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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

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Abstract:	<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>
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**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**

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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

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

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

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

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

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

Neither has biodegradation proved effective to decontaminate soils, even under laboratory conditions. In andosol microcosms sieved to < 2 mm and placed in aerobic conditions with an added solution of ¹⁴C-CLD in acetone, no more than 4.4 % of the initial dose of ¹⁴C-CLD was mineralised after 215 days (Fernandez-Bayo et al, 2013).

On the other hand, an adaptation of the In Situ Chemical Reduction principle (ISCR) to laboratory 80 kg mesocosms of the 3 main soil types of the French Caribbean contaminated by CLD has produced very encouraging results (Mouvet et al, 2017). The trial used the Daramend® amendment with added Zero Valent Iron filings (ZVI) in a series of cycles alternating reducing and oxidising conditions. After 6 months of treatment, CLD concentrations dropped by 74% in nitisol, 71 % in ferralsol and 22 % in andosol. Eleven dechlorinated products of CLD transformation were identified, from mono- (CLD -1Cl) to penta-dechlorinated (CLD - 5Cl). None accumulated during the trial and of the seven ecotoxicity tests implemented, six showed no difference between the treated soils and the untreated control samples.

The effect of ZVI alone, without the easily degradable organic material in Daramend®, was investigated using distilled water to which was added 100 mg/l of CLD dissolved in acetone

and 0.2 g of ZVI. The CLD was entirely transformed as from Day 14 into 14 dechlorinated degradates (Belghit et al, 2015) identical to those formed after ISCR treatment of actual soils in the laboratory (Mouvet et al, 2017).

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

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

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

MATERIAL & METHODS

Experimental plot and remediation treatments applied

The study parcel is a banana plantation in Martinique, located to the north-west of Fort-de-France at an altitude of 71m and growing on a nitisol with proven chlordecone contamination of the 0 - 40 cm soil horizon, at 0.71 ± 0.26 mg/kg, $n = 24$. Because of this contamination, cultivation of various subsistence crops is discouraged (Cabidoche & Lesueur-Jannoyer, 2012).

The ISCR patent (United States Patent, 2000) describes the process as involving multiple treatment cycles that alternate strongly reducing conditions with oxidizing conditions. The reducing conditions result from the addition of Daramend® amendments and water to obtain a soil moisture content close to its water holding capacity. The regular Daramend® soil amendment used for the study and purchased from the US company FMC, was a mixture of 70 % alfalfa and 30% ZVI. In order to test a soil amendment containing a local raw material instead of alfalfa, two other amendments containing bagasse were tested: Daramend® with bagasse (also developed by FMC with 70 % bagasse and 30 % ZVI) and a bagasse/ZVI mixture (developed by the BRGM with 70 % bagasse and 30 % "coarse" ZVI). Finally, two treatments with ZVI only were applied, coarse ZVI (30 % < 50 µm; Lövink Technocast b.v, 7060 AA Terborg, Netherlands, imported from Poland) and fine ZVI (98 % < 50 µm; Dousselin iron powder NC 100.24; Dousselin & Geoffray-Jacquet Réunion, 69270 Couzon au Mont D'Or, France).

The parcel was divided into 6 trial plots (105 m², 15 x 7 m): P1 with coarse ZVI; P2: control; P3: Daramend® with bagasse; P4: regular Daramend®; P5: fine ZVI; P6: bagasse + coarse ZVI.

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

An additional adjacent plot, PA, 100 m², was treated with 2.8 % (w/w) coarse ZVI in the second phase of the study. This plot was equipped with suction cups during the ISCR treatment to monitor concentrations of CLD and degradates in the soil water. As the background concentration in this plot was much higher than in the 1st control plot, P2, a second control plot, labelled P8, was used in addition to P2 for the agronomy part of the study.

