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Ronald Ranguin, Corine Jean-Marius, Christelle Yacou, Sarra Gaspard, Cyril Feidt, et al.. Reduction of chlordecone environmental availability by soil amendment of biochars and activated carbons from lignocellulosic biomass. Environmental Science and Pollution Research, 2020, 27 (33), pp.41093-41104. 10.1007/s11356-019-07366-2 . hal-02510064

HAL Id: hal-02510064
https://hal.univ-lorraine.fr/hal-02510064

Submitted on 8 Mar 2022

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Reduction of chlordecone environmental availability by soilamendment of biochars and activated carbonsfrom lignocellulosic biomass

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Published in Environmental Science and Pollution Research. Available online: 23/01/2020 https://doi.org/10.1007/s11356-019-07366-2

Keywords

Chlordecone . Environmental availability . Activated carbon . Biochar . Soil

Abstract

Chlordecone (kepone or CLD) was formerly used in French West Indies as an insecticide. Despite its formal ban in 1993, high levels of this pesticide are still found in soils. As such, sequestering matrices like biochars or activated carbons (ACs) may successfully decrease the bioavailability of halogenated compounds like CLD when added to contaminated soils. The present study intends (i) to produce contrasted sequestering matrices in order to (ii) assess their respective efficiency to reduce CLD environmental availability. Hence, the work was designed following two experimental steps. The first one consisted at producing different sequestering media (biochars and ACs) via pyrolysis and distinct activation processes, using two lignocellulosic precursors (raw biomass): oak wood (*Quercus ilex*) and coconut shell (*Cocos nucifera*). The chemical activation was carried out with phosphoric acid while physical activation was done with carbon dioxide and steam. In the second step, the CLD environmental availability was assessed either in an OECD artificial soil or in an Antillean contaminated nitisol (i.e. 2.1 µg CLD per g of soil Dry Matter, DM), both amended with 5wt% of biochar or 5wt% of AC.

These both steps aim to determine CLD environmental availability reduction efficiency of these medi a when added (i) to a standard soil material or (ii) to a soil representative of the Antillean CLD contami nation context. Textural characteristics of the derived coconut and oak biochars and ACs were determined by nitrogen adsorption at 77K. Mixed microporous and mesoporous textures consisting of high pore volume (ranging from 0.38 $cm^3.g^{-1}$ to 2.00 $cm^3.g^{-1}$) and specific (BET) surface areas from 299.9 $m^2.g^{-1}$ to 1285.1 $m^2.g^{-1}$, were obtained. Overall, soil amendment with biochars did not limit CLD environmental availability (environmental availability assay ISO/DIS 16751 Part B). When soil amended with ACs, a significant reduction of the environmental availability in both artificial and natural soils was observed. AC soil amendment resulted in a reduced CLD transfer by at least 65% ($P<0.001$) for all lignocellulosic matrices (excepted for coconut sample activated with steam, which displayed a 47% reduction). These features confirm that both pore structure and extent of porosity are of particular importance in the retention process of CLD in aged soil. Owing to its adsorptive properties, AC amendment of CLD contaminated soils appears as a promising approach to reduce the pollutant transfer to fauna and biota.

Introduction

Chlordecone (CLD) is a chlorinated persistent organic pollutant (POP) particularly recalcitrant to biochemical degradation due to its very stable bishomocubane structure (composed by two methylene groups on a cubane skeleton, a cubic cage of carbon atoms as described by Marchand

1989) (Cabidoche et al. 2009; Matolcsy et al. 1988). Its broad application as an insecticide from 1972 to 1993, especially in the French West Indies to control the proliferation of a banana pest (i.e. *Cosmopolites sordidus)*, resulted in high levels of CLD contamination in plantation soils (>1 mg/kg for CLD in numerous areas) (Cabidoche et al. 2009; Le Déaut and Procaccia 2009; Levillain et al. 2012). Despite CLD formal ban in 1993, soil contamination is expected to last several centuries due to its low water solubility and its high affinity for organic matter (with K_{OC} in the range of 2.5 - 20 $m^3.kg^{-1}$) (Cabidoche et al. 2009), if no remediation process is applied. In this context, CLD soil contamination constitutes a major transfer risk of CLD transfer to fauna and biota (Bouveret et al. 2013; Delannoy et al. 2018; Jurjanz et al. 2014, 2016, 2017).

A promising way to reduce soil-bound CLD transfer to biota and fauna is to sequestrate the pollutant within the soil matrix. Activated Carbons (ACs) have shown efficient long-term sequestration for halogenated compounds (Choi, et al. 2014; Hilber et Bucheli 2010; Jakob et al. 2012; Perelo 2010), little evidence is available regarding the effects of ACs on CLD environmental availability (as the soil pollutant fraction susceptible to be mobilized and accessible for biological uptake) in contaminated soils (Delannoy et al. 2018). Although successful AC amendment application trials for polychlorinated biphenyls' (PCBs) sequestration in soils were performed (Denyes et al. 2012; Denyes et al. 2013, 2016), so far, no attempt has been made concerning the immobilization of CLD in an Antillean soil.

Biochars, which can be defined as pyrolyzed biomass or organic waste materials under very low oxygen conditions (without any activation process), may also be of interest in this perspective (Ahmad et al. 2014). Biochars are usually characterized by lower specific surface area and microporosity volume than ACs, which could significantly limit the sequestration and subsequent bioavailability reduction factor of organic contaminants (Ahmad et al. 2014). In view of CLD-contaminated potential land management, *in-situ* soil pollutant sequestration methods based on the use of ACs or biochars, could be a valuable strategy to limit the contaminant transfer from soil to biota and fauna. The proposed strategy could further involve locally produced biochars and ACs. Indeed, the latter represents an eco-friendly solution seeking to solve the serious environmental problem of contamination by chlorinated pesticides while improving the value of residues. The production of ACs using locally available waste such as coconut coir (coconut fiber) via chemical and physical activation methods offers the great opportunity for future economic utilization of this cheap and abundant agriculture biomass.

This study intends (i) to produce contrasted sequestering matrices in order (ii) to assess their respective efficiency to reduce CLD environmental availability in both an OECD artificial soil and an Antillean contaminated nitisol. These both steps aim to determine CLD environmental availability reduc¬tion efficiency of these media when added (i) to a standard soil material (ii) or to a soil representative of the Antillean CLD contamination context. For this purpose, normalized a standardized ISO *in vitro* test (environmental availability assay ISO/DIS 16751) was used (ISO 2015).

Material and Methods

The work was set in two experimental steps. The first one consisted of the production of contrasted sequestering media (biochar and ACs) using different activation processes on two lignocellulosic precursors (raw biomass): oak wood (*Quercus ilex*) and coconut shell (*Cocos nucifera*). Then, their physico-chemical properties were characterized by N_2 sorption, scanning electron microscopy and thermogravimetric (TG) analysis. In the second step, the CLD environmental availability was assessed either in an OECD artificial soil or in an Antillean contaminated nitisol (2.1 µg CLD per g of soil Dry Matter), amended with 5wt% of biochar or 5 wt% of AC.

2.1. Production and characterization of experimental matrices

2.1.1. AC and biochar synthesis from raw materials

Coconut shells of the dwarf variety (Cocos nucifera), were harvested in Saint-Claude, Guadeloupe (French West Indies), then peeled and crushed. Oak wood/bark was obtained from Nancy, France. All samples were firstly cut and then dried in an oven at 105°C for 48 h to remove the moisture content until reaching a content around 10% as recommended in the literature for

the pyrolysis of biomasses (Daltro et al. 2018). They were then grounded using the Retsch SM 100 to pass through a 4-mm screen and sieved with the Retsch AS 200 sieve shaker (amplitude 2.00, 60-s interval time, and 30-min total running time) into particle size ranging from 0.4 to 1 mm (Altenor et al. 2009), and subsequently stored in the same oven. In this work, three types of matrices were obtained from coconut and oak including biochars, chemically activated carbons, and physically activated carbons.

