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USE OF BIOCHAR TO PROTECT THE VEGETABLES AGAINST THE CHLORDECONE CONTAMINATION: THE STRATEGY OF THE SEQUESTRATION

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Abstract: In the case of certain pesticides, the known decontamination methods are not always technically feasible (phyto or bio remediation) or financially and ecologically feasible (excavation, chemical decontamination). We offer an alternative to complete depollution: the sequestration of the pesticide in the soil with the aim of limiting the transfer of the contaminant to the ecosystems. In previous work we have shown that the incorporation of organic matter (compost) in the soil increases the sequestration in the soil of chlordecone. Thus, although contaminated, the soil only releases the pollutant more weakly in the vegetables grown and the water that passes through it. However, organic materials are not permanent and the process must be renewed at intervals of the order of 1 to 2 years. We propose to use Biochar, organic matter stabilized in solid form, which could fulfill the same role of sequestration with a longer duration of effectiveness. This agro-ecological management method (compost, biochars) makes it possible to offer a method that is easy to implement because it is mastered by farmers.

Keywords: Soil decontamination, chlordecone sequestration, biochars

Introduction

In the French West Indies, the public authorities have to deal with a problem of pollution of ecosystems, by an organochlorine pesticide (chlordecone [Jannoyer et al 2016]. Chlordecone is an insecticide from the DDT family (formula $C_{10}Cl_{10}O$) which has been widely used between 1972 and 1993 to fight against the banana weevil. Although banned for 30 years, this particularly persistent molecule in the soil is the cause of chronic pollution of soil, water, plants and animals. In Martinique, 40 to 50% of the water points monitored exceed the standard for drinking water. Carcinogenic, chlordecone makes the soil unsuitable for certain crops, in particular roots and tubers which absorb this pollutant.

Its impact has also been proven in humans (increased risk of prostate cancer, disruption of development in young children) for chronic exposure via food (Multigner et al, 2010). Given the intrinsic characteristics of chlordecone, very strong persistence and sorption on organic matter, several decades, even a century will pass before the state of soil pollution returns to normal if nothing is implemented to remedy this (Cabidoche et al, 2009).

Currently, we have no means of action to reduce contamination in natural environments. The management of this crisis poses a real challenge for research and the authorities because few similar cases exist in complex, specific environments (volcanic soils, humid tropical climate, island environment, dense population, etc.) and, therefore, fragile.

An alternative to depollution: the sequestration of chlordecone by adding organic matter.

Due to the physicochemical properties of this pesticide (low solubility, hydrophobicity, very low biodegradability, etc.) and the strong retention of chlordecone in clays], it will be difficult and costly to clean up the soil using simple excavation techniques. , chemical decontamination, phytoremediation (extraction by plants) or biodegradation (degradation by microorganisms). We have shown [Woignier et al, 2018, 2020] that in volcanic soils, the decontamination processes envisaged (use of bacteria [Chevallier et al, 2019] or “In Situ Chemical Reduction” ISCR [Mouvet et al, 2020] will be ineffective due to a physical limitation linked to the microstructure of the clay. Indeed for these soils called andosols (or allophane soil); the chlordecone is trapped in the allophane clays whose microstructure (porosity, pore size) very strongly limits the accessibility. These physical characteristics lead to the conclusion that it will be practically impossible physically to decontaminate these Andosols by the processes currently envisaged (bacteria, ISCR). However, these Andosols represent nearly 50% of the contaminated soils in Martinique.

Pending effective processes, one solution would be to strongly trap the molecule in the soil so that, although contaminated, it only releases this contamination weakly. We therefore propose an alternative to complete depollution: sequestration. The objective is to limit the transfer of the contaminant present in the soil to water and crops. Like many organic pesticides, chlordecone has a strong chemical affinity for organic matter in the soil: experimental results show that the ability of the soil to fix chlordecone depends directly on its concentration of organic matter [Woignier et al 2013].

The incorporation of organic matter into polluted soil is known as an agro-ecological lever for trapping various pesticides (atrazine, propachlor, simazine, etc.) [Beesley et al, 2010]. In previous work we have shown that the incorporation of organic matter (compost) in the soil increases the sequestration in the soil of chlordecone. Thus, although contaminated, the soil only releases the pollutant more weakly in the vegetables grown and the water that passes through it.

