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Categorizing chlordecone potential degradation products to explore their environmental fate

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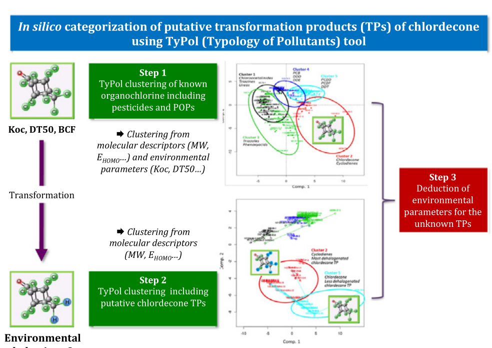
HIGHLIGHTS

- TyPol, an *in silico* typology, was used to categorize 170 organochlorine molecules.
- Clustering used both molecular descriptors and environmental behaviour.
- Parent and transformation products represented various chemical families.
- 20 chlordecone putative transformation products (TPs) were categorized.
- Combining two clustering allowed assessing the potential fate of chlordecone TPs.

GRAPHICAL ABSTRACT



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ABSTRACT

Chlordecone ($C_{10}Cl_{10}O$; CAS number 143–50-0) has been used extensively as an organochlorine insecticide but is nowadays banned and listed on annex A in The Stockholm Convention on Persistent Organic Pollutants (POPs). Although experimental evidences of biodegradation of this compound are scarce, several dechlorination products have been proposed by Dolfing et al. (2012) using Gibbs free energy calculations to explore different potential transformation routes. We here present the results of an *in silico* classification (TyPol - Typology of Pollutants) of chlordecone transformation products (TPs) based on statistical analyses combining several environmental endpoints and structural molecular descriptors. Starting from the list of putative chlordecone TPs and considering available data on degradation routes of other organochlorine compounds, we used different clustering strategies to explore the potential environmental behaviour of putative chlordecone TPs from the knowledge on their molecular descriptors. The method offers the possibility to focus on TPs present in different classes and to infer their environmental fate. Thus, we have deduced some hypothetical trends for the environmental behaviour of TPs of chlordecone assuming that TPs, which were clustered away from chlordecone, would have different environmental fate and ecotoxicological impact compared to chlordecone. Our findings suggest that mono- and di-

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hydrochlordecone, which are TPs of chlordecone often found in contaminated soils, may have similar environmental behaviour in terms of persistence.

1. Introduction

In the French West Indies (FWI), chlordecone ($C_{10}Cl_{10}O$; CAS number 143–50-0 - decachlorooctahydro-1,3,2-metheno-2Hcyclobuta[c,d]pentalen-2-one) has been largely used on banana plantations over the 1978–1993 period to control banana weewil. Its persistence in the agricultural soils of the FWI (i.e., 20,000 ha that represent up to 25% of the agricultural surface of the FWI) was estimated to last for several decades in Nitisol, centuries in Ferralsol, and half a millennium in Andosol soils (Cabidoche et al., 2009).

This organochlorine insecticide is now banned and listed on annex A of the Stockholm Convention on Persistent Organic Pollutants (POPs) but its former use has induced a general and important contamination of rivers, springs, and drinking water as well as coastal ecosystems of the FWI (Coat et al., 2011) as revealed by investigation of the French National Action Plan for chlordecone (PNAC 2008–2010). In such context, finding strategies to remediate and/or mitigate this contamination on the very long-term is a great challenge and, from this point of view, the FWI represent an open field for remediation (Cabidoche and Lesueur-Jannoyer, 2011; Levillain et al., 2012).

There is no clear cut evidence of microbial chlordecone degradation under aerobic conditions. Indeed Orndorff and Colwell (1980) proposed that *Pseudomonas aeruginosa strain KO3* and a bacterial consortium isolated from Hopewell plant sewage sludge under aerobic conditions transform chlordecone into mono-hydro-chlordecone and di-hydro-chlordecone. However, these results have been criticized by Cabidoche et al. (2009) because the initial contents in mono-hydro- and di-hydro-chlordecone, known to be by-products of the synthesis contaminating the chlordecone, have not been measured. This lack is compromising the proposed results because detection of chlordecone TPs can be the result of incomplete chlorination of chlordecone during synthesis and not to microbial biodegradation. Later on, George and Claxton (1988) studied chlordecone degradation catalyzed by three *Pseudomonas* spp. showing that after two weeks of incubation chlordecone reached only 15–25% of initial concentration with a relatively high uncertainty of 10% on chlordecone HPLC concentration measurements. In addition, in non-inoculated control, mono- and di-hydro-chlordecone were detected as well. A poor bacterial growth was recorded and, consequently, the authors concluded that due to its important chlorination, chlordecone was a poor carbon source for bacterial growth. However, a recent study based on a large data set of 881 field soils of the FWI showed a significant increase of the 5b-hydrochlordecone/chlordecone ratio in the soils 25 times greater than in commercial formulations which suggested that natural transformation into 5b-hydrochlordecone over the long term occurred in these soils (Devault et al., 2016).