Biochars were produced by pyrolysing the precursors at 700 °C for 1 h in a tubular furnace (Carbolite Gero® CTF 12/75/700) under a nitrogen flow of 80 mL.min^{-1}, and a heating rate of 10 C.min^{-1} and maintained at the final temperature for 1 h.. The resultant samples will be later labeled oak biochar or coconut biochar.

Chemically activated carbons were obtained following a procedure published in previous work (Altenor et al. 2009). Briefly, an appropriated amount of precursor was soaked during 24 h in phosphoric acid (H_3PO_4, 85 wt%), resulting in a impregnation ratio of 1.5:1 (g H_3PO_4:g precursor). Samples were subsequently dried in an oven at 110 °C during 4 h, followed by their pyrolysis using the same conditions as the above-mentioned biochars. This resulted in samples herein referred to as Oak P1.5 and Coco P1.5 for Oak and Coconut respectively.

For physical activation, the oak and coconut biochars were heat treated under three gasses, either steam alone, CO2 alone, or with CO_2/H_2O mixture, carried by a nitrogen flow (80 mL.min^{-1},), until a burn-off of approximately 50% was achieved. The burn-off (%) or degree of carbon loss refers to the percentage of mass loss, which indicates efficient activation (Chang, Chang, et Tsai 2000; Gaspard et al. 2007). The burn-off refers to the weight difference between the original char and the activated carbon divided by the weight of original char with both weights on a dry basis: this is calculated according to the following equation:

$$\text{« burn} - \text{off »\%} = 1 - \frac{W_{final}}{W_{initial}} * 100 \quad (1)$$

with $W_{initial}$: weight of biochar

W_{final} : mass of carbon after activation

Samples obtained from oak wood were labeled Oak CO_2, Oak CO_2/H_2O, Oak H_2O and from Coconut shell were labeled Coco CO_2, Coco CO_2/H_2O, Coco H_2O, depending of their physical activation conditions.

2.1.2. ACs and biochars characterization

Generally, thermal treatment in an inert atmosphere of lignocel-lulosic matters consists on the progressive degradation of their embedded biopolymers leading to the reorganization of the carbon phase. As such, thermogravimetric analysis (TG) repre¬sents a convenient semiquantitative technique for anticipating the preparation of the ACs and biochars. Thermogravimetric analysis of the two precursors (coconut *shell* and oak wood*)* were carried out using a LABSYS Evo-Setaram instrument under a nitrogen flow of 80 mL.min^{-1} and heating rate of 10 °C.min^{-1}.

Microstructural characteristics of the samples were evaluated via scanning electron microscopy**,** operating at 20 KV (SEM, Hitachi S 2500).

The textural structure of the carbonaceous materials was analyzed N_2 sorption at 77K in a Micromeritics ASAP 2020 apparatus. Prior to analysis, samples were degassed 24 h under vacuum at 300 °C (heating rate of 8 °C.min^{-1}). Specific surface area was determined according to the Brunauer, Emmett and Teller model (Brunauer, Emmett, et Teller 1938). Dubinin–Radushkevich (D-R) equation was used to evaluate the micropore volume whilst the mesopore volume was estimated using the Barrett–Joiner–Halenda (BJH) theory, calculated from the desorption branch (Barrett, Joyner, et Halenda 1951). Total pore volume was calculated by summing the micropores and mesopores volume. The mean pore diameter (Dp) was calculated according to the following equation $4 \times V_T/S_{BET}$ (Durimel et al. 2013).

2.2. Artificial soils preparation

Artificial soils were prepared as described in Table 1 accordingly to the OECD guideline 207 (OECD 1984). Briefly, the common fraction present in each artificial soil contains sand and kaolin (78:22, m:m dry basis) (Sigma-Aldrich, St Louis, USA) as well as 10% (dry mass basis of whole soil) of sphagnum peat (Tourbe de Sphaigne, Florentaise, Truffaut, Paris). An additional portion constituted by biochar or AC was then added (5% dry mass basis of whole soil) as described in Table 1. All artificial soils were spiked with 100 µg of CLD (Kepone, Supelco, Sigma Aldrich, Saint-Louis) per g of dry matter.

Briefly, a CLD mix was spread over artificial soils using an aqueous mixture of CLD (20:80; methanol:water vol:vol). After spiking, solvent traces were evaporated under an extractor hood overnight. At last, ultrapure water was added to reach 18% of mass of the wet soil. Then, all artificial soils were aged during 80 days at room temperature (20 ± 2°C) prior the following experimental parts.

2.3. Nitisol amendment

Contaminated nitisol soil (2.1 µg CLD per g of soil Dry Matter) was sampled in French West Indies in the previous "croissant bananier" as described elsewhere (Jurjanz et al. 2014) and dried at room temperature until mass stabilization. Then, 5% of the condensed materials (dry mass basis) was added to 2g subsamples of this soil (n=3). Six not amended subsamples were used as control. Finally, ultrapure water was added to reach 18% of mass of the wet soil. All soils were aged during 80 days at room temperature (20 ± 2°C) prior the following experimental parts.

2.4. Environmental availability assays

Environmental availability assays were performed on each subsamples of artificial and natural soils. These tests were performed on the Bioavailability-Bioactivity (Bio-DA) platform of Université de Lorraine (Vandoeuvre-lès-Nancy, France). The protocol was adapted from the XP ISO/TS 16 751 Part B to fit a 2g soil-sample instead of 5g (ISO 2015). Thus, 600 ± 25 mg of Tenax (60-80 mesh, Sigma-Aldrich, Saint-Louis) were added in an amber collection vial and 28 mL of ultrapure water were spread to preserve the soil:water ratio of the ISO strandar. After a 20h-agitation period at 150 rpm in a horizontal shaker, the tubes were centrifuged (2000 g during 15min) and tenax was recovered using Glass Pasteur pipettes and washed with ultrapure water. As CLD is poorly soluble in petroleum ether the ISO protocol was adapted as follow: tenax was dried during 1h in a 40± 0.5°C ventilated oven. Then, tenax was extracted three times with 10mL acetone using a 10-minutes ultrasonic bath. All extracts were combined and concentrated until 3mL prior GC-MS analyze (7 890A, Agilent Technologies, Santa Clara, USA). Briefly, the mass spectrometer was set at a resolution of 10 000, in electron ionization mode (70 eV electron energy) (5975C, Agilent Technologies, Santa Clara, USA). Single Ion Monitoring (SIM) was used to record the two most abundant signals. A DB5MS (25 m × 0.25 mm × 0.25 µm) capillary column from Agilent J&W (Agilent Technologies) was used in splitless mode. The GC temperature program for PCBs analysis was the following: 120 °C (1 min), 40 °C min^{-1} to 220 °C (10 min) and 2 °C min^{-1} to 250 °C and 10°C min^{-1} to 300°C (5 min). Signals were integrated using Chemstation (Chemstation E.02.00, Agilent Technologies, Santa Clara, USA). Quantitation was realized using isotopic dilution by adding ^{13}C CLD (Azur Isotope, 98% grade, Marseille, France) in each sample before analysis.

2.5. Statistical analysis

In order to assess the impact of biochars and ACs on CLD availability and bioavailability, an ANOVA was performed. The ANOVA procedure and the Tukey–Kramer post-hoc test of R version 3.2.3 (R Foundation for Statistical Computing, Vienna, Austria) running the package "car" (Fox and Sanford 2011). Differences were considered significant at $P<0.05$.

Results

3.1. ACs ans biochar characterization

3.1.1. Thermogravimetric behaviour of the precursors

Figure 1 shows the TG and the differential TG (DTG) curves obtained for both coconut and oak precursors. The TG curves highlight the mechanism of conversion of cellulose to carbon which comprises four successive steps. It starts with the desorption of moisture in the samples corresponding to a mass loss of 12.8wt% and 4.4wt% for the oak and coconut, respectively. This implies that a significant peak at around 120°C is observed in both DTG curves. The subsequent mass loss can be assigned to the decomposition of hemicelluloses and glycosidic linkage of cellulose (25.6wt% at around 290°C for oak and 18.0 wt% at around 275 °C for coconut). Likewise, the next region occurring at around 350 °C, is usually attributed to the degradation of cellulose (weight loss up to 50%). Finally, above 400 °C, depolymerization and rupture of C-O and C-C bonds leads to the aromatization and the formation of graphitic layers. Such behaviors are in good agreement with previous studies (Alvarez et Vázquez 2004), (Kim et al. 2006; Ncibi et al. 2014). In addition, it can be observed that thermal stability of the samples was reached from 700°C. As such, the temperature of pyrolysis was chosen

to be set at 700°C during the preparation of the biochars and activated carbon.

