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# Physico-chemical and agronomic results of soil remediation by In Situ Chemical Reduction applied to a chlordecone-contaminated nitisol at plot scale in a French Caribbean banana plantation

Christophe Mouvet, Bastien Collet, Jean-Marie Gaude, Luc Rangon, Sébastien Bristeau, Mathlide Senergues, Magalie Lesueur-Jannoyer, Alexandra Jestin, Jennifer Hellal, Thierry Woignier

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# Environmental Science and Pollution Research

## Physico-chemical and agronomic results of soil remediation by In Situ Chemical Reduction applied to a chlordecone contaminated nitosol in a French Caribbean banana plantation

--Manuscript Draft--

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<b>Abstract:</b>	<p>The In Situ Chemical Reduction process was tested in a nitosol in a French Caribbean banana plantation using five different soil amendments. The addition of 2.8% or 4.0% of ZVI (dw/dw, 2 different trial plots) in the 0 – 40 cm soil layer lowered the initial chlordecone (CLD) concentration by up to 74% or 69% in 37 days or 94 days, with 75% of the decrease achieved after only 21 or 24 days of treatment depending on each trial plot. The addition of commercially available Daramend® was also tested applying the 6% dose recommended by the manufacturer and using either the regular alfalfa-based product or a bagasse-based product specifically formulated for the study. Both significantly lowered CLD concentrations, but to a lesser extent than with the ZVI-only amendment. A bagasse-ZVI mixture prepared on site produced results slightly better than the two Daramend®. The percentage decreases in CLD concentrations were correlated with the negative redox potentials achieved. In all the trial plots, dechlorinated transformation products appeared in the soil and soil water as the CLD</p>

	<p>concentrations decreased, with H atoms replacing up to 4 and 7 of the 10 Cl atoms, respectively. None of these degradates appeared to accumulate in the soil or soil water during the treatment. Instead, the reverse occurred, with an overall downward trend in their concentrations over time. The effects of ISCR treatment on agronomic and human health-related parameters were measured in three different crops. The radishes produced with some treatments were visually of lower quality or smaller in size than those grown in the control plots. Lower yields were observed for the cucumbers and sweet potatoes grown after applying the bagasse-based amendments. Mortality among cucumber seedlings was observed after treatment with ZVI only. Simple operational solutions should suffice to remedy these negative agronomic effects. As regards human health-related effects, the CLD concentrations in radishes grown with three of the amendments were significantly lower than in the two control plots and well below the MRL, which was substantially exceeded in the radishes grown on untreated soil. For cucumbers, the treatments with regular Daramend® and with a local bagasse-ZVI mixture produced fruits with CLD below the MRL and also below the concentrations in one of the two control plots. As for the sweet potatoes, adding a bagasse-ZVI mixture had a significant positive effect by decreasing contamination to below the levels in the two control plots and below the MRL.</p>
<p><b>Suggested Reviewers:</b></p>	<p>Pierre Benoit, PhD INRA pierre.benoit@inra.fr Well aware of all aspects of the chlordecone issue in the French Caribbeans and (co-)author of 2 papers where the environmental fate of chlordecone and some of its degradates is considered. <a href="https://doi.org/10.1080/10643389.2014.955627">https://doi.org/10.1080/10643389.2014.955627</a>; <a href="http://dx.doi.org/10.1016/j.scitotenv.2016.09.094">http://dx.doi.org/10.1016/j.scitotenv.2016.09.094</a> TyPol – A new methodology for organic compounds clustering based on their molecular characteristics and environmental behavior. <i>Chemosphere</i>, Volume 111, September 2014, Pages 613-622.</p> <p>Mike Unger, PhD Virginia Institute of Marine Sciences munger@vims.edu Leader of an on-going project on the long-term monitoring of the fate and effects of TBT and Kepone in Chesapeake Bay. <a href="https://doi.org/10.21220/V5ZW35">https://doi.org/10.21220/V5ZW35</a></p> <p>Carmen Dominguez, PhD Universidad Complutense de Madrid carmdomi@ucm.es Research work on In situ chemical reduction for chlorinated compounds See for instance <a href="https://doi.org/10.1016/j.jwpe.2018.10.011">https://doi.org/10.1016/j.jwpe.2018.10.011</a></p>
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1  
2 **Physico-chemical and agronomic results of soil remediation by *In Situ* Chemical**  
3 **Reduction applied to a chlordecone contaminated nitosol in a French Caribbean banana**  
4 **plantation**  
5  
6

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## Abstract

The In Situ Chemical Reduction process was tested in a nitisol in a French Caribbean banana plantation using five different soil amendments. The addition of 2.8 % or 4.0 % of ZVI (dw/dw, 2 different trial plots) in the 0 – 40 cm soil layer lowered the initial chlordecone (CLD) concentration by up to 74 % or 69 % in 37 days or 94 days, with 75 % of the decrease achieved after only 21 or 24 days of treatment depending on each trial plot. The addition of commercially available Daramend® was also tested applying the 6 % dose recommended by the manufacturer and using either the regular alfalfa-based product or a bagasse-based product specifically formulated for the study. Both significantly lowered CLD concentrations, but to a lesser extent than with the ZVI-only amendment. A bagasse-ZVI mixture prepared on site produced results slightly better than the two Daramend®. The percentage decreases in CLD concentrations were correlated with the negative redox potentials achieved. In all the trial plots, dechlorinated transformation products appeared in the soil and soil water as the CLD concentrations decreased, with H atoms replacing up to 4 and 7 of the 10 Cl atoms, respectively. None of these degradates appeared to accumulate in the soil or soil water during the treatment. Instead, the reverse occurred, with an overall downward trend in their concentrations over time. The effects of ISCR treatment on agronomic and human health-related parameters were measured in three different crops. The radishes produced with some treatments were visually of lower quality or smaller in size than those grown in the control plots. Lower yields were observed for the cucumbers and sweet potatoes grown after applying the bagasse-based amendments. Mortality among cucumber seedlings was observed after treatment with ZVI only. Simple operational solutions should suffice to remedy these negative agronomic effects. As regards human health-related effects, the CLD concentrations in radishes grown with three of the amendments were significantly lower than in the two control plots and well below the MRL, which was substantially exceeded in the radishes grown on untreated soil. For cucumbers, the treatments with regular Daramend® and with a local bagasse-ZVI mixture produced fruits with CLD below the MRL and also below the concentrations in one of the two control plots. As for the sweet potatoes, adding a bagasse-ZVI mixture had a significant positive effect by decreasing contamination to below the levels in the two control plots and below the MRL.

**Keywords:** Chlordecone; degradates; soil decontamination; chemical reduction; plant; Maximum Residue Level

## INTRODUCTION

Cases of environmental contamination by chlordecone (CLD) have been documented for many years. This can result from industrial CLD production, as in the James River case (Borsetti and Roach, 1978; Carver and Griffith, 1979; Huggett & Bender, 1980), or from its application on farmlands as an insecticide, resulting, in Guadeloupe, in its proven presence in soils and rivers (Snegaroff, 1977), but also in a whole series of living organisms in the ecosystems of its banana-growing regions (Kermarrec, 1980).

Harmful effects of chlordecone on human health were reported as early as 1978 (Cannon et al, 1978; Cohn et al, 1978; Reuber, 1979). Subsequently, teratogenic and pro-carcinogenic effects in birds (Eroschenko 1981) and an effect on the incidence of hepatocellular carcinoma in rats (Sirica et al 1989) were identified. A synthesis of all studies on its toxicity in animals and humans up to 1995 was published that year (Faroon 1995). The oestrogenic activity of CLD, which can be responsible for endocrine disruption, was later demonstrated *in vitro* (Hammond

1 1979; Clere 2012; Alabed Alibrahim 2018). Epidemiological studies in the French Caribbean  
2 have shown an increased occurrence of prostate cancer (Multigner et al, 2010), a negative  
3 impact on the cognitive, visual and motor development of infants (Dallaire et al, 2012; Multigner  
4 et al, 2016) and pregnancy complications (Kadhel et al, 2014).  
5

6 In the last twenty years or so, sampling campaigns have been organised to collect data on  
7 CLD contamination of ecosystems in the French Caribbean and to investigate the mechanisms  
8 involved in its transfer between ecosystems and between ecosystem compartments. Data are  
9 now available for surface and ground waters (Bocquené and Franco, 2005), fisheries and  
10 seafood resources (Coat et al 2006; Bertrand et al 2009), freshwater fish and crustaceans  
11 (Monti and Coat 2007), soils (Brunet et al 2009, Cabidoche et al 2009), ducks (Jondreville et  
12 al 2014), bulls (Jurjanz et al, 2017) and bovine livers (Saint-Hilaire et al, 2018).  
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14

15 From 2002 to 2005, administrative measures were introduced to limit the exposure of  
16 populations by regulating the marketing of different types of vegetables (Achard et al 2007;  
17 Joly 2010), poultry and other animal foods (Official Journal of the French Republic, 2005;  
18 *Journal Officiel de la République Française*, 2005). Consumption and commercialisation of fish  
19 and seafood have also been partly banned (Guadeloupe Regional Prefecture, 2010;  
20 *Préfecture de la Région Guadeloupe*, 2010). Regarding vegetables consumed, studies on the  
21 mechanisms involved in soil-to-plant transfers have produced a major advance for crisis  
22 management by establishing threshold soil concentrations above which the cultivation of  
23 different types of crops should be either banned or discouraged (Cabidoche & Jannoyer,  
24 2012).  
25  
26

27 In view of the need to back up regulatory approaches to crisis management with measures to  
28 reduce contamination, a group of experts attempted to identify potential depollution methods  
29 that could be applied to soils, sediments and water in Martinique and Guadeloupe (Clostre et  
30 al, 2010). Although the central role, whether direct or indirect, of soil contamination in the  
31 degradation of all French Caribbean ecosystems is undeniable, few studies have yet been  
32 made on possible methods for decontaminating soils.  
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34

35 Phytoremediation by crop plants is limited by the very low soil-to-plant transfer rates (Clostre  
36 et al, 2014, 2015, 2016; Woignier et al, 2012, 2016). The potential of other plants also seems  
37 quite insufficient: over one growth cycle, two *Miscanthus* species could extract only 0.03 % of  
38 the mass of CLD added extemporaneously to a clay-loam soil to simulate contamination by 1  
39 mg of CLD/kg of dry soil (Liber et al, 2018).  
40  
41

42 Neither has biodegradation proved effective to decontaminate soils, even under laboratory  
43 conditions. In andosol microcosms sieved to < 2 mm and placed in aerobic conditions with an  
44 added solution of <sup>14</sup>C-CLD in acetone, no more than 4.4 % of the initial dose of <sup>14</sup>C-CLD was  
45 mineralised after 215 days (Fernandez-Bayo et al, 2013).  
46  
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48 On the other hand, an adaptation of the In Situ Chemical Reduction principle (ISCR) to  
49 laboratory 80 kg mesocosms of the 3 main soil types of the French Caribbean contaminated  
50 by CLD has produced very encouraging results (Mouvet et al, 2017). The trial used the  
51 Daramend® amendment with added Zero Valent Iron filings (ZVI) in a series of cycles  
52 alternating reducing and oxidising conditions. After 6 months of treatment, CLD concentrations  
53 dropped by 74% in nitisol, 71 % in ferralsol and 22 % in andosol. Eleven dechlorinated products  
54 of CLD transformation were identified, from mono- (CLD -1Cl) to penta-dechlorinated (CLD -  
55 5Cl). None accumulated during the trial and of the seven ecotoxicity tests implemented, six  
56 showed no difference between the treated soils and the untreated control samples.  
57  
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59 The effect of ZVI alone, without the easily degradable organic material in Daramend®, was  
60 investigated using distilled water to which was added 100 mg/l of CLD dissolved in acetone  
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1 and 0.2 g of ZVI. The CLD was entirely transformed as from Day 14 into 14 dechlorinated  
2 degradates (Belghit et al, 2015) identical to those formed after ISCR treatment of actual soils  
3 in the laboratory (Mouvet et al, 2017).  
4

5 This series of results for chemical reduction is consistent and promising but was obtained in  
6 the laboratory and therefore required validation under actual field conditions. This was the  
7 object of the study presented here, which had two main aims and was conducted using only  
8 facilities that were readily available in French Caribbean banana-growing areas.  
9

10 The first aim was to quantify the effects of an ISCR approach on CLD concentrations and the  
11 formation of degradates in the soil of a banana plantation under natural conditions. As indicated  
12 above, laboratory results using an aqueous matrix, compared to results with real soils, suggest  
13 that ZVI has a major role in CLD transformation. As well as the Daramend<sup>®</sup> amendment,  
14 promoted by the ISCR patent holders, a ZVI-only amendment was therefore tested *in situ*, in  
15 two different grain sizes. Since bagasse from sugar cane is locally available and could play the  
16 same role as the alfalfa in Daramend<sup>®</sup>, two other trial treatments with added bagasse and  
17 added ZVI, one provided by the Daramend<sup>®</sup> manufacturer (FMC) and one prepared on site by  
18 the project team, were also applied.  
19  
20

21 The second aim was to study the influence of the ISCR procedure on plants grown on the soil  
22 after treatment, since consumption of plants is one of the main sources of human exposure to  
23 CLD (Dubuisson et al, 2007; Guldner et al, 2010). A decrease in soil concentrations obtained  
24 without also lowering concentrations in plants would be only half a success. This study  
25 therefore addressed both agronomic criteria (yields, unit mass, visual quality) and human  
26 health-related criteria (CLD concentrations in parts consumed) for radishes, cucumbers and  
27 sweet potatoes grown on trial plots treated with the different ISCR variants and on two control  
28 plots.  
29  
30

## 31 32 33 34 **MATERIAL & METHODS**

### 35 36 **Experimental plot and remediation treatments applied**

37 The study parcel is a banana plantation in Martinique, located to the north-west of Fort-de-  
38 France at an altitude of 71m and growing on a nitisol with proven chlordecone contamination  
39 of the 0 - 40 cm soil horizon, at  $0.71 \pm 0,26$  mg/kg, n = 24. Because of this contamination,  
40 cultivation of various subsistence crops is discouraged (Cabidoche & Lesueur-Jannoyer,  
41 2012).  
42  
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44

45 The ISCR patent (United States Patent, 2000) describes the process as involving multiple  
46 treatment cycles that alternate strongly reducing conditions with oxidizing conditions. The  
47 reducing conditions result from the addition of Daramend<sup>®</sup> amendments and water to obtain a  
48 soil moisture content close to its water holding capacity. The regular Daramend<sup>®</sup> soil  
49 amendment used for the study and purchased from the US company FMC, was a mixture of  
50 70 % alfalfa and 30% ZVI. In order to test a soil amendment containing a local raw material  
51 instead of alfalfa, two other amendments containing bagasse were tested: Daramend<sup>®</sup> with  
52 bagasse (also developed by FMC with 70 % bagasse and 30 % ZVI) and a bagasse/ZVI  
53 mixture (developed by the BRGM with 70 % bagasse and 30 % "coarse" ZVI). Finally, two  
54 treatments with ZVI only were applied, coarse ZVI (30 % < 50  $\mu$ m; Lövink Technocast b.v,  
55 7060 AA Terborg, Netherlands, imported from Poland) and fine ZVI (98 % < 50  $\mu$ m; Dousselin  
56 iron powder NC 100.24; Dousselin & Geoffray-Jacquet Réunion, 69270 Couzon au Mont D'Or,  
57 France).  
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1 The parcel was divided into 6 trial plots (105 m<sup>2</sup>, 15 x 7 m): P1 with coarse ZVI; P2: control;  
2 P3: Daramend<sup>®</sup> with bagasse; P4: regular Daramend<sup>®</sup>; P5: fine ZVI; P6: bagasse + coarse  
3 ZVI.  
4

5 Based on FMC's expertise (J. Mueller, personal communication), a 6% dose (dw/dw) was  
6 applied in the P3 & P4 plots with Daramend<sup>®</sup>. The same dose was applied for the BRGM's  
7 bagasse + ZVI treatment. 300 kg of quicklime with 52 % CaO were also applied in the P3 and  
8 P4 trial plots to obtain the pH recommended by FMC, of about 6.5 (the final pH was quite close  
9 to the target, with the soil water pH for P3 and P4 at 6.9 on completion of the ISCR treatment).  
10 For the P1 & P5 trials using ZVI only, a smaller mass of amendment was used (4 % dw/dw),  
11 because the cost of the ZVI powder limited the amount that the study could afford.  
12

13 An additional adjacent plot, PA, 100 m<sup>2</sup>, was treated with 2.8 % (w/w) coarse ZVI in the second  
14 phase of the study. This plot was equipped with suction cups during the ISCR treatment to  
15 monitor concentrations of CLD and degradates in the soil water. As the background  
16 concentration in this plot was much higher than in the 1<sup>st</sup> control plot, P2, a second control plot,  
17 labelled P8, was used in addition to P2 for the agronomy part of the study.  
18

19 The total mass of each amendment was incorporated into the soil down to 35 - 40 cm, in two  
20 successive half-doses and cross-ploughing six times after each application from north to south  
21 and from east to west. A rotary spader was used in the P1, P5 and P6 trial plots, and an  
22 Adventus-FMC tractor-driven rotary tiller in the P3 and P4 trial plots.  
23

24 After ploughing to incorporate the amendments, the soil was compacted by driving an 8200 kg  
25 tractor across the entire parcel to reduce the amount of air that could compromise treatment  
26 efficiency by chemical reduction. This increased the apparent density of the 0-10 cm horizon  
27 from 0.8 to 1.2. After applying the treatment, a plough was again used to break up and aerate  
28 the soil.  
29

30 The parcel was irrigated with a system of 5 parallel sprinkler lines running down their length.  
31 Each line was fitted with 10 rotating sprinklers 10 m apart. This set-up produced an average  
32 discharge of 10.9 ± 1.3 mm/h, n = 12, as measured from the volumes of water collected in tubs  
33 distributed randomly across the entire study parcel. The parcel was irrigated for the first time  
34 just after incorporation of the soil amendments, until puddles of water appeared in several  
35 places. It was irrigated for the second time when the soil moisture content dropped below the  
36 water-holding capacity determined before treatment (0.42). To preserve soil moisture and  
37 minimise its re-oxygenation through exchanges with the atmosphere, the trial plots were  
38 covered with waterproof tarps after each irrigation phase.  
39

40 The total irrigation water height amounted to 154 mm over the 12 weeks of treatment of P1 to  
41 P6, or the equivalent of 8 weeks of conventional banana crop irrigation in the study zone.  
42 Accumulated rainfall over the parcel during the 3 months of study amounted to 610 mm  
43 (monthly average: 203 ± 35 mm, Mouvet et al, 2016 a). The total water height for PA and P8  
44 (control 2) amounted to 195 mm over the 8 weeks of treatment, during which accumulated  
45 rainfall amounted to 237 mm. In terms of added water height, the irrigation component in the  
46 process was therefore in no way unusual.  
47

## 48 **Soil sampling and characterisation, Eh determination and analyses of chlordecone and 49 degradates**

### 50 *Initial soil characterisation*

51 Twelve independent soil samples were taken at random locations across the 1000 m<sup>2</sup> plot.  
52 The main physico-chemical parameters were analysed by an accredited laboratory (SAS,  
53 Ardon, France) using standardised procedures previously reported (Mercier et al, 2013). Two  
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1 techniques were used to verify the presence of halloysite clay, the main mineralogical  
2 characteristic of nitisols. The crystal structure of halloysite was characterised by X ray  
3 diffraction using a Philips PW 1830 (Cu K $\alpha$ ) diffractometer. The diffraction angles studied  
4 ranged from 2 to 50 degrees and the inter-reticular distances investigated, d, were within the  
5 range of 1.1 to 11 Å. For infrared spectroscopy, an IR-FT Nicolet 510P (ThermoFischer  
6 Scientific Inc., Waltham, MA, USA) spectrometer was used and the soil samples were  
7 characterised in transmission mode after dilution in KBr pellets with a 5 10<sup>-3</sup> mass ratio. The  
8 IR spectra were obtained in the wavelength range of 400 - 4 000 cm<sup>-1</sup>.  
9

#### 10 *Subsequent soil sampling strategy*

11 The trial plots were subdivided into 3 zones of equal size. In each zone, 4 sampling points  
12 were located by a random selection of X - Y coordinates, keeping to a distance of 0.5 m from  
13 the plot edges (and from the suction cups used when soil moisture was investigated). 12  
14 samples were thus taken on each date in each trial plot.  
15

16  
17 At each sampling point, a 900 g soil sample was taken with a garden fork from the 0 - 20 cm  
18 horizon and two 450 g samples were taken with an auger, first from the 20 - 30 cm horizon (1<sup>st</sup>  
19 drilling), then from the 30 - 40 cm horizon (2<sup>nd</sup> drilling). These samples taken at 3 different  
20 depths were then thoroughly mixed together to produce a single sample for the 0 - 40 cm  
21 horizon. This procedure is repeated for each of the 4 sampling points of the zone, and an  
22 overall composite sample of the zone is produced from these 4 single samples. For each trial  
23 plot, we thus obtained 3 composite soil samples from the 0 - 40 cm horizon, each to be  
24 analysed separately for CLD and degradates.  
25  
26

#### 27 *Measurement of redox potential*

28 For each of the 12 sampling points, 5 redox measurements were taken for the 0 - 20 cm horizon  
29 in a hole made with a garden fork (1 measurement on each of the 4 sides of the hole and 1 at  
30 the bottom), 3 for the 20 - 30 cm horizon from hand-augered samples and 3 for the 30 - 40 cm  
31 horizon from samples taken by the second augering. The point of making so many  
32 measurements was to reduce the effects of soil heterogeneity. In our presentation of the  
33 results, the figures for the 20 - 30 cm and 30 - 40 cm horizons are averaged to represent the  
34 20 - 40 cm horizon.  
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38 The probe was calibrated before making the measurements using a standard 220 mV solution.  
39 The reference electrode was an Ag/AgCl (WTW, IDS ORP Electrode Sentix® ORP 900,  
40 supplied by VWR). The indicator electrode was a platinum ring and the reference electrolyte  
41 was KCl 3M (measurement range: - 1 250.0 to +1 250.0  $\pm$  0.2 mV). The electronic unit was a  
42 digital multi-parameter portable WTW® 3 420 (supplier: Val de Loire Labo, F-41220 Saint-  
43 Laurent-Nouan, France).  
44  
45

46 All readings were corrected for the potential of the hydrogen electrode with the following  
47 equation:  
48

$$49 \text{corrected Eh} = \text{measured Eh} + 224.6 - 0.71418 \times T \text{ (}^\circ\text{C)} + \text{DE}$$

50  
51 where DE is the difference between the measured value of the standard at the measurement  
52 T° (long-stem digital Multi Thermometer: - 50 °C to 150 °C,  $\pm$  0,5 °C) and the value that the  
53 standard should theoretically have at this T°.  
54  
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#### 56 *Determination of chlordecone and its transformation products in soil samples*

57 The samples were dried (40  $\pm$  1°C for 72 h) in aluminium trays before crushing and sieving to  
58 < 2 mm. A representative aliquot was further ground down to < 80  $\mu$ m, a grain size optimising  
59 the representativeness of the sample taken for analysis. Another representative aliquot was  
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1 dried at 105 °C to measure the residual moisture content after drying at 40 °C, and used to  
2 express results relatively to the actual dry mass.  
3

4 The extraction and analytical methods (Bristeau et al, 2014) are briefly summarised here. The  
5 determination of CLD and its transformation products started with Pressurised Liquid  
6 Extraction of the 5 g (dw) soil sample ground down to < 80 µm with a 50/50 v/v acetone/hexane  
7 mixture at 100 °C and 110 bars of pressure. CLD-C13 and transnonachlore were used as  
8 internal standards. GC/MS/MS analyses were performed with a Bruker GC450 gas  
9 chromatograph, a 1177 injector, a Combi Pal (CTC) automated sampler and a 300MS triple  
10 quadrupole mass spectrometer. Recovery rates from the 3 soil types ranged from 92 to 139%  
11 (mean = 114 %, standard deviation = 16%, n = 24), the quantification limit for CLD being 0.03  
12 mg kg<sup>-1</sup> (Bristeau et al, 2014).  
13  
14

