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Effects of particle size and amendment rates of Sargassum biochar on chlordecone sequestration in West Indian soils

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Abstract :

The use of biochars (BC) and activated carbons (AC) as a way of sequestering soil bound pollutants such as chlordecone (CLD) is increasingly being studied. This study aims at assessing the impact of Sargassum BC/AC particle size and Sargassum BC amendment rate on CLD adsorption in Nitisol and in Andosol. Four different types of carbonaceous matrices were tested: Sargasso carbon activated by phosphoric acid (SargH₃PO₄), Sargasso carbon activated by steam (SargH₂O), biochar of Sargasso (Ch Sarg700) and a commercial activated carbon (ORBOTM). In a first experiment, CLD contaminated Andosol and Nitisol were amended with 2% of each carbonaceous matrix divided into four particles size classes (<50µm; 50-150µm; 150-200µm and >200µm). In a second experiment, the contaminated soils were amended with the biochar of Sargasso at five application rates (0, 0.25, 0.5, 1 and 2 % (w/w)). After a four months ageing, environmental availability tests were carried out on the soils of both experiments. The results of the first experiment showed that the best reductions of CLD environmental availability were obtained in both soils with the biochar of Sargasso and the ORBOTM. More specifically, in Nitisol, particle size under 50 µm of biochar of Sargasso and AC ORBOTM showed a CLD environmental availability reduction up to 80% and 79%. In Andosol, there was no significant difference between the three particle sizes (<50µm, 50-150µm and 150-200µm) of Biochar of Sargasso on the reduction of environmental availability (average reduction of 43±2.5%). The results of the second experiment showed that an amendment rate increase improves the immobilization of CLD. When the amendment rate was increased from 0.25% to 2% the environmental availability was reduced by 43% in Nitisol and 50% in Andosol.

Keywords: *chlordecone, environmental availability, sequestration, biochar, activated carbon, Sargassum*

1. Introduction

The chlorinated Persistent Organic Pollutant Chlordecone (CLD) was widely used as a pesticide against the banana black weevil in the French West Indies from the 1970s until its prohibition in 1993. CLD appears to be very persistent in the Antillean volcanic soils (Nitisol, Ferralsol and Andosol) and the resulting pollution varies according to the soil characteristics but also on the history of CLD use (quantity applied and frequency of use). CLD is at the origin of a permanent pollution affecting agricultural (Cabidoche et al. 2009) production and population health in the contaminated areas (Multigner et al. 2010; Saunders et al. 2014; Yang et al. 2020). Nowadays, it is estimated that 1/5 of the used agricultural land in Guadeloupe is contaminated, whereas in Martinique this represents 2/5 of the same type of land (DAAF 2015, 2017). This environmental contamination may lead to contaminated food (Godard and Bellec 2002). Another environmental issue in the French West Indies is related to massive and irregular arrivals of *Sargassum spp.* These events cause negative economic impacts since they affect the tourism economy (Maréchal et al. 2017). These algae may also cause health damages when they decompose and release gases such as hydrogen sulfide and ammonia.

The use of biochars (BC) and activated carbons (AC) as a way to sequester pollutants such as CLD is increasingly being studied. BCs result from pyrolysis of biomass under an oxygen-limited environment, they can further on be activated by physical or chemical methods to obtain ACs (Kavitha et al. 2018). Previous studies have shown the impact of biomass on the characteristics of BCs and ACs and therefore on their sequestration efficiency (Zheng et al. 2017; Li et al. 2018; Ranguin et al. 2020). Indeed, the carbon matrix can be made out of different raw materials such as manure, wood and even algae (IBI 2012). Ranguin et al. 2021 have shown that *Sargassum spp.*, a brown alga, can be used as parent material for BCs and ACs. Indeed, this pilot study showed that BCs derived from *Sargassum spp.* and pyrolyzed at 700°C for 3 hours are characterized by a high degree of porosity, a large specific surface area and represent a suitable candidate for the adsorption of CLD with an important reduction of CLD environmental availability in artificial soil and Nitisols (Ranguin et al. 2021). These promising results need further investigations in order to confirm these results and study another French West Indies type of soil. optimize the efficiency of this strategy. Indeed, others factors may influence the effectiveness of