3.1.2. Microstructure analysis by scanning electron microscopy

Scanning electron microscopy (SEM° analysis was conducted to examine the microstructure of the samples. SEM images of the oak precursor shown in Figure 2 indicate a relatively homogeneous surface with the presence of spherical or elliptical macropores of various sizes (10 - 50 µm) homogeneously distributed in the cell wall of the precursor. The transverse section highlights the oak vessels oriented parallel to the axis of the wood. These observations are in agreement with the expected microstructure of hard woods which are characterized by the presence of these channels dedicated to the conduction of the sap. SEM micrographs of the resulting biochar suggest that high temperature pyrolysis led to a slight alteration of the sample morphology (some macropores are narrowed and the surface appears slightly damaged). However, no additional porosity could be observed at this stage, as pyrolysis is simply associated with loss of mass followed by clogged pore formation.

The coconut precursor (coir), for its part, exhibits a fibrous microstructure associated with a relatively rough surface (Figure 3). This cell wall is generally made of cellulose embedded in a non-crystalline matrix of lignin. The diameter of these fibers varies from 10 to 100 µm. After pyrolysis at 700 ° C, observations are similar to those of oak, namely no significant change in the porosity of the samples was detected.

3.1.3. Textural properties of ACs and biochars by N2 sorption

Liquid nitrogen adsorption/desorption at 77 K was measured for ACs and biochars . As shown in Figs. 4 and 5**Erreur ! Source du renvoi introuvable.**, the volume of N_2 adsorbed increases suddenly at low relative pressure, which clearly indicates the existence of micropores until a P/P_0 value of 1. The International Union of Pure and Applied Chemistry (IUPAC) classification of adsorption isotherms consists of two adsorption and desorption pathways. Samples Oak H_2O and Oak H_2O/CO_2, Coco CO_2 and Coco P1.5 shows a classical Type IV isotherm shape, associated with capillary condensation that occurs in mesopores. This suggests the coexistence of high microporosity and the presence of mesopores. The values of measured specific surface area are presented in the Table 2. Coco biochar exhibits the lower BET surface area of 299 $m^2.g^{-1}$, and the highest one is obtained for the physically activated samples, and especially Coco CO2, with a BET surface area of 998 $m^2.g^{-1}$.

Samples Oak H_2O, Oak CO_2/H_2O, CocoP1.5, Coco H_2O and Coco CO_2 sample show mesoporous-type porosity. The adsorption-desorption isotherms overlap completely at very low relative pressures and then become rapidly distinct and two different hysteresis loops appear at high relative pressures (P/Po> 0.45). Similarly Oak biochar presents the lower surface area among the Oak carbon samples, with a value of 424 $m^2.g^{-1}$. The BET surface area of the carbon samples obtained by physical activation is around 1000 $m^2.g^{-1}$, and Oak P1.5 has a much higher value of surface area of 1506 $m^2.g^{-1}$.

3.2. CLD environmental availability in artificial soils

The first set of assays involved 13 samples of OECD soils amended by either one of ACs or biochars in order to apprehend the potentialities of sequestration offered by condensed media on CLD availability. The results are presented in Figure 6. CLD environmental availability of the OECD standard soil was 75.7±1.8% indicating that the main part of soil CLD was available. No significant reduction of CLD availability ($P>0.05$) with both biochars in comparison to non-amended OECD standard soil was obtained (oak biochar: 65.2±5.6%; coconut biochar: 67.7±6.8%). A significant reduction (by a factor 2) of CLD-environmental availability was seen when the OECD soil was amended by activated matrices with the ex-ception of Coco H2O sample.

3.3. CLD environmental availability in Antillean nitisol

The second set of experiments involved one Antillean nitisol sample amended by either one of ACs or one of biochars. The results are presented in Figure 7. CLD environmental availability of the nitisol soil was set to 100%. No reduction of CLD availability from amended soils with biochar in comparison to nitisol soil was observed (oak biochar: 105±11%; coco biochar: 103±8%). In contrast, CLD environmental availability for 6 out of 7 activated carbons was in the range of 20 to 40% showing a major reduction compared to the control ($P<0.05$). Steam-activated coconut exhibited higher CLD-environmental availability than the 6 other ACs ($P<0.05$). ORBO activated carbon appeared to be the most effective sorbent reducing CLD-environmental availability to 16±11%.

Discussion

4.1. AC vs biochar characteristics and effectiveness to reduce environmental availability

As thoroughly described in the literature, ACs displayed higher porosity than biochars (Table 2) (Chai et al. 2012; Delannoy et al. 2018). Indeed, the activation process is known (i) to eliminate incomplete combustion materials and (ii) to increase the porosity. As a result, no reduction of environmental availability was obtained when soils were amended with biochars, whereas a significant reduction was obtained with activated carbons (Figs. 6 and 7). This result is in accordance with previous data obtained within OECD soil and for different organic pollutants (Delannoy et al. 2014a; Delannoy et al. 2014b) and CLD (Yehya et al. 2017). It indicates that the pyrolysis process on its own is not sufficient to reach an adequate basal porosity quality and a total surface area which would be needed to bound CLD and consequently to reduce its environmental availability.

Considering the results obtained after amendment of OECD soil (Fig. 8) and nitisol (Fig. 9), a similar pattern of CLD environmental availability reduction was observed for the different studied ACs. Indeed, except for the coconut activated by steam, reduction of environmental availability was in the same range for the OECD soils amended with the different ACs (reduction factor between 13 and 37%). The same trends were observed with AC-amended nitisol. The reduced distinctive sequestration efficiency of the steam-activated coconut could be explained by the low surface area in pore (706 $m2.g^{-}1$) compared to the majority of the activated carbons prepared exhibiting a specific surface values higher than 900 $m2.g^{-}1$. In contrast coco P1.5 prepared by phosphoric activation of coconut exhibiting a specific surface area of 642 $m2.g^{-}1$ was able to reduce CLD environmental availability to a value of 19%. These results may be linked to the higher amount of mesoporous volume than the other ACs. Overall it appears that the textural characteristics like specific BET surface area, total pore volume, and micro- and mesopore volume and mean pore diameter are positively correlated to the CLD environmental availability reduction (Figs. 9 and 10). Considering the total pore volume, a high reduction level of environmental availability was reached for values above 0.5 $cm3.g^{-}1$for both OECD soil and nitisol. Textural properties like micro- and mesopore volumes appear to play a role in this reduction. Indeed, these parameters were much lower for biochars than for ACs (Table 1, Figs. 2, 3, and 4b). As an illustration, the micropore volume appears to be significantly and negatively correlated to the CLD environmental availability (Fig. 8c). This trend was also previously noticed in another set of biochars and ACs (Delannoy et al. 2018).

4.2. Comparison of strategies applied to limit CLD transfer to flora and fauna

The in vitro “environmental availability” studies described and discussed above give interesting insight and perspective in order to limit the CLD transfer from soil to biota and fauna. Indeed, in the French West Indies, no sustainable solution has been found to tackle CLD transfer to flora or fauna. Such transfers pose a major threat for local production of vegetables and food producing animals.

It has to be noted that different research programs are still in place to investigate CLD sequestration by the use of organic amendments like compost (decayed organic material from plants) (Woignier et al. 2016). Regarding the use of compost, one major problem is related to its durability. Indeed, composts are mainly labile carbon sources which are degraded after a few decades (Schmidt et al. 2011), in contrast to ACs that have a time residence of several hundred years (Wang et al. 2016).

