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# In vitro and in vivo assessment of a CLD sequestration strategy in Nitisol using contrasted carbonaceous materials

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## Abstract

Chlordecone (Kepone) (CLD) is a highly persistent pesticide formerly used in the French West Indies. High levels of this pesticide may be found in soils and constitute a subsequent source of contamination for outdoor-reared animals due to involuntary ingestion of consistent amounts of soil. In that context, carbonaceous materials may be used to amend soil to efficiently decrease the bioavailability of such organic pollutants. The present study aims to assess the efficiency of diverse amendments of a contaminated Guadeloupe nitisol using two physiologically-based approaches. A set of 5 carbonaceous materials (ORBO, DARCO, Coco CO2, Oak P1.5, Sargasso biochar) was tested and used to amend Nitisol at 2% (mass basis). Bioaccessibility assessment was performed using the Ti-PBET assay (n=4). The relative bioavailability part involved 24 piglets randomly distributed into 6 experimental groups (n=4). All groups were exposed during 10 days to a contaminated soil, amended or not with carbon-based matrices. A significant decrease of relative bioaccessibility and CLD concentrations in liver were observed for all amended groups in comparison to the control group, with the exception of the biochar amended soil in the bioaccessibility assay ( $p < 0.05$ ). Extent of this reduction varied from 22% to more than 82% depending on the carbonaceous matrix. This decrease was particularly important for the ORBO™ activated carbon for which bioaccessibility and relative bioavailability were found lower than 10% for both methodologies.

## 1. Introduction

Among legacy organochlorine pesticides (DDT, dieldrin, HCH...), most of them present high hydrophobicity, chemical stability, persistence in soil (Tremolada et al., 2012), and are persistent organic pollutants (POPs) under the Stockholm Convention. These molecules can have a long residence time in soil and may be bioaccumulated by biota or even biomagnified in the trophic chain. The subject of this study is the pollution of tropical soils by a persistent organochlorine, chlordecone (CLD), recognized as a POP in 2006 and introduced to annex A in 2007 (UNEP, 2011). Chlordecone was used from the 1970s to the 1990s in French West Indies banana plantations to fight against the black weevil (UNEP, 2011). Thirty years later, soils are reservoirs of this contamination (Cabidoche et al., 2009) but

also sources of pollution for biota in surrounding ecosystems. This concerns both cultivated plants (Clostre et al., 2015) or farmed animals (Jurjanz et al., 2020) in the terrestrial environment, and crustaceans and fish in freshwater (Coat et al., 2011) or marine (Dromard et al., 2016) ecosystems. Exposed through their surrounding environment and food products, humans appear ultimately at risk to CLD health effects as noticed by epidemiological studies linking CLD exposure to prostate cancer increased incidence (Multigner et al., 2010) and child neurodevelopment impairments (Dallaire et al., 2012).

Despite of tangible proof of natural degradation due to transformation products observed in Antillean soils (Chevallier et al., 2019; Lomheim et al., 2020), no efficient process is currently available to degrade efficiently CLD *in*

*situ*. In this frame, transfer appears to be a key physiological mechanism explaining the subsequent contamination of biota, food products and ultimately humans. Acting directly on this transfer would prevent the contamination of the whole food chain. One possible strategy to reduce this CLD transfer to animals is to sequester it within the soil matrix. In this perspective, several amendment sources have already been evaluated and proven to be effective to limit the CLD transfer, as assessed using plants (Fernandes et al., 2010; Woignier et al., 2015, 2012) or through an *in vitro* assay (Ranguin et al., 2020) and confirmed in animal studies using artificial soils (Delannoy et al., 2019; Yehya et al., 2017). To limit transfer to plant, compost amendment of CLD-contaminated soils displayed a reduction of transfer to plants by a factor of 3 to 10 compared to non-amended soils (Woignier et al., 2012). Activated carbons (ACs) amendment showed also a reduction up to 90% in non-physiological based *in vitro* environmental availability assays (Ranguin et al., 2020) or 95% in *in vivo* relative bioavailability assays using spiked OECD artificial soils (Delannoy et al., 2019; Yehya et al., 2017). To date, no data are available concerning the sequestration potential of ACs in an historical Antillean contaminated soil using a combination of physiological based *in vitro* and *in vivo* assays.