BC/AC. It has been shown that a particle size reduction of BC is beneficial for certain heavy metals sequestration. Indeed, Zheng et al. 2017, have shown that the finest fraction (<0,5mm) of rice straw biochar has led to a significant reduction of Cd (-45%) and Zn (-70%) concentration in Pakchoi shoot. The potential effect of BC/AC particle size on pollutant sequestration as CLD remains understudied. Another factor that may alter the BC/AC effectiveness is the amendment rate. Indeed, in previous papers related to soil rehabilitation, this parameter

was found to vary from 0,25% to 10%. Thus, the optimal amendment rate needs to be assessed since it is dependent on multiple factors such as the type of BC/AC or the type of soil.

The aim of this study was to (i) characterize the effect of various particle sizes of Sargassum BC/AC on the CLD environmental availability and to (ii) study the effects of the amendment rate on CLD sequestration in Nitisol and Andosol.

2. Materials and methods

In a first experiment, CLD contaminated Andosol and Nitisol were amended with 2% of four carbonaceous matrix (3 ACs and 1 BC) divided into four particles size classes (<50µm, 50-150µm, 150-200µm and >200µm). In a second experiment, the contaminated soils were amended with the biochar at five application rates (0, 0.25, 0.5, 1 and 2 % (w/w)).

2.1. Preparation of the sequestering matrix

Three different types of carbonaceous matrices were prepared from *Sargassum spp.*: H₃PO₄ activated carbon (SargH₃PO₄), H₂O activated carbon (SargH₂O), biochar (Ch Sarg700). Each matrix was produced by COVACHIM M2E laboratory (Antillean University, Point-à-Pitre). Details of the production process of these matrices are already described in Ranguin et al. (2021). An additional commercial AC (ORBO™, Sigma-Aldrich CO. LLC) was also tested as a

positive control. A brief description can be found in Table 1, as well as their major textural properties.

2.2. Characterization of the BC/AC particle size

For the first experiment, each carbonaceous matrix was grinded for 2 minutes at 13000 rpm by an analytical grinder (IKA Tube-Mill 100, Staufen, Germany) using a stainless MMT40 bowl. The particle size was characterized using a laser diffraction analyzer (Mastersizer 3000, Malvern Panalytical, France). Distribution of the size of activated carbons and biochars samples were obtained from the device acquisition software as the mean of 15 analyses (Mastersizer 3000, version 3.81, Malvern Panalytical, France). Following this characterization, four classes of granulometry have been determined by sieving: <50µm, 50-150µm, 150-200µm and >200µm.

	Precursor	Pyrolysis	Activation	Textural parameters		
				BET Surface area (m ² .g ⁻¹)	V _{Micropores} (D-R) (cm ³ .g ⁻¹)	V _{Mesopores} (BJH) (cm ³ .g ⁻¹)
Ch Sarg700	<i>Sargassum spp.</i>	700°C for 3h	None	872	0.44	0.55
Sar H ₂ O	<i>Sargassum spp.</i>	700°C for 1h	Physical: Steam (H ₂ O) at 600°C	109	0.12	0.09
SargH ₃ PO ₄	<i>Sargassum spp.</i>	700°C for 3h	Chemical: Phosphoric acid H ₃ PO ₄ (0.5:1) ^a	877	0.30	0.46
ORBO™	Coconut	N/A	N/A	1121	0.46	N/A

Table 1: Manufacturing details and physical characterization of the different carbonaceous matrices (Ranguin et al. 2021) N/A: information no provided by the manufacturer

^a: g H₃PO₄ /g of Sargassum

2.3. Amendment of soil

For the experiment 1 an amendment rate at 2% was applied to Nitisol and Andosol samples. These samples were mixed for 10 minutes with 20 mg of one of the 4 different sequestering matrices and grinded to one of the 4 different particle sizes. At the end of this experiment the most efficient matrix (type of BC/AC and particle size) was selected for experiment 2. In this second experiment Nitisol and Andosol samples were amended with 4 different rates (0,25%-0,50%-1%-2%) with the selected matrix.