Some other studies investigated the in situ reduction of CLD using zero-valent iron compounds for CLD degradation (Mouvet et al. 2011). This approach consists in the addition of large amount of zero-valent iron in anoxic condition in order to modify CLD in less halogenated compounds. Such strategy was efficient to decrease CLD concentration in soil (Mouvet et al. 2011). However, no long-term studies assessed the toxicological and environmental impact of such extensive treatment on soil property and biota.

Several studies have proven that AC and biochar application to soils was able to significantly limit organic pollutants transfer to biota (Ghosh et al. 2011). As an example, reduction levels up to 94% of pollutant transfer were reported on earthworms when using ACs (Denyes et al. 2012, 2013; Langlois et al. 2011; Paul and Ghosh 2011; Wang

et al. 2012). The results of the present study confirm the adequacy of this sequestration strategy for CLD-contaminated soils (Delannoy et al. 2018). In the present study, the minimum environmental availability observed was of about 20% representing 80% reduction of CLD availability after AC amendment. Such reduction transfer implies a significant improvement in terms of CLD contamination of biota. These promising results could even been improved by the optimization of (i) the duration of the maturation and (ii) the rate of application of ACs or biochars.

The effectiveness of carbon amendments in the form of biochars has also been reported in several studies for PCBs, PAHs, and several pesticides (Chai et al. 2012; Denyes et al. 2013, 2016; Gu et al. 2016; Jakob et al. 2012; Kołtowski et al. 2016, 2017; Wang et al. 2012). In these studies, authors reported positive sequestration effects after biochar amendments. In the present study, such reduction was not observed when the soils were amended by biochars. It could be suggested that the bishomocubane structure or chemical characteristic of the CLD imped the sequestration for such matrices.

Another critical point to consider toward in further field application is to ensure the innocuity of soil-amendment by biochars or ACs. Literature assessed thoroughly the environmental toxicological aspect of AC and biochar amendment. Such amendment of soil is known to increase soil water holding capacity as well as microbial activities (Lehmann et al. 2011; Tammeorg et al. 2014). These elements are of benefit for agricultural practices and improve soil water retention (Karhu et al. 2011), as well as for specific fauna like earthworms (Zhang et al., 2019; Liesch et al. 2010). If no comprehensive ecological review is available to apprehend globally the impact of such strategy on ecosystems, the rate of application was proven to be correlated to the toxicity for the soil fauna (Zhang et al., 2019; Gomez-Eyles et al., 2011). Thus, levels equal or above to 10% biochar or ACs show adverse effects on earthworms (Zhang et al., 2019) as well as in plants (Lehmann et al. 2011). Another noteworthy observation is related to the precursor of the ACs or biochars: as an illustration, plant-derived biochars or ACs present lower toxicity than other precursors like manure, hence droppings by immobilization heavy metals and organic pollutants by induction of microbial pollutant degraders (Liu et al. 2018). Although reported toxicity of such strategy only appears at high application rates (higher than 10%), this suggests a wide range of safe application rates to avoid toxicity while ensuring a reduction of POPs transfer.

Conclusion

Soil amendment with 5% of ACs derived from lignocellulosic sources resulted in major reductions of CLD environmental availability (up to 80%). Biochars from the same lignocellu-losic precursors were not effective to reduce environmental availability of CLD as a minimal porosity was obtained. According to these results, the activation process appears to

be crucial to sequestrate CLD in soils. In terms of practical application in situ, the only valuable strategy would consist in soil amendment by ACs like coconut or oak. In order to valorize local green wastes, the production of coconut-based ACs and its amendment to Antillean CLD-contaminated soils will contribute to sustainably limit CLD transfer to ecosystems. For such purpose, the collection, the storage, and the AC production processes have to be locally organized.

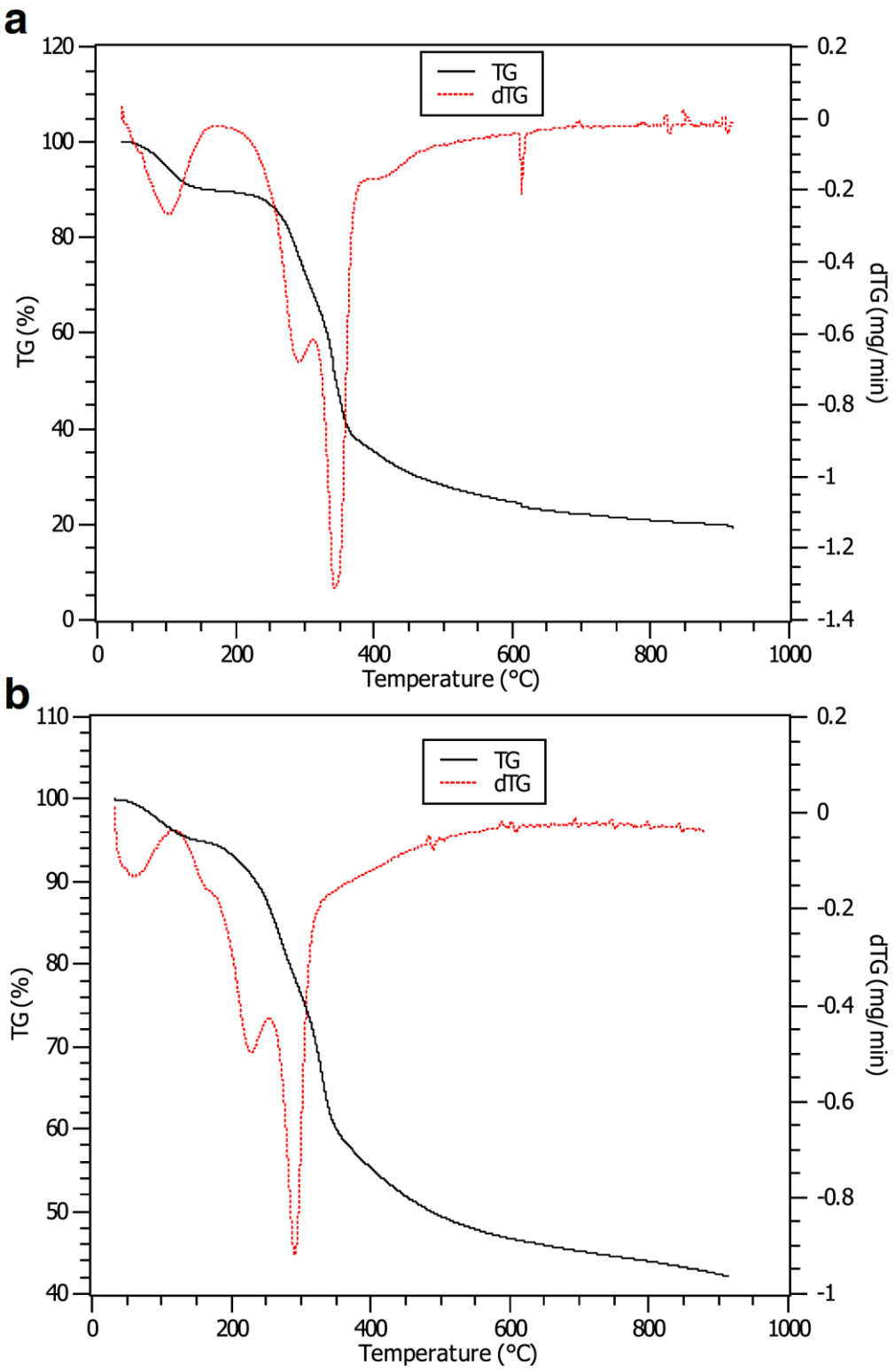

Figure 1 : TGA of (a) oak wood and (b) Coconut nucifera.