15 Three CLD transformation products were quantified thanks to available analytical standards:  
16 5b-monohydroCLD, another monohydroCLD for which the data available at the time of the  
17 study (Belghit et al, 2015) did not enable us to determine whether the dechlorination position  
18 is 5- or 5a (CAS nomenclature), and chlordecol, with QL of 0.03 mg/kg for the 3 compounds.  
19 Concentrations in mg/kg could not be calculated for the transformation products for which no  
20 standards were available. However, we were able to estimate their relative abundance by  
21 calculating their relative peak areas (Mouvet et al, 2017).  
22  
23

## 24 **Soil solution sampling and analyses**

### 25 *Sampling with suction cups*

26 Suction cups were installed in the PA trial plot (with 2.8 % ZVI) in order to determine  
27 concentrations of chlordecone and any degradation products in pore water in the soil. Various  
28 types of suction cup tips were tested in laboratory conditions: ceramic, stainless steel and  
29 glass. The glass type (item 4311.20/00 Ecotech, Germany, pore diameter: 20 µm) was  
30 selected as it sorbed the least CLD (data not presented here).  
31  
32  
33

34 Before they were installed, all the suction cups were soaked for about 12 hours in distilled  
35 water in order to clean off any particles of manufacturing residue. The spatial coordinates of  
36 the cups were determined by generating suites of random numbers (Excel), keeping to a  
37 distance of 0.5 m from the inner edges of the trial plots. Three pairs of suction cups were  
38 installed, with one at a depth of 35 cm and one at 50 cm, at an angle of 45° to minimise the  
39 preferential water flow that can lead directly to the tip if the cup is installed vertically. The  
40 diameter of the auger used to drill the hole was 1 cm larger than that of the suction cup: a  
41 silicone filler was used to seal the gap around the suction cup after installation.  
42  
43

44 Negative pressure (25 h, - 0.4 bar ± 0.02 bar) was applied first to eliminate the moisture from  
45 the silicone filler and a second time (48 h to 50 h, - 0.4 ± 0.02 bar) before sampling the water  
46 to be analysed. The water was collected in brown glass bottles, then transferred in the  
47 laboratory into 250ml flasks, adding analytical quality acetone at a rate of 0.1% of the water  
48 volume collected.  
49

### 50 *Analyses of soil solution*

51 The samples collected from the suction cups were spiked with 13C chlordecone (internal  
52 standard for chlordecone and its degradation products) and transnonachlor (internal standard  
53 for chlordecol). Liquid-liquid extraction as from a 100 mL sample was performed with twice 5  
54 mL of a hexane/acetone mixture (85/15, v/v) in the presence of sodium chloride (50 g/L) at a  
55 pH of 2.5 (± 0.5). The extract was evaporated and finalised to 0.5 mL in cyclohexane.  
56  
57

58 Analysis was by gas chromatography coupled with mass spectrometry, using the same  
59 parameters as for the soil analysis. The quantification limit for analysing chlordecone, 5b-  
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61  
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1 hydrochlordecone and 5- or 5a-hydrochlordecone is 0.07 µg/L. As with the analyses in soil  
2 samples, the other transformation products were semi-quantified through their relative  
3 chromatographic peak area.  
4  
5  
6

## 7 **Agronomy section**

### 8 *Plants tested, soil preparation before planting, establishing the crops*

9  
10 Three plants were tested: radishes (*Raphanus sativus*), cucumbers (*Cucumis sativus*, Var.  
11 EUREKA) and sweet potatoes (*Ipomoea batatas*). These 3 plants were chosen because they  
12 are reference crops in terms of their response to in soil pollution (Clostre et al, 2014) and  
13 because they contribute significantly to consumer exposure (Dubuisson et al, 2007 ; Guldner  
14 et al, 2010).  
15  
16

17 Soil preparation before planting involved rototilling three times to a depth of 40 cm in each trial  
18 plot. A ridging plough was then used to form four ridges 30 cm high and 1.2 m apart in each  
19 trial plot, in order to optimise plant growth and development and facilitate work in the plots.  
20 Finally, the soil was raked and hoed by hand to break up the clods and shape the ridges.  
21  
22

23 The interval between the ploughing that completed the ISCR treatment and plantation of the  
24 crops was 4 months for P1 to P7 and just 1 month for PA. To ensure that the trials reflected  
25 usual procedure, the planting method and density were established in accordance with the  
26 recommendations published by the Martinique Chamber of Agriculture. In each trial plot, the  
27 radishes were sown in two rows 15 cm apart in three beds 3 linear metres in length, making a  
28 total of 6 rows x 3 linear metres in each plot. 50 cucumber seedlings in mini soil blocks were  
29 transplanted into each plot in 5 beds of 10 seedlings 45 cm apart. The sweet potato cuttings,  
30 about 25 cm long on average with at least 3 buds, were taken from an experimental plot run  
31 by the Martinique Chamber of Agriculture. 50 cuttings were planted in each plot, in 5 beds of  
32 10 cuttings 25 cm apart.  
33  
34

### 35 *Irrigation system and analysis of irrigation water*

36 The irrigation system was typical of those used in banana plantations and comprised 12  
37 sprinklers with a 5-metre sprinkling radius, placed 9 metres apart so that each trial plot could  
38 be entirely irrigated with two sprinklers. The average flow rate of 2.6 mm/hour (n = 12, standard  
39 deviation = 0.8) was assessed using tubs placed randomly across the plot for one hour during  
40 irrigation. The water was pumped into the storage pond adjacent to the banana plantation  
41 studied, using a pump fitted with a suction strainer.  
42  
43

44 For the irrigation water analysis, due to local operational constraints and overall financial  
45 constraints, a sampling strategy had to be used involving composite integrating samplers. On  
46 each of the 8 sampling dates, one 1-litre sample was collected in a glass bottle from 4 randomly  
47 chosen sprinklers. The two samples taken on two successive dates (at 2, 4, 5 or 10 day  
48 intervals) were then mixed and homogenised to produce a composite sample. The four  
49 composite samples thus obtained, each corresponding to 8 sub-samples (4 sprinklers on 2  
50 dates), were then analysed. A 5<sup>th</sup> sample taken from 4 sprinklers on one day only was also  
51 analysed.  
52  
53

54 The analytical procedure combined solid-phase micro-extraction (SPME) for 10 minutes,  
55 separation by gas chromatography (GC) and identification by mass spectrometry (MS and  
56 MS/MS). Quantification was based on a standard addition method (Soler et al, 2014).  
57

### 58 *Fertilisation*

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1 To provide the crops with the necessary nitrogen, phosphorus and potassium, complete  
2 banana fertiliser mixtures (14 - 4 - 28), DAP (Di-Ammonium Phosphate) and KCl, all routinely  
3 used by farmers in the French Caribbean, were applied to all the trial plots (Table 1).  
4

#### 5 *Use of suction cups to investigate concentrations of chlordecone and degradates in the soil* 6 *solution*

7 The same suction cups as those used for the physico-chemical phase of the study were  
8 installed in P2 (control 1), P4 (regular Daramend®) and PA (ZVI only). Three suction cups were  
9 installed in each of these plots, each placed between 2 sweet potato plants at a depth of 30  
10 cm and at a 45° angle to minimise preferential vertical transport along the auger hole made for  
11 the suction cup.  
12

13 Pre-treatment of the suction cups before their installation, the installation method and the  
14 sampling protocol are described above. Samples were taken on three dates spread out over  
15 the growth cycle. For each sampling point (each suction cup), a composite sample was  
16 produced from the 3 sampling dates, priority having been given to spatial variability (3 different  
17 locations, 1 average sample per location) over a temporal variability approach (1 composite  
18 sample from the 3 suction cups for each of the 3 dates). Three analyses would therefore be  
19 available for each of the 3 trial plots.  
20  
21

22 CLD and its degradates were analysed in accordance with the protocol described above for  
23 the suction cups installed for the physico-chemical phase of the study.  
24

#### 25 *Harvest for the analysis of chlordecone and its degradates*

26 The radishes were carefully dug out with a mini-excavator to retain their fine roots. All radishes  
27 along a 1.5 metre row were collected in one repetition. The radishes were sorted into 2  
28 categories, those of marketable size (more than 1.2 cm in diameter) and the smaller  
29 individuals, then counted and weighed (Mettler PE600 precision scales). Chlordecone was  
30 analysed for each trial plot from a composite sample obtained from 75 homogeneous radishes  
31 of median size, corresponding to 25 radishes from each of the 3 beds of seedlings. After  
32 washing - first with tapwater, then with distilled water - and drying with absorbent tissue, the  
33 radishes were cut up axially into even-sized pieces, then stored in a freezer at - 18 °C until  
34 shipping to the laboratory in isotherm packages refrigerated with dry ice packs. Five sub-  
35 samples were taken from the composite sample and analysed separately.  
36

37 The cucumbers were harvested when the control cucumbers had reached their marketable  
38 size of 12 cm. Six more harvests then took place, one every 3 to 4 days over 3 weeks. Each  
39 time, the cucumbers were weighed, counted and sorted into marketable (L > 12 cm) and non  
40 marketable (L < 12 cm) fruits. The composite sample for the analysis was made up from each  
41 of the 5 beds in each trial plot, using 12 average-sized cucumbers chosen randomly from the  
42 batches comprising 4 cucumbers harvested on 3 different dates. Each cucumber was washed  
43 first in clean water, then in distilled water, then dried with absorbent tissue. Each was cut into  
44 8 pieces, with two longitudinal cuts along the axis and one cut across the width. Four pieces  
45 were chosen and added to the 12 pieces taken in the same way from the three other  
46 cucumbers harvested from the same bed on the same date, to produce a composite sample  
47 of 16 independent pieces from the same day's harvest. By combining the samples made up  
48 for each bed on three different dates, we obtained a final composite sample of 48 cucumber  
49 pieces. This composite sample was then vacuum packed and stored in a freezer until shipping  
50 to the laboratory in a refrigerated package. Five sub-samples were taken from the composite  
51 sample and analysed separately.  
52

53 The sweet potatoes were harvested 5 months after planting. All tubers dug out with a garden  
54 fork were collected. They were counted, weighed and sorted in the laboratory, separating out  
55 the non marketable tubers (L < 10 cm, or calibre < 5 cm, or damaged tubers), which would not  
56 be analysed. For each of the 5 beds, 10 uniform sweet potatoes of marketable size were  
57 chosen and carefully washed in clean and then distilled water, scrubbing them gently to  
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1 preserve the fine skin covering the tubers. Particular care was taken with crooked tubers to  
2 prevent any earth from contaminating the sample. 3 rounds 1 cm thick were cut from each of  
3 the 10 tubers. The 30 rounds were then cut in half along the axis to make up a composite  
4 sample, then placed in bags and stored in a freezer until shipping to the laboratory in  
5 refrigerated packages. Five sub-samples were taken from the composite sample and analysed  
6 separately.  
7

#### 8 *Analysis of chlordecone and certain degradation products*

9 The plant samples were analysed at the analytical laboratory of the Drôme *département* (LDA  
10 26 ; 37 Avenue de Lautagne, BP 118, F-26904 Valence cedex 9, France). The French Agency  
11 for Food, Environmental and Occupational Health & Safety standard method for CLD analysis  
12 in plant material was applied (Agence nationale de sécurité sanitaire de l'alimentation, de  
13 l'environnement et du travail, 2015). After extraction and purification, the concentrations of  
14 chlordecone, chlordecol and 5b-hydro CLD were measured with a high-performance liquid  
15 chromatograph mass spectrometer (Thermo, West Palm Beach, USA) TSQ Quantum). The  
16 quantification limits for these 3 micropollutants were respectively 0.5, 2.6 and 0.5 µg/kg of fresh  
17 material for cucumbers and sweet potatoes, and 1, 10 and 1 µg/kg of fresh material for  
18 radishes. The higher quantification limit for radishes is due to the smaller amount of total  
19 biomass available for each sample. By convention, the detection limit is equal to the  
20 quantification limit divided by 3.  
21  
22

#### 23 **Statistics**

24  
25  
26 All the statistical analyses and boxplots were performed with R (R Core Team, 2014), with a 5  
27 % p-value. The distribution of the values was assessed for normality with the Shapiro-Wilk test,  
28 with variance equality verified by the Bartlett test.  
29

30 For the values of redox and CLD and degradation products the following tests were applied:

- 31 - Comparison of redox values, CLD and degradation products at different sampling  
32 campaigns: non-parametric Kruskal-Wallis rank tests, using the R "agricolae" package.
- 33 - Comparison of different plots and depths at each sampling time: ANOVA followed by Tukey  
34 HSD test (Honest Significant Difference) to compare treatments using the R "stats"  
35 package.  
36  
37

38  
39 For the agronomy data the following tests were applied to assess the effects of the treatments  
40 on each plant:

- 41 - Dunnett test to compare treatments with a control sample, "multcomp" package (Torsten  
42 Hothorn et al, 2008),
- 43 - Tukey HSD test (Honest Significant Difference) to compare treatments, R "stats" package,
- 44 - LSD (Least Significant Difference) method to compare treatments by group, adjusted by  
45 Bonferroni, R "agricolae" package (Felipe de Mendiburu, 2014).

46  
47 The Wilcoxon-Mann-Whitney test comparing treatments was applied in cases of non-normal  
48 distribution or unequal variance.  
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## 54 **RESULTS & DISCUSSION**

### 55 **Main soil parameters**

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1 Overall, most values (Table 2) were similar to those measured for another nitisol sample from  
2 Guadeloupe (Mercier et al, 2013), suggesting that the present study would be representative  
3 of French Caribbean nitisols in general.  
4

5  $P_2O_5$ ,  $K_2O$  and  $CaO$  appeared to vary somewhat ( $15 \leq CV \leq 25 \%$ ) between the 12 replicates.  
6 These parameters are not very likely to influence the mechanisms involved in ISCR and their  
7 heterogeneity should therefore not influence the effects of the treatment applied to each plot.  
8 In contrast, the parameters likely to play an important role in ISCR (pH, total Fe and organic  
9 carbon) were fairly homogeneous ( $3 \leq CV \leq 10 \%$ ) across the study zone. The same  
10 parameters determined for P2, the additional plot treated with ZVI in the agronomy part of the  
11 study, did not differ significantly from those in table 2, with for instance a total iron content (%)  
12 of  $8.3 \pm 0.3 \%$  and a water pH of  $5.7 \pm 0.4$ .  
13  
14

### 15 **Presence of halloysite**

16 The X-ray diffractogram of all 6 plots shows diffraction peaks at 4.45 and 7.4 Å (Online  
17 Resource 1). These inter-reticular distances are characteristic of halloysite clays (Dubroeuq  
18 et al, 1998; Onodera et al, 2001). The IR spectrum for all plots shows 2 clear peaks in the OH  
19 region ( $3\ 500 - 3\ 800\ cm^{-1}$ ; Online Resource 2), which are characteristic of halloysite-type  
20 phyllosilicate clays (Colmet - Daage et al, 1965, Gustaffsson et al, 1995), unlike amorphous  
21 clays that do not present the same well-defined bands. The plots studied are therefore typical  
22 nitisols with respect to the types of constituent clays.  
23  
24

### 25 **Redox potential in the 0 - 20 cm soil layer**

26 The changes of Eh values throughout the duration of the experiment for all trial plots are  
27 illustrated in Figure 1. The full data set will be described and discussed below, focusing first  
28 on the comparison between treatments for each of the 7 measuring campaigns, and then on  
29 the changes over time for each of the 6 different treatments.  
30  
31

#### 32 *Comparison between treatments for each measuring campaign*

33 On the day before the experiment started, the mean Eh (mV vs. SHE) was  $581 \pm 54$  in P1  
34 (coarse ZVI),  $563 \pm 39$  in the control (P2),  $527 \pm 76$  in P3 (Daramend® bagasse),  $529 \pm 63$  in  
35 P4 (regular Daramend®),  $540 \pm 59$  in P5 (fine ZVI) and  $533 \pm 80$  in P6 (Bagasse with ZVI). In  
36 P3, P4, P5 and P6, the values do not differ from each other or from the control plot P2. The  
37 mean value in P1 is not statistically different from the control plot but slightly higher than in the  
38 4 other treated plots (Fig 2).  
39  
40

41 Two days after adding the amendments (T2), corresponding to 1 day after the end of the first  
42 irrigation, the mean redox potential in the control plot was  $628 \pm 52$  mV. The lowest mean Eh  
43 values, of  $-255 \pm 132$  mV and  $-254 \pm 58$  mV, were obtained with the fine (P5) and coarse ZVI  
44 (P1) treatments respectively. This range is very similar to the values obtained in optimised  
45 laboratory conditions with regular 2 to 12 % Daramend® and 1% additional ZVI (Mouvet et al,  
46 2017). The plot treated with the regular Daramend® (P4) yielded a mean Eh value,  $6.9 \pm 218$   
47 mV, very much lower than the control but higher than in the ZVI trials. Spot values below -  
48 300 mV were observed only in P1 (n = 2) and P5 (n = 5), the lowest spot value of all treatments  
49 being recorded at - 405 mV in P5 (fine ZVI plot). The two trials with bagasse and ZVI (P3 and  
50 P6) each had mean Eh values that were lower than in the control plot but still positive.  
51 Statistically, P1 and P5 do not differ from each other but show values significantly lower than  
52 all the other trials. P4 and P6 do not differ from each other but differ significantly from all the  
53 other trials. P2 and P3 differ from each other and from all the other trials (Fig 3).  
54  
55  
56

57 Although few changes occurred between the 3<sup>rd</sup> and 7<sup>th</sup> day (July 1, T2)) of treatment, the mean  
58 Eh values in the two ZVI-only trial plots did begin to increase during that period (Fig 1), leading  
59 to values in P1 becoming no more statistically different to those of P4 and P6 (Fig 4).  
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1 Between the 3<sup>rd</sup> and 21<sup>st</sup> day (July 18, T3) of treatment, the mean Eh decreased by 75 mV in  
2 the control plot and by 113 mV and 64 mV in the regular Daramend<sup>®</sup> and bagasse + ZVI plots  
3 respectively, but a slight increase, of 56 mV, occurred in the Daramend<sup>®</sup> bagasse plot. In  
4 contrast, the increase in mean Eh was very clear for the coarse ZVI, at + 293 mV, and for the  
5 fine ZVI at + 185 mV, which produced a slightly positive value for P1 (39 mV) and a slightly  
6 negative value for P5 (- 70 mV ; Fig 1). This increase can be attributed to a decrease in the  
7 reduction potential of the added amendments as a result of partial oxidation of the added ZVI  
8 and reoxygenation of the soil. Compared to the trials with ZVI only, the decrease (P4 and P6),  
9 or smaller increase (P3), in Eh in the trial plots with easily biodegradable organic matter can  
10 be attributed to the continuous consumption of this biomass and the associated oxidative  
11 species. On the 21st day of treatment (T3), the statistical analysis indicates that the mean Eh  
12 value for all the trial plots was significantly lower than that in the control plot. The drop in Eh  
13 compared to the control was smaller in P3 than in the other 4 trial plots. P3 mean value was  
14 significantly higher than in the other 4 trial plots in which the only difference was between P1  
15 and P4 (Fig 5).  
16  
17

18 On Day 35 (July 30, T4), despite a second irrigation (66 mm) between the 27<sup>th</sup> and 28<sup>th</sup> day of  
19 experimentation (July 22 and 23), Eh continued to increase in both ZVI-only plots (P1 and P5),  
20 reaching mean values of + 352 mV and + 308 mV respectively. In contrast, Eh remained fairly  
21 stable in all other plots. The failure of the 2<sup>nd</sup> irrigation to further decrease the Eh values, or at  
22 least to stop the increase in Eh, may be due to the fact that the mechanisms involved in  
23 lowering the Eh resulting from the oxidation of ZVI when added without easily biodegradable  
24 organic matter had exhausted their potential. At this time of the experiment, P4 and P6 do not  
25 differ significantly from each other but differ significantly from all the other trials, P1, P3 and P5  
26 do not differ significantly from each other but differ significantly from all the other trials, and P2,  
27 with a mean value of + 547 mV, differs significantly from all the other trials (Fig 6). These 3  
28 groups of Eh values match the 3 main types of treatments almost exactly: easily biodegradable  
29 organic matter (P4 and P6), ZVI only (P1 and P5), control (P2). The sole exception is P3,  
30 Daramend<sup>®</sup> bagasse.  
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32  
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34 Between the 44<sup>th</sup> and the 65<sup>th</sup> day of treatment (Online Resources 3 and 4), few changes  
35 occurred (Fig 1), as was the case between the 3<sup>rd</sup> and 7<sup>th</sup> days.  
36

37 At the end of 94 days of treatment (T7), P4 (regular Daramend<sup>®</sup>) and P6 (bagasse + ZVI) differ  
38 significantly from all the other trials, with much lower, slightly positive mean values of + 71 and  
39 + 86 mV respectively, but do not differ from each other (Fig 7). The easily biodegradable  
40 organic matter of these two treatments remained efficient in keeping mean Eh values below  
41 100 mV over a 3-month period in the experimental conditions of this study. The prolonged  
42 lowering of Eh values in the treatment with alfalfa or bagasse probably results from  
43 fermentation of these organic components producing organic acids that counter the production  
44 of hydroxyl ions resulting from the ZVI corrosion process (Dolfing et al, 2008). The trials P1,  
45 P3 and P5 do not differ significantly from each other. The control plot P2 differs significantly  
46 from all other plots except P1. Overall, the distribution of the various treatments into 3 distinct  
47 groups already observed on Day 35 was maintained at the end of the experiment.  
48  
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50

51 In order to provide an overall view covering the whole duration of the treatment, a statistical  
52 analysis was conducted on the basis of a single data-set pooling the 7 measuring campaigns.  
53 On this basis, the mean Eh values in P4 and P6 do not differ from each other but are lower  
54 than the 4 other trial plots which all differ from each other, with values increasing in the  
55 following order: P5 < P1 < P3 < P2 (Fig 8). The mean of all post-treatment Eh values in the plot  
56 treated with Daramend<sup>®</sup> bagasse, at  $363 \pm 173$  mV, was much higher than with the regular  
57 Daramend<sup>®</sup> treatment,  $- 8 \pm 218$  mV. This may be due to a lower reductive capacity of the ZVI  
58 in the regular Daramend<sup>®</sup> formulation, or to the poorer biodegradability of bagasse compared  
59 to alfalfa. However, the mean of all post-treatment Eh values in the plot treated with the  
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1 bagasse + ZVI mix prepared on site with the same % of ZVI as in the Daramend® bagasse, 33  
2 ± 41 mV, is much closer to the mean for the regular Daramend® than for the Daramend®  
3 bagasse. It is therefore tempting to attribute the difference in the mean Eh values of the two  
4 bagasse-based amendments to differences in ZVI efficiency. However, the characteristics (not  
5 measured) of the bagasse used in each of the two corresponding amendments may also have  
6 been different. The available data therefore cannot explain why the Eh values resulting from  
7 the Daramend® bagasse treatment differ so clearly from those obtained with the regular  
8 Daramend® and the bagasse + ZVI mix.  
9

#### 10 *Comparison between measuring campaigns for each treatment*

11 In addition to figure 1 providing an overview of all the data at a glance, we produced box and  
12 whisker plots to better visualise the changes in Eh over time for each treatment and to bring  
13 out the statistically significant differences between measuring campaigns. These plots are  
14 included in the manuscript for the coarse ZVI treatment (Fig 9), the control (Fig 10) and the  
15 regular Daramend® (Fig 11). The corresponding figures for the treatments with Daramend®  
16 bagasse (P3), fine ZVI (P5), and the mix Bagasse - ZVI (P6) are provided as Online Resources  
17 5 to 7.  
18  
19

20  
21 In the coarse ZVI trial P1 (Fig 9), all values after T0 are lower than at T0. The values for the  
22 T1, T2 and T3 dates do not differ from each other, with lower T1 and T2 values than on the  
23 last 4 dates, T4 to T7. T7 exhibits the highest value of all dates except T5 (T5 on the  
24 penultimate measurement date and T7 at the end of the treatment period). The T4 values are  
25 in an intermediate position, higher than at T1 and T2 but not higher than at T3, and lower than  
26 at T5 and T7 but not lower than at T6. These differences over time indicate an initial, rather  
27 short, period of time from T0 to T2, i.e. 7 days, when the Eh values were significantly lower  
28 than during the rest of the treatment. This is followed by an intermediate phase (T3) that shows  
29 Eh values returning close to zero and differs significantly from the previous and next phases.  
30 The third and final phase has Eh values in the 400 - 500 mV range, shows little significant  
31 change from T4 to T7 and leads to a mean value at the end of the treatment (T7) which is the  
32 highest of all trial plots but still significantly lower than the mean value before the treatment  
33 started (T0).  
34  
35

36 In the control P2 (Fig 10), only T1 and T2 differ significantly, with higher values, from the 6  
37 other measuring campaigns. The T1 and T2 values do not differ from each other but show a  
38 slight increase compared to T0. The values from T3 to T7 do not differ from each other and  
39 return to levels that are not different to T0, except the T6 value which is slightly lower than at  
40 T0. This somewhat erratic variation over time reflects the intrinsic heterogeneity of a field plot  
41 and the absence of any action in the control plot that could have had a consistent influence on  
42 mean Eh values.  
43  
44

45 In P3 (Daramend bagasse, Online Resource 5), all values after T0 are lower than at T0 and  
46 do not differ from each other, except the T4 value which is slightly lower than at T3, T6 and  
47 T7.  
48

49 In the regular Daramend® trial P4 (Fig 11), all values after T0 are much lower than at T0 and  
50 do not differ from each other, except the T7 value which is slightly higher than at T3 and T5.  
51 This very consistent effect of the treatment over time very probably reflects the lasting effect  
52 of the easily biodegradable organic matter making up 70 % of the amendment mass.  
53  
54

55 For the fine ZVI trial P5 (Online Resource 6), the changes over time are strikingly similar to  
56 those observed for P1. All values after T0 are lower than at T0. For three dates, T1, T2 and  
57 T3, the values do not differ from each other but are lower than for the 4 later dates. T7 exhibits  
58 the highest value of all dates except T6, from which it does not differ. T4, T5 and T6 do not  
59 differ from each other.  
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1 As in P6 (Online Resource 7), all values after T0 are much lower than at T0 and do not differ  
2 from each other.

