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Chlordecone fate and mineralisation in a tropical soil (andosol) microcosm under aerobic conditions

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HIGHLIGHTS

- More than 80% of chlordecone remained in soil in an extractable form.
- Aerobic mineralisation of chlordecone in soil microcosms was quantified.
- Degradation rate of chlordecone significantly decreased with time.

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ABSTRACT

Chlordecone is a persistent organochlorine insecticide that, even decades after its ban, poses a threat to the environment and human health. Nevertheless, its environmental fate in soils has scarcely been investigated, and elementary data on its degradation and behaviour in soil are lacking. The mineralisation and sorption of chlordecone and the formation of possible metabolites were evaluated in a tropical agricultural andosol. Soil microcosms with two different soil horizons (S-A and S-B) were incubated for 215 days with ^{14}C-chlordecone. At five different times (1, 33, 88, 150 and 215 days) the extractability of ^{14}C-chlordecone was analysed. Mineralisation was monitored using $^{14}CO_2$ traps of NaOH. The appearance of metabolites was studied using thin layer and gas chromatography techniques. At the end of the experiment, the water soluble ^{14}C-activity was 2% of the remaining ^{14}C-chlordecone for S-A and 8% for S-B. Only 12% of the remaining activity was non extractable and more than 80% remained extractable with organic solvents. For the first time to our knowledge, a significant mineralisation of chlordecone was measured in a microcosm under aerobic conditions (4.9% for S-A and 3.2% for S-B of the initial ^{14}C-activity). The drastically lower emission of $^{14}CO_2$ in sterilised microcosms indicated the biological origin of chlordecone mineralisation in the non-sterilised microcosms. No metabolites could be detected in the soil extracts. The mineralisation rate of chlordecone decreased by one order of magnitude throughout the incubation period. Thus, the chlordecone content in the soil remained large. This study confirms the existence of chlordecone degrading organisms in a tropical andosol. The reasons why their activity is restricted should be elucidated to allow the development of bioremediation approaches. Possible reasons are a heterogeneous distribution a chlordecone between sub-compartments with different microbial activities or a degradation of chlordecone by co-metabolic processes controlled by a limited supply of nutrients.

1. Introduction

The long-term environmental problems raised by the application of highly chlorinated pesticides have been of great concern since the 1960s (Arias-Estevez et al., 2008; Harrison, 1966; Miglioranza et al., 2002). However, some chlorinated compounds, whose pollution potential has long been underestimated, are now known to pose serious human health and environmental problems. Such is the case for chlordecone ($C_{10}Cl_{10}O$, Fig. 1a), who was extensively used to control a wide range of pests, mainly in banana plantations in tropical regions (UNEP, 2006). In May 2009, chlordecone was included in Annex A of the Stockholm Convention on Persistent Organic Pollutants.

Abbreviations: ASE, Accelerated Solvent Extraction; ECD, Electron Capture Detector; d.w.e, dry weight equivalent; FWI, French West Indies; GC-ECD, Gas Chromatography-Electron Capture Detector; GC–MS, Gas Chromatography–Mass Spectrometry; K_d, Soil sorption partition coefficient; LSC, Liquid Scintillation Counter; NER, Non Extractable Residues; OC, Organic Carbon; R_f, Retardation factor; S, Soil; TLC, Thin Layer Chromatography.

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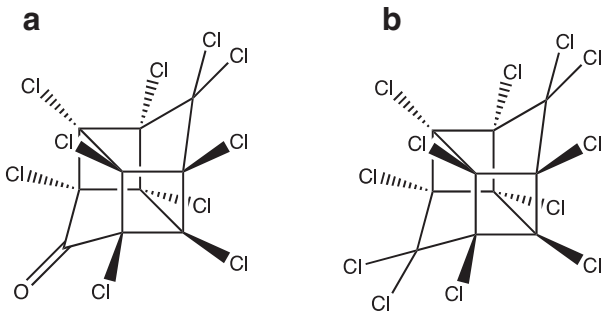

Fig. 1. Developed chemical formula of chlordecone (a) and mirex (b).

Notwithstanding, the current residual chlordecone contamination still has negative impacts on human health, the environment and local economy. An example of this is the French West Indies (FWI), where chlordecone was used in banana plantations to control the weevil, *Cosmopolites sordidus* (Cabidoche et al., 2009). Despite its prohibition in France in 1993, pollution surveys conducted in 2001 in the FWI by the French Department of Health revealed the presence of chlordecone in soils, rivers, springs and drinking water as well as in food crop products such as root vegetables (Cabidoche and Lesueur-Jannoyer, 2011; DSDS, 2001). More recent studies in the same area measured concentrations of chlordecone in soils between 0.2 and 37.4 mg kg^{-1} (Cabidoche et al., 2009).

