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Soil microstructure and organic matter: Keys for chlordecone sequestration☆

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HIGHLIGHTS

- Chlordecone (CHLD) sequestration in soils is a possible way to reduce plant contamination.
- CHLD sequestration in allophanic soils is improved by the addition of compost.
- SAXS show the closure of the fractal structure of allophane after compost addition.
- The mesopores collapsed and the CHLD is less susceptible to diffusion in crops and water.
- Proposal for a new strategy to limit the risk of contamination: enhancing CHLD sequestration.

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ABSTRACT

Past applications of chlordecone, a persistent organochlorine pesticide, have resulted in diffuse pollution of agricultural soils, and these have become sources of contamination of cultivated crops as well as terrestrial and marine ecosystems. Chlordecone is a very stable and recalcitrant molecule, mainly present in the solid phase, and has a strong affinity for organic matter. To prevent consumer and ecosystem exposure, factors that influence chlordecone migration in the environment need to be evaluated. In this study, we measured the impact of incorporating compost on chlordecone sequestration in andosols as a possible way to reduce plant contamination. We first characterized the transfer of chlordecone from soil to plants (radish, cucumber, and lettuce). Two months after incorporation of the compost, soil–plant transfers were reduced by a factor of 1.9–15 depending on the crop. Our results showed that adding compost modified the fractal microstructure of allophane clays thus favoring chlordecone retention in andosols. The complex structure of allophane and the associated low accessibility are important characteristics governing the fate of chlordecone. These results support our proposal for an alternative strategy that is quite the opposite of total soil decontamination: chlordecone sequestration

1. Introduction

Chlordecone (CHLD) is an environmentally persistent organochlorine insecticide that was intensively used in banana production in many parts of the world for more than 50 years [1–4]. Although many countries now forbid its use, CHLD has caused permanent pollution of soils which continue to contaminate crops [5–8] as well as fish and crustaceans [9–12]. CHLD impairs child development [13,14], contributes to abnormally high rates of prostate cancer [15] and is also suspected of being involved in the increasing incidence of breast cancer [16].

The persistence of chlordecone in soils is explained (i) by its physicochemical properties (low solubility in water $S = 0.2\,g\,L^{-1}$, hydrophobicity K_{oc} between 2500 and 17,500 $L\,kg^{-1}$) [2] resulting in a strong affinity for organic matter and (ii) by its poor biodegradability related to its peculiar chemical structure (bishomocubane "cage" $C_{10}Cl_{10}O$) and a high steric hindrance [17–19].

Widely used soil decontamination techniques such as solvent extraction and incineration are costly [20]. Microbial degradation

☆ In memory of Yves-Marie Cabidoche who pioneered chlordecone studies in the French West Indies.

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is thermodynamically possible [17] but is not yet even a promising technique as it has slow degradation rates, requires anoxic conditions and could result in degradation products whose toxicity is not known.

Previous works have shown that all soils are not equivalent in terms of CHLD pollution and in their ability to transfer this pollution to the environment. Andosols are generally more polluted than other kinds of volcanic soils but release less CHLD to percolating water and crops [2,5]. Andosols are young volcanic soils which contain amorphous clays like allophane. The structure and physical properties of allophane clays differ from those of usual clays: large pore volume and specific surface area, tortuous and fractal porous arrangement [21].

Chung and Alexander [22] showed that pesticide sequestration in soils was correlated with organic carbon content and nanoporosity. In a previous study [23] we showed that natural pesticide sequestration occurs in andosols which is attributed to their high organic content and the peculiar fractal structure of allophane and we considered the possibility of increasing the sequestration of CHLD in soils by adding compost [24]. The objectives of the present work were thus:

(1) From an agronomical point of view, the previous results obtained on a root crop (radish) needed to be tested using other crops, as the mechanisms and the intensity of pollutant transfer from the soil depend on the crop and on the organ harvested. Cucurbits are well-known for their ability to accumulate persistent organic pollutants even in fruits [25–27] while in the case of leaf crops, the pesticide taken up by the roots has to be translocated to the aerial part [26,28]. The amplitude of the sequestration process caused by organic amendment needed to be evaluated in different types of crops: a root crop, a cucurbit and a leaf crop.
(2) From a physical point of view, the role of allophane in the micro structural changes that occur upon addition of compost addition needed to be understood through a complete study, and the mechanisms responsible for the collapse needed to be investigated. In this study, we thus characterized the amplitude of structural changes (pore collapse and changes in fractal structure) in soils with different allophane contents, so as to demonstrate that the fragile allophane microstructure is sensitive to the addition of compost. In addition, we investigated the effect of adding compost on the microstructure of soils with a wide range of allophane concentration (6–18%). In conclusion, we propose a mechanism to explain the structural changes: capillary forces are responsible for the collapse of the micro aggregates, and this collapse of the allophane aggregates is likely involved in the whole sequestration process.

