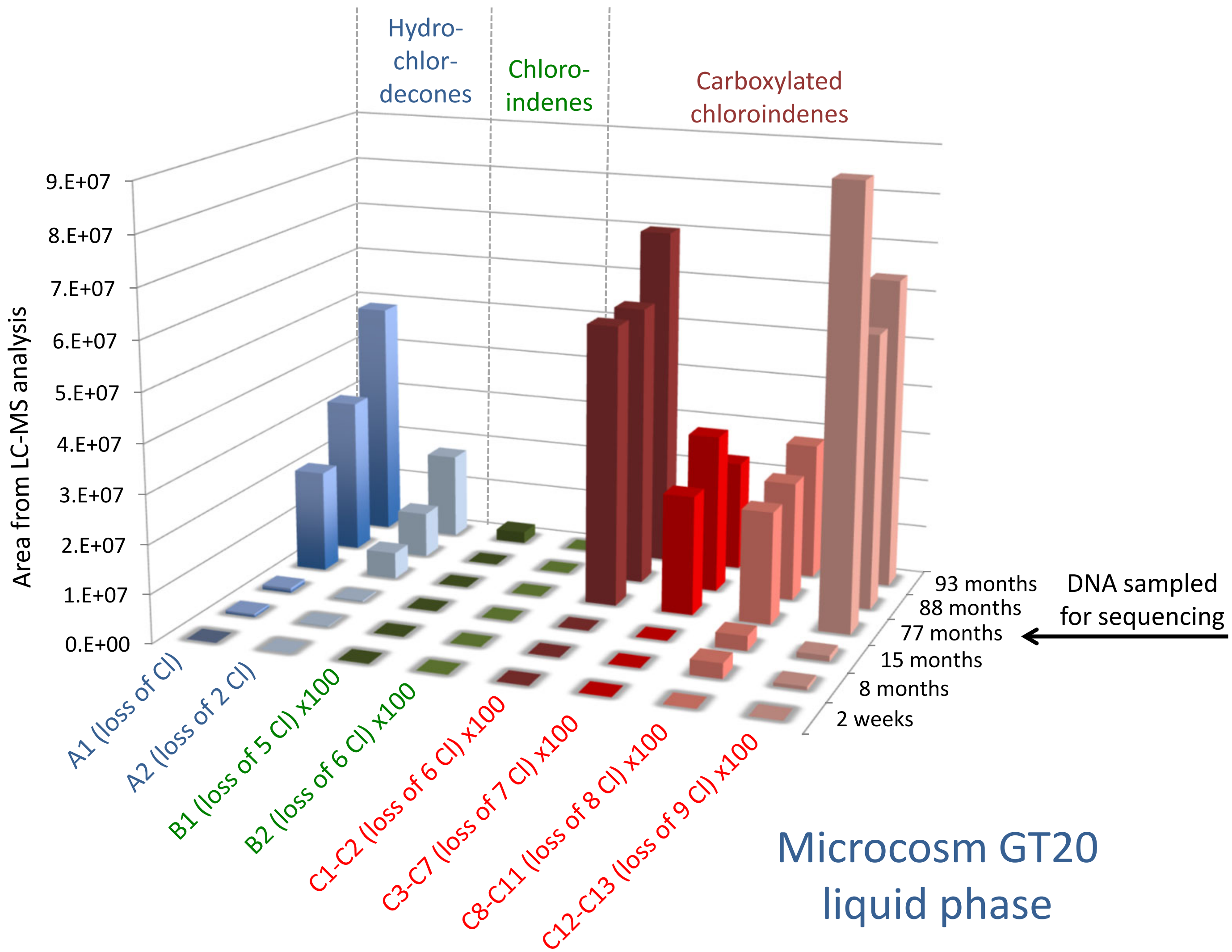


$C_{10}Cl_4O_2H_4$ (**C1-C2**)
$C_{10}Cl_3O_2H_5$ (**C3-C7**)
$C_{10}Cl_2O_2H_6$ (**C8-C11**)
$C_{10}ClO_2H_7$ (**C12-C13**)

Carboxylated chloroindenes

1. Schrauzer, G. N., & Katz, R. N. (1978). *Bioinorg Chem, 9*(2), 123-143.
2. Ranguin, R., et al. (2017). *Environ Sci Pollut Res Int*. doi: 10.1007/s11356-017-9542-z.
3. Chaussonnerie, S., et al. (2016). *Front Microbiol, 7*(2025), 2025.