Thus, the aim of the present paper is to assess the potential of five carbonaceous materials (of diverse origins and physical properties) to reduce the CLD transfer from a nitisol sampled in a CLD contaminated area. CLD transfer will be assessed *via in vitro* bioaccessibility assay and an *in vivo* relative bioavailability assay using piglets, as a relevant biological model of children.

## 2. Material and Methods

### 2.1. Experimental design

The experimental design aimed at comparing CLD bioaccessibility and relative bioavailability in contaminated antillean soils amended (2% dry mass basis) or not with one of five contrasted carbonaceous materials. After 80 days maturation period, the residual bioaccessible fraction of CLD was assessed using the Tenax-Improved Physiologically Based Extraction Test (Ti-PBET) (Li et al., 2016). This assay mimics the physiological conditions of the digestive system of monogastric animals. In order to validate *in vitro* data, a second step proceeded to the CLD relative bioavailability assessment of each amended soil in piglets.

### 2.2. Carbon sources preparation and characterization and nitisol amendment

Carbon sources were provided by Sigma-Aldrich (Saint-Louis, USA) for ORBO and DARCO or produced by COVACHIMM2E laboratory (Université des Antilles, Pointe-à-Pitre) : Coco CO<sub>2</sub>, Oak P 1.5 and SargBC. Extensive characterization (Delannoy et al., 2019; Ranguin et al., 2020) as well as reference of methodologies of production and characterization for non-commercial carbonaceous matrices are provided in Table 1. The Brunauer, Emmett et Teller (BET) surface areas, as the main physical parameters of the porosity of these matrices, are presented in Table 1. The CLD contaminated nitisol (0.58 µg CLD per g of soil Dry Matter) was sampled in French West Indies as described elsewhere (Jurjanz et al., 2014) and dried at room temperature until mass stabilization. Then, 2% carbonaceous material (dry matter basis of total amended soil) was added to four subsamples of soil (60 g). Four not amended subsamples were used as control. Finally, ultrapure water was added (18% of mass of the wet soil). All soils were aged during 80 days at 20 ± 2°C.

**Table 1 Physico-chemical characterization of condensed materials**

	Origin	BET surface area m <sup>2</sup> .g <sup>-1</sup>	Vmic cm <sup>3</sup> /g	Vmes cm <sup>3</sup> /g	Ref
DARCO®	Lignite based Activated Carbon, activated by H <sub>2</sub> O. Commercial AC supplied by Sigma-Aldrich	825	0.39	0.30	
ORBO™	Coconut based Activated Carbon, chemically activated. Commercial AC supplied by Sigma-Aldrich	1121	0.46	-	
Coco CO <sub>2</sub>	Coconut based Activated Carbon, activated by CO <sub>2</sub> gaz	998.58	0.50	0.58	Ranguin 2020
Oak P.1.5	Oak based Activated Carbon, activated by phosphoric acid	1506	0.53	0.80	Ranguin 2020
SargBC	SargBC	872	0.44	0.55	Ranguin, 2021

## 2.3. Bioaccessibility assays

To assess CLD bioaccessibility in contaminated soils, an aliquot of the Physiologically Based Extraction Test (PBET) gastric solution (20 mL; pH = 2.5) was placed into a 60 mL amber collection vial with 0.5 g of tested soil and shaken at 150 rpm, 37 °C as detailed by Li et al., 2016. After 1 h, NaOH was added to achieve a pH of 7 along 0.035 g of bile salts and 0.01 g of pancreatin. 0.5 g of Tenax (60-80 mesh, Sigma-Aldrich) was then added. This prepared intestinal phase was incubated for 4 h. Then, Tenax beads were collected using centrifugation at 2000 g for 15 min followed by a thorough rinse with deionized water (~10 mL). CLD bioaccessibility was determined by quantifying the concentration of CLD adsorbed onto the tenax beads. Tenax was dried during 1 h in a 40± 0.5°C ventilated oven and extracted 3 times with 10mL acetone using a 10 min ultrasonic bath. All extracts were combined and concentrated until 1 mL prior the following GC-MS analysis as described elsewhere (Ranguin et al., 2020).