2. Materials and methods

The experimental design comprised two complementary experiments to answer the two following questions: (i) can incorporating compost in a contaminated andosol reduce soil–plant transfer of chlordecone in three types of vegetable crops (experiment 1)? (ii) What are the effects of adding compost on the microstructure of a wide range of allophane contents (experiment 2)?

2.1. Experiment 1

2.1.1. Soil sampling and preparation

We chose andosols because they represent the majority of contaminated soils in the French West Indies (FWI) and are more contaminated than other types of soil [1,2]. A contaminated andosol containing 6% allophane (CHLD 4.7 mg kg^{-1} dry soil) was sampled in the A horizon, at a depth of 0 to 15–20 cm, in an agricultural field at Morne-Rouge, Martinique. This CHLD content is representative of the level of contamination of andosols in the FWI [1,29]. Moreover this soil is over the contamination thresholds which guarantees that harvested products comply with the European maximum residue limit [29]. The soil thus requires management of the risk of crop pollution [5,29]. This is why we chose it to test the effect of adding compost on CHLD sequestration.

The components of the compost used in this study (Vegethumus, manufactured by Fayssinet) are sheep manure, pulp and cake from fruits (olive, cacao, coffee, sunflower), wool stuffing and magnesium. Main characteristics of this organic amendment are 24.8% water content, 46.6% organic matter content, C:N ratio = 13, humifying capacity = 0.70; humic yield = 577 kg t^{-1} raw material. We chose this product because it best answered our initial selection criteria for the reference organic matter to be used: locally available, already used by farmers, high humic potential, CHLD free, and also compatible with certified organic production.

The soil was mixed with the compost (5% by weight) and incubated at 28–30 °C with constant humidity maintained at 90% of maximum water retention capacity throughout incubation. Five percent (corresponding to 70 t ha^{-1}) appeared to be a satisfactory compromise between the significant dose we needed to achieve results and a dose that would be easily adopted by the farmers. A control (non-amended soil) was also prepared and incubated in the same conditions. To monitor total CHLD content during incubation, CHLD content was measured three times for each treatment (compost and control): 0, 30 and 90 days after incubation (Table 1). The sampling dates were chosen because of the kinetics of decomposition of organic matter: a month for easily decomposable matter and three months for organic fertilizers. Organic amendments continue to mineralize after three months.

2.1.2. Management of vegetable crops

Three vegetables: a root crop, radish (*Raphanus sativus*), a fruit crop, cucumber (*Cucumis sativus*) and a leaf crop, lettuce (*Lactuca sativa*) were used for these experiments. These crops were chosen because different parts of the plant are consumed and because they are part of the island diet. Seeds were obtained from Tropica (France), a supplier of seed varieties adapted to tropical conditions. Two months after the compost was incorporated into the soil, the vegetables were sown in individual pots filled with soil with 0% or 5% added compost. For each crop, three to six replicates were grown under each treatment (no compost or added compost): five 10-L pots for radish, three 35-L pots for cucumber and six 10-L pots for lettuce. The size of the pot was chosen so as not to limit crop growth [28,30,31]. Plants were thinned to three radishes per pot, one cucumber per pot and one lettuce per pot 15 days after sowing. Soil moisture was maintained at field capacity under climatic chamber conditions (14:10 light/dark regime, 26 °C, drip irrigation) for radish and under greenhouse conditions for cucumber and lettuce (natural light, 25–31 °C, micro-sprinkler irrigation). Harvesting was carried out when the edible parts of plants were of a marketable size. This was 40 days for radish, 40 days for lettuce and 45 days for cucumber. The plants harvested in each pot were treated as a composite sample. The sample to be analyzed for each pot was the edible part of the crop: root tubers for radish, all the fruits of a plant for cucumber and all the leaves for lettuce. The vegetables were washed twice with nanopure water to avoid CHLD-contamination by tap water. CHLD content was measured in the prepared composite samples.

2.1.3. Chlordecone analyses

Soil and plant samples were analyzed by the LDA26 (Valence, France), a French laboratory which works under the standard NF17025 and is accredited for pesticide analysis by COFRAC,