### 3 4 **Redox potential in the 20 - 40 cm soil layer**

5 Most of the data for the 20 – 40 cm soil layer (Fig 12), whether on changes over time with any  
6 given treatment or on the differences between treatments at each measuring date, are very  
7 similar to the observations made for the 0 - 20 cm soil layer. The presentation and discussion  
8 concerning the 20 – 40 cm data is therefore much shorter than for the 0 – 20 cm layer.  
9 Accordingly, the focus is on the comparison between treatments for each measuring  
10 campaign, with a selection of box and whisker plots presented as Online Resources.

11  
12  
13 On the day before the experiment started, T0, the range of mean Eh values ( $563 \pm 39$  to  $610$   
14  $\pm 76$  mV) was very similar to that observed in the 0 – 20 cm layer ( $533 \pm 80$  to  $581 \pm 54$  mV).  
15 At T0, the statistical analysis (Online Resource 8) divided the 6 treatments into 4 groups in  
16 each of which no treatment results are statistically different to the other treatment results in the  
17 same group (P1 ; P4 ; P3 = P5 = P2 ; P5 = P2 = P6), while only some treatment results for any  
18 given group may differ from some treatment results in another group (example above: P3  $\neq$  P6  
19 but P5 and P2 = P6). This reflects an overall similarity between the trial plots, an interpretation  
20 which is further supported by the fact that no one treatment differs from all of the others.

21  
22  
23 Two days after adding the amendments, the ranking of the Eh values for the various plots was  
24 very similar to that observed in the 0 – 20 cm soil layer, with mean values of + 664 mV for the  
25 control plot, -111 and – 132 mV respectively for the coarse and fine ZVI plots, and positive  
26 values for the three treatments combining organic matter and ZVI, at + 112 mV in P6, + 80 mV  
27 in P4 and + 307 mV in P3. Statistically, P1 and P5 do not differ from each other but are different  
28 to all the others; the same holds for P4 and P6, while P2 and P3 differ from each other and  
29 from all the others (Online Resource 9). Interestingly, this division into 3 groups corresponds  
30 almost exactly (with the sole exception of P3) to the 3 different types of treatments, as also  
31 observed for the 0 – 20 cm layer.

32  
33  
34 Between Day 3 and Day 21 (July 18) the mean Eh in the control plot dropped slightly, while  
35 the mean redox potential in the ZVI-only plots increased, by 111 mV in P1 and by 46 mV in  
36 P5, although the mean values were still negative, at - 1 mV in P1 and – 86 mV in P5. Over the  
37 same period, the mean redox potential dropped by 160 mV to - 80 mV with the regular  
38 Daramend<sup>®</sup> treatment and by 25 mV to - 13 mV with the ZVI/bagasse mix. The redox potential  
39 in P3 (Daramend<sup>®</sup> bagasse) remained positive, at + 388 mV (Fig 12).

40  
41  
42 Subsequently, the redox potential in the ZVI-only trial plots continued to rise, remaining slightly  
43 negative up to Day 35 (30/07) in P5 but becoming clearly positive (+ 150 mV in P5 and  
44 + 390 mV en P1) by Day 64 (29/08) and beyond. During the same 5-week period, the redox  
45 potential in the plots with added organic matter did not vary significantly and up to the end of  
46 the treatment, on 25/09, remained slightly negative in the plot treated with regular Daramend<sup>®</sup>,  
47 slightly positive in the plot treated with the ZVI/bagasse mix, and clearly positive in the plot  
48 treated with Daramend<sup>®</sup> bagasse (Fig 12).

49  
50  
51 At Day 65, P4 (regular Daramend<sup>®</sup>) and P6 (bagasse + ZVI) differ significantly from all the  
52 other trials, with much lower, slightly positive mean values, but do not differ from each other  
53 (Online Resource 10). The trials P1 and P3, with values close to that of the control, do not  
54 differ significantly from each other but differ significantly from all the other trials. The control  
55 plot P2, with the highest mean value, differs significantly from all other plots. P5 is in an  
56 intermediate position with a mean value which makes it differ from all the other treatments.  
57 Overall, the distribution of the various treatments into 3 distinct groups already observed on  
58 Day 3 was maintained until this late stage of the experiment.

1 At the end of 94 days of treatment (T7), all the treatment results differed: the highest value was  
2 measured in the control plot P2 and the lowest values in P4 and P6. The value closest to P2  
3 was measured in P1, while the values for P3 and P5 came between P2 and P1 on the one  
4 hand and between P4 and P6 on the other hand (Online Resource 11).  
5

6 As also done for the 0 - 20 cm layer, a statistical analysis of a single data-set pooling the 7  
7 measuring campaigns provides an overall view covering the entire duration of the treatment.  
8 The mean Eh values in P5 and P6 do not differ from each other but are lower than the 4 other  
9 trial plots which all differ from each other with values increasing in the following order: P4 < P1  
10 < P3 < P2 (Fig 13). The overall picture is therefore very similar in the 2 soil layers.  
11

### 12 **Effect of the ploughing ending the treatment**

13 Ploughing in order to return the soil to its initial aerobic status caused the values for redox  
14 potential to rise to almost T0. For the 0 – 20 cm layer in P4 for instance, the mean Eh was 529  
15 ± 63 mV before the addition of the amendment and 474 ± 88 mV two weeks after the tilling that  
16 ended the treatment. Given that the mean Eh in P4 had dropped to - 106 ± 194 mV 21 days  
17 after the start of the treatment, the quite drastic effect of applying an ISCR treatment on redox  
18 conditions in soils is therefore easily and quickly reversible.  
19  
20  
21

### 22 **Synthesis and link with literature data**

23 Despite the fact that ISCR clearly relies on reducing conditions, most papers published on the  
24 use of Daramend® or ZVI for the remediation of soil polluted by chlorinated contaminants do  
25 not include data on soil redox potential (Abbey et al, 2003; Kim et al, 2010; Phillips et al, 2005;  
26 Zhuang et al, 2014). In a clayey soil with a water content set in laboratory conditions to 80 %  
27 of the water-holding capacity (Dalgren et al, 2009), the lowest, transitory, redox potential of –  
28 300 mV (relative to the standard hydrogen electrode) was obtained by the 20<sup>th</sup> week of  
29 treatment after the addition of 2% Daramend® and an additional 1.5 % of ZVI (w/w). In another  
30 case study with a silty loam soil, a total of 11% (w/w) Daramend® amendment and 0.2%  
31 granular ZVI (Phillips et al, 2006) resulted in redox potentials as low as -553 mV (values  
32 probably not corrected for the standard hydrogen electrode potential; when corrected for this  
33 potential, a - 553 mV is in fact around – 330 mV). The lowest negative values recorded here  
34 are lower than these published values. In the case of our two treatments with ZVI only, the  
35 higher percentage of ZVI added may explain the lower Eh reached. The same reasoning holds  
36 in our trial with an added 6% dose of Daramend®, compared to the study with the clayey soil.  
37 As in the study by Philipps et al, this involved a double dose of Daramend® compared to the  
38 one we used, but a much lower ZVI dose. The lower Eh reached in our study suggests that  
39 ZVI plays a major role in achieving very low Eh values. However, because the soils treated in  
40 the 3 studies were all different, this suggestion must be taken as only an indication of the  
41 relative contribution of ZVI to the overall effect observed on Eh values.  
42  
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45

46 The trials with ZVI only produced the most negative values and had average values more  
47 negative than the Daramend® treatments up to the seventh day of treatment (Fig 4). This may  
48 be correlated with the higher percentage of ZVI in the ZVI-only treatments (4% with coarse  
49 and fine ZVI) vs. 1.8 % for the regular Daramend® and Daramend® bagasse. In contrast, the  
50 easily biodegradable organic matter in the regular Daramend® and the mix bagasse – ZVI  
51 succeeded in maintaining much lower Eh values than in the control plot for the entire duration  
52 of the experiment, and lower values than in the ZVI plots from Day 35 onwards (Figs 6 and 7).  
53  
54

55 Over the duration of the treatment, the coefficient of variation (CV) of all Eh values in the control  
56 plot was 10 % for the 0 – 20 cm layer (n = 233) and 9% for the 20 – 40 cm layer (n = 305). In  
57 the treated plots, the variability was much higher, with, for instance, CVs of 146 % and 153 %  
58 respectively for the 0 – 20 cm and 20 – 40 cm layers in P1, with a maximum of 2725 % for the  
59 0 – 20 cm layer in P4 (mean ± standard deviation: - 8 ± 218 mV, n = 230). This very high  
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1 variability of the Eh values in the trial plots reflects the fact that despite the effort of multiple  
2 cross-ploughing just after adding the amendments, their incorporation did not result in  
3 homogeneous redox conditions on the scale of the volume (a few tens of cm<sup>3</sup>) in which redox  
4 is measured.  
5

6 In view of the results presented below on the analyses for CLD and its degradates in the soil  
7 samples, taken together with the Eh measurements, the abundant Eh data collected needed  
8 to be synthesized. This was achieved by grouping together, for each treatment, the values of  
9 both the 0 – 20 and 20 – 40 cm layers for all post-treatment dates in a single data set. This  
10 simplification was possible because for 5 of the 6 trial plots, P5 being the exception, the Eh  
11 data after addition of the amendments do not differ significantly in the 0 - 20 cm layer from the  
12 results for the 20 - 40 cm layer (Online Resources 12 to 17). In addition, taking Eh values for  
13 the whole 0 – 40 cm layer is fully consistent with the fact that the analyses for CLD and its  
14 degradates were performed on samples representing the 0 – 40 cm layer (see Materials &  
15 Methods). This dataset was then used to allow direct comparisons between the treatments by  
16 calculating the percentage of Eh values below certain thresholds (Table 3). When the 3 lowest  
17 thresholds were considered, the trial plots ranked as follows: P5 > P4 > P1 >> P6 >>> P3 >  
18 P2. When the percentage of values < 0 mV was considered instead, the ranking changed  
19 slightly: P4 > P5 > P6 > P1 >> P3 > P2. Lastly, when the lowest mean value was considered,  
20 the ranking was P5 = P1 > P4 > P6 > P3 >> P2 (Fig 21).  
21  
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#### 24 **Chlordecone and its degradation products in the soil**

25  
26 Three soil sampling campaigns were conducted 24, 64 and 94 days after incorporating the  
27 amendments.  
28

##### 29 *24 days after incorporation of the amendments (Table 4)*

30 A clear drop in CLD concentrations was observed in the P1 and P5 plots where ZVI only had  
31 been added and, to a lesser extent, in P6. In terms of lowering CLD concentrations, 63 %  
32 efficiency was achieved in the best of cases (fine ZVI, Table 8). The second best result, a 45  
33 % reduction, was obtained with coarse ZVI. The two commercial amendments were  
34 substantially less effective (11 and 14 %), while the local bagasse with a coarse ZVI mixture  
35 produced an intermediate result (39 %).  
36  
37

38 Chlordecol concentrations were very similar in most trial plots, the lowest value being recorded  
39 in the fine ZVI plot P5, significantly lower than in P2 and P3.  
40

41 No 5b-hydroCLD was detected in any of the plots. It can however be quantified in soils where  
42 CLD concentrations are higher than those in the parcel analysed here, as it has two possible  
43 sources: impurities in the commercial formula containing the CLD or natural degradation of the  
44 CLD (Devault et al, 2015). On the other hand, concentrations of 5- or 5a-hydroCLD (another  
45 mono-hydroCLD, CLD – 1 Cl, absent from the commercial formulas of chlordecone) were  
46 clearly quantifiable (at least twice the quantification limit of 0.03 mg/kg), the value in the fine  
47 ZVI trial plot P5 representing 67 % of the residual CLD concentration and being the highest of  
48 all trials and significantly higher than P2, P3 and P6.  
49  
50

51 Four other products of dechlorination (two dihydroCLD, one trihydroCLD and one  
52 tetrahydroCLD) were observed in the treated plots. They could not be quantified in mg/kg given  
53 the absence of analytical standards, but the relative peak area provided a semi-quantitative  
54 descriptor. TetrahydroCLD appeared only in the coarse ZVI plot P1, which ranked second only  
55 to P5 for the trihydroCLD. For the two dihydroCLD, the highest values were again observed in  
56 P1 and P5, together with P4 for the 5,6- or 5a-hydroCLD.  
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1 The two trial plots in which the drop in CLD concentrations and the formation of most  
2 degradates seemed least apparent were those treated with the commercial Daramend®  
3 amendments P3 and P4, even though the 6 % treatment dose applied was larger than the 4  
4 % dose used in the P1 and P5 ZVI-only plots. On the other hand, the ZVI dose involved in both  
5 Daramend® treatments is lower (1.8 %) than that in the ZVI-only treatments (4 %). As observed  
6 for the Eh values, the role of ZVI in the transformation of CLD therefore appears to be quite  
7 important. The amendment P6 prepared on the spot with local bagasse and ZVI (1.8 % ZVI of  
8 dry soil weight) had a slightly better effect than the commercial amendments.  
9

#### 10 *64 days after incorporation of the amendments (Table 5)*

11 There were no significant differences in CLD concentrations compared to t = 24 days in any of  
12 the plots. This is not surprising for the control plot, but a continuing decrease in CLD  
13 concentrations would have been expected in the treated plots. On the other hand, a reduction  
14 did appear in 14 of the 15 quantifiable peak areas of the 4 degradation products, and was  
15 particularly clear in the P1 and P5 trial plots. Tetrahydro CLD, which had appeared only in P1,  
16 was no longer detected. The absence of accumulation of partially dechlorinated intermediates,  
17 generally observed with the ISCR, can be linked to the extreme Eh conditions, in terms of  
18 readily available electrons, induced by the technology (Dolfing et al, 2008).  
19

20 For chlordecol, the only value significantly lower than in the control plot was observed in P5.  
21

#### 22 *94 days after incorporation of the amendments (Table 6)*

23 Few substantial changes appeared compared to the two previous sampling dates. The CLD  
24 concentrations continued to diminish slightly in the two ZVI trial plots where the largest  
25 percentage decreases in CLD concentrations (Table 8) were again observed. The continuation  
26 of slightly negative redox conditions (Figs 1 & 12) in the P3 and P4 plots thanks to the presence  
27 of exogenous plant material thus seems less effective than achieving - albeit in a shorter time  
28 - more negative redox values thanks to a higher dosage of ZVI in P1 and P5. It is not possible  
29 to assign the dechlorination of CLD observed here to a single one of the various mechanisms,  
30 reductive dehalogenation versus dichloroelimination for example, involved in the  
31 dechlorination of chlorinated organic compounds as a result of adding strongly reducing  
32 elements such as ZVI (Dolfing et al, 2008). The rate of decrease in CLD concentrations from  
33 Day 24 to Day 94 shows a maximum relative gain of 20 % for the trials that proved most  
34 effective after just 24 days. On the other hand, in the plot treated with regular Daramend®,  
35 prolonging treatment for a further 70 days doubled the rate of decrease, but it still remained  
36 considerably lower than in the conditions with ZVI only (Table 8).  
37

38 Chlordecol concentrations had remained stable, and were lower than in the control plot only in  
39 P5. Ten of the 12 peak areas of the transformation products that were quantifiable on the  
40 previous sampling date continued to diminish. Regarding the largest peak areas observed after  
41 the first sampling date, the compound had either disappeared completely (dihydro in P1 and  
42 P5; tetrahydro in P1) or had dropped by a factor of 9 (tetrahydro in P5). These changes in peak  
43 areas over the duration of the test period could reflect different phenomena. One could be the  
44 transformation of these degradation products into others that were not detected. The signals  
45 from the products recorded on the first monitoring date were very weak, so that a further  
46 transformation of just a fraction of these products would make the initial signal undetectable.  
47 Transformation should in fact be understood as comprising additional dechlorination  
48 processes, or as a functionalisation or opening of the bis-homocubane cage structure  
49 generating products that are not detectable by gas chromatography (Chaussonnerie et al,  
50 2016; Chevallier et al, 2018). An additional transformation of identified products resulting in  
51 higher levels of dechlorination would be consistent with the results obtained with an aqueous  
52 matrix, where changes in the signals indeed suggest a formation in sequence from -1 to --5  
53 Cl (Belghit et al, 2015). This transformation process would have significant environmental  
54 implications if, for example, microbial degradation was indeed being promoted by a high level  
55 of dechlorination.  
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1 A second hypothesis is leaching of the transformation products to a depth greater than where  
2 the samples were taken. The mobility of dechlorinated CLD products has been shown to be  
3 greater than that of CLD (Mouvet et al, 2016 b). This supports the leaching hypothesis, which  
4 is also backed up by thermodynamic calculations showing that the solubility in water of  
5 dechlorinated CLD degradates increases as the level of dechlorination increases (Dolfing et  
6 al, 2012).  
7

8 A complementary statistical analysis was conducted on a data-set pooling the results of three  
9 sampling campaigns for each plot trial. This was carried out at the expense of a vision of the  
10 evolution over time (illustrated previously in Figs 1 and 12) in order to increase the number of  
11 samples per trial plot and improve the robustness of the analysis. To avoid multiple repetitions  
12 of the words "statistically significant" all the differences mentioned in the section illustrated  
13 below by box and whisker plots are given as statistically significant at the p value < 0.05  
14  
15

16 For chlordecone, the greatest fall in concentrations compared to the control plot (P2) is  
17 obtained in plots P5 (fine ZVI) and P1 (coarse ZVI), followed by P6 (bagasse – ZVI), that does  
18 not differ from P1 but is more efficient than P4 (regular Daramend<sup>®</sup>) and P3 (Daramend<sup>®</sup>  
19 bagasse) that do not differ from each other. Values in P3 do not differ from those of the control  
20 plot P2 (Fig 14).  
21

22 For 5- or 5a-chlordecone, which results from the reductive dechlorination of chlordecone, the  
23 greatest concentration is observed in P5, followed by P4 and P1 that do not differ from each  
24 other. P1, P3 and P6 concentrations do not differ from each other, all three producing less 5a-  
25 CLD than P5. No 5a-chlordecone can be detected in the control plot P2 (Fig 15).  
26  
27

28 For chlordecol, P5 and P1 are the only 2 treatments with concentrations lower than the control  
29 plot P2 (Fig 16).  
30

31 For 5,6- or 5a,6- dihydrochlordecone, the largest relative peak areas were observed in P1 and  
32 P5 that do not differ from each other, followed by P4 that does not differ from P5. P4 does not  
33 differ from P6 either. The lowest signal was measured in P3, no signal at all being recorded in  
34 the control plot P2 (Fig 17).  
35  
36

37 For the second dihydrochlordecone identified, the only two treatments differing from the control  
38 P2 are P1 and P5 that do not differ from each other. The peak areas of the samples from P3,  
39 P4 and P6 are not different to that of P1. No trace of dihydrochlordecone was detected in the  
40 control plot (Fig 18).  
41  
42

43 For the tetrahydrochlordecone identified, P1, the only trial where the compound produced a  
44 measurable signal, differs significantly from the other trials (Fig 19).  
45

46 For the trihydrochlordecone identified, the greatest relative peak areas are measured in P5  
47 and P1 that do not differ from each other. P6 value is lower than P1 and P5 but not different to  
48 P4. P3 does not differ from P4. No trace of trihydrochlordecone was detected in the control  
49 plot (Fig 20).  
50

51 The results obtained in the neighbouring plot PA treated with 2.8 % coarse ZVI (Table 7)  
52 strengthened all the observations for P1 treated with 4 % of the same ZVI. The first was a  
53 decrease in CLD concentrations of around 70 %, with a 40 % drop after just 9 days of  
54 treatment. Interestingly, the larger decrease in CLD concentrations compared to P1, 74 % vs.  
55 54 %, was obtained despite the lower dose of added ZVI in PA. Secondly, 5b-hydroCLD was  
56 again not formed in amounts > 0.05 mg/kg and chlordecol decreased after 21 days, but  
57 subsequently did not decrease further. Thirdly, the formation of CLD -1Cl and the same 4 other  
58 transformation products with, for 3 of these, gradual formation (higher values after 21 days  
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1 than after 9 days) and subsequent disappearance (lower values after 37 days than after 21).  
2 At the end of the study, 37 days of treatment, a decrease in relative peak areas compared to  
3 Day 21 was observed for 4 of the 5 compounds. The decrease for the trihydroCLD was very  
4 limited, while the tetrahydroCLD disappeared completely and the values for 5.6- or 5a.6-  
5 hydrochlordecone (for the second dihydroCLD, no clear trend appeared between Days 9, 21  
6 and 37) and the pentahydroCLD decreased by a factor of 1.6 and 7.4, respectively. A fifth  
7 dechlorinated compound was observed, a penta-hydroCLD that had been reported previously  
8 in laboratory conditions for soils treated with Daramend® and ZVI (Mouvet et al, 2017) and in  
9 an aqueous matrix treated with ZVI (Belghit et al, 2015). The initial CLD concentration of 1.5  
10 mg/kg probably allowed this highly dechlorinated degradate to be detected in PA but not in P1  
11 and P5, where the initial CLD concentrations were lower. Like the other polydechlorinated CLD  
12 derivatives, this degradate evolved over time, with a clear peak quite soon after the treatment  
13 started, on Day 21, followed by an abrupt decrease resulting in a much weaker signal after 37  
14 days. Such a high level of dechlorination, - 5 Cl atoms, in a soil matrix under field conditions,  
15 is remarkable as it is close to the best level, -6 to -8 Cl atoms, obtained for an aqueous CLD  
16 solution with 5 % NaOH (pH = 14) in laboratory conditions with a UV + H<sub>2</sub> treatment in the  
17 absence of any substantial amount of oxidising agent (United States Patent, 1979).  
18  
19

20 The decrease over time for most degradates suggests either the formation of other degradation  
21 products, possibly dechlorinated to a higher level and which were not detected, or leaching of  
22 the identified substances to below the 40 cm layer as a consequence of the irrigation applied,  
23 or because the compounds had become completely mineralised.  
24