Development of dechlorination products over time



Microcosm GT20
liquid phase

Proposed degradation pathways for CLD

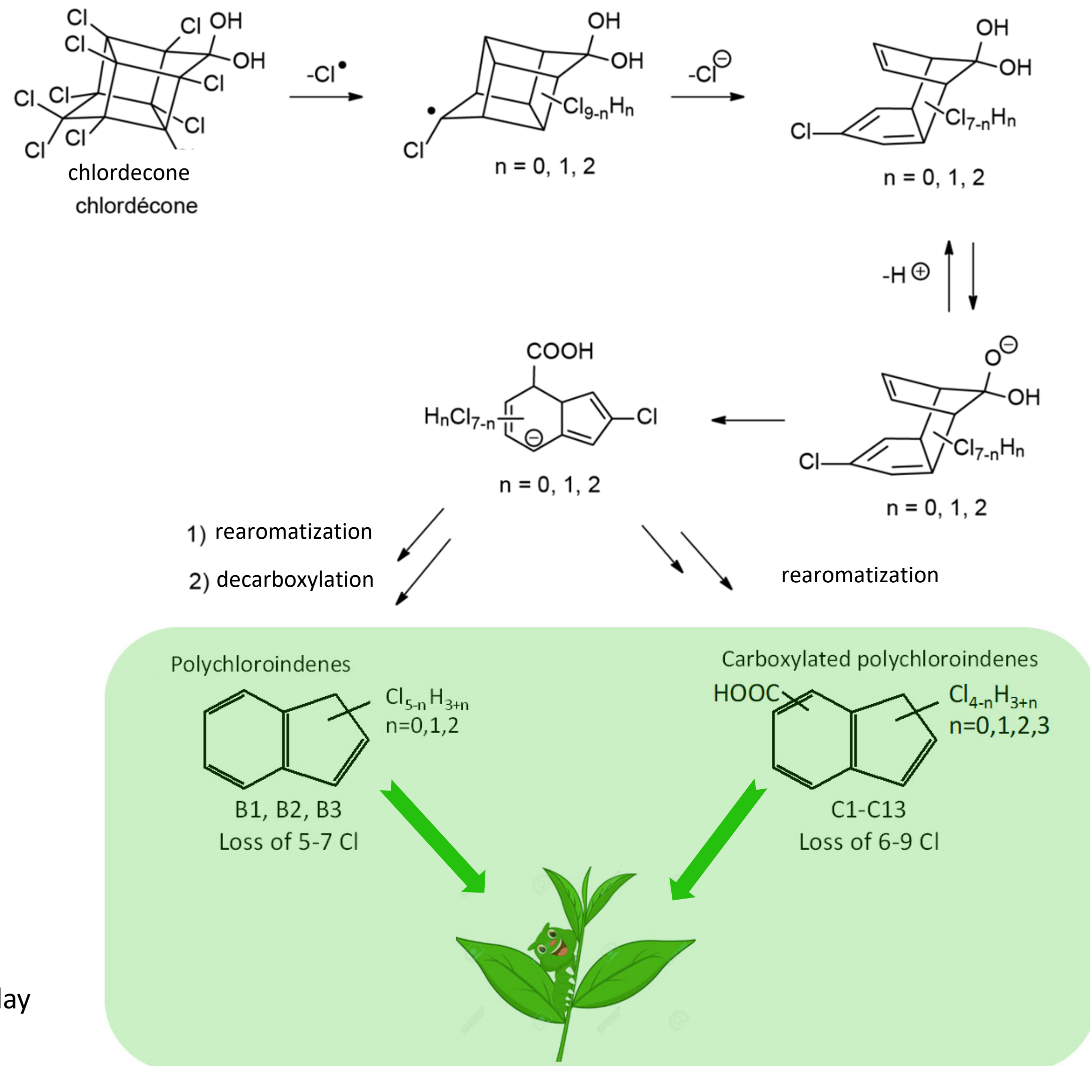


Figure from PhD thsis of Marion Chevallier: 2018

Etude de la dégradation biologique et chimique d'un pesticide persistant : la chlordécone