## 2.4. Relative bioavailability assays

The experimental protocol was approved by the Ethical Committee of Lorraine (Permit Number: EU0387, delivered by French Ministry of Higher Education, Research and Innovation). This study was carried out in strict accordance with the recommendations of the Guide for the Care and Use of Laboratory Animals of the French Ministry of Agriculture for Animal Research (MAAR) and European Council Directive (European directive 2010/63/EU) in the recognized animal facility of the Bioavailability - Bioactivity platform (Bio-DA). Briefly, twenty-four 40 days-old castrated male piglets (Saint-Maurice-aux-Forges, France) followed a 8-days acclimation period was realized (temperature kept to 22-24°C). Similar exposure and organ collection methods were performed as described previously (Delannoy et al., 2018, 2014). As the liver was found to be the most contaminated tissue after CLD exposure of piglets (Bouveret et al., 2013), this target organ was used to assess relative bioavailability. Livers were collected, chopped, stored at -20°C and freeze-dried.

## 2.5. Analyses of biological matrices

The current reference analytical method (French Ministry of Agriculture, 2015) was applied to control CLD in liver against the maximum residue levels established in European regulation (Commission of the European Communities, 2008). This methodology is described elsewhere (Yehya et al., 2017) and was performed by a COFRAC accredited laboratory (Laboce, Quimper, France).

## 2.6. Data analyses

### 2.6.1. Quality control

CLD quantification through bioaccessibility assay (n=4) was performed after a daily calibration of the apparatus. Two kind of blank controls were introduced in each analytical run: Method blanks (which undergo all the bioaccessibility

test without introduction of contaminated soil) and Equipment blanks (constituted by the reconstitution solvent). Two method blanks were introduced in each method run whereas one Equipment blank was introduced between two samples on the analytical tray. No evidence of cross contamination was observed from the analysis of these blanks. Limit of Quantification (LOQ) obtained from the methodology were below 2 % of bioaccessible CLD. Bioaccessible concentrations below LOQ were replaced by LOQ in the dataset. CLD quantification in animal tissues (n=4) were carried out in strict accordance with the COFRAC quality accreditation of LDA 56. Values below LOQ (2.0 ng g<sup>-1</sup> of dry matter) were replaced by LOQ value in the data set.

### 2.6.2. Tissues concentrations of CLD

In order to assess the impact of ACs on CLD bioavailability an analysis of variances (ANOVA) was performed. The experimental unit was the piglet. Concentrations of CLD in liver were compared between the five treatment groups: Nitisol versus ORBO or DARCO, Coco CO<sub>2</sub>, SargBC, or Oak P 1.5 using the Analysis of Variance (ANOVA) procedure and the Tukey–Kramer post-hoc test of R version 3.2.3 (R Foundation for Statistical Computing, Vienna, Austria).

### 2.6.3. Relative Bioaccessibility and Relative bioavailability (RBA) factor calculation

Relative bioaccessibility was calculated by dividing CLD bioaccessible concentrations for each amended soil by CLD bioaccessible concentrations from non-amended nitisol group. Similarly, The RBA was calculated by dividing “CLD-concentrations in liver of piglets exposed by an amended soil” by “CLD concentrations obtained in liver from piglets exposed to non-amended soil (set as a 100% reference)”, adapted from a method previously described (Delannoy et al., 2014a; Wittsiepe et al., 2007; Yehya et al., 2017). Linearity between the CLD-dose of exposure and CLD-concentrations in the liver was a prerequisite of this method (Littell et al., 1997) and was demonstrated already in a similar assay on piglets (Bouveret et al., 2013). The corresponding equation to calculate RBA of CLD after one AC-treatment in the liver is provided below (Yehya et al., 2017).

$$RBA_{treatment,liver} = \frac{C^{\circ}_{treatment}}{C^{\circ}_{Nitisol}}$$

$RBA_{treatment}$ : Relative bioavailability of CLD after one AC – treatment in the liver

