Deciphering the chemical and microbiological degradation pathways of a recalcitrant molecule: the case of chlordecone

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EUGLOH Annual Student Research Conference

Global Health Challenges: Diseases of Modern Life

September 28th – 30th 2020

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Chlordecone is an organochlorine insecticide, classified as a Persistent Organic Pollutant (POP) in 2009 by the Stockholm convention. It was massively used in the French West Indies (FWI) from 1972 to 1993[1]. Its application on banana plantations is responsible for long-term pollution of environmental compartments (soils, sediments and water ressources), contaminating the whole food chain[1-3]. The high population impregnation associated with the chronic toxicity of chlordecone causes serious public health, socio and economic problems[4-7].

Because of its hydrophobic properties and low chemical reactivity, chlordecone readily binds in soils and sediments rich in organic matter and persists in the environment. Its specific structure, made of a bis-homocuban cage, makes it very stable and highly difficult to degrade. Chlordecone persistence predictions, taking into account leaching and infiltration phenomenon, estimated its presence in the FWI environment for several decades to hundreds of years[8]. Until recently, only two studies mentioned a marginal chlordecone transformation in FWI soils, thus confirming the previous predictive models[9-10].

Several laboratory studies have demonstrated a possible microbial degradation of chlordecone in liquid media[11-13]. In the recent years, we succeeded to completely transform chlordecone into several transformation products (TPs) in anaerobiosis, using bacterial consortia or isolated bacteria (*Citrobacter* sp.86 and *Desulfovibrio* sp.86)[14-17]. The present work aims at elucidating every TP formed within microbial chlordecone transformation and deciphering the mechanisms involved.

The use of several analytical tools (gas or liquid chromatography coupled with a mass spectrometer) enabled to detect several chlorinated TPs generated during chlordecone bacterial transformations. Interestingly, in specific incubation conditions, *Citrobacter* sp.86 and *Desulfovibrio* sp.86 completely degraded chlordecone into three families of TPs that corresponded to hydrochlordecones (A), polychloroindenes (B) and polychloroindenecarboxylic acids (C). Structural elucidation of these TPs was done through chemical biomimetic reactions enabling to produce enough quantity of each of them to perform nuclear magnetic resonance experiments.

In microbial conditions, the hypothesis of the involvement of corrinoids was put forward, and mutants of *Citrobacter* sp.86 containing deleted genes involved in anaerobic corrinoid biosynthesis pathway were done. *Via* this technic, we successfully managed to show that these cofactors contributed to chlordecone ring-opening dechlorination[18].

In a second time, it was also noticed that *Desulfovibrio* sp.86 placed in different incubation conditions did not generate A, B and C families, but an extra family named F. Instead of opening and dechlorinating chlordecone, the gem-diol function was transformed into a thiol function[17]. It was the first time that such an activity was observed and is under investigation to understand the underlying mechanism.

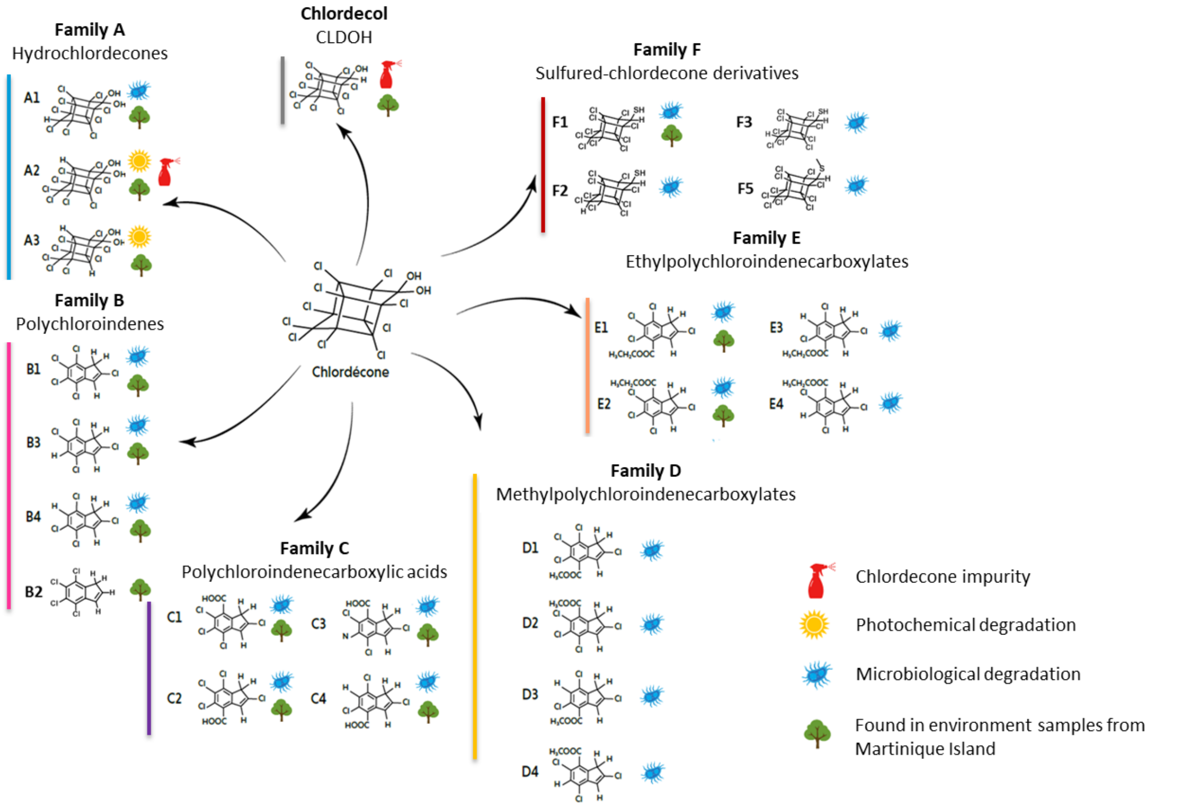

Figure 1: Chlordecone transformation product structures

After all these results, it was wondered whether such microbiological transformation could take place directly in FWI environment. We benefit from the home-made library of chlordecone TPs to search for them in environmental samples from Martinique Island. The dual GC-MS and LC-MS analysis revealed the systematic presence of one or more TPs in all the samples originally contaminated by chlordecone[16-17]. This prospective study shows that the paradigm of absolute persistence of chlordecone, taken for granted for decades, now seems obsolete. From now on, new monitoring and risk priorities need to be set up and a more in-depth field study should be conducted. It also questions the extent of the microbial ring-opening dechlorination and the reductive sulfidation processes that were discovered. Indeed, both microbiological activities have proven effective on other substrates such as mirex, another chlorinated POP that shares the same bishomocuban structure as chlordecone, and a number of carbonyl compounds, respectively.

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