Thèse de doctorat de l'Université Paris-Saclay

Analysis of CLD and dechlorination products in microcosms

	Microcosm ID	CLD aded to date	CLD remaining after 8 years	CLD Recovered	Sum MHCLD, DHCLD and THCLD*	Sum CINs (B1 and B2)**	Sum CCINs (C1-C13)**	Sum products (HCLDs, CINs and CCINs)	Products/ $CLD_{remaining}$	Total Mass Recovered
		(µmol)	(µmol)	%	(µmol)	(µmol)	(µmol)	(µmol)	%	%
CONTROLS	G28_poisoned	1.63	1.13	69%	0.002	ND	ND	0.002	0.0%	70%
	G30_poisoned	1.63	0.97	59%	0.001	ND	ND	0.001	0.0%	59%
	G41_poisoned	1.63	1.06	65%	0.004	ND	ND	0.004	0.0%	65%
	G50_poisoned	1.63	0.90	55%	0.002	ND	ND	0.002	0.0%	55%
	G59_poisoned	1.63	1.07	66%	0.001	ND	ND	0.001	0.0%	66%
	AVERAGE	1.63	1.03	**63%**	0.00	ND	ND	0.002	0%	**63%**
ORIGINAL MICROCOSMS	G4	3.26	1.36	42%	0.14	0.01	0.11	0.26	19%	50%
	G19	3.26	1.75	54%	0.45	0.04	0.24	0.73	42%	76%
	G31	3.26	1.73	53%	0.13	0.05	0.05	0.22	13%	60%
	G45	3.26	0.83	25%	0.24	0.03	0.05	0.32	39%	35%
	G54	3.26	1.18	36%	0.51	0.04	0.10	0.65	55%	56%
	G63	3.26	1.81	56%	0.03	0.01	0.78	0.82	45%	81%
	G14_TCE	1.62	1.05	65%	0.62	0.09	0.20	0.91	87%	121%
	AVERAGE	3.03	1.39	**47%**	0.30	0.04	0.22	0.56	43%	**68%**
MICROCOSM TRANSFERS AMENDED REGULARLY	GT15_TCE	17.9	5.60	31%	2.43	0.65	1.08	4.2	74%	54%
	GT3_TCE	15.8	5.70	36%	4.13	0.12	1.37	5.6	98%	72%
	GT5	23.6	7.37	31%	1.29	0.51	1.12	2.9	40%	44%
	GT20	25.7	8.42	33%	2.71	1.02	1.13	4.9	58%	52%
	GT33	19.6	6.11	31%	1.54	0.23	1.14	2.9	48%	46%
	GT4	22.4	5.99	27%	0.48	0.16	0.63	1.3	21%	32%
	AVERAGE	20.8	6.53	**32%**	2.10	0.45	1.08	3.6	56%	**49%**

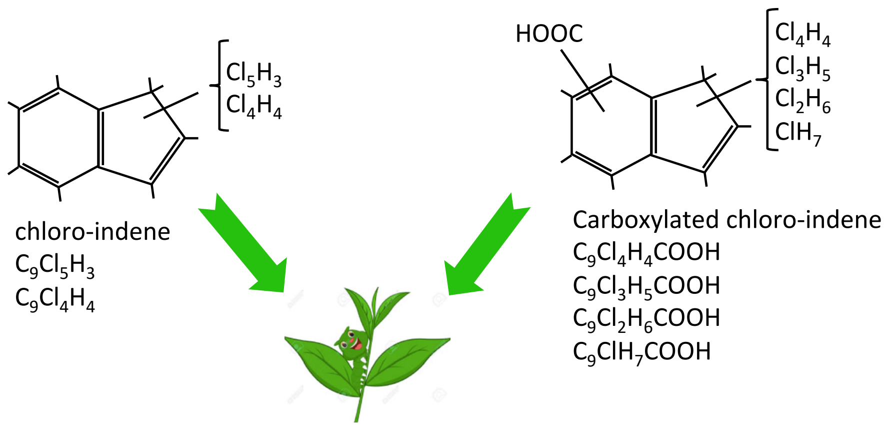
Analysis of field samples

Sample	Chlordecone		Hydrochlordecones	Chloroindenes	
	CLD		MHCLD (A1) & DHCLD (A2)	$C_9Cl_5H_3$ (B1)	$C_9Cl_4H_4$ (B2)
	ng/g solids	area/g solids	%CLD area/g solids	ng/g solids	%B1 area/g solids
Soils:					
River	122	7.2E+06	6%	0.45	ND
Banana	133	1.3E+07	7%	2.1	20%
Stream	1020	9.3E+07	3%	2.1	3.2%
Coco	267	3.1E+07	8%	22	14%
Sea	191	2.9E+07	7%	8.1	23%
Bridge	435	1.8E+07	1%	1.0	ND
Activated Carbon Samples:					
AC-1	24	7.3E+06	10%	ND	ND
AC-2	6032	1.8E+09	8%	ND	ND
AC-3	8416	2.5E+09	4%	ND	ND

Conclusions and Future Work

- Observation of open cage structures in soil samples from Guadeloupe
- Demonstration of almost complete dechlorination in microcosms (up to 9 Chlorine atoms lost)
- Possibility of complete degradation of chlordecone and bioremediation by addition of electron donor substrates – But rates are slow

Need for a better understanding of the mechanism of formation of the indenes to accelerate the dechlorination process



Acknowledgements

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University des Antilles

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- Region Guadeloupe
- SIAEAG Guadeloupe
- AIP DEMICHLORD