Under anaerobic conditions, a pure culture of *Methanosarcina thermophila* grown on acetate was shown to convert chlordecone to polar and non-polar products (Jablonski et al., 1996). Interestingly, similar pattern of soluble chlordecone decomposition products were obtained with reduced vitamin B12 and reduced coenzyme F430 isolated from *M. thermophila*. More recently, *Pseudonocardia* sp. KSF27 isolated from a soil repeatedly treated with endosulfan was shown to also degrade dieldrin and other organochlorine insecticides such as chlordecone but without providing information on the degradation pathway (Sakakibara et al., 2011).

In France, giving the environmental and health problems caused by chlordecone contamination in the West Indies, several research programs have recently been carried out on soil bioremediation. Search for chlordecone-degrading microorganisms under anaerobic and aerobic conditions remains a big challenge due to the lack of experimental evidences of degradation products in soil environment. Indeed, only few measured data on the identification of chlordecone TPs are available showing traces of the TP 5b-hydrochlordecone in some Andosol, Nitisol, and Ferralsol soil samples (Devault et al., 2016; Martin-Laurent et al., 2014). Recently, Fernández-Bayo et al. (2013) gave evidence for a weak but measurable mineralization of ^{14}C-chlordecone in an Andosol from Guadeloupe in aerobic conditions reaching 4.9% of the ^{14}C-chlordecone initially added in the topsoil (0–20 cm) and 3.2% in the below horizon (30–60 cm) over a 230d period of incubation. The absence of $^{14}CO_2$ evolution in sterile soil microcosms led the authors to conclude that chlordecone mineralization was biotic being most likely catalyzed by microorganisms (Fernández-Bayo et al., 2013).

Dolfing et al. (2012) conducted a theoretical study using Gibbs free energy calculations to explore the thermodynamic feasibility of different chlordecone potential degradation routes. By performing ab initio quantum chemical calculations to estimate molar values of $\Delta fHm°$ and $\Delta fGm°$ for chlordecone and selected dechlorination products, they have estimated the energetics of the degradation and dechlorination of chlordecone under a variety of redox conditions. They ended up with the proposal of a list of 20 potential TPs and concluded that there were no thermodynamic reasons why chlordecone-respiring or -fermenting organisms should not exist.

Complementary information could be brought by clustering approaches based on the relationships between molecular properties and environmental fate of organic compounds. With this aim, we recently developed ‘TyPol’ (Typology of Pollutants), a classification method based on statistical analyses combining several environmental endpoints (i.e. environmental parameters such as sorption coefficient, degradation half-life or bioconcentration factor), and structural molecular descriptors (number of atoms in the molecule, molecular surface, dipole moment, energy of orbitals…). This approach also allows to focus on TPs present in different classes and to infer possible changes in environmental fate consecutively to different degradation processes (Servien et al., 2014). Starting from the list of chlordecone TPs proposed by Dolfing et al. (2012) and considering available literature data on degradation routes of other organochlorine compounds, we conducted a study using TyPol to explore the potential environmental behaviour of chlordecone TPs based on their molecular properties.

2. Materials and methods

2.1. Clustering methodology

The TyPol tool permits to classify organic compounds, and their transformation products, according to both their behaviour in the environment and their molecular properties. The calculation of molecular descriptors is performed using an *in silico* approach, while the environmental endpoints (i.e. environmental parameters) are extracted from several available databases and literature. The strategy relies on partial least squares analysis and hierarchical clustering (see below 2.5. Statistical treatments). The robustness of the TyPol method was assessed on a list of 215 organic compounds using a cross-validation algorithm. The information system is based on a management system for relational database MySQL DBMS-R (version 5.1), an Apache web server (version 2.2), and the statistical R software (also used for graphs). More details concerning TyPol can be found in Servien et al. (2014).