In both experiments, water was added to reach up to 15% of humidity and were let aged for 4 months at 4±1°C. For

both experimental phases, each amendment was realized in quadruplicate.

2.4. Assessment of chlordecone environmental availability

The used method was an adaptation of the Test ISO/DIS 16 751 method A (Delannoy et al. 2018). This method was realized in the platform Bio-DA (Vandoeuvre-lès-nancy, France). All chemicals used during the analytical processes were of Pesticide Residues grade and glassware equipment was cleaned with an alkaline detergent, (RBS T 105, Carl Roth GmbH, Karlsruhe, Germany). Briefly, for each

sampling, 400 ± 1 mg were weighed into a test tube to which was added 4 mL of an ultra-pure aqueous solution of cyclodextrin (hydroxypropyl- β - cyclodextrin, CAS: 128446-35-5). After a 20-hour horizontal agitation $50 \mu\text{L}$ of ^{13}C -CLD (Azur Isotope, Istres, France) at $10 \mu\text{g}\cdot\text{mL}^{-1}$ was added and left to decant for 1 hour and then extracted 2 times with ethyl acetate (liquid-liquid extraction) then evaporated under nitrogen. At last $500 \mu\text{L}$ of acetonitrile were added and the tube was vortexed. The final solution was transferred to a GCMS tube.

2.5. GC-MS/MS analysis

Chlordecone analysis was performed on a gas chromatograph coupled to a triple quadrupole mass spectrometer (TSQ 9000 GC-MS/MS ThermoFisher Scientific, Massachusetts, USA), equipped with silica capillary column (TG-5SilMS, 30m length, 0.25mm internal diameter, 0.25 μm film thickness, ThermoFisher Scientific). Splitless injection was performed on a programmable temperature vaporizing injector at 75°C with a gradual heating to 300°C at the rate of $2.5^\circ\text{C}/\text{s}$ and 3 min at 300°C . The cleaning of the injector was at 330°C since 20min. A constant flow of $1.2\text{mL}/\text{min}$ of helium was used as carrier gas and argon was used as collision gas. The analyze was performed as follows: 1.5 min at 40°C , gradual heating to 90°C at the rate of $25^\circ\text{C}/\text{min}$, 1.5min at 90°C , gradual heating to 180°C at the rate of $25^\circ\text{C}/\text{min}$, gradual heating to 280°C at the rate of $5^\circ\text{C}/\text{min}$. The transfer line temperature and the ion source temperature were set at 250°C and

3. Results

First, the results highlight the differences between the two types of soil. Indeed, the reduction of CLD environmental availability was more important in Nitisol than in Andosol. Secondly, a matrix effect was statistically observed $P < 0.001$ for both soils. Finally, a particle size effect was also statistically noted ($P < 0.002$ in Nitisol and $P < 0.001$ in Andosol).

3.1. Soils effect on CLD sequestration

For Nitisol, the environmental availability of CLD was of $28 \pm 5.0\%$ (mean \pm SE, $n=4$), $61 \pm 2.5\%$, $73 \pm 2.6\%$ and $79 \pm 2.7\%$ for AC SargH₂O, AC SargH₃PO₄, Biochar of Sargasso and AC ORBOTM, respectively. For Andosol the following results were obtained: $10 \pm 4.3\%$, $32 \pm 3.7\%$ and $47 \pm 6.5\%$ for AC SargH₃PO₄, Biochar of Sargasso and AC ORBOTM, respectively. Thus, the sequestration strategy performed differently in the two types of soil (Andosol and Nitisol). For all four carbonaceous materials the sequestration was more efficient in Nitisol.