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

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

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

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

Soil sampling and characterisation, Eh determination and analyses of chlordecone and degradates

Initial soil characterisation

Twelve independent soil samples were taken at random locations across the 1000 m² plot. The main physico-chemical parameters were analysed by an accredited laboratory (SAS, Ardon, France) using standardised procedures previously reported (Mercier et al, 2013). Two

techniques were used to verify the presence of halloysite clay, the main mineralogical characteristic of nitisols. The crystal structure of halloysite was characterised by X ray diffraction using a Philips PW 1830 (Cu K α) diffractometer. The diffraction angles studied ranged from 2 to 50 degrees and the inter-reticular distances investigated, d, were within the range of 1.1 to 11 Å. For infrared spectroscopy, an IR-FT Nicolet 510P (ThermoFischer Scientific Inc., Waltham, MA, USA) spectrometer was used and the soil samples were characterised in transmission mode after dilution in KBr pellets with a 5 10⁻³ mass ratio. The IR spectra were obtained in the wavelength range of 400 - 4 000 cm⁻¹.

Subsequent soil sampling strategy

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

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

Measurement of redox potential

For each of the 12 sampling points, 5 redox measurements were taken for the 0 - 20 cm horizon in a hole made with a garden fork (1 measurement on each of the 4 sides of the hole and 1 at the bottom), 3 for the 20 - 30 cm horizon from hand-augered samples and 3 for the 30 - 40 cm horizon from samples taken by the second augering. The point of making so many measurements was to reduce the effects of soil heterogeneity. In our presentation of the results, the figures for the 20 - 30 cm and 30 - 40 cm horizons are averaged to represent the 20 - 40 cm horizon.

The probe was calibrated before making the measurements using a standard 220 mV solution. The reference electrode was an Ag/AgCl (WTW, IDS ORP Electrode Sentix® ORP 900, supplied by VWR). The indicator electrode was a platinum ring and the reference electrolyte was KCl 3M (measurement range: - 1 250.0 to +1 250.0 $\pm$ 0.2 mV). The electronic unit was a digital multi-parameter portable WTW® 3 420 (supplier: Val de Loire Labo, F-41220 Saint-Laurent-Nouan, France).

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

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

where DE is the difference between the measured value of the standard at the measurement T° (long-stem digital Multi Thermometer: - 50 °C to 150 °C, $\pm$ 0,5 °C) and the value that the standard should theoretically have at this T°.

Determination of chlordecone and its transformation products in soil samples

The samples were dried (40 $\pm$ 1°C for 72 h) in aluminium trays before crushing and sieving to < 2 mm. A representative aliquot was further ground down to < 80 μ m, a grain size optimising the representativeness of the sample taken for analysis. Another representative aliquot was

dried at 105 °C to measure the residual moisture content after drying at 40 °C, and used to express results relatively to the actual dry mass.

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

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

Soil solution sampling and analyses

Sampling with suction cups

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

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

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

Analyses of soil solution

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

Analysis was by gas chromatography coupled with mass spectrometry, using the same parameters as for the soil analysis. The quantification limit for analysing chlordecone, 5b-

hydrochlordecone and 5- or 5a-hydrochlordécone is 0.07 µg/L. As with the analyses in soil samples, the other transformation products were semi-quantified through their relative chromatographic peak area.

Agronomy section

Plants tested, soil preparation before planting, establishing the crops

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

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

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

Irrigation system and analysis of irrigation water

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

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

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

Fertilisation

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

Use of suction cups to investigate concentrations of chlordecone and degradates in the soil solution

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

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

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

Harvest for the analysis of chlordecone and its degradates

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

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

The sweet potatoes were harvested 5 months after planting. All tubers dug out with a garden fork were collected. They were counted, weighed and sorted in the laboratory, separating out the non marketable tubers ($L < 10$ cm, or calibre < 5 cm, or damaged tubers), which would not be analysed. For each of the 5 beds, 10 uniform sweet potatoes of marketable size were chosen and carefully washed in clean and then distilled water, scrubbing them gently to

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.
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24 **Statistics**

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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.
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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.
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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).
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49 The Wilcoxon-Mann-Whitney test comparing treatments was applied in cases of non-normal
50 distribution or unequal variance.
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54 **RESULTS & DISCUSSION**

55 **Main soil parameters**

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

P₂O₅, K₂O and CaO appeared to vary somewhat ($15 \leq CV \leq 25 \%$) between the 12 replicates. These parameters are not very likely to influence the mechanisms involved in ISCR and their heterogeneity should therefore not influence the effects of the treatment applied to each plot. In contrast, the parameters likely to play an important role in ISCR (pH, total Fe and organic carbon) were fairly homogeneous ($3 \leq CV \leq 10 \%$) across the study zone. The same parameters determined for P2, the additional plot treated with ZVI in the agronomy part of the study, did not differ significantly from those in table 2, with for instance a total iron content (%) of $8.3 \pm 0.3 \%$ and a water pH of 5.7 ± 0.4 .