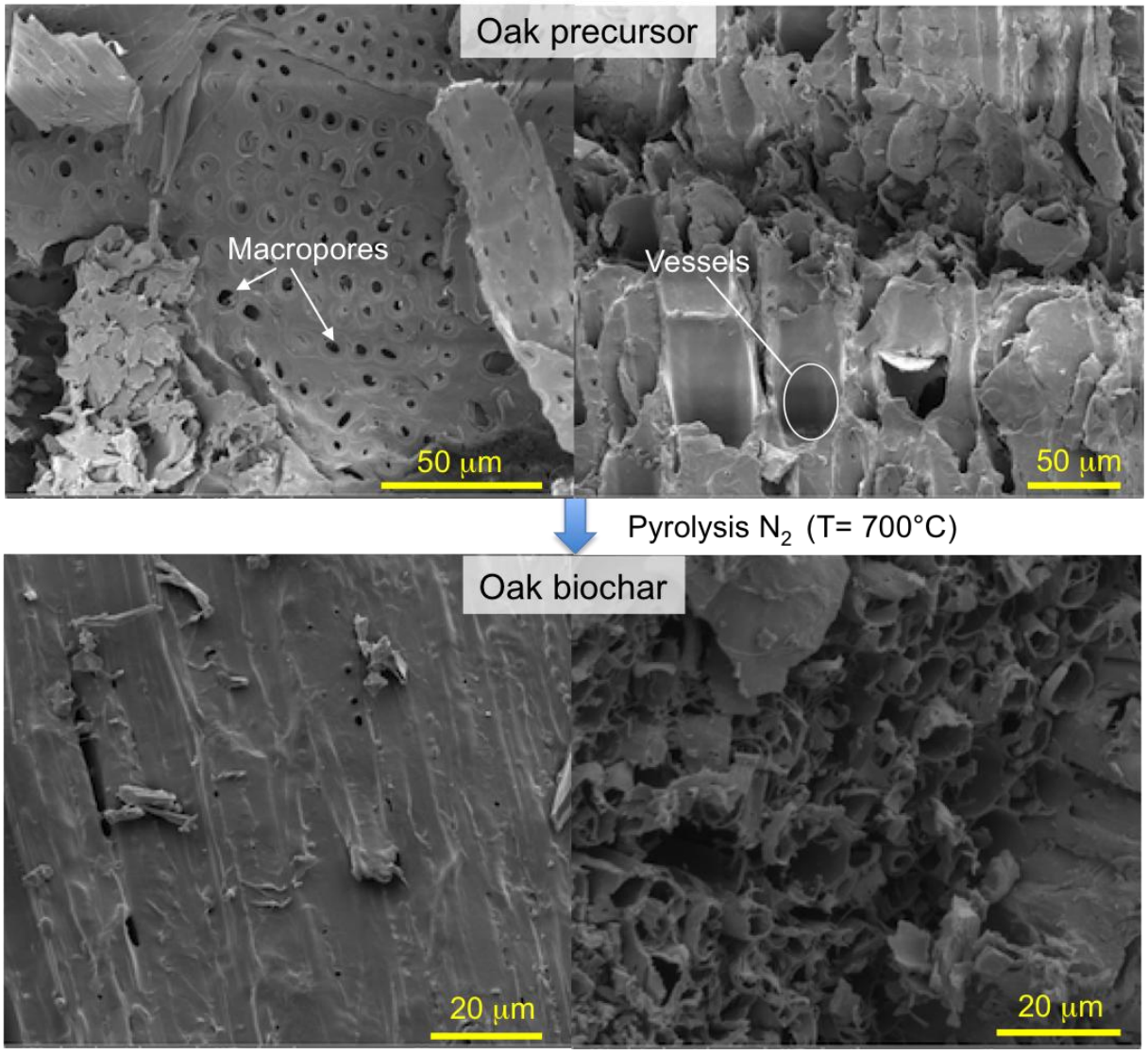

Figure 2 : SEM images of oak wood before and after pyrolysis.

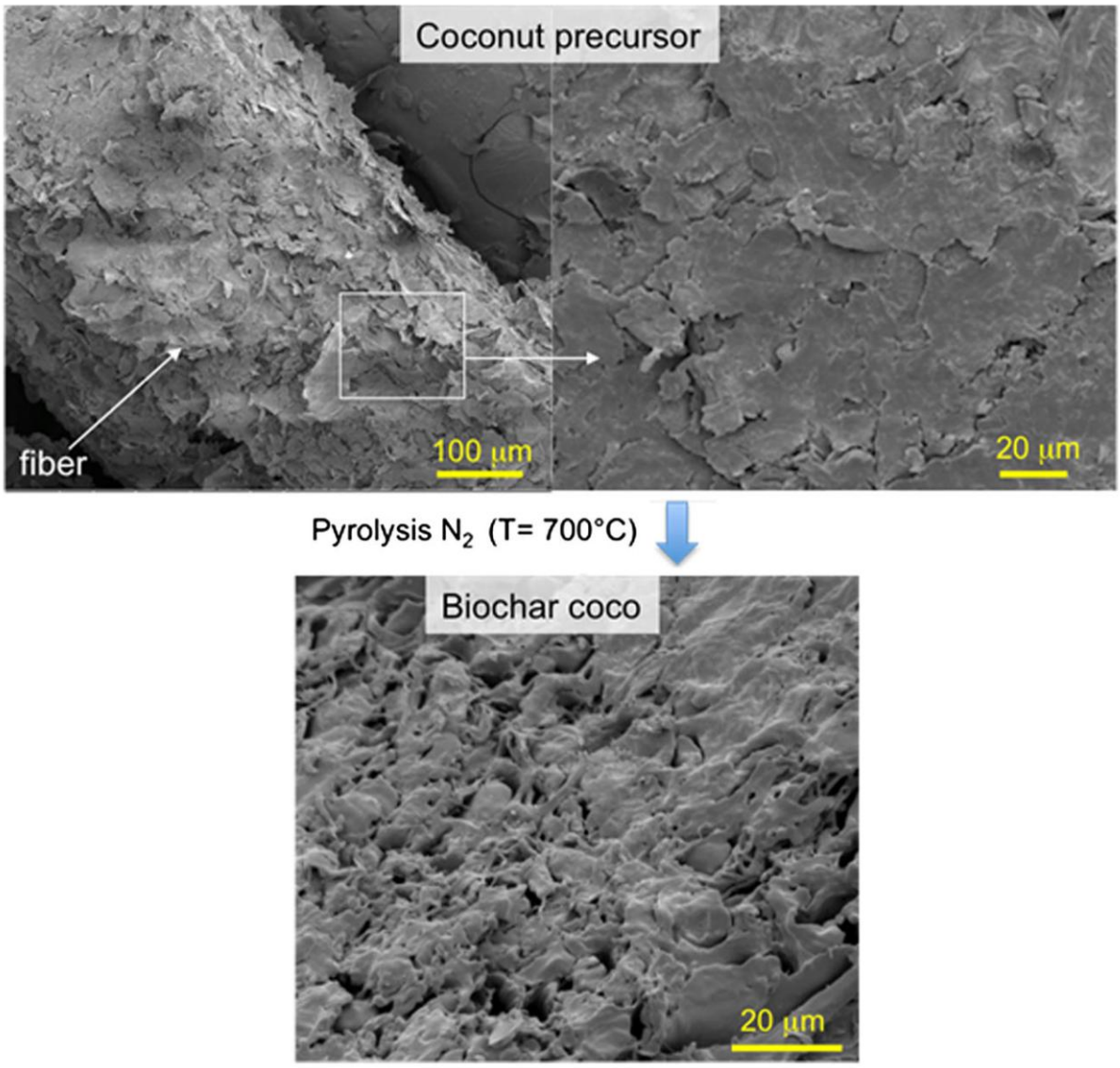

Figure 3 : SEM images of coconut shell precursor before and after pyrolysis.