3.2. Matrices effects on CLD sequestration

Figure 1 and 2 showed that for both soils, two matrices were more effective in reducing the CLD environmental availability. These matrices were the ORBOTM and the biochar of Sargasso. The contrast of effectiveness of the carbonaceous matrices was very striking in Nitisol. Indeed, by considering all particle size classes, ORBOTM and Biochar of Sargasso, allowed a reduction of $79 \pm 2.7\%$ and $73 \pm 2.6\%$, whereas AC SargH₃PO₄ and AC SargH₂O showed a smaller reduction of $61 \pm 2.5\%$ and $28 \pm 5.0\%$

300°C , respectively. The mass spectrophotometer was operated in electron impact ionization mode with electron energy of 70eV. Three transitions were selected, one for quantitation (Q) and two for qualification. For chlordecone, (Q) $269.8 > 234.9$, $269.8 > 140.9$, $234.8 > 140.9$ were chosen with collision energy 12, 34, 24 respectively. For ^{13}C -CLD used as the internal standard, (Q) $291.8 > 221.9$, $276.8 > 241.8$, $276.8 > 239.8$ were chosen with collision energy 26, 12 and 12 respectively. Blank with solvent were analyzed between each sample to confirm the absence of interferences peaks. Calibration standard solutions were analyzed at the beginning and end of each sequences. The calibration curve was constructed with concentration versus the ratio (peak analyte area)/(peak internal standard area).

2.6. Statistical analysis

For the first experiment, a three-factor ANOVA was used with the CLD concentration as the quantitative factor and the matrix type and particle size as qualitative factors. For the second, a two-factor ANOVA was used with the CLD concentration as quantitative factor and the amendment rate as qualitative factor. Both ANOVA tests were followed by a Tukey-Kramer test, performed with R software (4.0.1, Vienna). Differences were considered significant at $P < 0.05$. For both experiments, the number of replicates for each modality was equal to 4 except for the control which was equal to 5 (for the first experiment) and 2 (for the second experiment). Differences were considered significant at $P < 0.05$.

respectively. For Andosol, the results were less obvious but the two matrices still stand out from the others. In fact, for Andosol, ORBOTM and biochar of Sargasso allowed a reduction of $47 \pm 6.5\%$ and $32 \pm 3.8\%$ when the other two matrices showed reductions of less than 10% or no reduction at all.

In view of the results, an efficiency gradient appeared between the matrices for the two soils: AC ORBOTM \geq Biochar of Sargasso $>$ AC SargH₃PO₄ \geq AC SargH₂O

3.3. Particle size effects on CLD sequestration

For Nitisol, two scenarios appeared concerning the impact of the particle size of the carbonaceous matrices on CLD environmental availability. For the first, no particle size impact was observed. This was the case for ORBOTM and SargH₂O activated carbon for which, no significant difference for CLD environmental availability were observed between the four particle size classes (Figure 1). In the second case, for biochar of Sargasso and the H₃PO₄ activated carbon, a difference in efficiency was seen between certain particle size classes. For biochar of Sargasso, the smallest particle size ($< 50 \mu\text{m}$) showed a reduction up to $80 \pm 1.0\%$ of the environmental availability, much larger than that caused by the largest particles size class ($> 200 \mu\text{m}$) which was up to $68 \pm 2.3\%$. In the case of AC SargH₃PO₄, the results of the two largest particle size classes ($< 200 \mu\text{m}$; $200-150 \mu\text{m}$) were statistically similar and the two smallest ($< 50 \mu\text{m}$; $50-150 \mu\text{m}$) also. However, these two groups were different, the smallest particles showed a CLD environmental availability reduction more important