Presence of halloysite

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

Redox potential in the 0 - 20 cm soil layer

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

Comparison between treatments for each measuring campaign

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

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

Although few changes occurred between the 3rd and 7th day (July 1, T2) of treatment, the mean Eh values in the two ZVI-only trial plots did begin to increase during that period (Fig 1), leading to values in P1 becoming no more statistically different to those of P4 and P6 (Fig 4).

Between the 3rd and 21st day (July 18, T3) of treatment, the mean Eh decreased by 75 mV in the control plot and by 113 mV and 64 mV in the regular Daramend[®] and bagasse + ZVI plots respectively, but a slight increase, of 56 mV, occurred in the Daramend[®] bagasse plot. In contrast, the increase in mean Eh was very clear for the coarse ZVI, at + 293 mV, and for the fine ZVI at + 185 mV, which produced a slightly positive value for P1 (39 mV) and a slightly negative value for P5 (- 70 mV ; Fig 1). This increase can be attributed to a decrease in the reduction potential of the added amendments as a result of partial oxidation of the added ZVI and reoxygenation of the soil. Compared to the trials with ZVI only, the decrease (P4 and P6), or smaller increase (P3), in Eh in the trial plots with easily biodegradable organic matter can be attributed to the continuous consumption of this biomass and the associated oxidative species. On the 21st day of treatment (T3), the statistical analysis indicates that the mean Eh value for all the trial plots was significantly lower than that in the control plot. The drop in Eh compared to the control was smaller in P3 than in the other 4 trial plots. P3 mean value was significantly higher than in the other 4 trial plots in which the only difference was between P1 and P4 (Fig 5).

On Day 35 (July 30, T4), despite a second irrigation (66 mm) between the 27th and 28th day of experimentation (July 22 and 23), Eh continued to increase in both ZVI-only plots (P1 and P5), reaching mean values of + 352 mV and + 308 mV respectively. In contrast, Eh remained fairly stable in all other plots. The failure of the 2nd irrigation to further decrease the Eh values, or at least to stop the increase in Eh, may be due to the fact that the mechanisms involved in lowering the Eh resulting from the oxidation of ZVI when added without easily biodegradable organic matter had exhausted their potential. At this time of the experiment, P4 and P6 do not differ significantly from each other but differ significantly from all the other trials, P1, P3 and P5 do not differ significantly from each other but differ significantly from all the other trials, and P2, with a mean value of + 547 mV, differs significantly from all the other trials (Fig 6). These 3 groups of Eh values match the 3 main types of treatments almost exactly: easily biodegradable organic matter (P4 and P6), ZVI only (P1 and P5), control (P2). The sole exception is P3, Daramend[®] bagasse.

Between the 44th and the 65th day of treatment (Online Resources 3 and 4), few changes occurred (Fig 1), as was the case between the 3rd and 7th days.

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

In order to provide an overall view covering the whole duration of the treatment, a statistical analysis was conducted on the basis of a single data-set pooling the 7 measuring campaigns. On this basis, the mean Eh values in P4 and P6 do not differ from each other but are lower than the 4 other trial plots which all differ from each other, with values increasing in the following order: P5 < P1 < P3 < P2 (Fig 8). The mean of all post-treatment Eh values in the plot treated with Daramend[®] bagasse, at 363 ± 173 mV, was much higher than with the regular Daramend[®] treatment, $- 8 \pm 218$ mV. This may be due to a lower reductive capacity of the ZVI in the regular Daramend[®] formulation, or to the poorer biodegradability of bagasse compared to alfalfa. However, the mean of all post-treatment Eh values in the plot treated with the

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.
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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).
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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.
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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.
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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.
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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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As in P6 (Online Resource 7), all values after T0 are much lower than at T0 and do not differ from each other.