Among the strategies for in situ incorporation of exogenous inputs, the use of biochars (porous carbonaceous product resulting from the pyrolysis of biomass) constitutes an alternative with promising potential, based in particular on its particular physicochemical properties (high porosity, specific surface, surface chemistry, habitat for microorganisms, etc.). Although biochar has primarily been studied as a soil amendment due to its positive role in carbon sequestration, reduction of greenhouse gas emissions [K.R.Reddy et al] and improvement of soil fertility , it is attracting increasing attention for its ability to reduce the bioavailability of pesticides [Ahamad et al., 2014,]. It has also been recognized that the presence of biochar in the soil not only enhances the sorption of different pesticides but affects the mechanisms of bioavailability of pesticide residues to living organisms (. Moreover, the application of biochar in contaminated agricultural soils can limit the risk of groundwater contamination by reducing the leaching of applied pesticides [Ahmad et al., 2014].

1. Materials and Methods

1.1 Preparation of biochars and soils

We synthesized from the same precursor (STEP sludge representative of a large part of the deposit generated in Martinique) 5 different biochars from 5 different pyrolysis operating conditions: 400°C, 500, 600, 700, and 800 °C. The soils (nitisols) were sampled in the municipality of Trinité (Vert Pré). Bins of 150 kg of soil were mixed with the 5 biochars in a proportion of 8 and 10% by weight, i.e. 11 modalities with the control soil.

After 3 months of maturation at a constant humidity level (86%), the amended soils were taken from 7 kg pots in which radishes (*Raphanus sativus*) were planted (10 per pot). After 30 days of growth, we recovered the radish bulbs as well as the rootlets which were weighed and sent

for CHLD measurement at LDA26 (Drome Analysis Laboratory). The measurement of chlordecone in the bulbs (5 measurements) and rootlets (1 measurement) was made by HPLC/MS [Woignier et al, 2018]. The measurement of the weight of the bulbs made it possible to quantify the influence of the biochars on the agronomic yield.

2. Results

The results obtained are very encouraging and indicate that in the presence of biochars in polluted soils, the level of chlordecone in the bulb of the radish decreases by a factor of 6, for the most effective (800°C), concentration equal to 10 % by weight of biochar in the soil. In addition, interesting potentialities from an agronomic point of view have been confirmed (higher yield, larger and more leafy radishes, etc.).

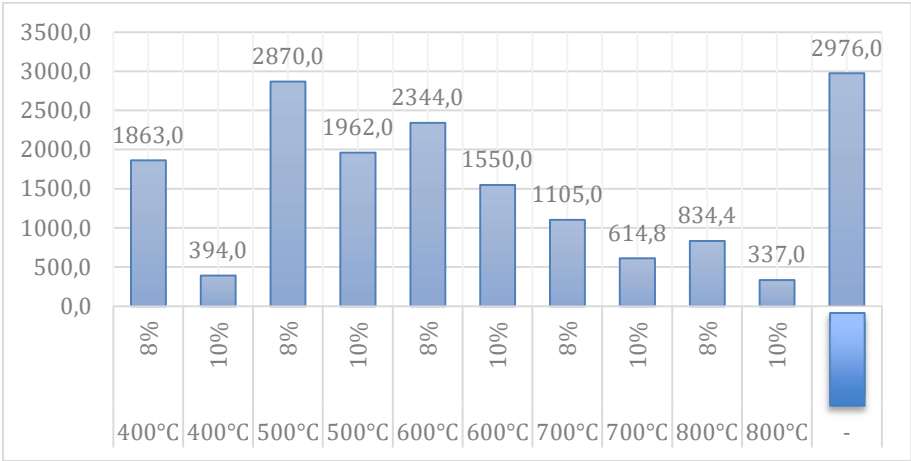


Figure 1. Chlordecone rate (µg/Kg) in radish roots (*Raphanus sativus*): Influence of concentration and temperature of biochar production. The last column is the control.