Furthermore, the extensive use of the similarly highly toxic insecticide mirex ($C_{10}Cl_{12}$, Fig. 1b), extended the problem because chlordecone is the main degradation product and it was also co-applied as an impurity of mirex (Faroon et al., 1995). For instance, Carlson et al. (1976) have shown that twelve years after the last application of mirex to soil, 3–6% of the remaining mirex-related organochlorine compounds detected in the soil was chlordecone. Moreover, mirex, which was already included in Annex A of the Stockholm Convention in 2001, was still in use in China until 2009 (Wang et al., 2010). Surprisingly, the environmental fate of both chlordecone and mirex has been barely investigated. Gambrell et al. (1984) studied the effect of variations in the redox potential (from anaerobic to aerobic conditions) and pH (from mildly alkaline to moderately acid) in kepone (trade name of chlordecone) transformation in the James River sediments, an area heavily contaminated by the chlordecone produced at the nearby Hopewell plant, Virginia, USA, from 1966 to 1975 (Faroon et al., 1995). After 56 days of microcosm incubation the level of kepone in the sediments, determined by Gas Chromatography-Electron Capture Detector (GC-ECD), did not change significantly under any of the combinations of imposed pH and redox potential conditions. The formation of metabolites was not monitored. In another qualitative study, Francis and Metcalf (1984) detected up to 6 different compounds that could potentially be chlordecone degradation products in the organisms (vertebrates and invertebrates) of a terrestrial-aquatic laboratory model ecosystem after 1 month of incubation. Only two of these compounds were detected in the water of the system. One of these compounds was only detected at trace levels and the second compound presented a concentration of only 0.02 ppm. However, the total concentration of chlordecone determined in water at the end of the experiment was not clear (0.17 ppm or 10 ppb) and the exact nature of the metabolites was not identified in this study. Borsetti and Roach (1978) studied the degradation products of chlordecone in soils collected in the vicinity of the Hopewell plant and in mullets from the James River. The concentration of chlordecone extracted from both the soils and mullets was 60 and 0.56 ppm, respectively. The authors identified 9-chloro and 8-chloro homologs of chlordecone in soils at concentrations of 1.0 and 0.01 ppm, respectively. In the mullets, only a 9-chloro homolog was observed at concentrations of 0.04 ppm. The appearance of the metabolites was rather attributed to the photodegradation of chlordecone in the river, although biodegradation or impurities with chlordecone could also be a reason for these results. A study investigating the potential degradation of ^{14}C-chlordecone in estuarine microcosm under static and continuous flow from 42 to 60 days, failed to show any transformation of the compound (Garnas et al., 1978). Skaar et al. (1981) found no direct evidence of degradation of mirex or chlordecone after 56 days of incubation in freshwater sediments under aerobic or anaerobic conditions, nor metabolism or co-metabolism of ^{14}C-labelled chlordecone in sediments that had long-term pre-exposure to chlordecone. Orndorff and Colwell (1980) studied the biodegradation of chlordecone with a mixed aerobic culture obtained by enrichment from a sludge lagoon of the municipal sewage treatment plant of Hopewell and with a *Pseudomonas aeruginosa* strain K03 isolated from this enrichment. They found that after 12 weeks of incubation, 14 and 16% of the applied chlordecone was transformed to mono-hydro-chlordecone, and 4 and 16% was transformed to di-hydro-chlordecone, by *P. aeruginosa* and the mixed enrichment culture, respectively. They also suspected an alcohol-derivate of chlordecone in the mixed enrichment culture, however, they were not able to confirm this result because they did not have a standard of it or a GC–MS confirmation. Despite all these studies, none of them provided evidence of microbial mineralisation of chlordecone. To the best of our knowledge, the mineralisation of chlordecone in an aquatic simulated environment has only been reported once (Portier and Meyers, 1982). This study, carried out in a static microcosm with sediments from Lac des Allemands (Louisiana, US), slightly found a formation of 1.4–1.7% of $^{14}CO_2$ from chlordecone incubated during 30 days.

Finally, based on the low degradation rate of chlordecone in soil and water stated in the literature, Cabidoche et al. (2009) hypothesised that the decontamination of chlordecone from soil would only occur by leaching. Therefore, according to their calculations within the context of the FWI case, chlordecone would persist in the soil several decades or even centuries depending on the soil type and initial level of contamination.

Within this alarming context, the objective of this work was to study the degradation of recently applied ^{14}C-chlordecone and its environmental fate in different soil compartments in a tropical soil microcosm experiment. The demonstration of a potential for degradation of chlordecone in the soil and a better knowledge of its distribution within the soil compartments in controlled conditions is of great importance in the search for possible options for soil decontamination. Two horizons of an agricultural andosol where banana plants had been cropped and chlordecone extensively applied were chosen. Among the soil types occurring in the banana cropping areas of the FWI, andosols are those that exhibit the highest stocks of chlordecone (Cabidoche et al., 2009). The rates of mineralisation and distribution within the soluble, extractable and non-extractable residues (NER) fractions were measured over 215 days of incubation under aerobic conditions. The possible appearance of metabolites was also investigated.

2. Materials and methods

2.1. Chemicals

[^{14}C U]-chlordecone was purchased from Moravek Biochemical (Brea, CA, USA) at a specific activity of 1443 MBq $mmol^{-1}$ (radiochemical purity 99.9%). Non-labelled chlordecone Pestanal® was purchased from Sigma-Aldrich (Schnelldorf, Germany) with a purity of 99.7% (area). Chlordecone is a non-ionic organochlorine insecticide with low water solubility — the poor solubility leads to variable data ranging from 0.35 to 3 μg mL^{-1} (UNEP, 2006). Chlordecone is readily soluble in apolar organic solvents as indicated by the high log K_{ow} 4.5–5.4 (UNEP, 2006).