Redox potential in the 20 - 40 cm soil layer

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

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

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

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

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

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

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

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

Effect of the ploughing ending the treatment

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

Synthesis and link with literature data

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

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

Over the duration of the treatment, the coefficient of variation (CV) of all Eh values in the control plot was 10 % for the 0 – 20 cm layer (n = 233) and 9% for the 20 – 40 cm layer (n = 305). In the treated plots, the variability was much higher, with, for instance, CVs of 146 % and 153 % respectively for the 0 – 20 cm and 20 – 40 cm layers in P1, with a maximum of 2725 % for the 0 – 20 cm layer in P4 (mean $\pm$ standard deviation: -8 ± 218 mV, n = 230). This very high

variability of the Eh values in the trial plots reflects the fact that despite the effort of multiple cross-ploughing just after adding the amendments, their incorporation did not result in homogeneous redox conditions on the scale of the volume (a few tens of cm³) in which redox is measured.

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

Chlordecone and its degradation products in the soil

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

24 days after incorporation of the amendments (Table 4)

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

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

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

Four other products of dechlorination (two dihydroCLD, one trihydroCLD and one tetrahydroCLD) were observed in the treated plots. They could not be quantified in mg/kg given the absence of analytical standards, but the relative peak area provided a semi-quantitative descriptor. TetrahydroCLD appeared only in the coarse ZVI plot P1, which ranked second only to P5 for the trihydroCLD. For the two dihydroCLD, the highest values were again observed in P1 and P5, together with P4 for the 5,6- or 5a-hydroCLD.

The two trial plots in which the drop in CLD concentrations and the formation of most degradates seemed least apparent were those treated with the commercial Daramend® amendments P3 and P4, even though the 6 % treatment dose applied was larger than the 4 % dose used in the P1 and P5 ZVI-only plots. On the other hand, the ZVI dose involved in both Daramend® treatments is lower (1.8 %) than that in the ZVI-only treatments (4 %). As observed for the Eh values, the role of ZVI in the transformation of CLD therefore appears to be quite important. The amendment P6 prepared on the spot with local bagasse and ZVI (1.8 % ZVI of dry soil weight) had a slightly better effect than the commercial amendments.

64 days after incorporation of the amendments (Table 5)

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

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

94 days after incorporation of the amendments (Table 6)

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

Chlordecol concentrations had remained stable, and were lower than in the control plot only in P5. Ten of the 12 peak areas of the transformation products that were quantifiable on the previous sampling date continued to diminish. Regarding the largest peak areas observed after the first sampling date, the compound had either disappeared completely (dihydro in P1 and P5; tetrahydro in P1) or had dropped by a factor of 9 (tetrahydro in P5). These changes in peak areas over the duration of the test period could reflect different phenomena. One could be the transformation of these degradation products into others that were not detected. The signals from the products recorded on the first monitoring date were very weak, so that a further transformation of just a fraction of these products would make the initial signal undetectable. Transformation should in fact be understood as comprising additional dechlorination processes, or as a functionalisation or opening of the bis-homocubane cage structure generating products that are not detectable by gas chromatography (Chaussonnerie et al, 2016; Chevallier et al, 2018). An additional transformation of identified products resulting in higher levels of dechlorination would be consistent with the results obtained with an aqueous matrix, where changes in the signals indeed suggest a formation in sequence from -1 to -5 Cl (Belghit et al, 2015). This transformation process would have significant environmental implications if, for example, microbial degradation was indeed being promoted by a high level of dechlorination.

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).

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

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[®]) and P3 (Daramend[®]
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).

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).

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

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).