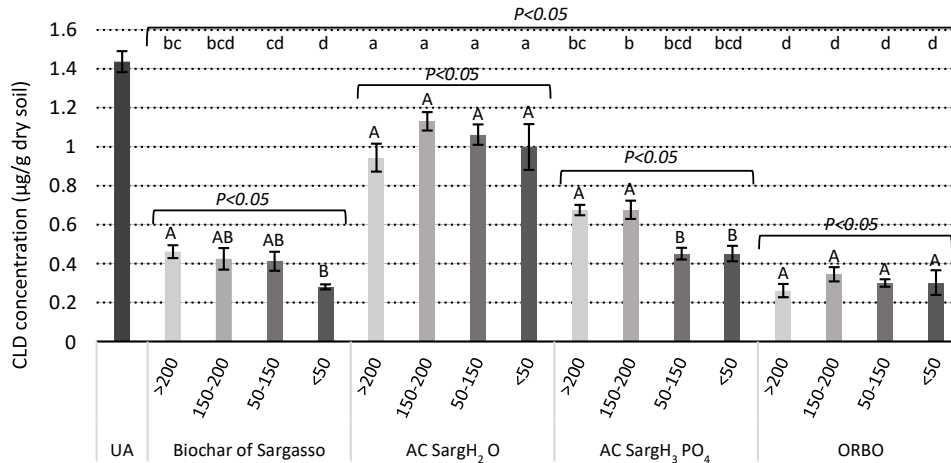


Figure 1: Particle size effect on the environmental availability of chlordecone using different carbonaceous matrices as a sequestration strategy in Nitisol

UA = unamended soil

Values correspond to the mean \pm SE (n=4)

Mean values with different superscript letters (a, b, c, d) are statistically different ($P < 0.05$) between size classes of all matrices (from ANOVA test).

Mean values with different superscript letters (A and B) are statistically different ($P < 0.05$) between size classes of the same type of matrix (from ANOVA test)

The control group was statistically different from the others ($P < 0.05$) using Dunnett test.

ANOVA results: Particle size effect ($P < 0.002$), Type of matrix effect ($P < 0.001$), Interaction ($P < 0.04$)

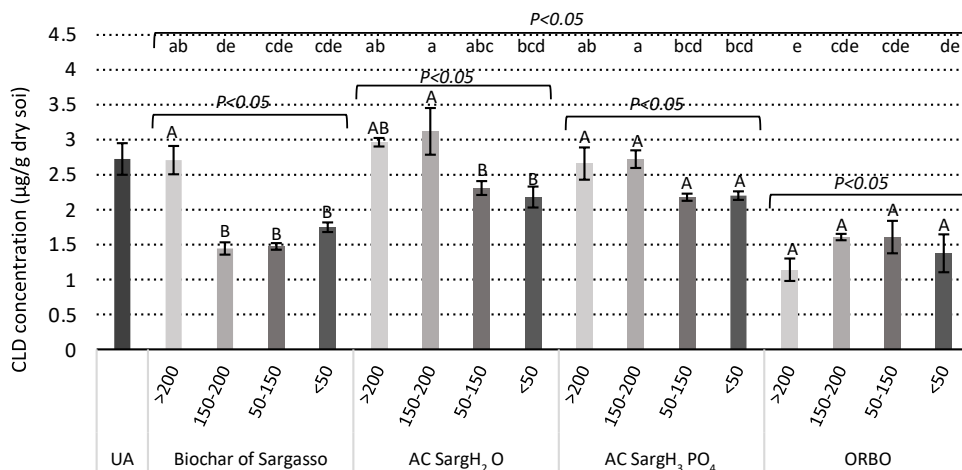


Figure 2: Particle size effect on the environmental availability of chlordecone using different carbonaceous matrices as a sequestration strategy in Andosol

UA = unamended soil

Values correspond to the mean \pm SD (n=4)

Mean values with different superscript letters (a, b, c, d) are statistically different ($P < 0.05$) between size classes of all matrices (from ANOVA test).

Mean values with different superscript letters (A and B) are statistically different ($P < 0.05$) between size classes of the same type of matrix (from ANOVA test)

The control group was statistically different from the others ($P < 0.05$) using Dunnett test.

ANOVA results: Particle size effect ($P < 0.001$), Type of matrix effect ($P < 0.001$), Interaction ($P < 0.001$)

than for the largest particles. Thus, the classes $>200\mu\text{m}$ and $150-200\mu\text{m}$ allowed a reduction up to $53\pm 1.9\%$ and $53\pm 3.3\%$ and the classes $50-150\mu\text{m}$ and $<50\mu\text{m}$ showed a reduction of $69\pm 2.1\%$ and $69\pm 2.8\%$.