$C^{\circ}_{treatment}$ : CLD concentration in liver after one AC treatment

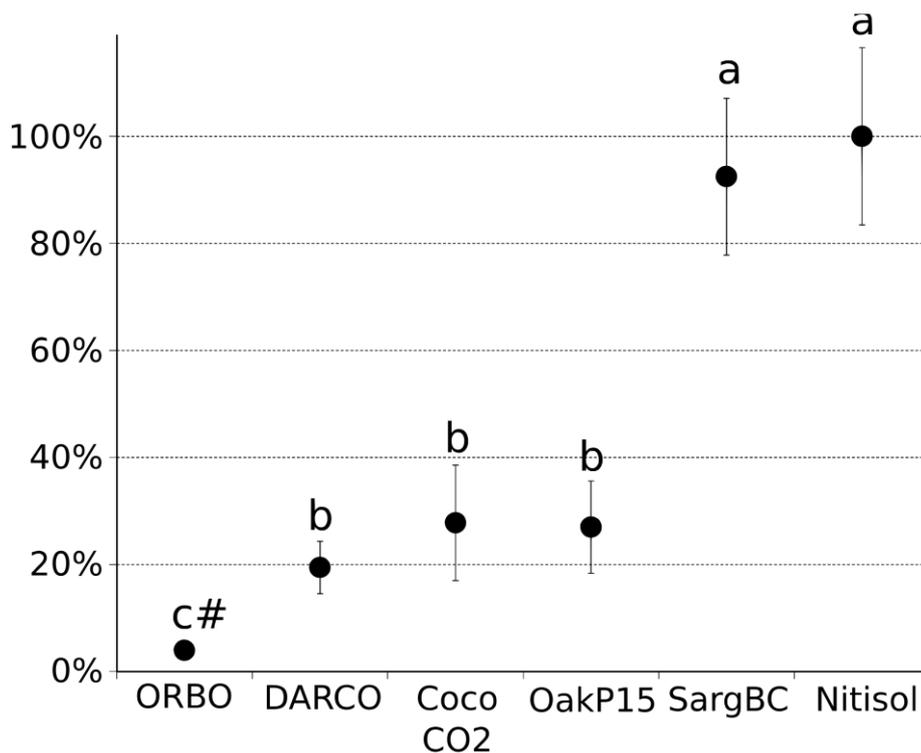
$C^{\circ}_{Nitisol}$ : CLD concentration in liver without amendment

### 3. Results

#### 3.1. Determination of the CLD Relative Bioaccessible fraction

CLD Relative Bioaccessibility was assessed using Ti-PBET assay (Figure 1). As expected, highest CLD concentrations ( $0.26 \mu\text{g L}^{-1}$ ) were obtained from the non-amended Nitisol group (100% relative bioaccessible reference group). The ANOVA and the post-hoc Tukey test allowed to distinguish three significantly different groups of treatments as described below (Figure 1;  $p\text{-value} < 0.001$ ). Firstly,

ORBO™ amended soil showed the lowest relative bioaccessibility values, all concentrations found were under LOQs, *i.e.* suggesting the highest level of CLD sequestration. Then DARCO®, Coco CO<sub>2</sub>, Oak P1.5 amended soil displayed similar relative bioaccessibility values between  $19 \pm 5\%$  to  $27 \pm 9\%$  (mean  $\pm$  SD). SargBC appeared to be the less efficient matrix regarding CLD sequestration as no significant difference was found compared to the non-amended nitisol. It has to be reminded that biochar does not fulfill an activation process in contrast to AC, consisting to use physical or chemical treatment to enhance the porosity of the material.