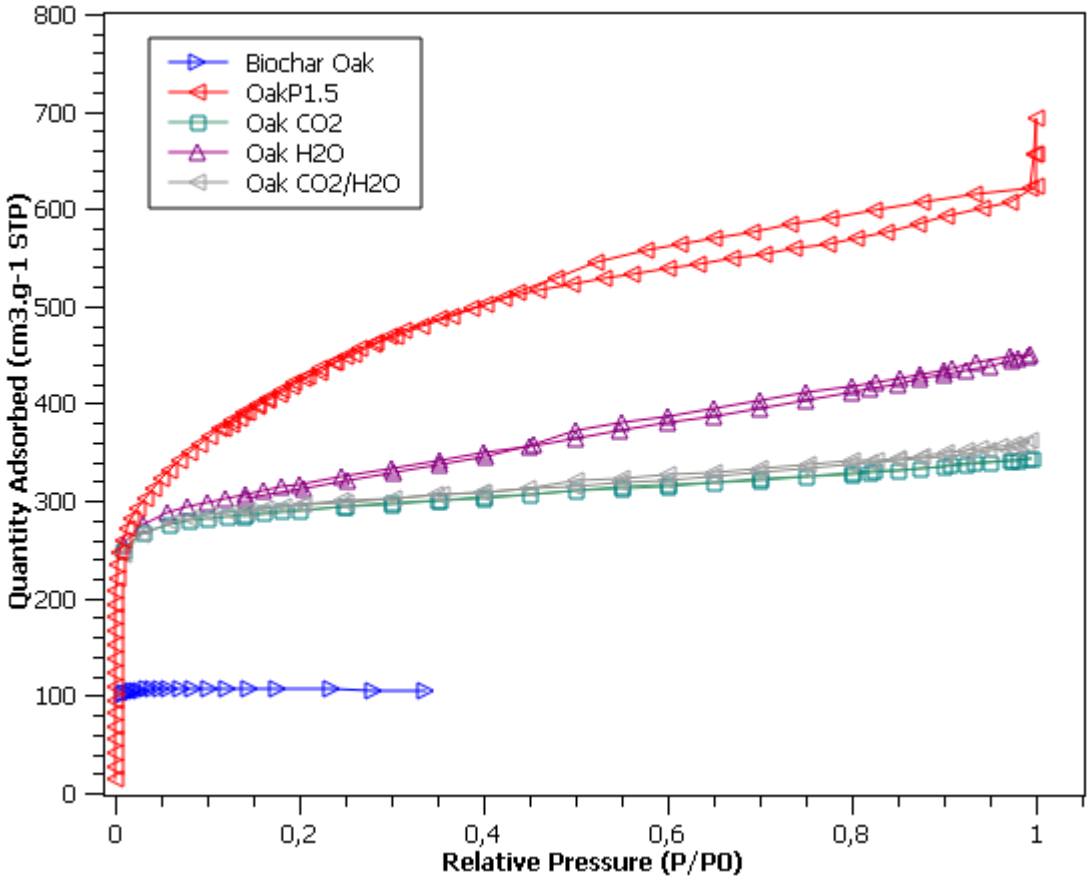

Figure 4: Adsorption isotherm of nitrogen at 77 K by AC of *Quercus ilex* pyrolyzed at 700 °C during 1 h.

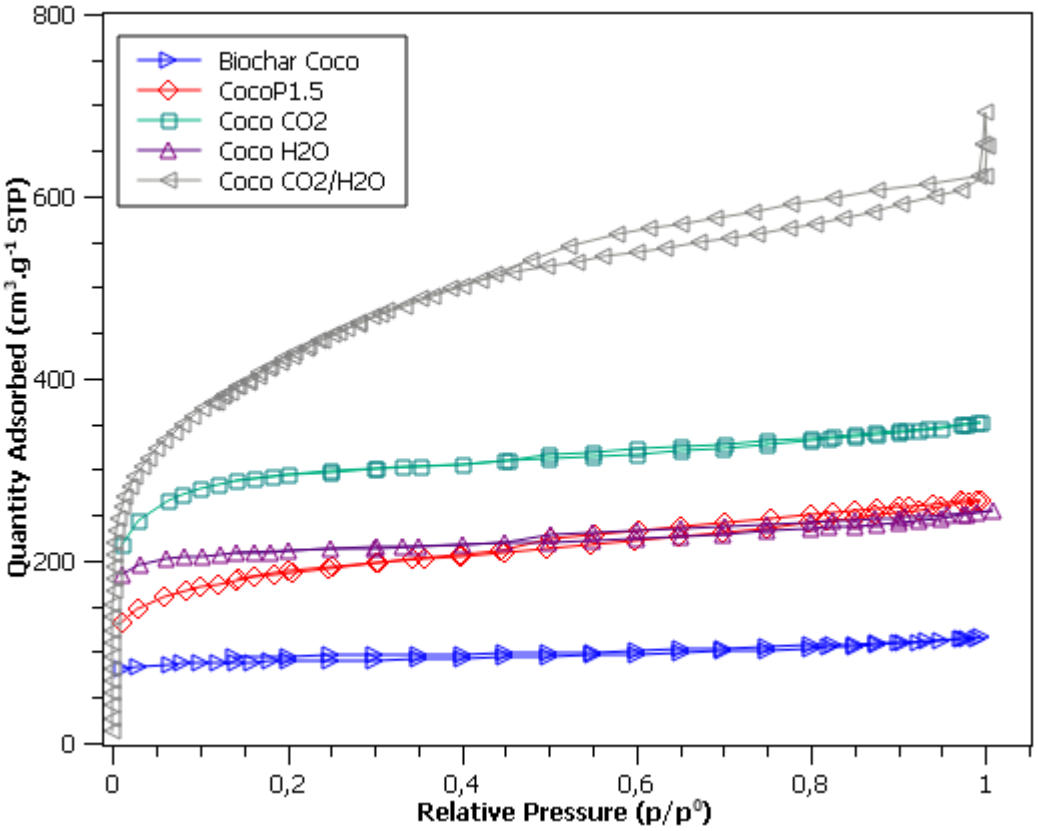

Figure 5: Adsorption isotherm of nitrogen at 77 K by AC of Coconut *nucifera* pyrolyzed at 700°C during 1 h.

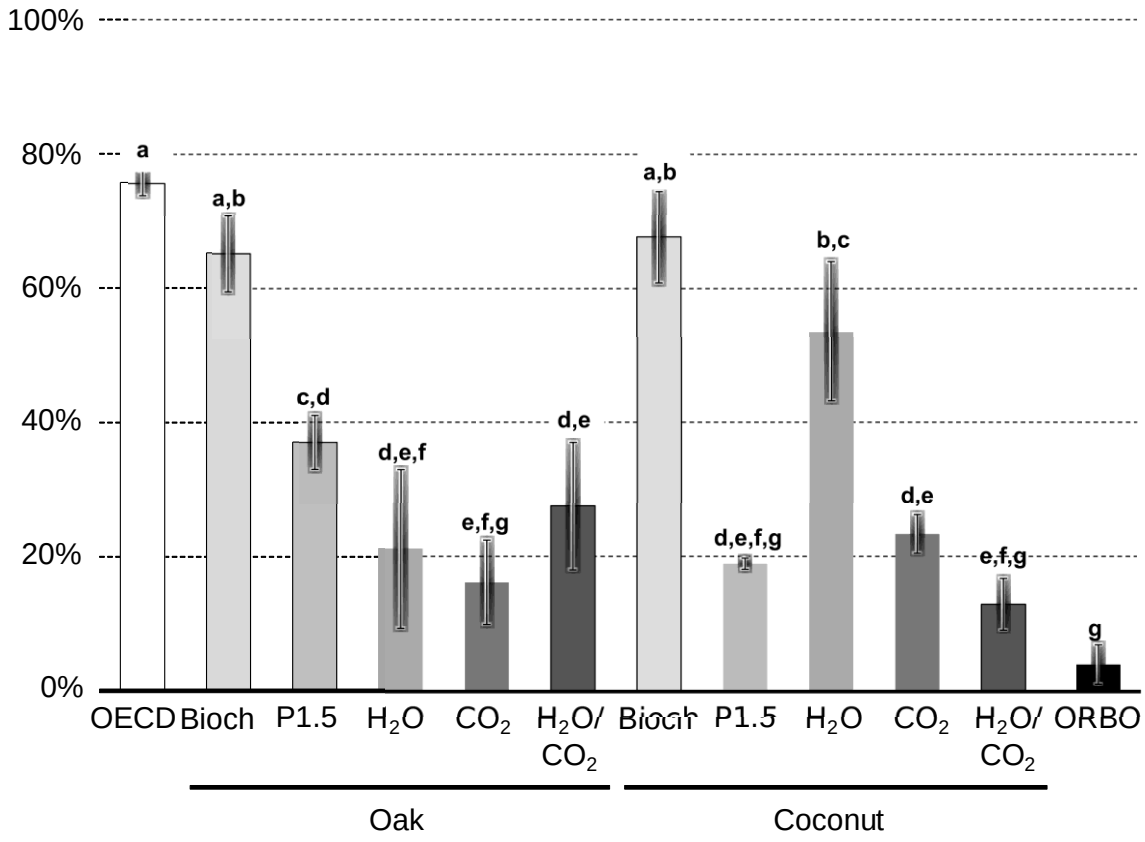

Figure 6 : CLD availability in OECD soils.