25 Further analyses of the water in the suction cups may suggest answers as regards the first two  
26 hypotheses, in particular because the matrix effects in water are much weaker than in soils.  
27 This lowers the quantification limit to 0.07 µg/L, or by a factor of almost 500 compared to  
28 analyses in soil. The complete mineralisation hypothesis, on the other hand, cannot be verified  
29 with the data collected in the present study.  
30

### 31 *Overall treatment efficiency*

32 The consistent ranking of efficiency in the trial plots over the 3 sampling dates, with P5 and P1  
33 always ahead of the other 3 treatments, suggests that the observation of greater efficiency of  
34 the ZVI-only treatments is quite robust (Table 8).  
35  
36

37 The 54 % and 69 % efficiencies are noteworthy because they exceed the percentages reported  
38 for 5% NaOH aqueous solutions of CLD using a dedicated apparatus for the dehalogenation  
39 of halogenated compounds (US Patents, 1979).  
40

### 41 *Relation between treatment efficiency and redox potential*

42 Plotting the % decrease in CLD concentration as a function of the lowest Eh mean value  
43 observed in each plot whatever the date (7 available) and soil layer (0 – 20 and 20 – 40 cm)  
44 points at a statistically very significant (1 %) inverse linear relationship (Fig 16). The same  
45 type of relation has been reported for the halogenated methanes CFCl<sub>3</sub>, CCl<sub>4</sub>, and CHCl<sub>3</sub>, with  
46 a statistically significant inverse linear relation between the degradation rates and Eh values  
47 in the range of– 104 to – 348 mV (Olivas et al, 2002).  
48  
49

50 The relation between the treatments efficiency and the lowering of redox potential achieved by  
51 the various amendments can be further illustrated by considering the % of the total number of  
52 Eh values (n = 337 to 468 according to the treatment) below certain threshold values. The  
53 linear relationships observed for - 350 mV, - 300 mV and - 250 mV are statistically significant,  
54 but at a 5 % level (Fig xx for – 250 mV), which is lower than when considering the lowest Eh  
55 mean value, significant at the 1 % level (Fig xx). When considering the % of values < 0 mV,  
56 the linear relationship is not significant at the 5 % level.  
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1 Knowing that the mechanism involved in ISCR relies on Eh values sufficiently low to lead to  
2 reductive dechlorination, the relations observed could be expected. Rather surprising, though,  
3 is the consistency of the trend based on 6 completely independent trial plots. This does not of  
4 course mean that Eh is the sole parameter involved in the dechlorination of CLD. Other  
5 parameter, not monitored, could be involved. One may for instance think of microbial  
6 degradation. This mechanism is however unlikely to have played a major role here, since the  
7 time elapsed to obtain 75 % of the maximum treatment efficiency is much shorter than the  
8 biodegradation rates reported in laboratory conditions. Nevertheless, the extreme conditions  
9 imposed by the treatments may lead to the expression by dehalogenating microorganisms of  
10 unique genes that could produce enzymes catalyzing the dechlorination reactions (Dolfing et  
11 al, 2008).  
12

13  
14 With the aim of further increase the ISCR efficiency in decreasing the CLD concentration of  
15 nitisol, one may consider lowering the Eh to even lower values. It would however prove difficult  
16 to further improve the procedures setup here without negative side-effects, for instance an  
17 increase in cost price and possible negative effects on soil functions if the application dose  
18 was increased. The results obtained do not suggest either that increasing the duration of the  
19 treatment is a promising route. As for modifying the amendments used by turning for instance  
20 to nanoscale ZVI, either alone or combined with easily biodegradable organic matter, it would  
21 also raise major issues of cost price and social acceptability.  
22

### 23 **Chlordecone and dechlorinated degradates in water from the suction cups**

24  
25 Due to limitations on financial resources available for this part of the study, suction cups were  
26 installed in the coarse ZVI PA plot only, at depths of 35 and 50 cm. The concentrations of 5b-  
27 hydrochlordecone are below the quantification limit in all the samples and not shown in the  
28 tables 9 & 10. Some of the sampling dates for some points (T2 at point 2 at depths of 35 and  
29 50 cm; T3 at point 3 at 50 cm) are not given in the tables as the water volumes collected were  
30 too small to be analysed (and sometimes nil).  
31

32  
33 In addition to the degradates observed in the PA soil samples treated with ZVI, three new  
34 dechlorinated CLD degradates appeared in the water from the suction cups (Tables 9 & 10):  
35 one pentahydroCLD differing from that found in the soils, one heptahydroCLD that could not  
36 be identified with complete certainty (problem of background noise and imperfectly resolved  
37 chromatographic peak), and one "unknown" for which the dechlorination level is very probably  
38 above 5, given that its retention time was shorter by 0.7 to 1.6 minutes than for the other two  
39 pentahydroCLD that were identified unequivocally; furthermore, except in the case of one  
40 tetrahydroCLD, the retention times under our chromatography conditions shortened  
41 consistently as dechlorination proceeded.  
42

43  
44 The water collected in the suction cups therefore provided important additional information: the  
45 drop over time in the concentrations (or relative peak areas) of products identified in the soils  
46 is at least partly due to the formation of other still more dechlorinated products, some to a  
47 dechlorination level > 5. As the detection limits in the soil samples were much higher than in  
48 the water samples, these compounds may have been present in the soil but had remained  
49 undetected.  
50

51  
52 The change over time in the concentration (or peak area) values can be investigated by  
53 considering, for instance, at what sampling date the degradation products can first be detected,  
54 and how the signals evolve over time. This could provide some insights into the dynamics of  
55 degradate formation and leaching. For each sampling date, 27 occurrences have to be  
56 considered (9 substances resulting from ISCR x 3 sampling points).  
57

58  
59 At a depth of 35 cm (Table 9), the degradates were detectable from the first sampling date, 9  
60 days after the start of the treatment, for all 27 occurrences. When comparing between the first  
61 and last sampling dates, the signals weakened systematically for the compounds with up to -  
62 4Cl (15 possible cases, 5 substances x 3 sampling points), while an almost equally systematic  
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65

1 reverse trend (11 cases out of 12) was found for compounds with a dechlorination level higher  
2 than 5. Of the 18 cases (9 degradates x 2 sampling points) where 3 sampling dates were  
3 available, 17 were at their maximum on the second sampling date, Day 21. This pattern of  
4 change over time may have resulted from the same mechanisms as those discussed for  
5 concentrations in the soil. Whatever the mechanism involved, the absence of accumulation  
6 (no continuous increase in concentration or relative peak area) of any of the degradates  
7 monitored is worthy of note.  
8

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9 At a depth of 50 cm (Table 10), 22 of the 27 possible occurrences had already materialised 9  
10 days after treatment had started. By the end of the monitoring period (Day 37), all possible  
11 occurrences had materialised. When comparing the first and last sampling dates, the  
12 decreasing trend in the signals over time for compounds with up to -4Cl is less systematic than  
13 at 35 cm (8 of 15 possible trends). The trend is mainly weakened by the results from sampling  
14 point 2, where in all 5 cases, the signal on Day 37 was equal or stronger than on Day 9. The  
15 increasing signal strength between Day 9 and Day 37 for compounds with 5 or more Cl was  
16 as marked as at a depth of 35 cm. Of the 18 cases (9 degradates x 2 sampling points) for  
17 which 3 sampling dates are available, 17 were at their maximum strength on the second  
18 sampling date, Day 21.  
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21 The rapid formation of most degradates, within 9 days at most (earlier sampling might have  
22 already shown the compounds) in the field conditions of this study, has also been reported in  
23 laboratory studies, in which all degradates appeared after just 7 days in aqueous batches  
24 (Belghit et al, 2015) and after 20 days (1<sup>st</sup> sampling date) in soil mesocosms (Mouvet et al,  
25 2017; Dictor et al, 2011). Such rapid transformations, all the more so in field conditions,  
26 suggest that the mechanism involved is physico-chemical rather than microbial, because even  
27 in optimised laboratory conditions with a highly favourable growth medium and anaerobic  
28 conditions, multiple enrichments over weeks (Orndorff & Colwell, 1980) or months  
29 (Chaussonnerie et al, 2015) are required before the microbial transformation of CLD becomes  
30 significant. The synchronicity of the formation of all degradates, from mono- up to hepta-  
31 hydroCLD, suggests formation pathways either in parallel or in quite rapid succession.  
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34 Another important and consistent result in studies on ZVI and CLD is the unequivocal absence  
35 of degradate accumulation over time, whatever the matrix studied and the degradate  
36 considered (Fig. 6, Belghit et al, 2015 ; fig. 3, Mouvet et al, 2016 a; tables 5 to 8 in this paper).  
37 Whether this results from leaching, further transformation or mineralisation is yet to be  
38 determined.  
39

40 The possibility of increased biodegradability of dechlorinated CLD degradates compared to the  
41 parent molecule is a very important question that remains entirely open. No work has yet been  
42 published on this issue, in particular because of the limited number of degradates available in  
43 sufficient mass and purity to conduct experiments addressing this question. In the case of  
44 polychlorinated biphenyls (PCB), the biodegradation of thirty-one isomers by two species of  
45 *Alcaligenes* and *Acinetobacter* decreases as chlorine substitution increases (Furukawa et al,  
46 1978). Additionally, mono- and dichlorobiphenyls from commercial PCB mixtures have been  
47 shown to undergo primary biodegradation by activated sludge microorganisms, while the  
48 biodegradation rates decrease as the levels of tri-, tetra-, and pentachlorobiphenyl increase  
49 (Tucker et al, 1975). The very specific bis-homocubane structure of CLD prevents  
50 unambiguous extrapolation of the results from studies on PCB. The hypothesis that variously  
51 dechlorinated CLD degradates have quite different, and probably greater, rates of  
52 biodegradation than CLD, must however be considered.  
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## 58 **Agronomic effects of the different treatments applied**

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1 The PA plot for which the physico-chemical results are described above was set up to provide  
2 a large enough area of soil treated with coarse ZVI only to study the 3 crops. Analyses of this  
3 area before treatment showed higher levels of contamination than in the initial control plot P2,  
4 labelled control 1 in this section. It was therefore decided to monitor all the crops in a second  
5 control plot adjacent to PA, called Control 2, which appears in the tables below in addition to  
6 the 4 trial treated plots and Control 1. There are only 4 trial plots, not 5, because the budget  
7 allocated to the study did not allow us include the P5 plot treated with fine ZVI in the agronomic  
8 part of the project.  
9

### 10 *Radishes (Table 11)*

11 In all the trials, the germination rate was above 80 %, which is considered highly satisfactory  
12 by professionals who grow this crop. The ISCR treatments applied therefore had no negative  
13 effects on germination of the radishes.  
14

15 The average unit mass of the radishes in the P3 (Daramend® Bagasse) and P6 (mix Bagasse  
16 + coarse ZVI) plots was similar, but differed from those in the other plots (control 1, regular  
17 Daramend®, control 2 and ZVI only), and their average yields were significantly lower than in  
18 the two control plots ( $P = 0.0119$ , Fisher LSD test), which showed a negative effect with  
19 bagasse. The C/N ratio in the bagasse can be higher than 100 (Torkashvand et al, 2008) as  
20 opposed to about 10 for the organic matter initially present in the soil in this study (Table 2).  
21 This caused nitrogen deficiency in the relevant plots, because in the presence of organic matter  
22 with such a high C/N ratio, micro-organisms take up nitrogen from reserves in the soil instead  
23 of releasing it. It is very likely that an additional input of mineral nitrogen in these plots would  
24 have limited the loss of yield: for the cucumber crop (see below), where the soil received a  
25 three times larger unit dose of added mineral nitrogen than the radish and sweet potato crops,  
26 no differences in yields were observed between the bagasse trials and the others. On plots  
27 amended with bagasse, sowing a legume crop after the ISCR treatment could be considered  
28 (e.g. *Crotalaria juncea*). When crushed and incorporated a few months before sowing or  
29 planting a cash crop, this would provide enough nitrogen for the soil micro-organisms to break  
30 down the bagasse. Alfalfa, the organic component in the regular Daramend® amendment, has  
31 a C/N ratio of 15 (Silva A., 2005) and did not cause any nitrogen deficiency effect.  
32  
33

34 According to standard FFV-59 issued by the United Nations Economic Commission for Europe  
35 (UNECE, 2017), the radishes in trial plots P3, P4 and P6 did not have the required quality to  
36 be classified in category I. However, from the purely visual point of view, the radishes from  
37 these plots were entirely fit for consumption. The radishes from the other plots (Control 1, ZVI  
38 only, Control 2) were classified in Category I because the few defects (reddish or translucent  
39 flesh) were present in less than 10 % of the radishes.  
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### 42 *Cucumbers (Table 12)*

43 Transplanting of the cucumber seedlings was entirely successful, with 100 % of the 350  
44 seedlings well established within 7 days after planting. Subsequently, fertiliser applied too  
45 close to the seedlings caused burns around the collar, which resulted in varying degrees of  
46 mortality in the different plots. A new batch of seedlings was then transplanted and successfully  
47 established in all the plots. Unfortunately, a high degree of mortality was subsequently  
48 observed in the ZVI plot, with only a single cucumber harvested from it. However, this seems  
49 to have been a temporary one-off problem. A subsequent experiment in greenhouse conditions  
50 and on a different soil treated with ZVI produced a perfectly normal cucumber harvest with an  
51 interval of just 1 month between ending the treatment and planting out the seedlings (Mouvet  
52 et al, 2016 a). A key factor in this respect seems to be finely controlled irrigation.  
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55 No significant differences were found (Wilcoxon test) between the trial plots in the average  
56 percentage of marketable cucumbers, their average unit mass and the average percentages  
57 of dry matter. No significant differences were found (Wilcoxon test) between the average  
58 commercial yields of the two control plots and the three treated trial plots, the only significant  
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1 difference being between the regular Daramend® and the Daramend® bagasse. No negative  
2 agronomic effects were therefore observed with any treatment in the trials that produced a  
3 harvest.  
4

#### 5 *Sweet potatoes (Table 13)*

6 Regarding the number of tubers per plant, the lowest values were for the P3 and P6 trials with  
7 a bagasse amendment (P3: Daramend® bagasse ; P6: mix bagasse – coarse ZVI). This again  
8 reflects the negative effect of bagasse discussed in the case of the radishes. However, none  
9 of the trial results differed significantly from those in the two control plots (Fisher LSD test).  
10

11 Regarding the percentage of marketable tubers per plant, there was no significant difference  
12 between the trial plots (Fisher LSD test), as most of the averages had a high standard  
13 deviation, producing coefficients of variation ranging from 33 to 55 %.  
14

15 Regarding the average unit mass measured on 50 marketable tubers, the Wilcoxon test  
16 showed no significant difference between treatments, with coefficients of variation ranging from  
17 24 to 64 %. Regarding the percentage of dry matter, the Fisher LSD test showed no significant  
18 differences between treatments, with much lower variability in the results (coefficients of  
19 variation from 5 to 13 %) than for the two parameters above.  
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22 Concerning marketable yields, the averages for the plots treated with the Daramend® bagasse,  
23 the regular Daramend® and coarse ZVI only were statistically no different to the averages for  
24 the two control plots. Plot 6, treated with bagasse + ZVI, had by far the lowest yield, but this  
25 was statistically different only from Control 2 and the ZVI-only plot (Wilcoxon test).  
26  
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#### 28 *CLD and degradate concentrations in irrigation and soil water during plant growth*

29 With the means available for the study, we were able to place suction cups in 3 trial plots:  
30 Control 1, regular Daramend® and coarse ZVI. In the two treated plots, the chlordecone  
31 concentrations in the soil solution, of about 1 µg/L (Table 14), were significantly lower  
32 (respectively 2.2 and 5.3 times lower) than those in control plot 1. Concentrations of CLD -1CI  
33 were significantly higher in the two treated plots than in the control plot, but no different to each  
34 other. Concentrations of CLD -3CI were significantly higher than in the control plot, with the  
35 ZVI-only trial producing a higher concentration than the treatment with regular Daramend®.  
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38 The average concentration of chlordecone in the irrigation water varied from 3.8 to 8.2 µg/L,  
39 with a mean ± standard deviation, n = 5, of 5.0 ± 1.8 µg/L. This is equivalent to the average  
40 concentration in the soil solution collected by the suction cups in the control plot, and indicates  
41 that there was no particular risk of irrigation water contamination affecting CLD concentrations  
42 in the crops grown in this plot. On the other hand, irrigation supplied water with a CLD  
43 concentration 2.7 to 4.8 times higher than in the soil solution from the treated plots. It is  
44 therefore likely that irrigation with contaminated water partially masks the positive effects of  
45 these two treatments on the transfer of chlordecone to plants. This is an artefact to the  
46 detriment of these treatments which is probably at least partly transferable to the other trial  
47 treatments. No system was set up to pre-treat the irrigation water in order to eliminate any CLD  
48 contamination. Appropriate systems do exist, but are unlikely to be brought into widespread  
49 use for operational ISCR implementation. Therefore, the experimental study conditions should  
50 be considered as entirely in accordance with real conditions in the field.  
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#### 56 *Concentrations of chlordecone and its degradation products in plant organs*

57 All results will be presented (Table 15) and discussed here from two angles: inter-comparison  
58 of the different treatments to assess their respective merits with a view to possible operational  
59 implementation, and secondly in relation to the Maximum Residue Limit of 20 µg/kg fresh  
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1 weight (Anses, 2018), which is a very important criterion given that plant consumption is a  
2 major factor in the population's exposure to chlordecone.  
3

#### 4 Radishes

5 The average concentration of chlordecone in the radishes from the two control plots were  
6 above the Maximum Residue Limit, 20 µg/kg. Therefore, none of these control radishes were  
7 marketable under the regulations in force.  
8  
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10 Average chlordecone concentrations in the radishes from the bagasse + ZVI and ZVI -only  
11 plots were significantly below those from the two control plots ( $P < 0.05$ ) and the MRL (Shapiro  
12 test, 0.1 %). The average chlordecone concentrations in the radishes from the regular  
13 Daramend® trial plot were also significantly below the 2 controls, but not below the MRL. The  
14 reason why the average value is not significantly lower than the MRL may be found in the  
15 highly variable values for this trial plot ( $n = 5$ ; 1 outlier at 23.2 mg/kg; without the outlier, the  
16 average drops to  $11.7 \pm 3.0$ ). The average concentration for the Daramend® bagasse trial is  
17 not significantly different to the control plots and significantly higher than the MRL (Shapiro  
18 test, 1% level). The majority of the treatments therefore reduced contamination in the radishes,  
19 with particularly outstanding results in the case of two trials, with which concentrations dropped  
20 not only below the values in the two control plots, but also below the MRL. The large reduction  
21 in contamination of the radishes is accounted for by the mechanism involved in CLD transfer,  
22 which occurs preferentially by contact (Woignier et al, 2012 b).  
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25 Two CLD by-products originally present in the untreated soil were analysed in the radishes.  
26 Chlordecol (CLDOH) was not detected in any of the radishes, and 5b-hydroCLD was detected  
27 only in two of the 10 samples of radishes in the control plot. This absence of contamination  
28 should be considered relatively to the low concentrations of these compounds in the soil  
29 samples, with both 5b-hydroCLD and CLD-OH always below 0.05 mg/kg and 0.10 mg/kg  
30 respectively. The available literature unfortunately does not provide data to which our results  
31 can be compared. The only paper with data on 5b-hydroCLD in plants addresses its fate in  
32 soils (andosol and nitisol) and in different plants (cabbages, cucumbers, radishes, bell  
33 peppers, sugarcane, sweet potatoes and lettuces) and plant organs (fine roots, tubers, corms,  
34 leaves, stems and fruits), compared to CLD. The authors note that 5b-hydroCLD  
35 concentrations exceeded 10 µg/kg fresh weight only in dasheen and sweet potato (Clostre et  
36 al, 2015). Given the detection limit of 0.33 µg/kg for 5b-hydroCLD in our study, it is not  
37 surprising that it was never detected. As with CLDOH, we are not aware of any published data  
38 to which ours could be compared.  
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#### 41 Cucumbers

42 Average chlordecone concentrations in cucumbers from all plots, including the control plots  
43 with untreated soil, were below the MRL. Control plot 1 and the Daramend® bagasse plot  
44 formed a group in which the average concentrations differed statistically from those in the other  
45 plots and included some samples > MRL: two from Control 1 (21.2 and 21.4 µg/kg) and 1 from  
46 the Daramend® Bagasse plot (22.3 µg/kg). All the other plots formed a homogeneous group  
47 with average concentrations in the range of 5 to 10 µg/kg, and no samples above the MRL.  
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50 The difference between the two control plots was striking and statistically significant  
51 (Dunnnett test:  $Pr > |t| = 0.000141$ ). At the time of writing, we had no evidence enabling us to  
52 account for the difference between the cucumbers harvested from the two control plots.  
53  
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55 Two of the trials, with regular Daramend® and with bagasse + ZVI, produced cucumbers with  
56 significantly lower CLD concentrations than in one of the two control plots. The surprisingly low  
57 CLD concentrations in the cucumbers from Control 2 are the reason why the values for the two  
58 treated plots do not differ significantly from those for this second control plot. A field trial with  
59 the same soil type (nitisol) and the same level of CLD contamination (0.91 mg/kg) as control  
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1 plot 2 plot produced cucumbers with an average CLD concentration of 19 µg/kg (Clostre et al,  
2 2014 b). In view of the CLD concentrations in the soil of control plot 2 in this study (0.77 mg/kg),  
3 values of around 20 µg/kg would have been expected in the cucumbers from that plot. The  
4 much lower average value measured, of 8.1 µg/kg, is yet to be explained.  
5

6 Chlordecone 5b-hydro was detected (detection limit = 0.17 µg/kg) in 52 % of the samples (14  
7 samples out of 27). The quantified values were very low, with a maximum concentration of  
8 2.5 µg/kg in a sample from the plot treated with Daramend® bagasse. No statistically significant  
9 difference appeared (Wilcoxon test) between the different trial plots.  
10

11 Chlordecol was quantified in 48 % of the samples analysed (13 samples out of 27). The  
12 maximum value (13.0 µg/kg) was measured in control plot 1, where the average concentration  
13 in cucumbers was 7.6 µg/kg, with one sample < 0.87 µg/kg. The cucumbers in the second  
14 control plot, P8, had a much lower average concentration of 2.0 µg/kg. The averages for the  
15 other plots ranged from 0.9 to 3.7 µg/kg. The only statistically significant differences (Wilcoxon  
16 test) were between control plots 1 and 2 (control 1 > control 2) and between control plot 1 and  
17 the regular Daramend® trial plot (Daramend® < control 1). The high proportion of values below  
18 the 0.87 µg/kg (detection limit) and the very wide dispersion of values for the same trial plot  
19 (e.g. Daramend bagasse: < 0.87, 3.00, 6.30, 7.40, < 0.87) makes their interpretation rather  
20 difficult.  
21  
22

### 23 Sweet potatoes

24 With an average of 21.0 µg/kg (standard deviation = 11.3), plot 4 (regular Daramend®) was  
25 close to the MRL and its average level of contamination was 2.3 to 3 times lower than in the  
26 control plots. However, these differences compared to the control plots were not statistically  
27 significant. Average chlordecone concentrations in the tubers from the other two plots  
28 (Daramend® bagasse and ZVI only) were in the range of 30 to 60 µg/kg, values that are similar  
29 and not significantly different to each other or from the values for the two control plots. The  
30 treatments applied to these three plots did not limit the transfer of chlordecone from the soil to  
31 the sweet potato tubers.  
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34 The lowest average concentration of chlordecone was observed in the bagasse + ZVI plot, at  
35 9.2 µg/kg, which is below the MRL (20 µg/kg) and significantly lower (Dunnett test:  $Pr(>|t|) = <$   
36  $0.001$ ) than in control plot 1, P2 (64.0 µg/kg) and control plot 2, P8 (47.9 µg/kg de MF). This is  
37 also the only plot in which all samples had concentrations below the MRL. The question arises  
38 as to whether it is indeed the beneficial effect of the ISCR treatment that produces values  
39 below the MRL, or whether other factors such as the effects of limited growth or, conversely,  
40 dilution, are involved. Given that in this bagasse + ZVI plot (Table 15), i) the yield was not  
41 significantly different to that from the two control plots, ii) the number of tubers was the smallest  
42 among all trial plots although the difference was not significant compared to the two control  
43 plots, and iii) the average unit mass was the smallest among all trial plots, it is most likely that  
44 the bagasse + ZVI treatment did indeed have an effect on CLD transfer.  
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48 Neither chlordecol nor 5bhydroCLD was detected in any sample. The study by Clostre et al,  
49 2015, does not have any data on 5b-hydroCLD in sweet potatoes grown on nitisol. Our results  
50 can therefore not be compared to any other similar dataset.  
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## 53 **CONCLUSIONS AND OUTLOOK**