**Figure 1. Relative Bioaccessibility obtained from each soil sample**

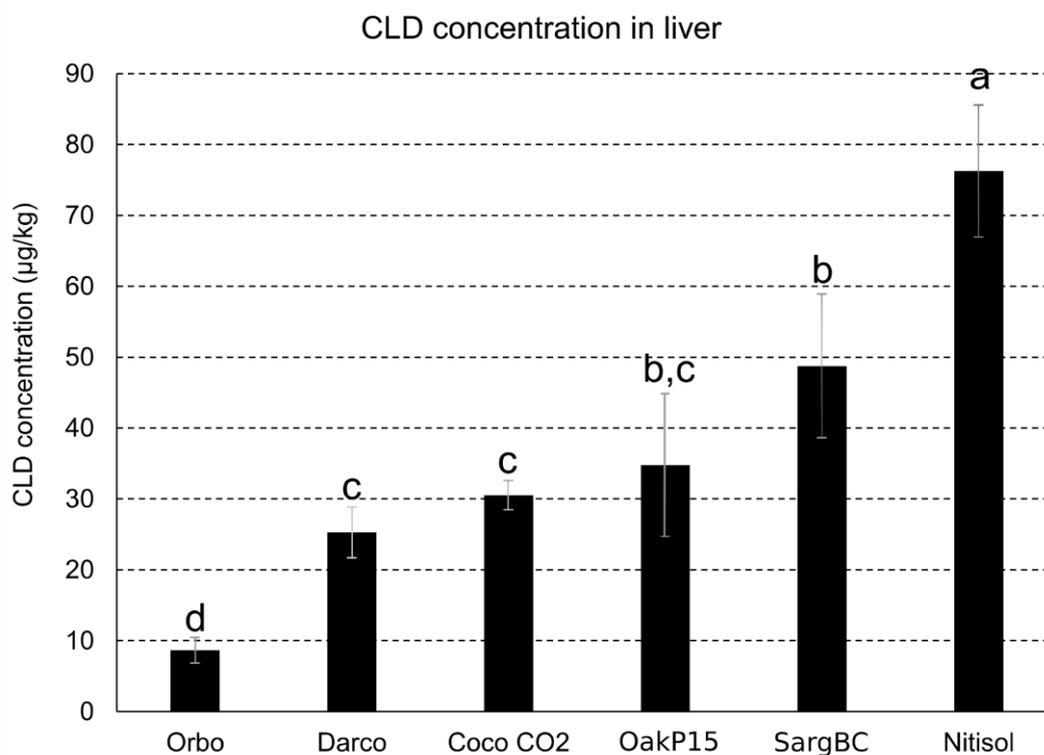
Relative bioaccessibility of CLD is expressed in % relatively to non-amended Nitisol. Values correspond to the mean  $\pm$  SD ( $n=5$ ). Mean values with different superscript letters (a, b, c) are statistically different ( $P < 0.05$ ). Statistical analysis was performed using a variance analysis and a Tukey post-hoc test.  
#: all values were below limit of quantification.

#### 3.2. Determination of the CLD relative bioavailability (RBA) fraction

CLD concentrations in biological matrices showed differences between the treatment groups as presented in Figure 2. As expected, and already observed in 3.1, the highest CLD concentrations were obtained in the non-amended Nitisol group (control):  $76 \pm 7.3 \text{ ng g}^{-1}$  of Dry Matter (DM) (mean  $\pm$  SD) (Figure 2). All amended Nitisol groups displayed significantly lower CLD concentrations in liver than in non-amended Nitisol, demonstrating the relevance of this amendment strategy. ORBO™ and DARCO® exhibited the lowest levels of CLD concentrations:  $10 \pm 1 \text{ ng g}^{-1}$  and  $27 \pm 3 \text{ ng g}^{-1}$  respectively (mean  $\pm$  SD). Coco CO<sub>2</sub> and Oak P 1.5, two of the three laboratory sourced ACs displayed similar levels of CLD concentrations

in liver:  $31 \pm 2 \text{ ng g}^{-1}$  and  $35 \pm 8 \text{ ng g}^{-1}$  respectively. At last, in agreement with the results obtained for the bioaccessibility assays, SargBC sample displayed the highest CLD concentrations of the amended soil groups:  $49 \pm 7 \text{ ng g}^{-1}$ , nevertheless this biochar exhibited significant reduction of CLD when compared to the control. The post-hoc Tukey test demonstrated significant differences between amended groups and the non-amended nitisol ( $p\text{-value} < 0.001$ ), as well as ORBO™ vs the other groups ( $p\text{-value} < 0.043$ ).

