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Chlordecone retention in the fractal structure of volcanic clay

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HIGHLIGHTS

- Allophanic soils are highly polluted but less contaminant for cultivated vegetables.
- SAXS and TEM show the fractal structure of allophane aggregates at the nanoscale.
- Allophane aggregates play the role of a labyrinth which fixes and traps chlordecone.
- Allophane physical properties contribute to chlordecone retention in andosols.

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ABSTRACT

Chlordecone (CHLD), a soil and foodstuff pollutant, as well as an environmentally persistent organochlorine insecticide, was used intensively in banana fields. The chlordecone uptake of three crops was measured for two types of polluted soils: allophanic and non-allophanic. The uptake is lower for allophanic soils even if their chlordecone content is higher than with non-allophanic soils. The fractal structure of the allophane aggregates was characterized at the nanoscale by small angle X-rays scattering, pore size distribution and transmission electron microscopy. We showed that clay microstructures should be an important physico-chemical factor governing the fate of chlordecone in the environment. Allophanic clays result in two counterintuitive findings: higher contaminant trappings yet lower contaminant availability. We propose that this specific, tortuous structure, along with its associated low accessibility, partly explains the low availability of chlordecone confined in allophanic soils.

Capsule

The fractal and tortuous microstructure of allophane clay favours the chlordecone retention in soils and disfavours the crop uptake.

1. Introduction

Chlordecone (CHLD) is an organochlorine insecticide, used in order to control different pests and detected in Africa, the Caribbean, Europe, Latin America, North America and French Polynesia [1–5]. Several years after the prohibition of its use, the molecule still persists in the soil [1,6], and continues to contaminate crops, water resources and ecosystems [5,7–11]. While the population remains exposed to this food contaminant, [12–14], the global impact of chronic exposure is not well known [15] despite its contribution to an abnormally higher rate of prostate cancer [16]. As the main CHLD reservoir is polluted soil, mechanisms of CHLD fate in the environment and food chains are useful to manage population exposure.

The persistence of CHLD in soils is explained by:

1. Its physicochemical properties (low solubility in water, hydrophobicity) giving it a high affinity for organic matter (high K_{oc}) [1,17], and
2. Its poor biodegradability related to its peculiar chemical structure (bishomocubane "cage") and the high steric hindrance caused by the ten chlorine atoms.

Banana crops in the French West Indies were mainly cultivated in the vicinity of volcanoes and were grown on two types of soils: allophanic (andosol) and non-allophanic (nitisol and ferralsol) [18]. These soils are not equivalent in terms of CHLD contamination and in their ability to transfer the pollutant to water and to plants. Andosols are generally more polluted than the two other kinds

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of volcanic soils but, surprisingly, preliminary results suggest that andosols release less CHLD to percolating water and crops than nitisol and ferralsol [1,19]. Andosols contain amorphous clays (allophane), which present unique structures and physical properties compared to usual clays: large pore volume and specific surface area, tortuous and fractal porous arrangement [20–23]. Our study hypothesizes that allophane would favour pesticide accumulation in soils, even if organic matter plays an important role. The purpose of this study is to: (1) demonstrate that andosols release less CHLD than other kinds of soils for a set of root and leaf vegetables and, (2) put forth the importance of the allophane fractal microstructure for CHLD soil trapping.

2. Material and methods

2.1. Field experiment

For these experiments, we studied two root and tuber vegetables and a leaf crop: yam [*Dioscorea* spp.], dasheen [*Colocasia antiquarum*] and lettuce [*Lactuca sativa*]. These crops were chosen for their diversity of edible parts, their importance in local food consumption and their levels of contamination measured over 20 μg/kg FM (fresh matter) [14]. This value is the Maximum Residue Level (MRL) fixed for CHLD in European Union countries [24].

For each crop, the same local variety was used on each experimental plot in order to limit crop response variability. For each trial, experiments were carried out in Martinique on two types of volcanic soils: allophanic soils (andosol, AS) and non-allophanic soils (ferralsol and nitisol, NAS). Yams and dasheens were grown on 300 m^2 plots at Morne-Rouge (AS) and Ducos and Sainte Marie (NAS), lettuces were grown on 100 m^2 plots in Ajoupa Bouillon (AS) and Le Lamentin (NAS).

Those plots were selected according to previous soil analyses in order to obtain a range of CHLD concentrations representative of the local pollution. Contamination ranged from 0.28 to 11.3 mg/kg of dry soil in AS and from 0.95 to 5.77 mg/kg of dry soil in NAS. Four plots (two AS and two NAS) were planted with 30 seedlings of yam and dasheen. Twenty lettuces were cultivated on two plots (one AS and one NAS). Crops were conducted as farmers do (crops density, fertilization, harvest). Thus, conditions were very similar to those of the local agriculture. Distances between plants were 1.3 m × 0.3 m for yam, 1 m × 1 m for dasheen and 0.2 m × 0.2 m for lettuce. Each crop was harvested at commercial maturity: 7 months for yam, 5 months for dasheen and 4 weeks for lettuce.