54 The first aim of this study was to test the effectiveness of the In Situ Chemical Reduction  
55 (ISCR) process to lower chlordecone (CLD) concentrations in a nitisol in a French Caribbean  
56 banana plantation. Five soil amendments capable of triggering the mechanisms involved in  
57 chemical CLD reduction were tested using facilities and operating procedures that could be  
58 readily implemented locally. The best results were obtained with the addition of Zero Valent  
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1 Iron (ZVI), followed by temporary and reversible compaction of the 0 - 20 cm soil layer and  
2 irrigation consistent with precipitation in the Caribbean rainy season. Adding 4 % ZVI (as a  
3 proportion of dry soil weight) to the soil in the parcel studied lowered the initial CLD  
4 concentration in the 0 – 40 cm soil layer ( $0.7 \pm 0.3$  mg/kg) by as much as 69 % in 94 days, with  
5 the effectiveness achieved after just 24 days of treatment remaining almost constant  
6 thereafter. The commercial Daramend<sup>®</sup> amendments tested, using the doses recommended  
7 by the manufacturer, also lowered CLD concentrations but to a lesser extent. In the second  
8 trial nitisol plot treated with 2.8 % of ZVI, the initial CLD concentration in the 0 – 40 cm soil  
9 layer ( $1.35 \pm 0.13$  mg/kg) decreased by 74 % in 37 days, with the treatment already 75 %  
10 effective after just 21 days. There was a statistically very significant correlation between the  
11 percentage decrease in CLD in the soil and the lowest mean redox potential measured.  
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14 As the CLD concentrations decreased, transformation products appeared in the soil and soil  
15 water, with H atoms replacing up to 4 and 7 of the 10 Cl atoms respectively. None of the  
16 dechlorinated CLD degradates appeared to accumulate in the soil or soil water during the  
17 treatment. Instead, the reverse occurred, with a clear overall downward trend over time. This  
18 result raises two main questions: the fate of these transformation products and their ecotoxicity  
19 and toxicity. The only experimental data available on the adsorption of these products by a  
20 nitisol show that they are less sorbed than the parent compound (Mouvet et al, 2016 b). The  
21 risk of groundwater contamination by these products needs to be assessed, taking particular  
22 account of the thickness of the non-saturated zone lying beneath the 40 cm topsoil layer  
23 studied here. The reason is that although the signal probably only weakens slightly in passing  
24 through a few tens of centimetres of soil, it could weaken much more over tens of metres.  
25 Unfortunately it is not possible to provide a complete mass balance because for several of  
26 these degradates there is no analytical standard available for their quantification, and nor are  
27 analytical standards available for products that might have resulted from bacterial CLD  
28 degradation and which require extraction and analytical methods (Chaussonnerie et al, 2016;  
29 Chevallier et al, 2018) other than those that could be used for this study. Regarding the  
30 ecotoxicity of these dechlorinated CLD degradates, the results obtained in six of seven tests  
31 conducted after applying the ISCR procedure in a 2017 laboratory study did not show any  
32 greater ecotoxicological response in the three treated soil types than in the controls (Mouvet  
33 et al, 2017). As for the toxicity of these degradates, this has been given particular attention in  
34 parallel studies because of the serious human health issues raised by CLD contamination. No  
35 *in vitro* tests have shown any greater toxicity in the degradates compared to the parent  
36 compound, and several tests have even shown that toxicity decreases as CLD dechlorination  
37 proceeds (Legeay et al, 2018). An *in vivo* test, which matched the human model most closely  
38 (Alibrahim et al, 2019), showed a significant decrease in toxicity for CLD-3Cl and CLD-4 Cl  
39 compared to CLD.  
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44 The second aim of this study was to quantify the effects of the ISCR treatment on three different  
45 crops regarding agronomic parameters, e.g. yields and visual quality, and a key parameter  
46 linked to the human health issue, the CLD concentrations in the edible part of the crops. The  
47 radishes produced with some treatments were visually of lower quality or smaller in size than  
48 those grown in the control plots. Yields from the cucumber and sweet potato crops were lower  
49 than in the control plots when the amendment contained bagasse as the organic ingredient.  
50 Almost 100 % mortality was observed in the cucumber seedlings planted out 3 months after  
51 applying the treatment in the ZVI trial plot. Simple operational solutions, e.g. additional inputs  
52 of nitrogen fertiliser to counteract the soil nitrogen deficiency caused by the very high C/N ratio  
53 of decomposing bagasse, a longer interval between ending the treatment and planting the  
54 seedlings and/or optimising irrigation to avoid mortality after planting out the seedlings, should  
55 remedy the negative effects resulting from the treatment. As regards the human health-related  
56 aspect, a very positive effect was noted in the radishes, with CLD concentrations significantly  
57 lower than in the control plots and even dropping below the Maximum Residue Level, which  
58 was substantially exceeded in the radishes grown on untreated soil. The human health-related  
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1 effects were less marked in the cucumbers and sweet potatoes due to the high variability of  
2 the results (both crops) and the generally low level of contamination (cucumbers). For the  
3 cucumbers, however, two ISCR trials produced fruits with CLD concentrations below the MRL  
4 and also below those in one of the two control plots. As for the sweet potatoes, one of the four  
5 ISCR trials, with a bagasse-ZVI amendment, produced a significant positive effect by  
6 decreasing contamination to below the levels in the two control plots and below the MRL.  
7

8 Obviously, the question of implementation costs has to be considered. On the scale of the  
9 100 m<sup>2</sup> trial with a 4 % dose of coarse ZVI applied to a 40 cm layer of nitisol, the cost price  
10 amounted to 19 €/m<sup>2</sup>. This includes purchase of the ZVI, customs duties, delivery to the site,  
11 hours of use and fuel for the agricultural machinery and the cost of the labour required to  
12 plough in the amendment, compact the soil and irrigate the crops. With application on a larger  
13 scale, a reduction of around 20 % can be expected in the cost of raw materials and overheads  
14 such as bringing agricultural machinery in and out. The unit cost could therefore drop to  
15 17 €/m<sup>2</sup>, even 12 €/m<sup>2</sup> if the dosage is reduced to 2.8 %, which was the dose applied in the 2<sup>nd</sup>  
16 nitisol plot that produced good results both in terms of lowering CLD concentrations in the soil  
17 and for the various crop criteria. With a unit cost of this order, it would not be possible to  
18 consider applying the treatment to the entire area affected by CLD contamination of the soils.  
19 Targeting treatment to zones where the issue is of particular concern, such as household  
20 gardens and catchments around water abstraction points, should therefore be considered to  
21 back up the current crisis management approach that relies on regulatory constraints and  
22 informing the population about good practices to be applied. A study on the social acceptability  
23 of implementing soil decontamination, of whatever kind, would however be required in the first  
24 place.  
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28 Over and above these socio-economic perspectives, several additional lines of research can  
29 already be identified. One of these concerns the transfer into plants of CLD degradates  
30 produced by the ISCR process. Unfortunately, this question can only be addressed for the  
31 degradates for which analytical standards are available. The analyses conducted in a later  
32 study showed that one CLD-1CL, one CLD -3Cl and one CLD-4Cl were present in the plants  
33 but that the sum of the molar concentrations of all the quantifiable substances, obviously  
34 including CLD itself, was lower in the plants grown on ISCR-treated soil than on the control  
35 soil (Mouvet et Bristeau, 2016). More detailed and exhaustive studies are still needed on this  
36 subject. Combining the ISCR approach with simultaneous or subsequent activation of  
37 microbiological activity could also be considered, as there is a possibility that with the partial  
38 dechlorination observed, the resulting molecules could biodegrade more efficiently than the  
39 parent molecules. To undertake these studies, analytical standards for the main CLD  
40 transformation products would again be required, but obtaining the mass and purity needed  
41 for these standards would be a project in itself.  
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45 Finally, decontaminating soils to eliminate CLD is not the only way of preventing CLD from  
46 being washed away by rainwater and thus contaminating aquatic environments, or of reducing  
47 contamination in plants grown on polluted soil. An alternative is CLD sequestration by adding  
48 organic matter. A 10 % dose of compost (dw/dw) added to the soil of one plot in this study  
49 reduced CLD concentrations in radishes to below the MRL, as also observed in several of the  
50 ISCR trials implemented. For two of the three crop plants tested, the addition of compost also  
51 improved yields and accelerated the harvest compared to the control and ISCR plots (Mouvet  
52 et al, 2016 a). The dosage was 10 times higher than that recommended by the compost  
53 manufacturer, but positive results have been obtained in some soils and some crops with a  
54 5 % dose (Woignier et al, 2012, 2013) and even with 1 % (Clostre et al, 2014 b). The 10 %  
55 dose may therefore not be necessary. However, the question arises as to how long the effect  
56 of the added compost would last, as it results on the one hand from CLD sorption onto the  
57 organic matter, and on the other hand from a physical restriction of porosity (Woignier et al,  
58 2013). The physical effect is active in andosols but not in nitisols (Woignier et al, 2013). As for  
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1 the chemical sorption phenomenon, there is every reason to expect that it would weaken as  
2 the added compost becomes mineralised, which would occur rapidly in a tropical climate.  
3 Repeated inputs would therefore be required, with the costs of treatment rising accordingly  
4 and a possibly negative effect on soil properties in the medium term. *A contrario*, the lasting  
5 positive effect of just a single ISCR treatment is not open to question.  
6

7 Pending conclusive results on CLD biodegradation and phytoremediation of soils in true field  
8 conditions, the range of options for remediating CLD-contaminated soils is limited. It may  
9 therefore be advisable to acknowledge this situation and to implement targeted ISCR and  
10 sequestration approaches on a larger scale than that described here. Remediation  
11 approaches, introduced together with strengthened awareness-raising and public information  
12 to promote a low-risk dietary intake, would help to lower levels of chlordecone exposure and  
13 reduce its harmful effects on human health.  
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1 **Figure captions**

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4 **Fig 1** Change over time in the mean Eh values in the 0 – 20 cm soil layer. Only 1 standard  
5 deviation (+ or -) is presented in order to clearly distinguish the range of values for each  
6 treatment. Blue arrows: irrigation. Red arrows: analysis of CLD and degradates  
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10 **Fig 2** Box and whisker plot of Eh values in the 0 - 20 cm layer for each trial plot at T0 before  
11 the experiment started. Plots identified by the same letter are not different at the 0.05 level  
12 (Post hoc Tukey HSD test)  
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16 **Fig 3** Box and whisker plot of Eh values in the 0 - 20 cm layer for each trial plot at T1, two  
17 days after the experiment started. Plots identified by the same letter are not different at the  
18 0.05 level (Post hoc Tukey HSD test)  
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22 **Fig 4** Box and whisker plot of Eh values in the 0 - 20 cm layer for each trial plot at T2, seven  
23 days after the experiment started. Plots identified by the same letter are not different at the  
24 0.05 level (Post hoc Tukey HSD test)  
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28 **Fig 5** Box and whisker plot of Eh values in the 0 - 20 cm layer for each trial plot at T3, twenty-  
29 one days after the experiment started. Plots identified by the same letter are not different at  
30 the 0.05 level (Post hoc Tukey HSD test)  
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34 **Fig 6** Box and whisker plot of Eh values in the 0 - 20 cm layer for each trial plot at T4, thirty-  
35 five days after the experiment started. Plots identified by the same letter are not different at the  
36 0.05 level (Post hoc Tukey HSD test)  
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40 **Fig 7** Box and whisker plot of Eh values in the 0 - 20 cm layer for each trial plot at T7, ninety-  
41 four days after the experiment started. Plots identified by the same letter are not different at  
42 the 0.05 level (Post hoc Tukey HSD test)  
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46 **Fig 8** Box and whisker plot of Eh values in the 0 - 20 cm soil layer throughout the duration of  
47 the treatment in each trial plot. Plots identified by the same letter are not different at the 0.05  
48 level (Post hoc Tukey HSD test)  
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52 **Fig 9** Box and whisker plot of Eh values in the 0 - 20 cm layer for each measuring campaign  
53 in the coarse ZVI trial P1. Plots identified by the same letter are not different at the 0.05 level  
54 (Post hoc Tukey HSD test)  
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1 **Fig 10** Box and whisker plot of Eh values in the 0 - 20 cm layer for each measuring campaign  
2 in the control trial P2. Plots identified by the same letter are not different at the 0.05 level (Post  
3 hoc Tukey HSD test)  
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7 **Fig 11** Box and whisker plot of Eh values in the 0 - 20 cm layer for each measuring campaign  
8 in the regular Daramend trial P4. Plots identified by the same letter are not different at the 0.05  
9 level (Post hoc Tukey HSD test)  
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13 **Fig 12** Change over time in the mean Eh values in the 20 – 40 cm soil layer. Only 1 standard  
14 deviation (+ or -) is presented in order to clearly distinguish the range of values for each  
15 treatment. Blue arrows: irrigation. Red arrows: analysis of CLD and degradates  
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20 **Fig 13** : Box and whisker plot of Eh values in the 20 - 40 cm soil layer throughout the duration  
21 of the treatment in each trial plot. Plots identified by the same letter are not different at the 0.05  
22 level (Post hoc Tukey HSD test)  
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26 **Figure 14:** Box and whisker plot of chlordecone concentrations (mg/kg dw) in the 0 - 40 cm  
27 soil layer. Data for each plot covers the 3 sampling campaigns, i.e. 24, 64 and 94 days following  
28 the beginning of the experiment. Plots identified by at least one letter in common are not  
29 different at the 0.05 level (Kruskal-wallis test)  
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34 **Figure 15:** Box and whisker plot of chlordecol concentrations (mg/kg dw) in the 0 - 40 cm soil  
35 layer. Data for each plot covers the 3 sampling campaigns, i.e. 24, 64 and 94 days following  
36 the beginning of the experiment. Plots identified by at least one letter in common are not  
37 different at the 0.05 level (Kruskal-wallis test)  
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41 **Figure 16:** Box and whisker plot of 5a-chlordecone concentrations (mg/kg dw) in the 0 - 40  
42 cm soil layer. Data for each plot covers the 3 sampling campaigns, i.e. 24, 64 and 94 days  
43 following the beginning of the experiment. Plots identified by at least one letter in common are  
44 not different at the 0.05 level (Kruskal-wallis test)  
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48 **Figure 17:** Box and whisker plot of 5,6- or 5a,6-dihydrochlordecone relative peak area in the  
49 0 – 40 cm soil layer. Data for each plot covers the 3 sampling campaigns, i.e. 24, 64 and 94  
50 days following the beginning of the experiment. Plots identified by at least one letter in common  
51 are not different at the 0.05 level (Kruskal-wallis test)  
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55 **Figure 18:** Box and whisker plot of the second identified dihydrochlordecone relative peak  
56 area in the 0 - 40 cm soil layer. Data for each plot covers the 3 sampling campaigns, i.e. 24,  
57 64 and 94 days following the beginning of the experiment. Plots identified by at least one letter  
58 in common are not different at the 0.05 level (Kruskal-wallis test)  
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1 **Figure 19:** Box and whisker plot of the tetrahydrochlordecone relative peak area in the 0 - 40  
2 cm soil layer. Data for each plot covers the 3 sampling campaigns, i.e. 24, 64 and 94 days  
3 following the beginning of the experiment. Plots identified by at least one letter in common are  
4 not different at the 0.05 level (Kruskal-wallis test)  
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8 **Figure 20:** Box and whisker plot of the trihydrochlordecone relative peak area in the 0 - 40  
9 cm soil layer. Data for each plot covers the 3 sampling campaigns, i.e. 24, 64 and 94 days  
10 following the beginning of the experiment. Plots identified by at least one letter in common are  
11 not different at the 0.05 level (Kruskal-wallis test)  
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15 **Fig 21** Relationship between the % decrease in CLD concentration at the end of the treatment  
16 period and the % of Eh values < - 250 mV measured during the whole duration of the treatment  
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20 **Fig 22** Relationship between the % decrease in CLD concentration at the end of the treatment  
21 period and the lowest mean Eh values measured during the treatment  
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1 **Table captions**

2 **Table 1** Fertiliser quantities (in kg/100 m<sup>2</sup>) applied to each crop

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6 **Table 2** Physico-chemical characteristics of the nitisol studied

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9 **Table 3** Percentages for each trial plot of Eh values below certain threshold values

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12 **Table 4** Chlordecone (CLD) concentrations and transformation products concentrations or  
13 relative peak areas in the 0 – 40 cm soil layer in the 6 trial plots 24 days after incorporation of  
14 the amendments. Values followed by at least one letter in common are not statistically different  
15 at the 1 % level (Kruskal-wallis test)

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20 **Table 5** Chlordecone (CLD) concentrations and transformation products concentrations or  
21 relative peak areas in the 0 – 40 cm soil layer in the 6 trial plots 64 days after incorporation of  
22 the amendments. Values followed by at least one letter in common are not statistically different  
23 at the 1 % level (Kruskal-wallis test)

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27 **Table 6** Chlordecone (CLD) concentrations and transformation products concentrations or  
28 relative peak areas in the 0 – 40 cm soil layer in the 6 trial plots 94 days after incorporation of  
29 the amendments. Values followed by at least one letter in common are not statistically different  
30 at the 1 % level (Kruskal-wallis test)

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35 **Table 7** Change over time in Chlordecone (CLD) and 5- or 5a-hydro CLD (CLD -1Cl)  
36 concentrations and the relative peak areas of the other CLD degradation products detected in  
37 the soil samples from the PA plot treated with coarse ZVI. The degradates are listed from left  
38 to right in descending order of their retention time in the chromatographic column

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42 **Table 8:** Percentage decrease in CLD soil concentration in the 6 trial plots on the 3 sampling  
43 dates

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48 **Table 9** Chlordecone (CLD), 5 or 5a-hydro CLD (CLD -1Cl) and, 5,6- or 5a,6-hydroCLD (CLD  
49 -2Cl) concentrations and relative peak areas of the other CLD degradation products detected  
50 in the water samples from the suction cups installed at 35 cm depth in the plot treated with  
51 coarse ZVI only. The degradates are listed from left to right according to their decreasing  
52 retention time on the chromatographic column

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56 **Table 10** CLD (chlordecone), 5 or 5a-hydro CLD (CLD -1Cl) and, 5,6- or 5a,6-hydroCLD (CLD  
57 -2Cl) concentrations and relative peak areas of the other CLD degradation products detected  
58 in the water samples from the suction cups installed at 50 cm depth in the plot treated with  
59 coarse ZVI only. The degradates are listed from left to right according to their decreasing  
60 retention time on the chromatographic column

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2 **Table 11** Values (mean  $\pm$  standard deviation) of three agronomic parameters determined for  
3 radishes in the 6 trial plots  
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7 **Table 12:** Agronomic parameters measured for each treatment applied to the cucumbers. For  
8 the yield (g/metre), which is considered the most important parameter, the Wilcoxon test was  
9 applied. Mean values followed by at least 1 letter in common are not statistically different to  
10 each other at the 5 % level  
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14 **Table 13:** Agronomic parameters measured for the sweet potatoes after each treatment. Mean  
15 values followed by at least 1 letter in common are not statistically different to each other at the  
16 5 % level. The Wilcoxon test was applied for the yield (kg/plant), and the LSD test for the other  
17 parameters  
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22 **Table 14** Concentrations (mean  $\pm$  standard deviation,  $n = 3$ ) of CLD and degradates quantified  
23 in the soil water sampled with the suction cups during growth of the sweet potatoes. Values  
24 followed by same letter are not statistically different from each other (Wilcoxon test,  $\alpha =$   
25 20 %)  
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29 **Table 15** Chlordecone concentrations ( $\mu\text{g}/\text{kg}$  fresh weight, mean  $\pm$  standard deviation,  $n = 5$ )  
30 in the three plants studied in the six different trial plots. Mean values followed by at least 1  
31 letter in common are not statistically different to each other at the 5 % level.  
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Fig 1