The RBA factors were calculated in order to estimate the residual CLD bioavailable fraction after Nitisol amendment. For amended soils RBAs of 11%, 33%, 40%, 46% and 64% were obtained respectively for ORBO™, DARCO®, Coco CO<sub>2</sub>, Oak P1.5 and SargBC (Table 1).



**Figure 2: Concentrations of CLD in biological matrices (ng of CLD per g of DM)**

Concentrations of CLD are expressed in  $\mu\text{g}\cdot\text{kg}^{-1}$  of DM. Values correspond to the mean  $\pm$  SD (n=4). Mean values with different superscript letters (a, b, c, d) are statistically different ( $P < 0.05$ ). Statistical analysis was performed using variance analysis and a Tukey post-hoc test.

## 4. Discussion

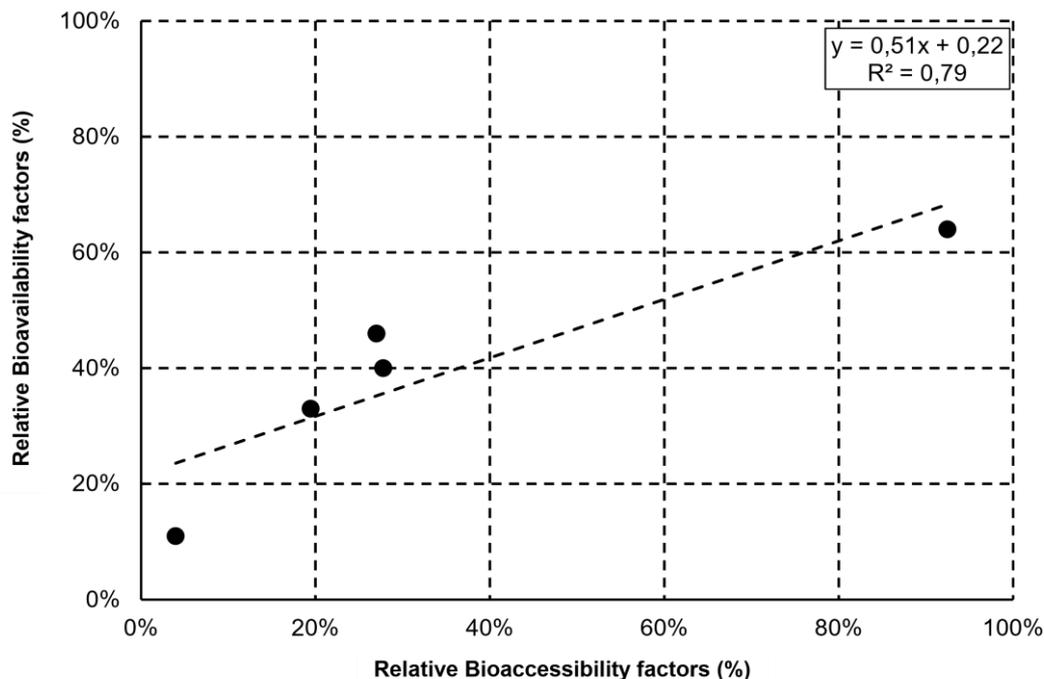
### 4.1. Bioaccessibility and relative bioavailability as complementary exposure assessment tools

Refining POPs exposure by *in vitro* and *in vivo* methodologies is of key importance to manage polluted areas for both humans and animals who may ingest involuntary soil particles. Involuntary ingestion of soil is being addressed by numerous protection agencies and public policies like the Environmental Protection Agency for USA (EPA, 2017), United Kingdom (Saikat et al., 2007), France (ANSES, 2019; MEEM, 2017) and Germany (BBodSchV, 1999; DIN, 2017) since the 80's. Numerous protocols were designed and investigated for both *in vitro* and *in vivo* assays (ANSES, 2019). Considering *in vitro* assays numerous published protocols demonstrated their ability to predict *in vivo* results for trace metals (ANSES, 2019). However, most of these frequently used methodologies minimize bioavailability of lipophilic POPs (Kademoglou et al., 2018; Li et al., 2016), and solubilization of these hydrophobic POPs was pointed out as one of the most limiting step (ANSES, 2019; Collins et al., 2013; Kademoglou et al., 2018; Li et al., 2016). In this frame, novel methodologies implement sorptive phases to enhance the solubilization and mobilization of POPs also reproducing the on-going absorption during the intestinal phase. The novel Ti-PBET methodology showed promising results to predict *in vivo* transfer using a mouse assay (Li et al., 2016).