For Andosol, two scenarios were also observable. For ORBO™ and AC SargH₃PO₄, no particle sizes effect was observed. Indeed, as shown in figure 2 there was no difference between the four particle sizes classes of each carbonaceous matrices. For the two others tested matrices the particle size had an impact. Biochar of Sargasso data

showed that the largest particles size class was statistically different from the other three classes. For the particle size >200µm, there was no reduction in CLD environmental availability (reduction up to 0.6±7.4%), when three others classes (200-150µm; 150-50µm and <50µm) allowed a more important reduction up to 47±3.2%, 46±1.7% and 36±2.5%. For SargH₂O activated carbon a similar trend is observed; the >200µm and 200-150µm classes were similar just as 150-50µm and <50µm classes. Indeed, the first group of SargH₂O showed non CLD environmental availability reduction when the second group allowed a reduction up to 15±3.6% (50-150µm), 20±5.5% (<50µm) for SargH₂O.

Finally, for both soils, when a particle size effect was observed, the classes less than 150µm led to the largest reduction in CLD environmental availability.

3.4. Amendment rate impact on CLD sequestration

To study the impact of the amendment rate on the environmental availability of chlordecone, the most efficient granulometries (50µm and 50-150µm) of the Biochar of Sargasso were chosen (Figure 1 and 2). Table 2 indicates the results of the environmental availability in CLD for the two soils according to the BC amendment rate.

In Andosol, the greatest reduction of CLD environmental availability, 67±4.3%, was achieved with a 2% amendment rate followed by 1% with a reduction of 57±1.6%. For Nitisol, there was no significative difference between 0.5%, 1% and 2% amendment (Table 2). But in both soils, the results showed that the higher the rate of amendment, the higher the sequestration efficiency.

BC type	Amendment rate (%)	CLD environmental availability ([CLD] µg/g dry soil)	
		Nitisol	Andosol
BioSarg ≤150µm	0 (UA)	1.15 ± 0.07 ^a	4.26 ± 0.58 ^a
	0.25	0.70 ± 0.04 ^b	2.80 ± 0.08 ^b
	0.5	0.55 ± 0.06 ^{bc}	2.43 ± 0.12 ^b
	1	0.59 ± 0.17 ^c	1.85 ± 0.07 ^c
	2	0.41 ± 0.08 ^c	1.41 ± 0.18 ^d

Table 2: Amendment rate effect of biochar of Sargasso on the environmental availability of chlordecone in Nitisol and Andosol

UA = unamended soil

Values correspond to the mean ± SE (n=8)

Mean values with different superscript letters (a, b, c, d) are statistically different (P<0.05), with an ANOVA test.

The control group was statistically different from the others (P<0.05) using Dunnett test.

4. Discussion

4.1. Particle size impact on CLD sequestration

Overall, a decrease of BC/AC particles size leads to a decrease in the environmental availability of CLD in soils (Fig.1 and 2), being significant for biochar of Sargasso in both soils and AC SargH₂O in Andosol. The improved efficacy on CLD sequestration may be related to the BC/AC's specific surface area variation when the particle size diminishes. Indeed, Zheng's (2017) publication showed that a decrease in particle size is correlated with an increase in the specific surface area of rice straw and corn stalk biochar's. Furthermore, the sequestration power of BC/AC is, among other thing, positively related to the specific surface area of these carbonaceous materials (Ranguin et al. 2021). The sequestration of organic pollutants by carbon geosorbents involves several phenomena such as physical-sorption on the surface of BC/AC. This immobilization process has therefore to be linked to the BC/AC's specific surface area. The reduction of particle size, due to an increase of the specific surface area of the carbon matrices, may increase the number of bonds between the surface of BC/AC and CLD resulting in increased immobilization of organic pollutants. Grinding biochar may also have increased the access to the matrix porosity and thus leads to a better reduction of the chlordecone environmental availability.

4.2. Amendment rate impacts

As expected, an increase in the BC amendment rate in both soils leads to a stronger decrease in the available CLD

concentration (Table 2). These results are in line with previous data which demonstrated the impact of the amendment rate on the ability of the DDTs to be sequestered by activated carbons (Tomaszewski et al. 2007). Thus, the rise of the biochar amount in soils logically increases contact surfaces with contaminated soil and result in a higher trapping of CLD molecules.