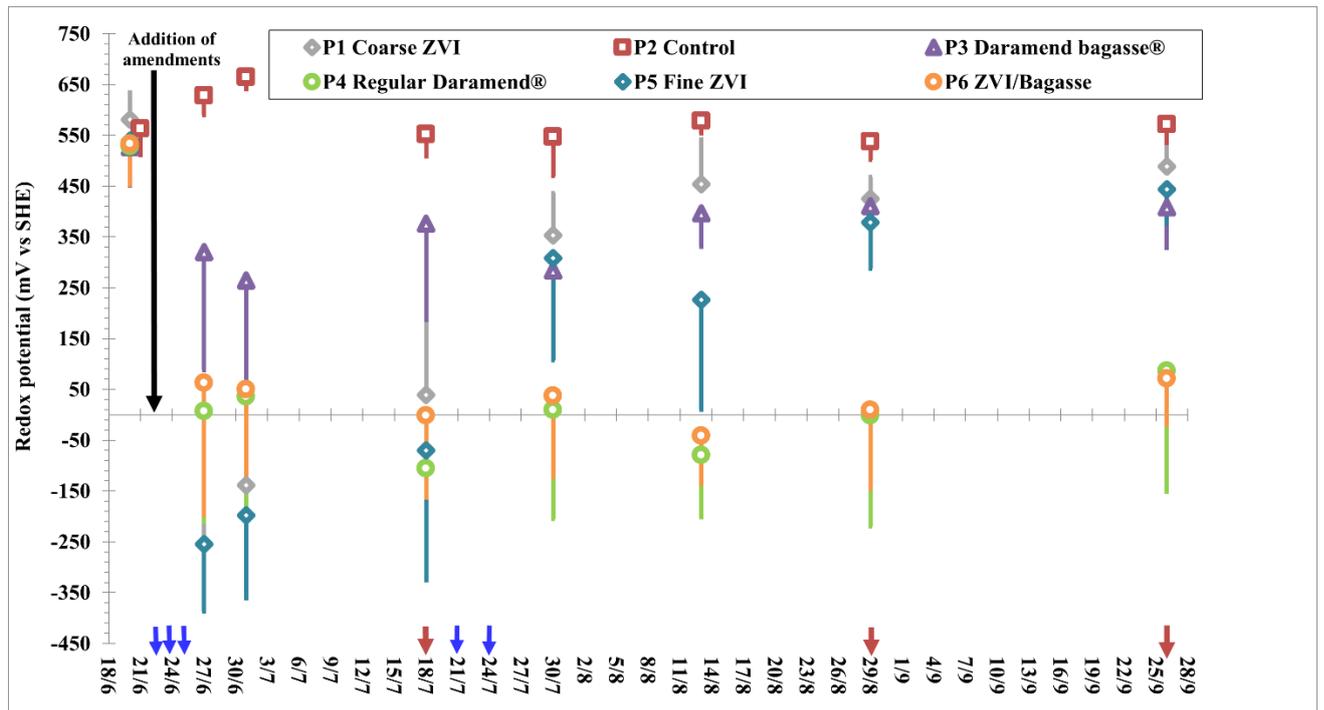


Fig 2

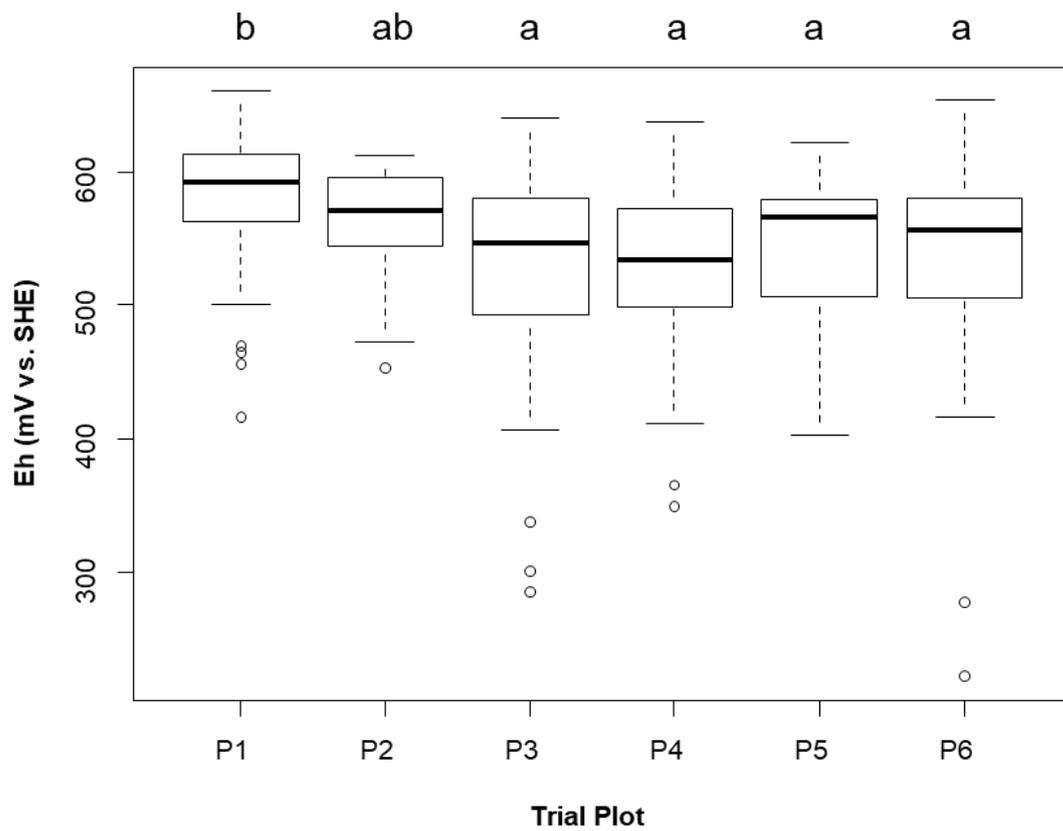


Fig 3

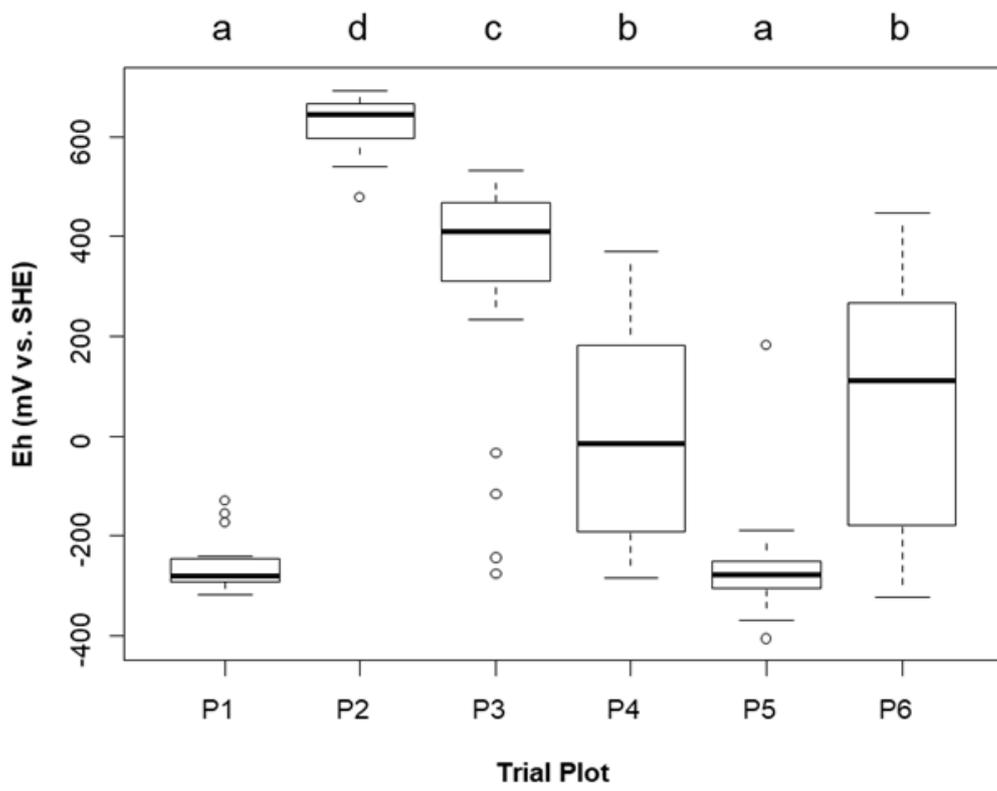


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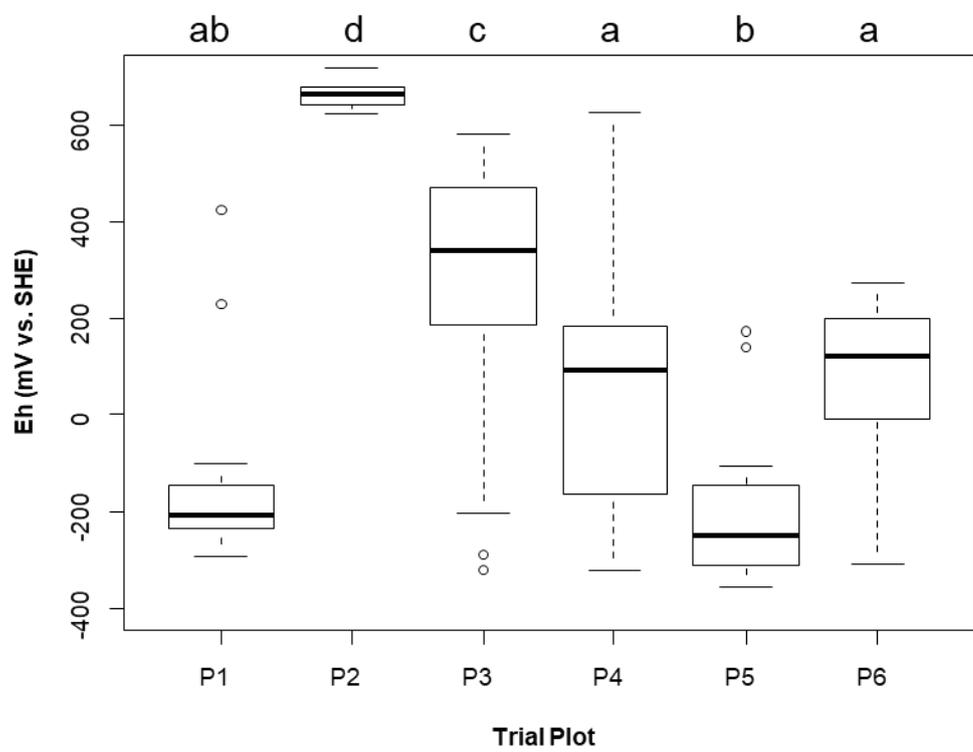


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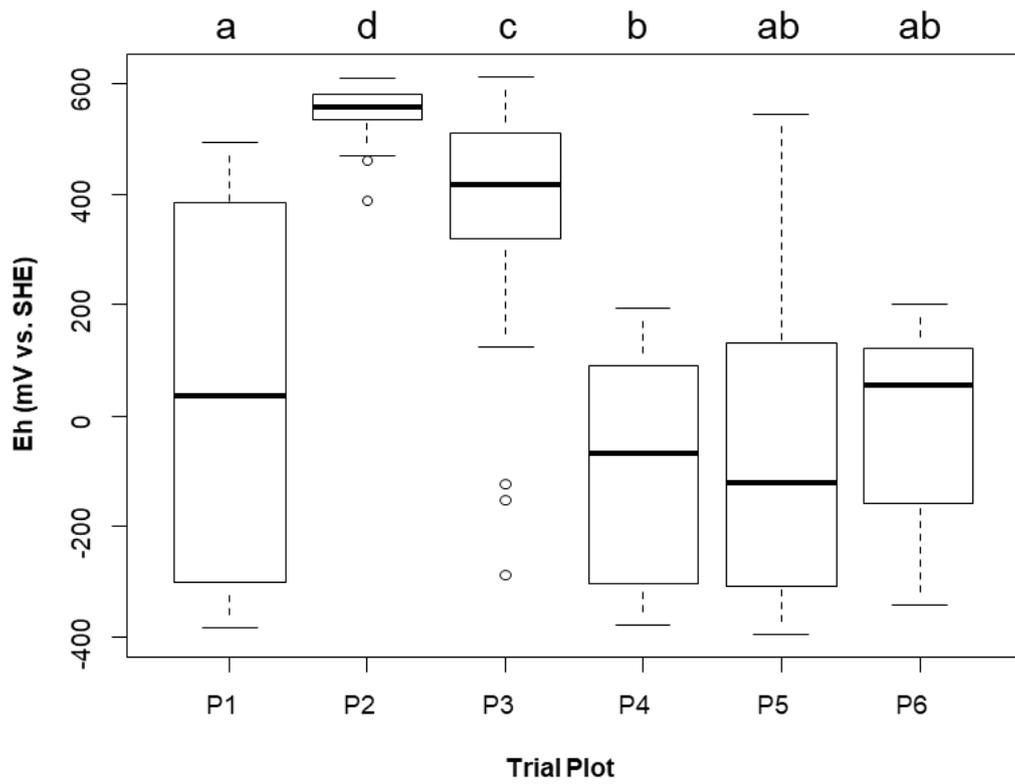


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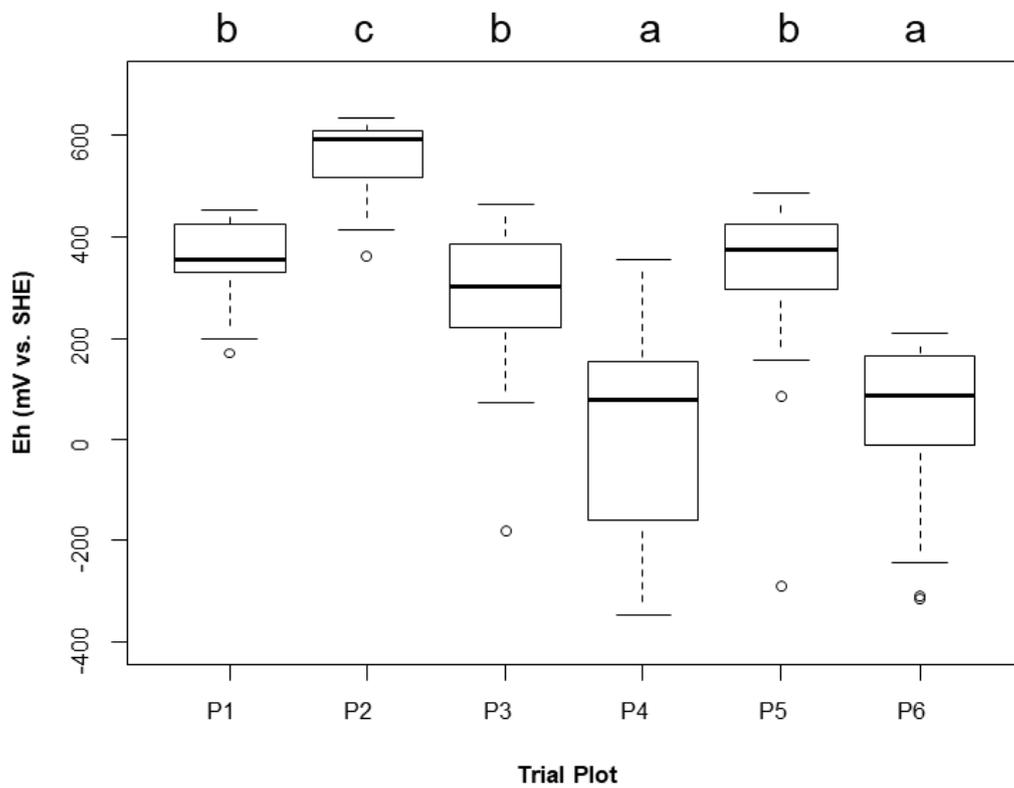


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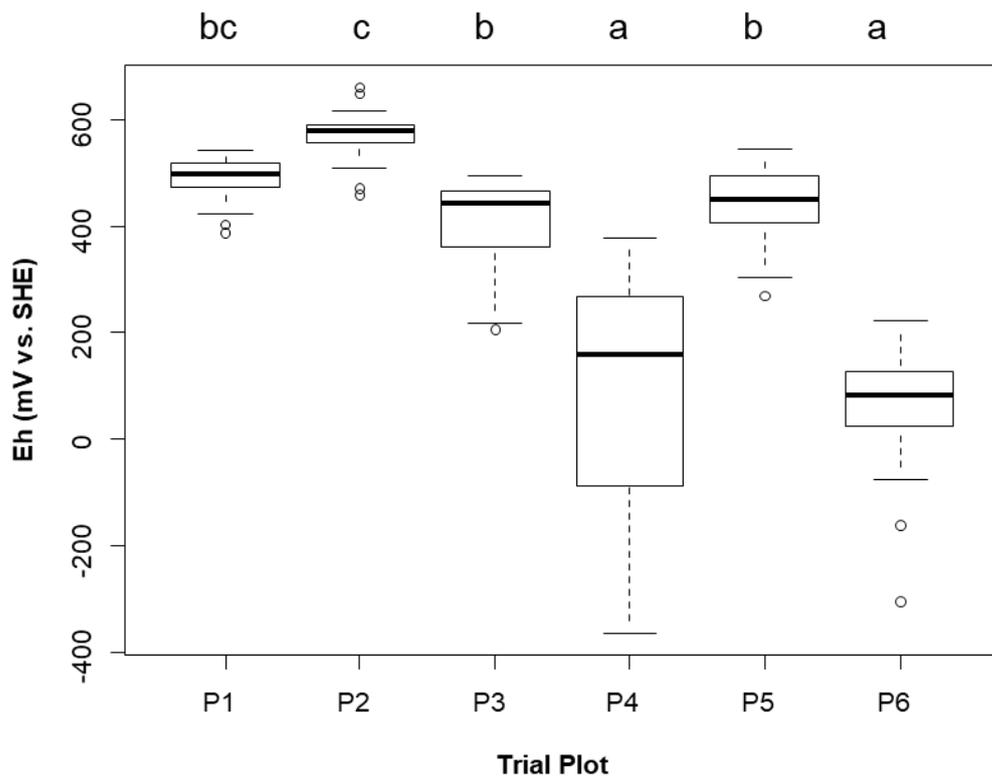


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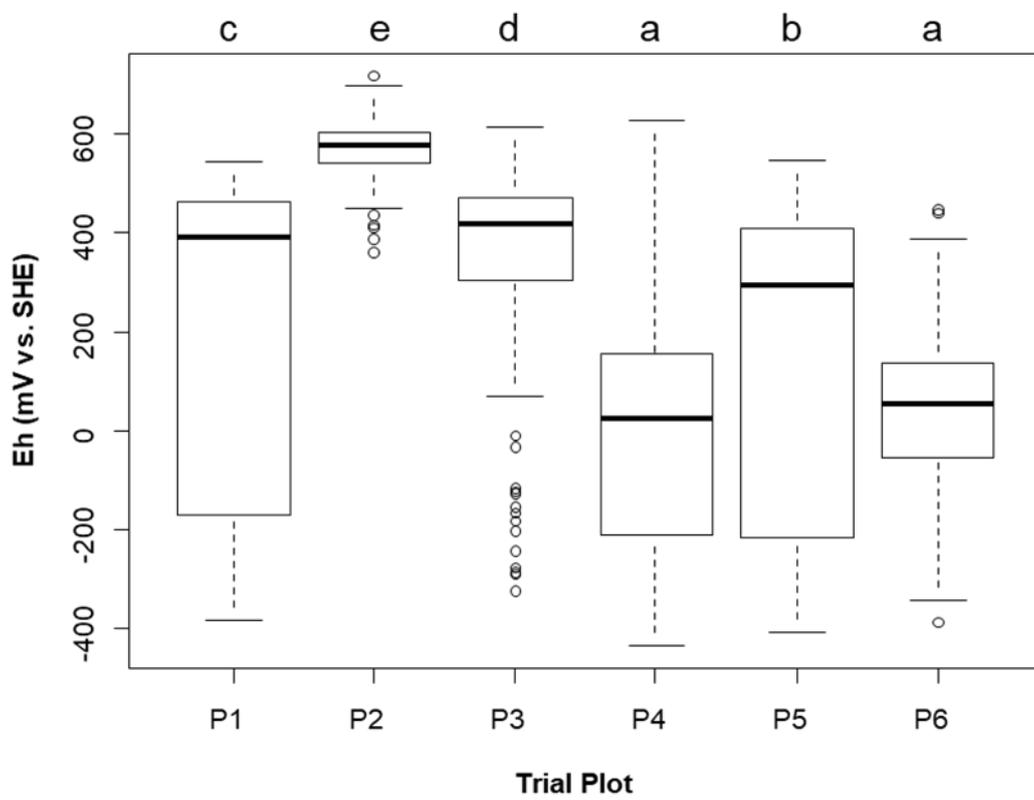


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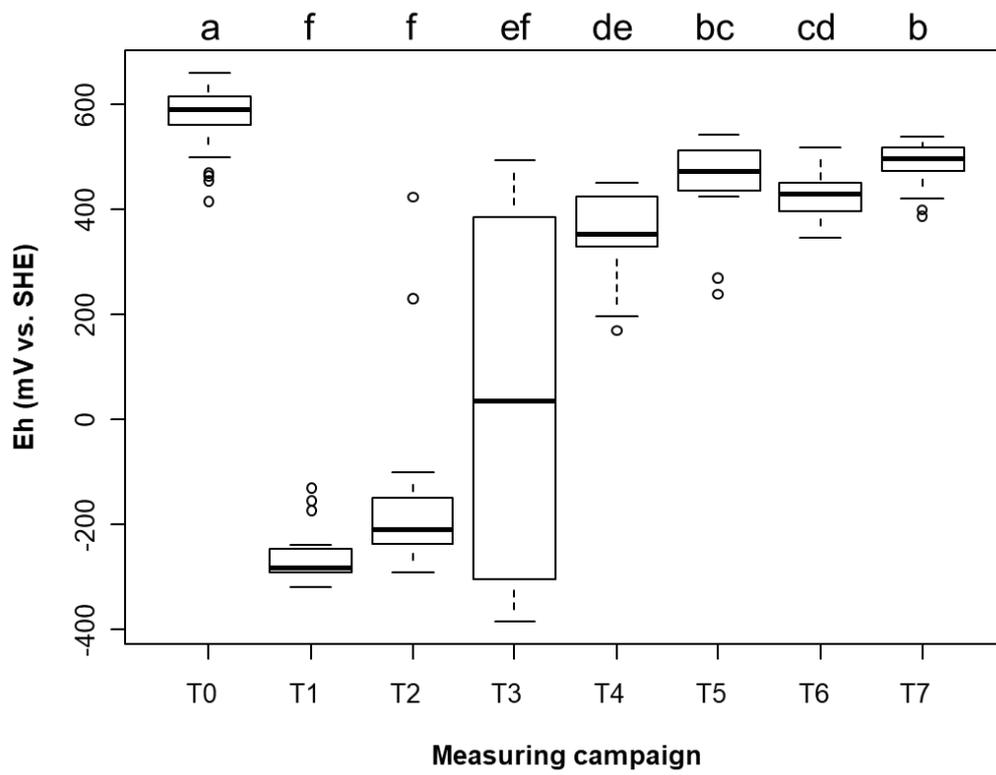


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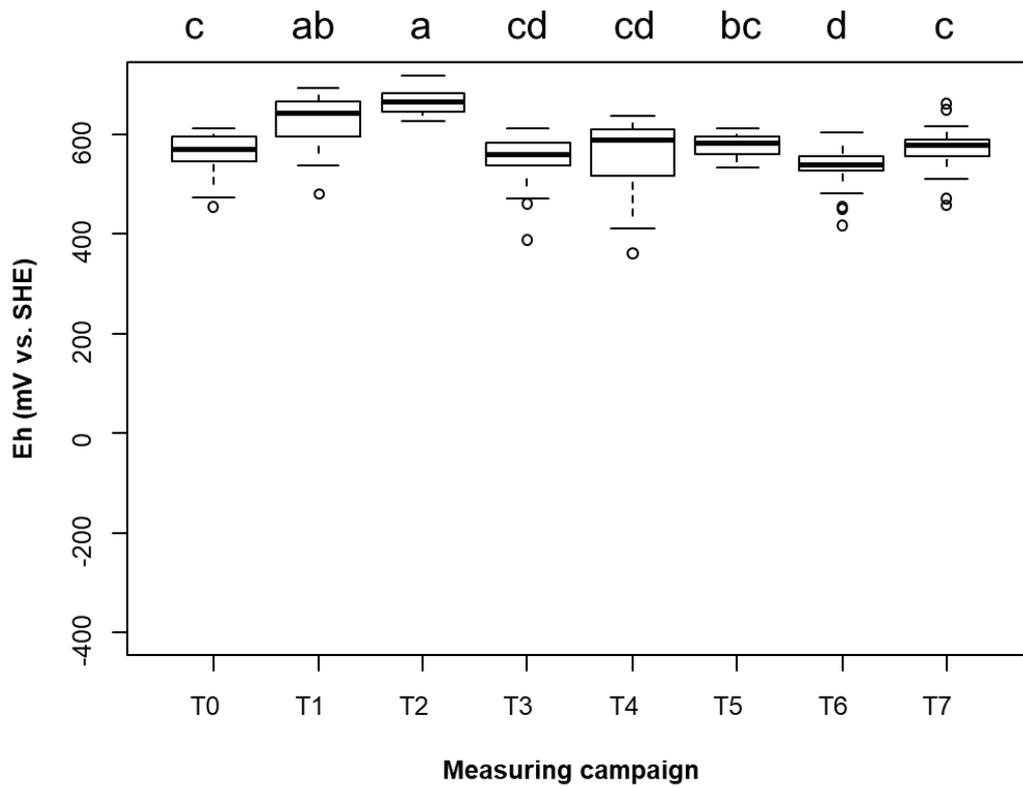


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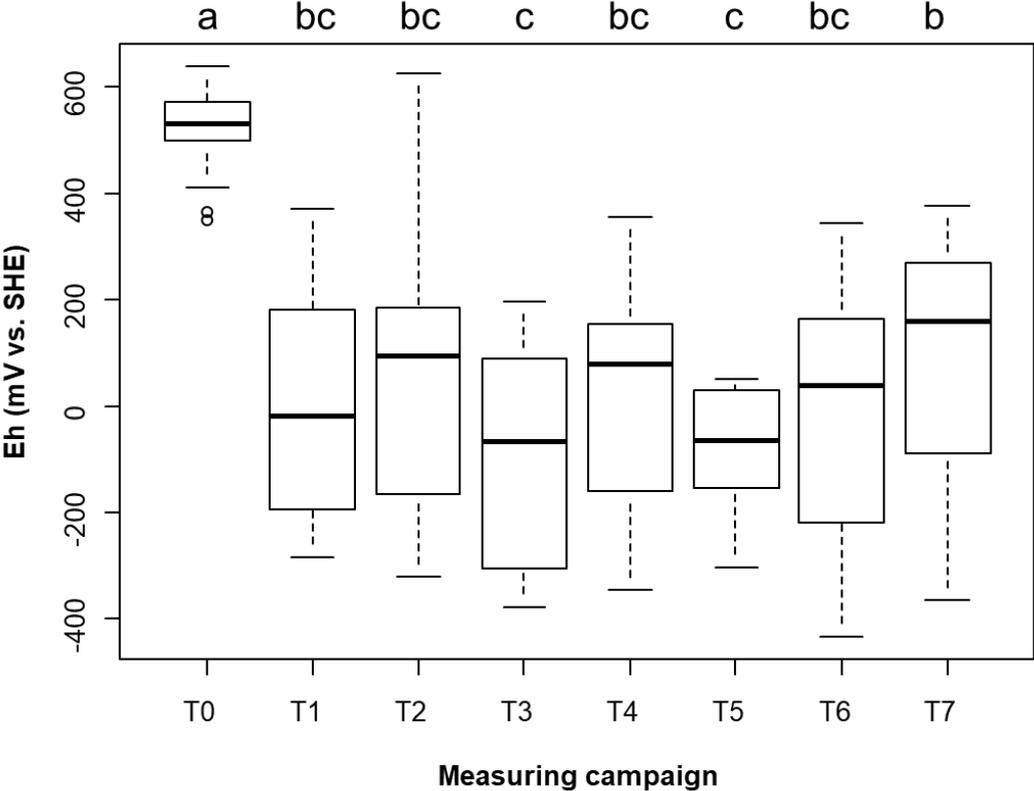