Concerning *in vivo* methodologies, a conservative approach (*ie* not minimizing the exposure assessment) should be implemented when facing this problem (ANSES, 2019). In this frame the present study used (i) the piglets as a relevant biological model for humans (ii) a physiological status which maximizes the intestinal permeability of lipophilic POPs (weaned) (Becker et al., 1950; Flores et al., 1989; Holt and Balint, 1993) mimicking the infant digestive tract (iii) a daily soil ingestion rate close to that found and recommended in literature (U.S. EPA, 2011)..

This assay is the first attempt to correlate Ti-PBET assay to a piglet's assay for CLD contaminated soil. A significant  $R^2$  correlation above 0.7 was found between *in vivo* and *in vitro* results for DDT and PCBs. However, bioaccessibility data underestimated the bioavailability ones (Li et al., 2016). As an illustration, present *in vivo* – *in vitro* correlation is in line with these previous results with a  $R^2$  of 0.79 despite a limited number of soil-treatments (cf Figure 3). However, a notable minimization of *in vivo* data by *in vitro* ones has also to be noticed as a slope of only 0.51 was obtained from the linear regression. This weak correlation could be explained by the particular results obtained from SargBC. These elements do not comply to validation criteria previously formalized for validation of bioaccessibility assays (Wragg et al., 2011). It may be hypothesized that the chemical characteristics of CLD presenting log Kow of 4.7 (UNEP, 2011) may be challenging for this Ti-PBET methodology, previously validated for molecules presenting higher Kow. Specific interactions with some constituents of the PBET test may also limit the adsorption of CLD onto Tenax beds (Collins et al., 2013; Kademoglou et al., 2018; Li et al., 2016). Further assessment is needed to conclude on the

adequacy of this physiological *in vitro* assay for CLD contaminated soils, but some improvements of the methodology (e.g modification of the resin nature) may enhance the capacity of this test to predict CLD relative bioavailability.



**Figure 3: Correlation between Relative Bioaccessibility and Relative Bioavailability factors**

Concentrations of CLD in biological matrices (ng of CLD per g of DM) Concentrations of CLD are expressed in  $\mu\text{g kg}^{-1}$  of DM. Values correspond to the mean  $\pm$  SD (n = 4). Mean values with different superscript letters (a, b, c, d) are statistically different ( $p < 0.05$ ). Statistical analysis was performed using variance analysis and a Tukey post hoc test

#### 4.2. Carbonaceous material characteristics limiting CLD transfer

When using the soil amendment strategy, CLD remained mainly adsorbed on carbonaceous materials even during the digestive processes limiting ultimately its absorption. Thus, the present results demonstrated for the first time a real potential of CLD sequestration in historically contaminated soils. Characteristics of the carbonaceous products, overall their specific surfaces and porosity repartition, are known to be relevant parameters (Ranguin et al., 2020). The current set of biochars and ACs was selected upon their respective efficiencies as detailed previously (Ranguin et al., 2020).

As expected a significant sequestration was obtained with all biochars and ACs amendments as these carbonaceous matrices displayed high BET Surface areas (Table 1). The activated carbons DARCO, Coco CO<sub>2</sub> and OakP1.5 presented similar extent of sequestration, although their BET Surface areas were quite different (793 to 1506 m<sup>2</sup> g<sup>-1</sup>). Interestingly, SargBC had a similar BET Surface than DARCO® but the extent of sequestration was significantly lower. Contrarily to previous hypotheses (Ranguin et al., 2020), the BET Surface could not be considered as the main explaining parameter of the sequestration potential in

the present study. Indeed, all tested carbonaceous materials were reported to display preponderantly a microporosity characterized by the narrowness of their pores (<2 nm) fitting the size of CLD (i.e. 0.652 nm) (Durimel et al., 2013) except SargBC (4.5 nm).