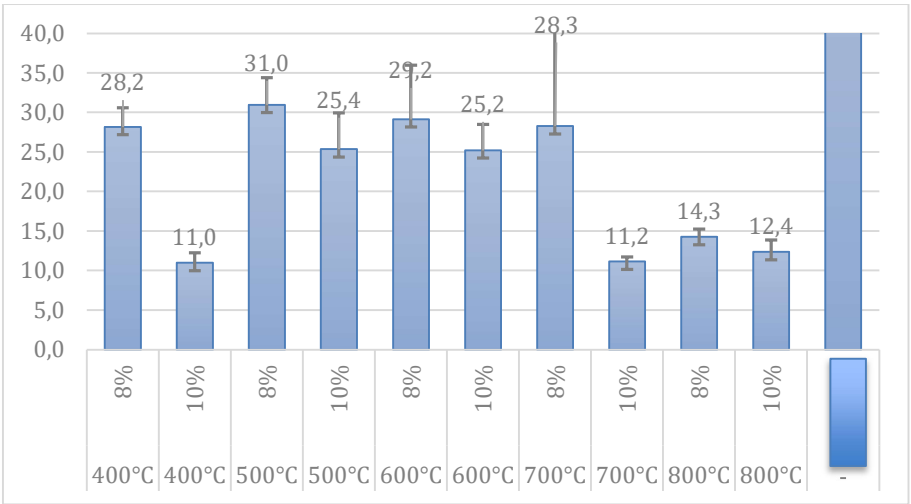


Figure 2. Chlordecone rate (µg/Kg) in radish bulbs (*Raphanus sativus*): Influence of concentration and production temperature of Biochar. The last column is the control.

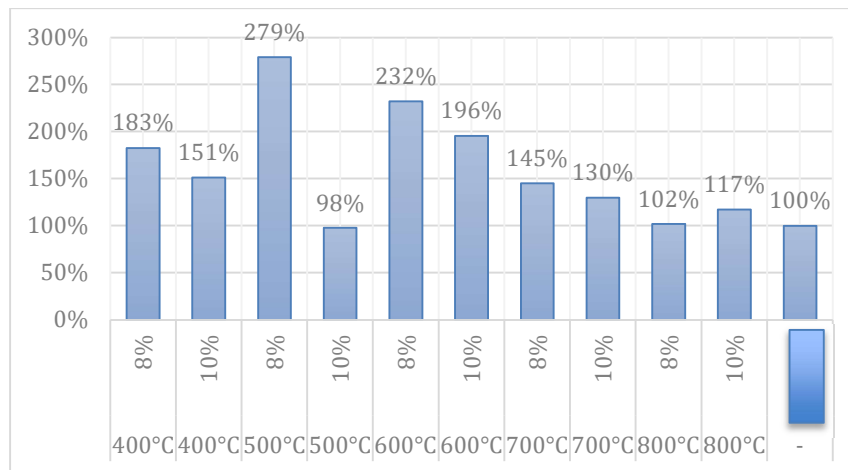


Figure 3. Agronomic yield for radish (*Raphanus sativus*): Influence of Biochar concentration and production temperature. The last column; is the control.

Regarding the central point of the study, namely the sequestration capacity of the biochar for the chlordecone molecule, a decrease in the amount of the pollutant is observed for almost all the biochar samples; CLD rate between 1.5 and 8.8 times lower than in the control (for the roots and CLD rate between 2 and 6 times lower than in the control) for the bulbs. These results confirm our expectations and indicate that in the presence of biochars in polluted soils, the rate of chlordecone in the bulb and the roots of radish decreases sharply. The 10% 700°C biochar confirms to be the most promising, the rate of chlordecone in the radish bulbs remains low. Biochar 10% 400°C also remains a very interesting alternative with the lowest rate of chlordecone in radish bulbs. As a reminder of the regulations in force, only 20 µg/kg of chlordecone fresh weight of vegetable foodstuffs are authorized by law. The marketing of foodstuffs which exceed this Maximum Residue Limit (MRL) is strictly prohibited. We can thus see that the biochars 400°C at 10%, 700°C at 10% and 800°C at 8% and 10% make it possible to be below this MRL with an edible radish bulb, where the control is not (with a rate 3 times higher than the regulatory MRL).

The yield in terms of the harvestable biomass of *Raphanus sativus* is also effectively influenced by the rate of biochars mixed in the soil, the yield being able to be 2.7 times higher. The feasibility of the method in open fields must now be demonstrated and this is the next step that we are planning with pilot farmers who will test the biochars in real conditions.

Conclusion

There is currently no decontamination solution offered to farmers. After the development of the biochar supply plan, this process will limit transfers to water and crops. Thus, it will be possible to recultivate contaminated soils and limit the pollution of water resources at strategic points. This process has other advantages. First of all, the addition of organic matter, generally in the form of compost, is part of good agricultural practice. On the other hand, this process does not have the disadvantages of conventional decontamination processes (chemical, biodegradation) which can lead to a deterioration of the properties of the soil but also to the appearance of degradation products whose harmfulness is poorly understood. Finally, it is easy to implement for farmers and does not present any health risk for the user. This method should make it possible to manage pollution and pollutant transfer pending definitive processes.

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