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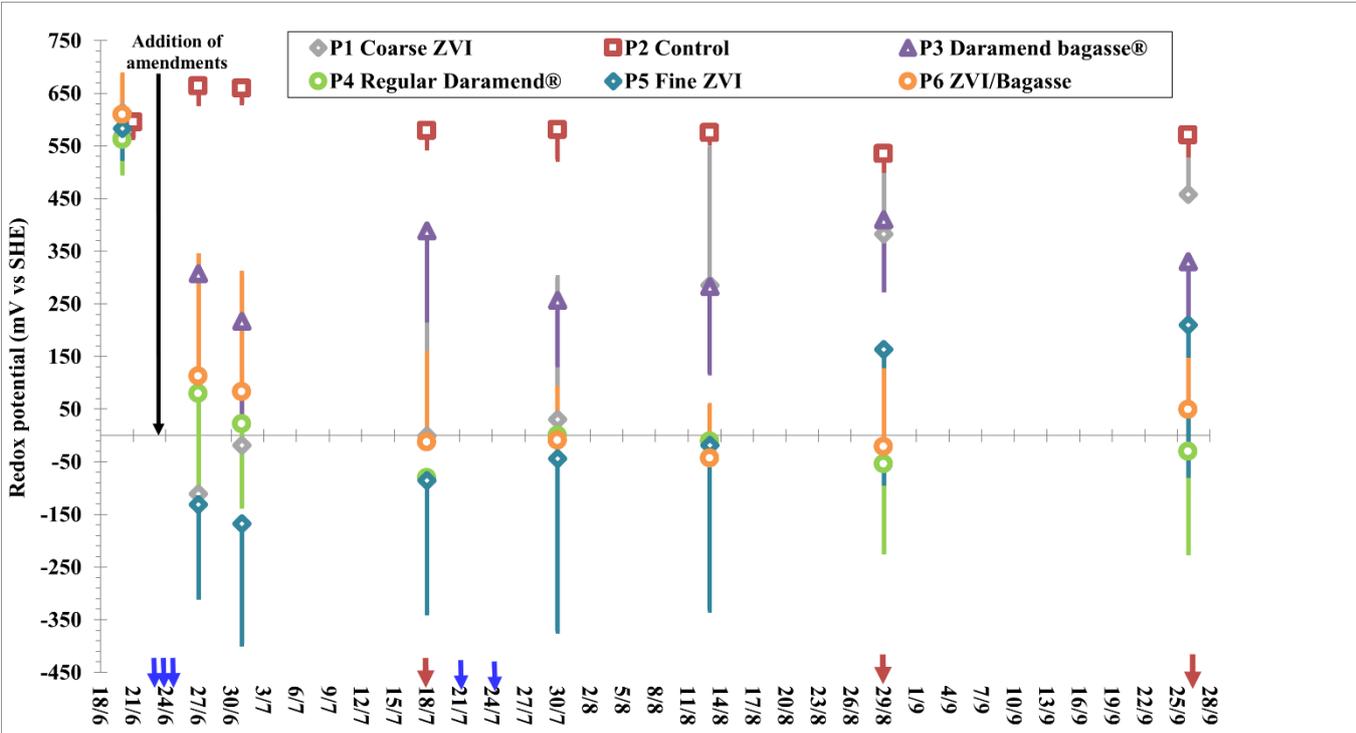


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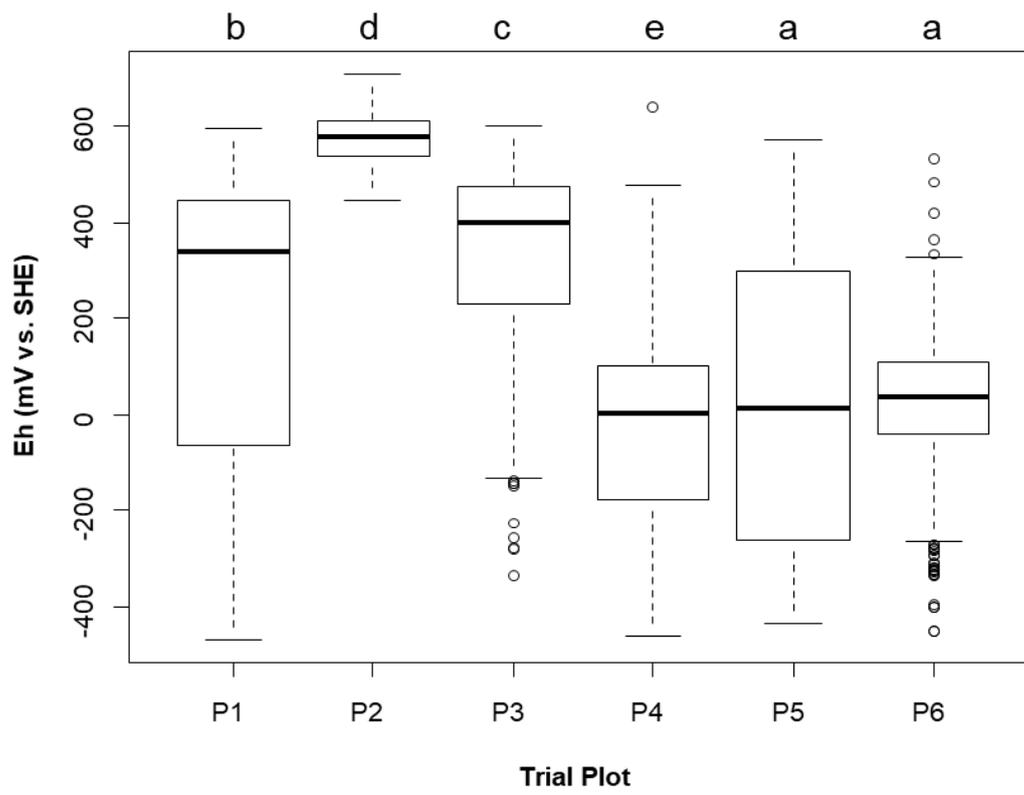


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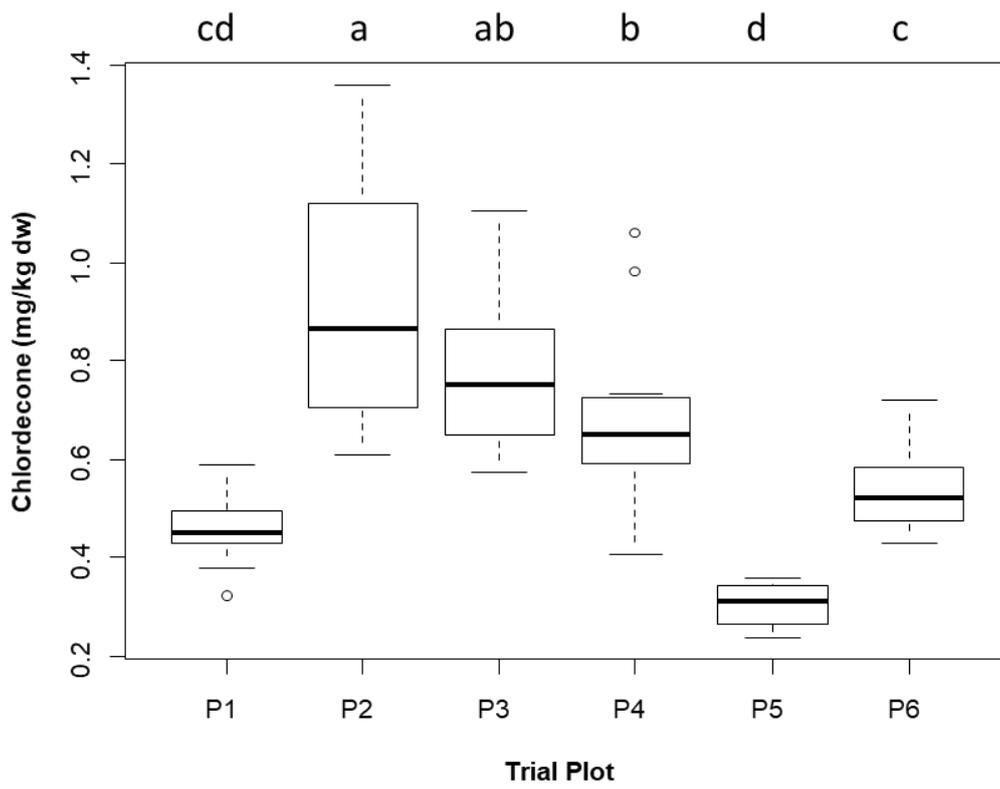


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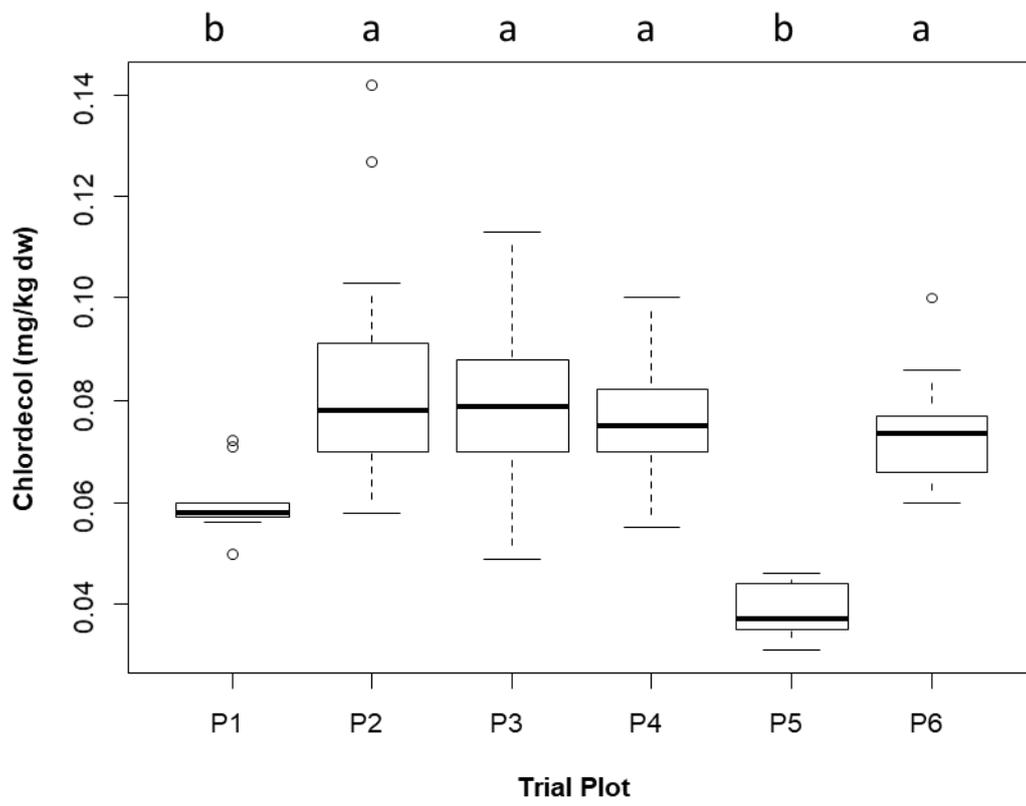


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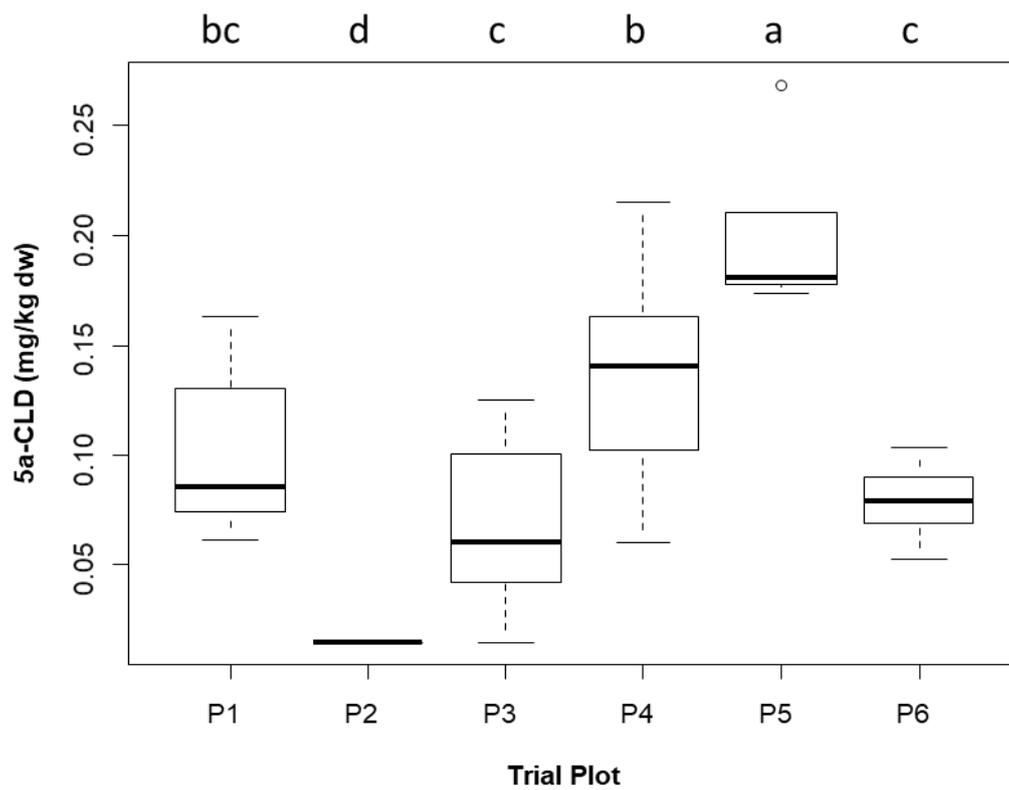


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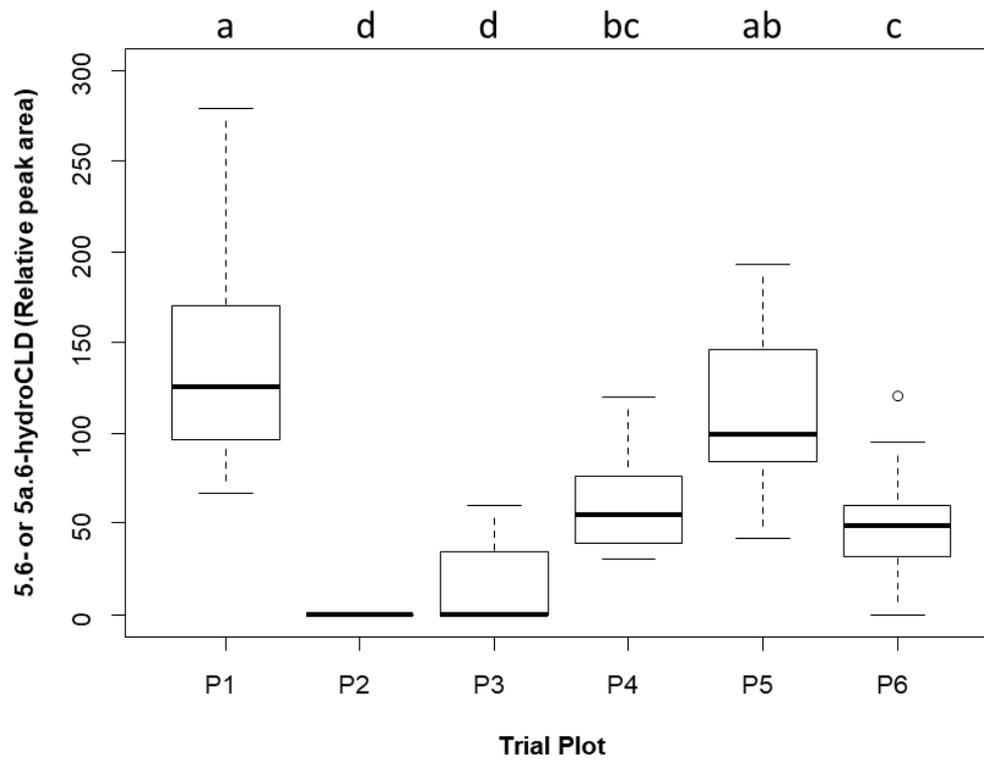


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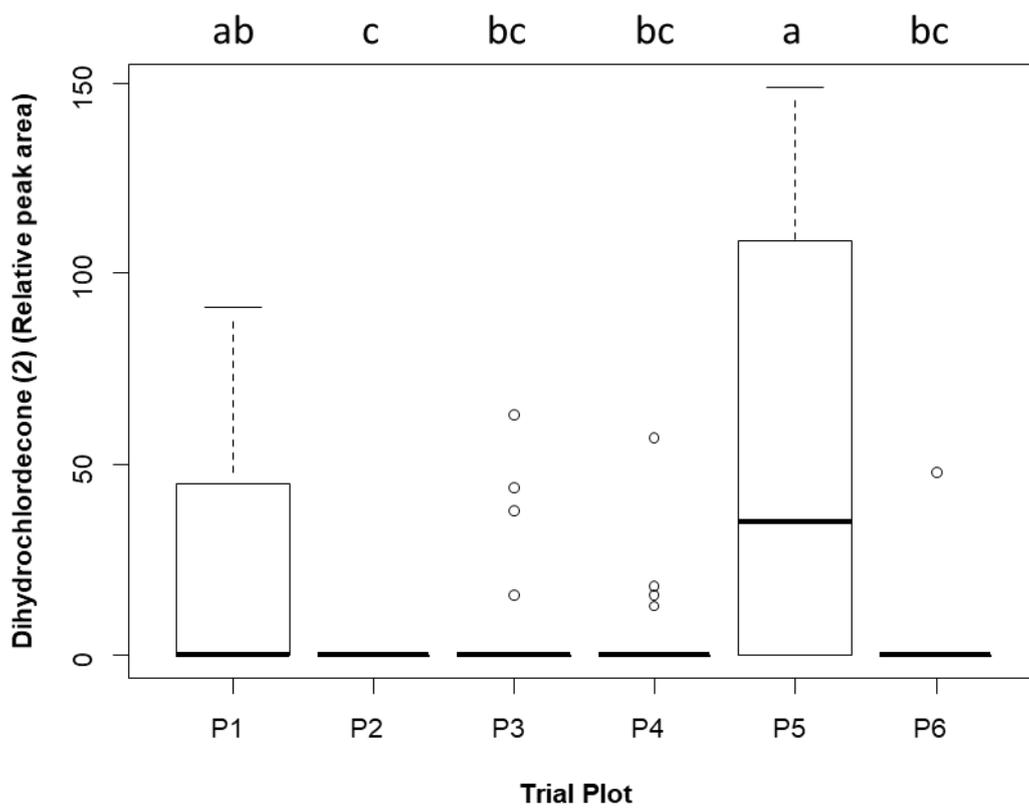


Fig 19

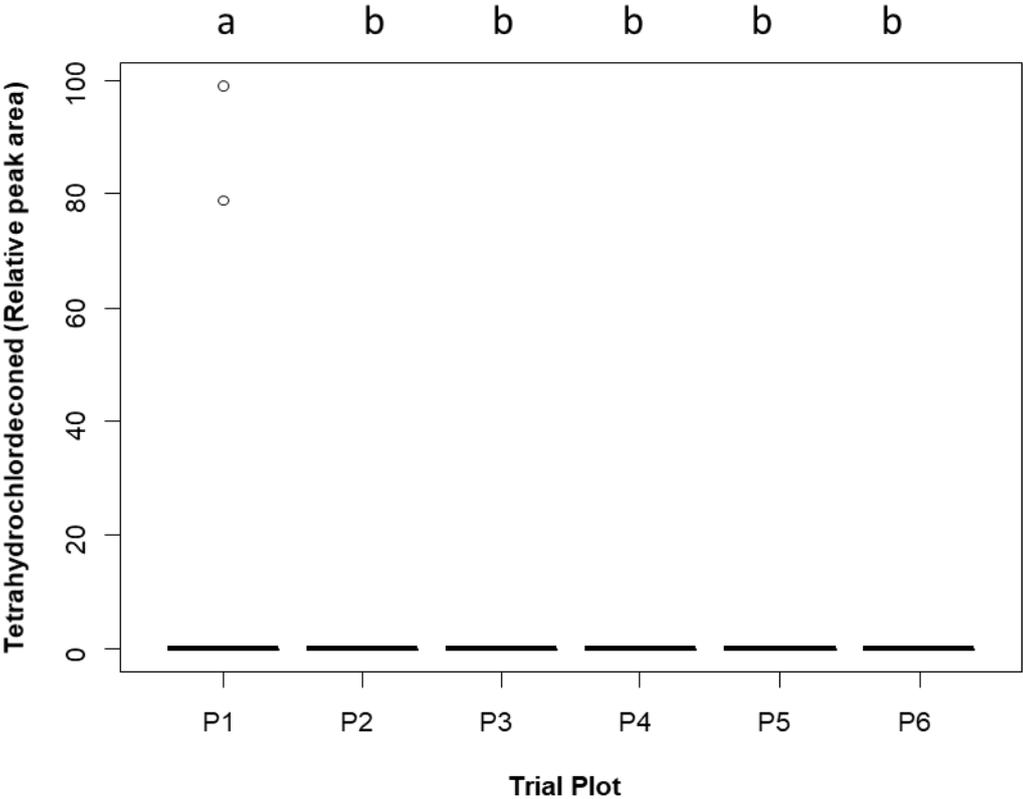


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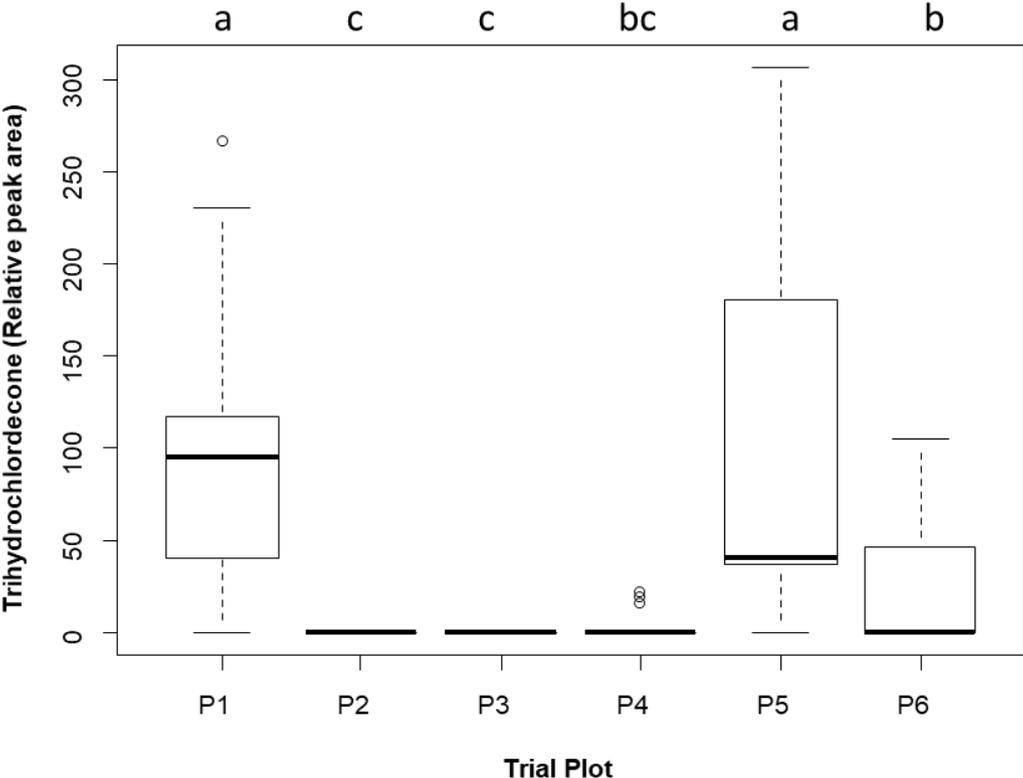