CLD availability is expressed in %. Values correspond to the mean ± SD (n=3 or 6 (OECD, ORBO). *Mean values* with different superscript *letters (a, b, c, d, e, f, g)* are statistically different (P<0.05). Statistical analysis was performed using the one-way ANOVA procedure of R software and Tukey post-hoc test.

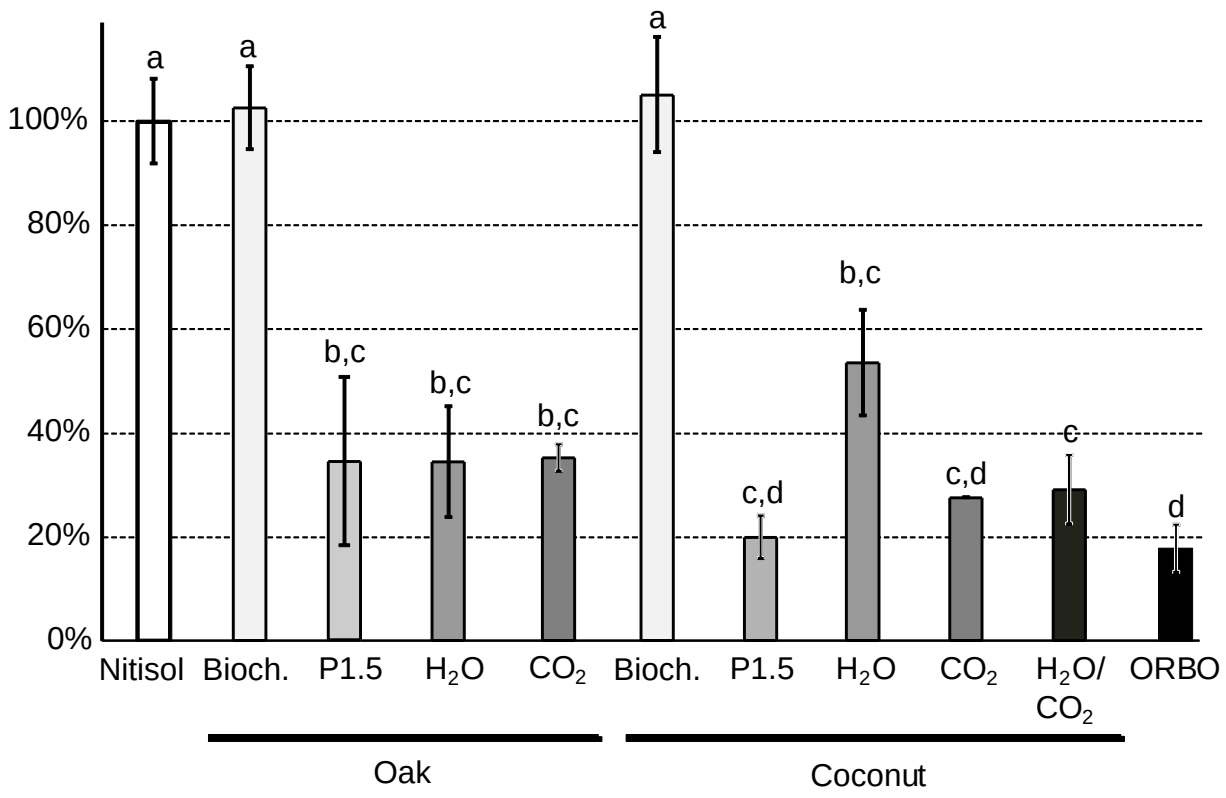

Figure 7: CLD availability in nitisol after amendment.

CLD availability is expressed in %. Values correspond to the mean ± SD (n=3 excepted for OECD and OFRBO where n= 6 (OECD, DARCO, ORBO). Mean values with different superscript letters (a, b, c, d) are statistically different (P<0.05). Statistical analysis was performed using the one-way ANOVA procedure of R software and Tukey post-hoc test.

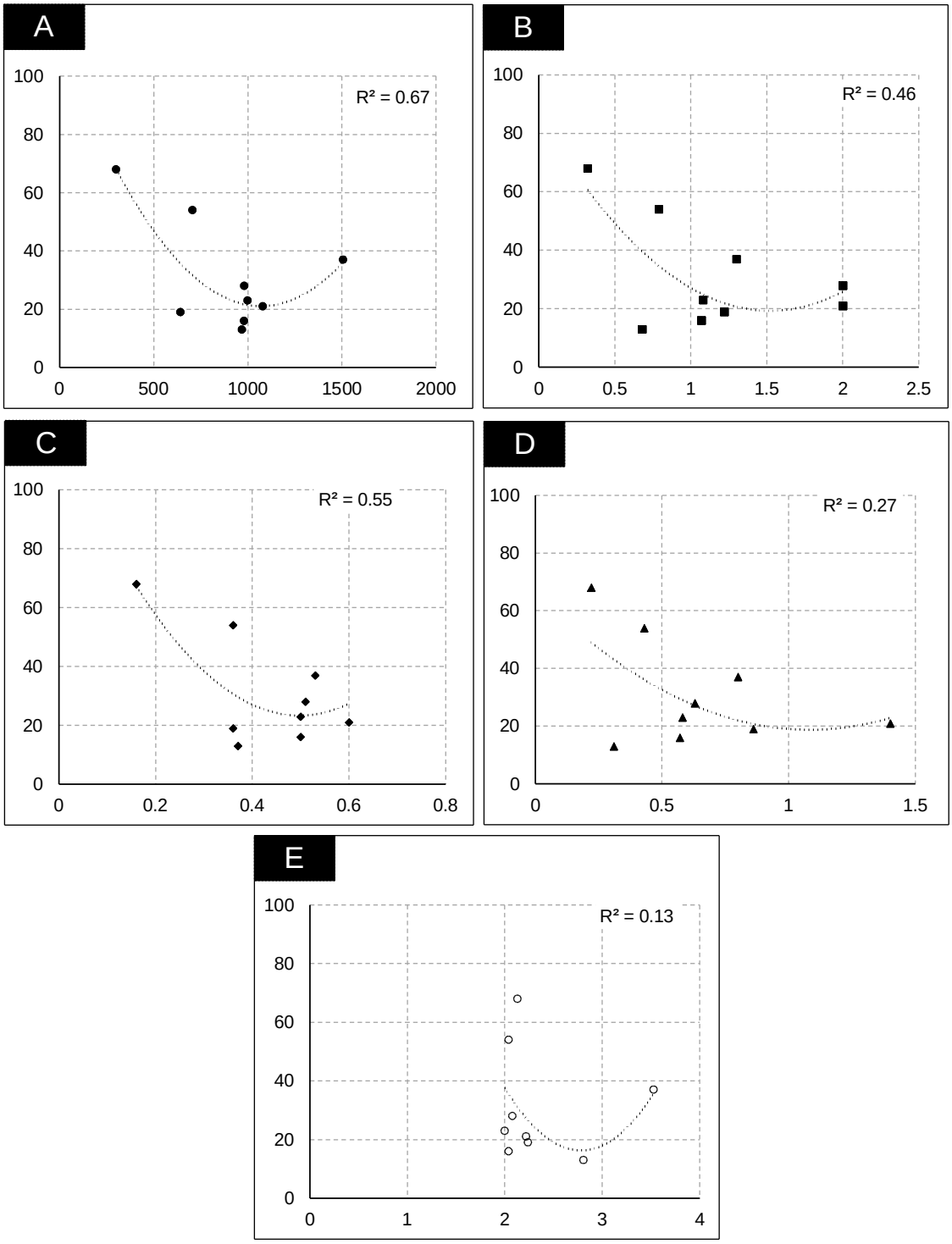

Figure 8. Textural characteristics and relation with CLD environmental availability reduction for artificial soils

x-axis corresponds respectively (A) to the BET surface area ($m^2.g^{-1}$), (B) to the total pore volume ($cm^3.g^{-1}$), (C) to the micropore volume ($cm^3.g^{-1}$), (D) to the mesopore volume ($cm^3.g^{-1}$) (E) to Mean pore with Dp (nm). y-axis corresponds to the mean of CLD environmental availability reduction (% of reduction compared to control) and error bar 95th confidence interval (n=4).