Whenever possible, ten replicates were selected at harvest-time from each plot. Vegetables were thoroughly washed twice with distilled water so as to eliminate any soil residues. Concentrations in the whole commercial vegetable were studied in order to be consistent with MRL references. For each selected plant, an aliquot of the harvested organ (tubers or corn with skin for yam and dasheen and leaves for lettuce) was made. Vegetal samples were frozen and stored at −20 °C until they were shipped to the analytical laboratory.

Soil was collected in the vicinity of the roots using a 30 cm hand auger (SDEC, France). For each plant, two samples, one in the planting row and the other in the inter-row, were taken. Composite samples were obtained by mixing (1/2 in volume) soil of the two sample points. Soil samples were air dried, manually crushed, sieved at 2 mm and finally crushed in a rotor beater mill (model SR200 by Retsch).

2.2. Analysis

Organic carbon (OC) and CHLD contents were determined by independent laboratories. OC content of soil samples was ascertained at the Amis-Cirad laboratory (Montpellier, France) by dry combustion (NF ISO 10694) using a Flash EA – 1112 Series (Thermo Electron Corporation, Waltham, MA) elemental analyser.

The CHLD content of soils was determined at the laboratoire départemental d'analyses de la Martinique (LDA972, Fort-de-France). The analytical method used for CHLD was MPO-MO.02/13. The CHLD content of plant samples was analysed at laboratoire départemental d'analyses de la Drôme (LDA26, Valence). The analytical methods used for solid phase extractions were AFSSA LERHQUA-CENPOP/06 and AFSSA/VEGETAUX HPLCMS developed by l'Agence nationale de sécurité sanitaire de l'alimentation, de l'environnement et du travail (French Agency for Food, Environmental and Occupational Health and Safety) (http://www.anses.fr/PNR5I0.htm). Both LDA972 and LDA26 comply with ISO 17025 standards for testing and calibration laboratories. Each has been accredited by COFRAC, the French Accreditation Committee for CHLD analyses thus providing guarantees for their technical skills and reliability.

At LDA972, extraction was carried out with an accelerated solvent extractor (Dionex ASE200, Sunnyvale, CA, USA) at 120 bars and 100 °C (heat time: 5 min, static time: 5 min, purge time: 300 s), using dichloromethane and acetone (volume ratio 50/50). Extract was then concentrated with pentanol (100 μL) and purified with concentrated sulphuric acid (200 μL, centrifugation for 5 min at 2000 tr/min). Concentration and purification are carried out in a centrifugal evaporator (GENEVAC, Ipswich, UK). Chlordecone content was measured using a Gas Chromatograph - Electron Capture Detector (GC-ECD) VARIAN (Palo Alto, CA, USA) GC 3800 and GC–MS–MS method (gas chromatography coupled with mass spectrometric detection) with VARIAN GC 450 and MS 240. Standard addition method and tracers (hexabromobiphenyl and PCB 193) allowed validation of extraction efficiencies. To perform identification, three transitions from precursor ion m/z 272 were monitored: m/z 235, 237 and 239 (excitation storage level: m/z 74.9 and excitation amplitude: 1.6 V). For confirmation, m/z 237 was used as a quantifier and m/z 235 (25%) and 239 (15%) as qualifiers. Quantification was achieved using internal standards: PCB101 and m/z 237 products ion from m/z 272 precursor ion. The performance for CHLD recovery was 85%.

At LDA26, plant sample extraction was carried out with acetone under constant agitation for 2 h at room temperature. After filtration a liquid–liquid extraction was carried out for 20 min with 25 mL of extract, 75 mL of water, 10 mL of saturated salted water and 20 mL dichloromethane. Extract purification is achieved with a silica cartridge. Chlordecone content was measured either by using VARIAN (Palo Alto, CA, USA) and Agilent (Santa Clara, CA, USA) Gas Chromatographs with Electron Capture Detector (GC-ECD) or Thermo (West Palm Beach, FL, USA) TSQ Quantum Ultra High Performance Liquid Chromatograph–Mass Spectrometer (HPLC–MS), depending on the matrix. When matrix interferences were too high with the GC–ECD, the LDA26 used HPLC–MS method with a tracer in order to realize the set of calibrations and to correct the matrix effects. For GC-ECD methods, calibration was achieved using the standard addition method along with two internal standards: hexabromobenzene and triphenylphosphate. For mass method, two transitions were monitored: 272 > 237 and 274 > 239 (excitation storage level: m/z 74.9 and excitation amplitude: 1.6 V. C_{13} CHLD was used as an internal standard for quantification. A standard curve with 5 points was established. The CHLD recovery performances were 84%.

CHLD soil and vegetal limits of quantification (LOQ) are respectively 10 μg/kg of dry soil (DS) and 1 μg/kg of fresh matter (FM). The resulting CHLD data are given with a 30% confidence interval.