Fig 21

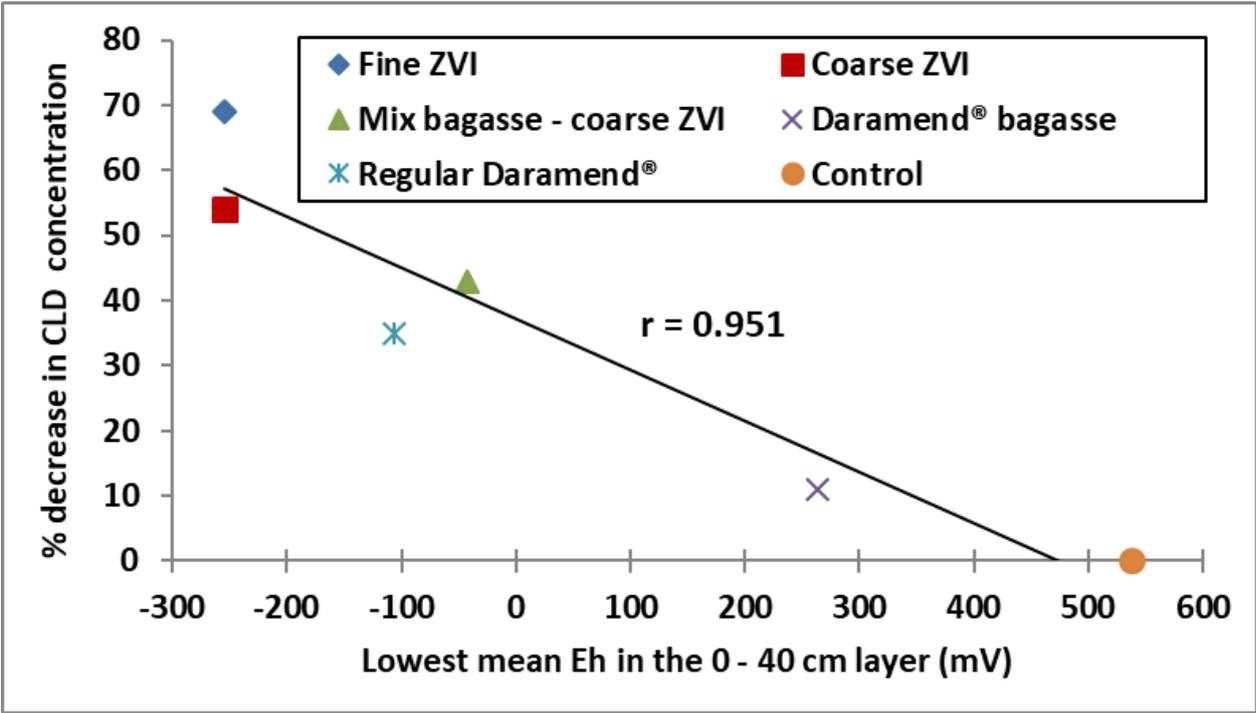
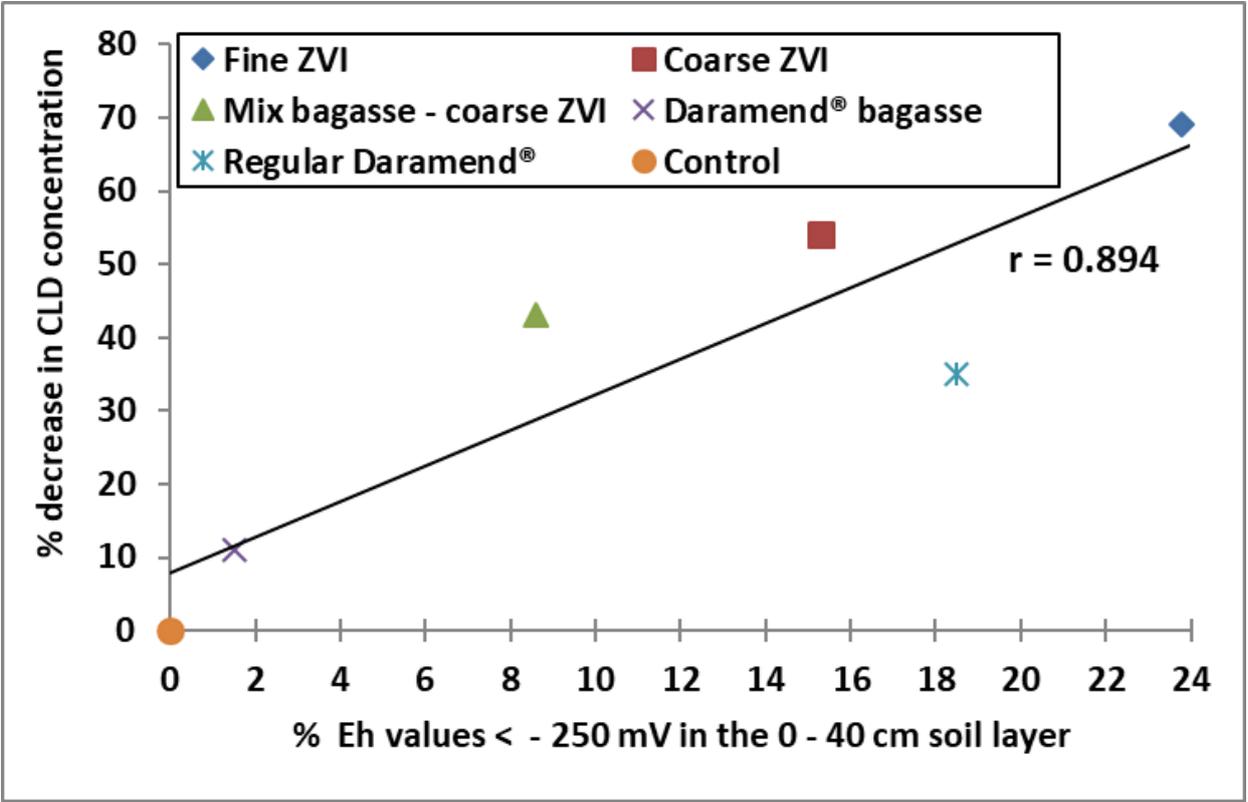


Fig 22



## Tables

**Table 1**

Crop	Complete 14 – 4 -28 fertiliser	DAP	KCl
Sweet potatoe	0,15	0,30	0,45
Cucumber	2,92	1,25	0,75
Radishes	0,05	0,11	0,11

**Table 2**

Parameter	Mean $\pm$ std. dev. (n = 12)	Coefficient of Variation, CV (%)
Organic Carbon (%)	1.3 $\pm$ 0.1	10
N Total (%)	0.14 $\pm$ 0.01	8
C/N ratio	9.5 $\pm$ 0.5	5
P <sub>2</sub> O <sub>5</sub> Olsen (mg/kg )	49 $\pm$ 9	17
K <sub>2</sub> O exchangeable (mg/kg )	962 $\pm$ 241	25
pH water	5.7 $\pm$ 0.4	6
pH KCl	4.6 $\pm$ 0.3	7
Cation Exchange Capacity (meq/100g)	18.9 $\pm$ 0.7	3
MgO exchangeable (mg/kg )	400 $\pm$ 46	11
CaO exchangeable (mg/kg )	1758 $\pm$ 327	19
CaCO <sub>3</sub> total (%)	< 0.1	0
Fe Total (%)	8.4 $\pm$ 0.3	3
% Coarse sand (200 - 2000 $\mu$ m)	5.9 $\pm$ 0.7	12
% Fine sand (50 - 200 $\mu$ m)	8.4 $\pm$ 0.5	6
% Coarse silt (20 - 50 $\mu$ m)	13.2 $\pm$ 1.8	13
% Fine silt (2 - 20 $\mu$ m)	8.6 $\pm$ 1.3	15
% Clay (< 2 $\mu$ m)	61.5 $\pm$ 1.8	3

**Table 3**

<b>Treatment</b>	<b>% of Eh values &lt; - 350 mV</b>	<b>% of Eh values &lt; - 300 mV</b>	<b>% of Eh values &lt; - 250 mV</b>	<b>% of Eh values &lt; 0 mV</b>
<b>P1, fine ZVI</b>	4.0	6.3	15.3	30
<b>P2, control</b>	0.0	0.0	0.0	0.0
<b>P3, Daramend® bagasse</b>	0.0	0.4	1.5	5
<b>P4 regular Daramend®</b>	4.7	10.4	18.5	49
<b>P5, fine ZVI</b>	8.4	16.0	23.8	42
<b>P6, mix bagasse – coarse ZVI</b>	1.2	4.6	8.6	36

Table 4

Treatment	CLD	5b-hydroCLD	5- or 5a-hydroCLD (mg/kg)	CLDOH	5,6- or 5a,6-hydroCLD	Dihydro-CLD (2) (relative peak area)	Tetrahydro-CLD	Trihydro-CLD
P1	0.50 ± 0.08 <sup>b</sup>	< 0.05	0.13 ± 0.03 <sup>ab</sup>	0.07 ± 0.01 <sup>ab</sup>	209 ± 67 <sup>a</sup>	73 ± 25 <sup>ab</sup>	60 ± 53 <sup>a</sup>	205 ± 78 <sup>a</sup>
P2	0.92 ± 0.23 <sup>a</sup>	< 0.05	< 0.03 <sup>c</sup>	0.09 ± 0.03 <sup>a</sup>	0 <sup>c</sup>	0 <sup>c</sup>	0 <sup>b</sup>	0 <sup>b</sup>
P3	0.82 ± 0.18 <sup>a</sup>	< 0.05	0.08 ± 0.02 <sup>b</sup>	0.09 ± 0.01 <sup>a</sup>	31 ± 25 <sup>bc</sup>	27 ± 26 <sup>bc</sup>	0 <sup>b</sup>	0 <sup>b</sup>
P4	0.80 ± 0.18 <sup>a</sup>	< 0.05	0.09 ± 0.02 <sup>ab</sup>	0.08 ± 0.01 <sup>ab</sup>	50 ± 14 <sup>ab</sup>	12 ± 23 <sup>c</sup>	0 <sup>b</sup>	7 ± 11 <sup>b</sup>
P5	0.34 ± 0.00 <sup>b</sup>	< 0.05	0.23 ± 0.03 <sup>a</sup>	0.04 ± 0.00 <sup>b</sup>	23 ± 14 <sup>a</sup>	125 ± 21 <sup>a</sup>	0 <sup>b</sup>	236 ± 65 <sup>b</sup>
P6	0.57 ± 0.08 <sup>b</sup>	< 0.05	0.08 ± 0.02 <sup>b</sup>	0.07 ± 0.01 <sup>ab</sup>	52 ± 45 <sup>bc</sup>	12 ± 20 <sup>c</sup>	0 <sup>b</sup>	44 ± 43 <sup>b</sup>

Table 5

Treatment	CLD	5b- hydroCLD	5- or 5a- hydroCLD	CLDOH	5,6- or 5a,6- hydroCLD	Dihydro- CLD (2)	Tetrahydro- CLD	Trihydro- CLD
	<i>(mg/kg)</i>				<i>(relative peak area)</i>			
<b>P1</b>	0.51 ± 0.07 <sup>cd</sup>	< 0.05	0.09 ± 0.03 <sup>abc</sup>	0.06 ± 0.00 <sup>ab</sup>	138 ± 27 <sup>a</sup>	12 ± 22 <sup>b</sup>	0	99 ± 10 <sup>a</sup>
<b>P2</b>	1.03 ± 0.23 <sup>a</sup>	< 0.05	< 0.03 <sup>d</sup>	0.08 ± 0.01 <sup>a</sup>	0 <sup>c</sup>	0 <sup>b</sup>	0	0 <sup>c</sup>
<b>P3</b>	0.75 ± 0.14 <sup>ab</sup>	< 0.05	0.07 ± 0.03 <sup>cd</sup>	0.07 ± 0.02 <sup>ab</sup>	9 ± 22 <sup>c</sup>	0 <sup>b</sup>	0	0 <sup>c</sup>
<b>P4</b>	0.67 ± 0.06 <sup>bc</sup>	< 0.05	0.15 ± 0.05 <sup>ab</sup>	0.08 ± 0.01 <sup>a</sup>	71 ± 31 <sup>ab</sup>	2 ± 5 <sup>b</sup>	0	3 ± 7 <sup>c</sup>
<b>P5</b>	0.33 ± 0.03 <sup>d</sup>	< 0.05	0.18 ± 0.01 <sup>a</sup>	0.04 ± 0.01 <sup>b</sup>	74 ± 34 <sup>ab</sup>	47 ± 29 <sup>a</sup>	0	62 ± 48 <sup>ab</sup>
<b>P6</b>	0.56 ± 0.07 <sup>cd</sup>	< 0.05	0.07 ± 0.01 <sup>bc</sup>	0.08 ± 0.01 <sup>a</sup>	53 ± 32 <sup>b</sup>	0 <sup>b</sup>	0	18 ± 24 <sup>bc</sup>

Table 6

Treatment	CLD	5b- hydroCLD	5- or 5a- hydroCLD	CLDOH	5.6- or 5a.6- hydroCLD	Dihydro- CLD (2)	Tetrahydro- CLD	Trihydro- CLD
	<i>(mg/kg)</i>				<i>(relative peak area)</i>			
<b>P1</b>	0.38 ± 0.05 <sup>bc</sup>	< 0.05	0.07 ± 0.01 <sup>b</sup>	0.06 ± 0.01 <sup>bc</sup>	83 ± 15 <sup>a</sup>	0 <sup>b</sup>	0	24 ± 21 <sup>b</sup>
<b>P2</b>	0.82 ± 0.29 <sup>a</sup>	< 0.05	< 0.03 <sup>c</sup>	0.08 ± 0.03 <sup>ab</sup>	0 <sup>b</sup>	0 <sup>b</sup>	0	0 <sup>b</sup>
<b>P3</b>	0.73 ± 0.11 <sup>a</sup>	< 0.05	0.07 ± 0.04 <sup>b</sup>	0.08 ± 0.02 <sup>a</sup>	7 ± 11 <sup>b</sup>	0 <sup>b</sup>	0	0 <sup>b</sup>
<b>P4</b>	0.54 ± 0.10 <sup>b</sup>	< 0.05	0.16 ± 0.02 <sup>a</sup>	0.07 ± 0.01 <sup>abc</sup>	62 ± 30 <sup>a</sup>	3 ± 7 <sup>b</sup>	0	0 <sup>b</sup>
<b>P5</b>	0.25 ± 0.01 <sup>c</sup>	< 0.05	0.18 ± 0.00 <sup>a</sup>	0.04 ± 0.01 <sup>c</sup>	89 ± 9 <sup>a</sup>	0 <sup>b</sup>	0	25 ± 22 <sup>b</sup>
<b>P6</b>	0.47 ± 0.03 <sup>bc</sup>	< 0.05	0.09 ± 0.01 <sup>b</sup>	0.07 ± 0.01 <sup>abc</sup>	37 ± 21 <sup>a</sup>	0 <sup>b</sup>	0	8 ± 19 <sup>b</sup>

**Table 7**

Sampling date	CLD	5b- hydroCLD	5- or 5a- hydroCLD	CLDOH	5,6- or 5a,6-- hydroCLD	Dihydro- CLD (2)	Tetrahydro- CLD	Trihydro- CLD	Pentahydro- CLD
		<i>(mg/kg)</i>				<i>(relative peak area)</i>			
<b>T0 = 0 day</b>	1.50 ± 0.16	< 0.05	< 0.03	0.10 ± 0.01	0	0	0	0	0
<b>T1 = 9 days</b>	0.91 ± 0.16	< 0.05	0.11 ± 0.02	0.09 ± 0.01	128 ± 39	63 ± 14	0	176 ± 47	88 ± 16
<b>T2 = 21 days</b>	0.71 ± 0.13	< 0.05	0.09 ± 0.02	0.06 ± 0.01	252 ± 68	50 ± 12	45 ± 27	214 ± 48	133 ± 28
<b>T3 = 37 days</b>	0.39 ± 0.06	< 0.05	0.07 ± 0.01	0.06 ± 0.01	157 ± 37	81 ± 20	0	201 ± 35	18 ± 30

**Table 8**

<b>Treatment</b>	<b>24 days</b>	<b>64 days</b>	<b>94 days</b>
<b>P1</b>	45	50	54
<b>P2</b>	0	0	0
<b>P3</b>	11	27	11
<b>P4</b>	14	35	35
<b>P5</b>	63	68	69
<b>P6</b>	39	46	43

Table 9

Sampling point	Sampling date	Concentration ( $\mu\text{g/L}$ )			Relative peak areas						
		CLD	5- or 5a-hydroCLD	5,6- or 5a,6-hydroCLD	Dihydro-CLD (2)	Tetrahydro-CLD	Trihydro-CLD	Pentahydro-CLD	-5Cl (2)	-7Cl?	Unknown 5
Point 1	T1= 9 d	0.6	2.0	15.7	3.8	1.2	12.4	0.4	0.1	2.0	5.5
	T2= 21 d	0.7	3.1	51.5	9.6	7.1	75.4	6.0	6.5	37.0	55.7
	T3= 37 d	0.3	1.0	5.0	2.3	0.4	6.6	0.9	0.9	23.9	25.7
Point 2	T1= 9 d	0.7	5.2	54.6	15.4	2.9	43.2	1.4	0.4	3.1	5.4
	T3= 37 d	0.3	1.2	8.4	4.3	< 0.7	8.6	2.8	1.4	11.7	2.0
Point 3	T1= 9 d	1.1	3.8	48.1	10.0	4.0	46.4	1.9	0.4	2.2	3.3
	T2= 21 d	1.3	3.8	34.1	11.8	3.2	54.7	6.1	4.1	47.2	56.3
	T3= 37 d	0.9	2.8	10.4	5.8	0.6	14.9	0.6	1.0	30.4	38.9

Table 10

Sampling point	Sampling date	Concentration ( $\mu\text{g/L}$ )			Relative peak areas						
		CLD	5- or 5a-hydroCLD	5,6- or 5a,6-hydroCLD	Dihydro-CLD (2)	Tetrahydro-CLD	Trihydro-CLD	Pentahydro-CLD	-5Cl (2)	-7Cl?	Unknown 5
Point 1	T1= 9 d	2.0	5.2	15.1	10.3	0.5	10.6	0.3	<	2.0	3.2
	T2= 21 d	2.0	5.8	25.3	12.6	1.4	24.7	4.9	2.4	7.7	1.7
	T3= 37 d	0.9	1.9	4.9	2.8	< 0.5	4.3	1.1	0.6	2.2	0.7
Point 2	T1= 9 d	5.0	6.5	7.6	6.0	<	4.0	<	<	0.5	1.2
	T3= 37 d	6.3	6.9	9.0	8.6	0.3	8.1	1.1	0.6	5.8	2.3
Point 3	T1= 9 d	0.5	2.5	12.0	5.6	0.3	9.9	0.5	<	1.4	4.6
	T2= 21 d	0.9	1.6	20.7	7.2	2.5	30.0	6.0	3.3	29.0	24.1
	T3= 37 d	0.8	1.2	8.3	4.3	0.7	11.7	0.9	1.2	21.9	13.0

Table 11

Agronomic parameter	Control 1	Daramend® bagasse	Daramend®	Bagasse + ZVI	Control 2	ZVI only
% germination	97 ± 3	84 ± 19	93 ± 3	87 ± 7	93 ± 3	85 ± 6
Unit mass (g)	7.3 ± 0.9	3.8 ± 1.1	8.2 ± 1.0	3.6 ± 0.5	6.8 ± 1.6	7.0 ± 1.5
Yield (g/m)	239 ± 31 <sup>bc</sup>	80 ± 49 <sup>d</sup>	312 ± 37 <sup>b</sup>	105 ± 16 <sup>d</sup>	243 ± 36 <sup>c</sup>	223 ± 51 <sup>c</sup>

Table 12

Agronomic parameter	Control 1	Daramend® bagasse	Daramend®	Bagasse + ZVI	Control 2	ZVI only
Mean marketable %	85	86	89	81	83	0
Mean unit mass (kg)	0.30	0.31	0.28	0.29	0.30	0
Mean dry matter (%)	4.4	3.9	4.1	4.4	4.4	0
Yield (kg/plant)	1.4 ± 0.4 <sup>bc</sup>	1.3 ± 0.2 <sup>b</sup>	1.1 ± 0.2 <sup>c</sup>	1.3 ± 0.7 <sup>bc</sup>	1.2 ± 0.5 <sup>bc</sup>	0

Table 13

Agronomic parameter	P2, Control 1	P3, Daramend® bagasse	P4, Daramend®	P6, Bagasse + ZVI	P8, Control 2	P1, ZVI only
Tubers/plant	5.0 ± 1.6 <sup>abc</sup>	3.4 ± 0.7 <sup>bc</sup>	5.7 ± 1.3 <sup>ab</sup>	2.8 ± 0.8 <sup>c</sup>	4.7 ± 2.0 <sup>abc</sup>	4.2 ± 1.2 <sup>abc</sup>
Marketable tubers (%)	66 ± 31 <sup>a</sup>	58 ± 32 <sup>a</sup>	61 ± 20 <sup>a</sup>	50 ± 17 <sup>a</sup>	64 ± 23 <sup>a</sup>	48 ± 20 <sup>a</sup>
Marketable tuber unit mass (kg)	0.50 ± 0.17 <sup>a</sup>	0.63 ± 0.31 <sup>a</sup>	0.43 ± 0.16 <sup>a</sup>	0.34 ± 0.08 <sup>a</sup>	0.48 ± 0.16 <sup>a</sup>	0.47 ± 0.30 <sup>a</sup>
Dry matter (%)	26.0 ± 1.0 <sup>a</sup>	24.9 ± 2.1 <sup>a</sup>	25.1 ± 2.0 <sup>a</sup>	25.0 ± 3.2 <sup>a</sup>	26.6 ± 2.9 <sup>a</sup>	26.1 ± 1.2 <sup>a</sup>
Marketable yield (kg/plant)	1.7 ± 0.9 <sup>ab</sup>	1.3 ± 0.9 <sup>ab</sup>	1.7 ± 1.0 <sup>ab</sup>	0.4 ± 0.1 <sup>b</sup>	1.3 ± 0.6 <sup>a</sup>	0.9 ± 0.7 <sup>a</sup>

Table 14

Plot	CLD, µg/L (mean ± std. dev)	CLD -1 Cl, µg/L (mean ± std. dev)	CLD -3Cl, µg/L (mean ± std. dev)
Control 1	5.3 ± 0.4 <sup>a</sup>	< 0.10 <sup>a</sup>	< 0.10 <sup>a</sup>
Regular Daramend®	1.0 ± 0.6 <sup>b</sup>	1.7 ± 0.6 <sup>b</sup>	0.1 ± 0.1 <sup>b</sup>
Coarse ZVI only	1.3 ± 0.4 <sup>b</sup>	1.7 ± 0.4 <sup>b</sup>	0.4 ± 0.2 <sup>c</sup>

Table 15

Plant	Control 1	Daramend® bagasse	Regular Daramend®	Bagasse + ZVI	Control 2	ZVI only
Radishes	28.9 ± 4.2 <sup>a</sup>	28.8 ± 5.8 <sup>a</sup>	14.0 ± 5.8 <sup>bcd</sup>	15.7 ± 0.6 <sup>b</sup>	28.8 ± 10.7 <sup>a</sup>	11.5 ± 2.0 <sup>c</sup>
Cucumbers	19.2 ± 2.0 <sup>a</sup>	15.7 ± 4.2 <sup>a</sup>	7.2 ± 1.9 <sup>b</sup>	5.8 ± 1.2 <sup>b</sup>	8.1 ± 3.8 <sup>b</sup>	No data
Sweet potatoes	64.0 ± 42.7 <sup>a</sup>	59.5 ± 28.0 <sup>a</sup>	21.0 ± 11.3 <sup>ab</sup>	9.2 ± 5.3 <sup>b</sup>	47.9 ± 22.6 <sup>a</sup>	49.4 ± 19.0 <sup>a</sup>



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