4.3. Influence of soil characteristics on the environmental availability of CLD

The addition of biochars and activated carbons to soils resulted in a greater decrease in relative environmental availability in Nitisols than in Andosols. Indeed, even if the two soils are composed mainly of clay, the shape and composition of these are different. The Nitisols are made of halloysite clays arranged in sheets while Andosols are made of allophane clays in globular structure. Allophanes are particular clays with a high capacity to retain and protect organic matter and therefore pollutants related to this material. Moreover, the higher the rate of allophane in a soil, the greater the specific surface area of the soil and the possibility of allophane aggregate formation. These aggregates have specific properties resulting in a large ability to bind chemical species (Woignier et al. 2007). Therefore, CLD is much more bound and retained in Andosols than in Nitisols as previously shown by Cabidoche et al. 2009. These authors estimated the depollution time of CLD by leaching in Nitisols of 60-100 years and in Andosols of 500-700 years. This information certainly explains the

difference in efficiency of the same BC/AC between the two soils.

4.4. Further investigation needed

Overall, the results of both experiments give interesting perspective in terms of CLD sequestration, by carbonaceous matrix, in Antillean soils. They demonstrate the potential of some carbonaceous matrices originated from *Sargassum* to limit the environmental availability of chlordecone. However, the experiments considered only the sequestration component of the BC/AC without testing the impact on soil fertility. In fact, BC/AC may, on the one hand, immobilize chemical elements in the soil that will no longer be available to plants and thus affect crop production. The

work of (Kim et al. 2015) showed for example that 0.5 and 1% amendment rates of orange pulp biochar's caused an increase in lettuce biomass while 2, 5 and 10% rates caused a decrease on this biomass. On the second hand, the raw material used for the BC/AC production may negatively impact the soils dynamics. For example, *Sargassum spp* is known to be a material with variable amounts of heavy metals. Thus BC/AC derived from sargassums may also contain heavy metals that could be released into soil and affect its fertility. Thus, in coming studies it appears important to take into consideration the impact of BC/AC on soil life when choosing the amendment rate. Overall, a compromise as to be find between the efficiency of sequestration and the modification of soil fertility.

5. Conclusion

Addition of biochar or activated carbons derived from *Sargassum spp.* to CLD contaminated soils reduced the chlordecone availability in soil. The results showed that the reduction level depends on the type of carbonaceous matrix. Indeed, the highest levels of reduction were achieved, in both soils, with the biochar of Sargasso and the ORBO™ (a commercial activated carbon). These matrices are characterized by a large specific surface area and a large volume of micropore, two important parameters in sequestration processes. Regarding particle size, 3 of the 4 carbonaceous matrices (SargH₂O, SargH₃PO₄ and ORBO™) did not show significant differences in both soils. For the Sargasso biochar a reduction of particle size under 150µm leads to a reduction of chlordecone environmental

availability of 76±2.2% in Nitisol and 41±2.1% in Andosol. The different result in the two soils is related to the physical characteristics and more precisely to the clays proprieties. Indeed, Andosol are made of allophane clays in globular structure that protect organic matter and therefore pollutants related to this material. Chlordecone is better retained in Andosols and therefore the same carbon matrix leads to a greater decrease in environmental availability in Nitisol. An increase of biochar of Sargasso amendment rate allows a decrease of CLD environmental availability in both soils. In Nitisol, there is no significant difference between 1% and 2% amendment rate, when in Andosol there is a significant difference between these two rates.

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Ethical Approval: Not applicable

Consent to Participate: All authors were agreed to participate to this study

Consent to publish: All authors read and approved the final manuscript.

Author Contributions: The study conception and design were developed by Matthieu Delannoy, Cyril Feidt, and Guido Rychen. Material preparation and data collection were performed by Barbara Souza Rodrigues, Sarra Gaspard, Florentin Michaux, and Claire Soligot. Data analysis was carried out by Barbara Souza Rodrigues, Matthieu Delannoy, Yves Le Roux, and Perrine Stephan. The first draft of the manuscript was written by Perrine Stephan and all authors commented on the previous version of the manuscript. All authors read and approved the final manuscript.

Availability of data and materials: The data presented in this study are available on request from the corresponding author.

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