When considering the additional parameters (V<sub>mic</sub>, V<sub>mes</sub>) (Table 1), no specific link could be established also between the characteristics of OakP15, Coco CO<sub>2</sub> and SargBC and the bioaccessibility and bioavailability results. Indeed, a similar V<sub>mic</sub> is given (Table 1) for Coco CO<sub>2</sub>, Oak P15 and SargBC. For V<sub>mes</sub>, OakP1.5 presented a much higher V<sub>mes</sub> and the sequestration potential of OakP1.5 was intermediate when compared to Coco CO<sub>2</sub> and SargBC. Thus, these specific microporosity parameters do not fully explain the different CLD sequestration observed. It has to be recalled that all ACs and Biochars have been incorporated in the same CLD contaminated Nitisol, at the same levels (2% mass basis) and were similarly matured during a 80-day period.

Mechanistically, this CLD sequestration resulted from adsorption of this POP onto carbonaceous matrices surface. This adsorption relies on physico-chemicals weak bindings between chemical functions of CLD and the surface of these matrices. Such a mechanism is also

depicted when a POP is adsorbed onto different soil organic matters (OMs) (Ahmad et al., 2014; Delannoy et al., 2014b; Woignier et al., 2012). More precisely, it has been recently theorized that their porosity, along with chemical surface groups, can interact tightly with the CLD molecule, resulting in a binding strength which could be compared to a covalent one (Durimel et al., 2013). Thus, other parameters such as granulometry, surface chemical groups, should also be

further investigated to better understand the obtained differences between matrices. Since coconut and Sargasso are low-cost and renewable AC sources especially in the French West Indies (Arsène et al., 2013), these raw materials are of particular interest to tackle the CLD transfer problem to animals and humans. Then, the implementation of a CLD sequestration strategy based on local biomasses could be a real remediation option.

## 5. Conclusion

Carbonaceous material amendment appears to be an interesting strategy to limit CLD transfer to animals. This reduction potential may be useful in terms of animal rearing as well as in terms of human safety, as they both may be exposed by involuntary ingestion of soil. Although, a wide range of RBAs was observed between the amended nitisol by such matrices, this study demonstrated that all investigated matrices resulted in relevant limitations of CLD transfer. The largest reduction of transfer were obtained with commercial ACs (90%). ACs produced from local biomass in laboratory condition displayed also an important

reduction (60-85%). However, biochar produced from an *algae* was less efficient (35%) than the ACs, and would need further developments. Overall, the results of this study are of great interest and presage further investigations of locally-based sequestering materials in order to assess the on-field efficiency, and the lasting of CLD sequestration with the different soil types known to be contaminated in French West Indies. In this frame, such strategy may be locally implemented and surveyed to assess on-field and over time the impact of climate on the CLD sequestration along the assessment of OM and carbonaceous materials lability.

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## Conflict of Interests

The authors have no conflicts of interest to declare. All co-authors have seen and agree with the contents of the manuscript and there is no financial interest to report. We certify that the submission is original work and is not under review at any other publication.

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Data availability

The data that support the findings of this study are available from the corresponding author, MD, upon reasonable request.

## Author contribution

Study conception and design: MD, GR, CF, NEW, SG (supporting)

Acquisition of data: NEW, MD, RR, CY

Analysis and interpretation of data: MD, RR, NEW, CY

Drafting of manuscript: MD, GR, CF, NEW, CY (supporting), RR (supporting), SG (supporting)

Critical revision: CF, MD, GR, SG, CY, RR

## Animal research

The experimental protocol was approved by the Ethical Committee of Lorraine (Permit Number: EU0387, delivered by French Ministry of Higher Education, Research and Innovation). This study was carried out in strict accordance with the recommendations of the Guide for the Care and Use of Laboratory Animals of the French Ministry of Agriculture for Animal Research (MAAR) and European Council Directive (European directive 2010/63/EU) in the recognized animal facility of the Bioavailability - Bioactivity platform (Bio-DA).

## Consent to participate

Not applicable

## Consent to publish

Not applicable