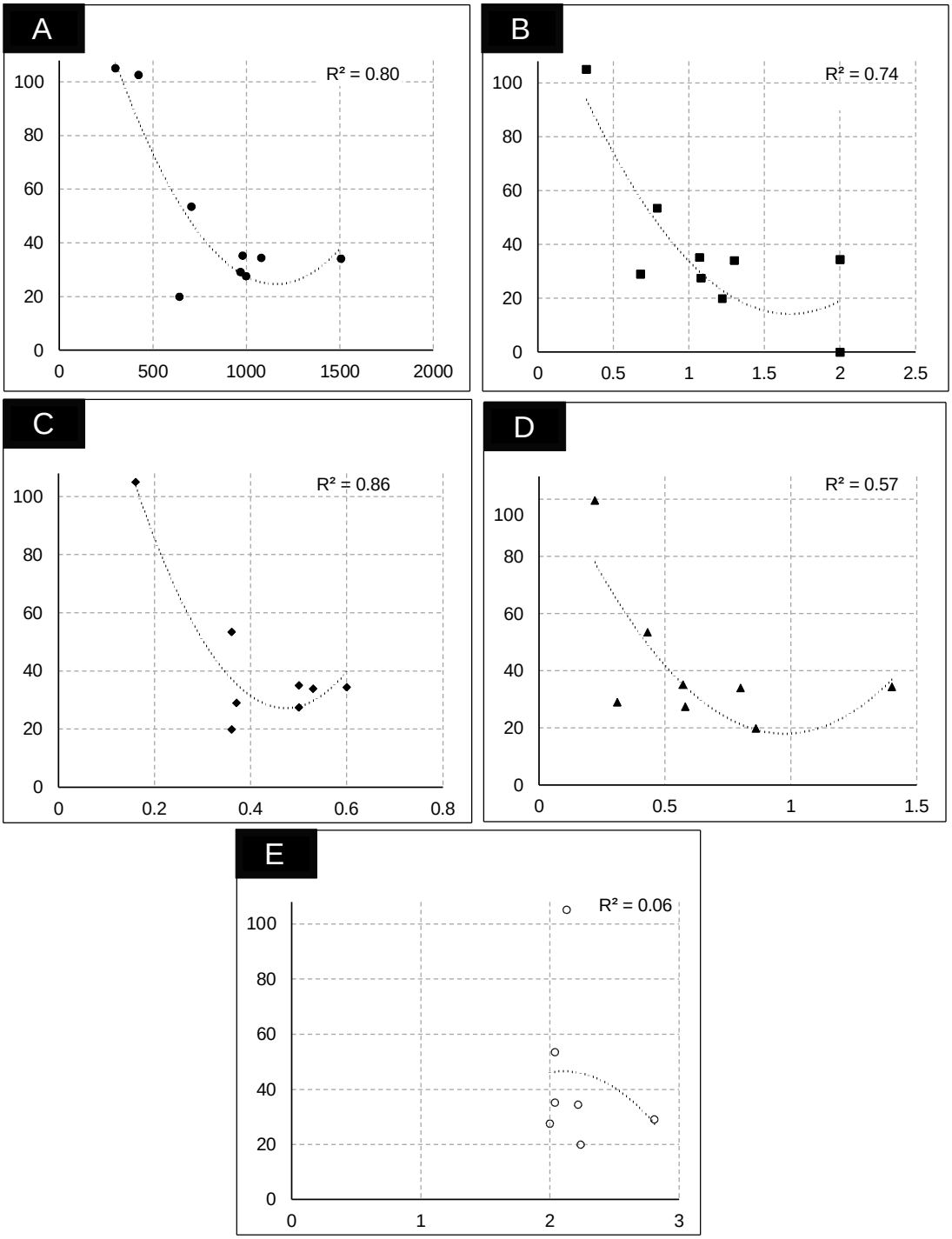

Figure 9. Textural characteristics and relation with CLD environmental availability reduction for natural soils

x-axis corresponds respectively (A) to the BET surface area ($m^2.g^{-1}$), (B) to the total pore volume ($cm^3.g^{-1}$) (C) to the micropore volume ($cm^3.g^{-1}$) , (D) to the mesopore volume ($cm^3.g^{-1}$) (E) to Mean pore with Dp (nm). y-axis corresponds to the mean of CLD environmental availability (n=4).

Table 1 : Composition of the different artificial soils and treatment of the experiment

Biochar column presents name and weight percentage of each biochar (source and pyrolyse temperature). Percentages are DM basis of artificial soil. Kepone concentration of each soil is 5 µg.g^{-1} of soil DM.

	Sand	Kaolin	*Sphagnum* peat	Activated carbon	Biochar
OECD standard soil	70.0%	20.0%	10%	-	
OECD with oak biochar	66.5%	19.0%	9.5%		5% (oak biochar)
OECD with Oak P1.5	66.5%	19.0%	9.5%	5% (Oak P1.5)	
OECD with Oak CO2	66.5%	19.0%	9.5%	5% (Oak CO2)	
OECD with Oak H2O	66.5%	19.0%	9.5%	5%(Oak H2O)	
OECD with coconut biochar	66.5%	19.0%	9.5%		5% (coconut biochar)
OECD with coconut P1.5	66.5%	19.0%	9.5%	5% (Coconut P1.5)	
OECD with coconut CO2	66.5%	19.0%	9.5%	5% (Coconut CO2)	
OECD with coconut H_2O	66.5%	19.0%	9.5%	5%(Coconut H2O)	

Table 2: Textural parameters of the lignocellulosic ACs and biochars.

Sample	Burn-off (%)	BET Surface area ($m^2.g^{-1}$)	$V_{Micropore}$ (D-R) ($cm^3.g^{-1}$)	$V_{Mesopore}$ (BJH) ($cm^3.g^{-1}$)	Total volume in pore ($cm^3.g^{-1}$)	Average pore width Dp (nm)
Biochar Oak	76	424.63	-	-		
OakP1.5	74	1506.19	0.53 (39.85%)	0.80 (60.15%)	1.33	3.53
Oak CO_2	54	979.62	0.50 (46.73%)	0.57 (53.27%)	1.07	2.04
Oak H_2O	53	1079.78	0.60 (30%)	1.40 (70%)	2.00	2.22
Oak CO_2/ H_2O	51	980.70	0.51 (44.74%)	0.63 (55.26%)	1.14	2.08
Biochar Coco	64	299.92	0.16 (42.10%)	0.22 (57.90%)	0.38	2.13
CocoP1.5	77	642.49	0.36 (29.51%)	0.86 (70.49%)	1.22	2.24
Coco CO_2	54	998.58	0.50 (46.30%)	0.58 (53.70%)	1.08	2.00
Coco H_2O	52	706.38	0.36 (45.57%)	0.43 (54.43%)	0.79	2.04
Coco CO_2/ H_2O	51	968.44	0.37 (54.41%)	0.31 (45.59%)	0.68	2.81

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Acknowledgements

We thank C. Soligot and P. Hartmeyer (Université de Lorraine, EA 3998) for their valuable technical support.

Funding information

We acknowledge the financial support of the Martinique Prefecture (PITE convention n° DRRT-2015-02) and the ANR (ANR-16 CE210008-01).