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

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

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

50 The results obtained in the neighbouring plot PA treated with 2.8 % coarse ZVI (Table 7)
51 strengthened all the observations for P1 treated with 4 % of the same ZVI. The first was a
52 decrease in CLD concentrations of around 70 %, with a 40 % drop after just 9 days of
53 treatment. Interestingly, the larger decrease in CLD concentrations compared to P1, 74 % vs.
54 54 %, was obtained despite the lower dose of added ZVI in PA. Secondly, 5b-hydroCLD was
55 again not formed in amounts > 0.05 mg/kg and chlordecol decreased after 21 days, but
56 subsequently did not decrease further. Thirdly, the formation of CLD -1Cl and the same 4 other
57 transformation products with, for 3 of these, gradual formation (higher values after 21 days
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than after 9 days) and subsequent disappearance (lower values after 37 days than after 21). At the end of the study, 37 days of treatment, a decrease in relative peak areas compared to Day 21 was observed for 4 of the 5 compounds. The decrease for the trihydroCLD was very limited, while the tetrahydroCLD disappeared completely and the values for 5.6- or 5a.6-hydrochlordecone (for the second dihydroCLD, no clear trend appeared between Days 9, 21 and 37) and the pentahydroCLD decreased by a factor of 1.6 and 7.4, respectively. A fifth dechlorinated compound was observed, a penta-hydroCLD that had been reported previously in laboratory conditions for soils treated with Daramend® and ZVI (Mouvet et al, 2017) and in an aqueous matrix treated with ZVI (Belghit et al, 2015). The initial CLD concentration of 1.5 mg/kg probably allowed this highly dechlorinated degradate to be detected in PA but not in P1 and P5, where the initial CLD concentrations were lower. Like the other polydechlorinated CLD derivatives, this degradate evolved over time, with a clear peak quite soon after the treatment started, on Day 21, followed by an abrupt decrease resulting in a much weaker signal after 37 days. Such a high level of dechlorination, - 5 Cl atoms, in a soil matrix under field conditions, is remarkable as it is close to the best level, -6 to -8 Cl atoms, obtained for an aqueous CLD solution with 5 % NaOH (pH = 14) in laboratory conditions with a UV + H₂ treatment in the absence of any substantial amount of oxidising agent (United States Patent, 1979).

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

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

Overall treatment efficiency

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

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

Relation between treatment efficiency and redox potential

Plotting the % decrease in CLD concentration as a function of the lowest Eh mean value observed in each plot whatever the date (7 available) and soil layer (0 – 20 and 20 – 40 cm) points at a statistically very significant (1 %) inverse linear relationship (Fig 16). The same type of relation has been reported for the halogenated methanes CFCl₃, CCl₄, and CHCl₃, with a statistically significant inverse linear relation between the degradation rates and Eh values in the range of– 104 to – 348 mV (Olivas et al, 2002).

The relation between the treatments efficiency and the lowering of redox potential achieved by the various amendments can be further illustrated by considering the % of the total number of Eh values (n = 337 to 468 according to the treatment) below certain threshold values. The linear relationships observed for - 350 mV, - 300 mV and - 250 mV are statistically significant, but at a 5 % level (Fig xx for – 250 mV), which is lower than when considering the lowest Eh mean value, significant at the 1 % level (Fig xx). When considering the % of values < 0 mV, the linear relationship is not significant at the 5 % level.

Knowing that the mechanism involved in ISCR relies on Eh values sufficiently low to lead to reductive dechlorination, the relations observed could be expected. Rather surprising, though, is the consistency of the trend based on 6 completely independent trial plots. This does not of course mean that Eh is the sole parameter involved in the dechlorination of CLD. Other parameter, not monitored, could be involved. One may for instance think of microbial degradation. This mechanism is however unlikely to have played a major role here, since the time elapsed to obtain 75 % of the maximum treatment efficiency is much shorter than the biodegradation rates reported in laboratory conditions. Nevertheless, the extreme conditions imposed by the treatments may lead to the expression by dehalogenating microorganisms of unique genes that could produce enzymes catalyzing the dechlorination reactions (Dolfing et al, 2008).

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

Chlordecone and dechlorinated degradates in water from the suction cups

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

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

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

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

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

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

At a depth of 50 cm (Table 10), 22 of the 27 possible occurrences had already materialised 9 days after treatment had started. By the end of the monitoring period (Day 37), all possible occurrences had materialised. When comparing the first and last sampling dates, the decreasing trend in the signals over time for compounds with up to -4Cl is less systematic than at 35 cm (8 of 15 possible trends). The trend is mainly weakened by the results from sampling point 2, where in all 5 cases, the signal on Day 37 was equal or stronger than on Day 9. The increasing signal strength between Day 9 and Day 37 for compounds with 5 or more Cl was as marked as at a depth of 35 cm. Of the 18 cases (9 degradates x 2 sampling points) for which 3 sampling dates are available, 17 were at their maximum strength on the second sampling date, Day 21.

The rapid formation of most degradates, within 9 days at most (earlier sampling might have already shown the compounds) in the field conditions of this study, has also been reported in laboratory studies, in which all degradates appeared after just 7 days in aqueous batches (Belghit et al, 2015) and after 20 days (1st sampling date) in soil mesocosms (Mouvet et al, 2017; Dictor et al, 2011). Such rapid transformations, all the more so in field conditions, suggest that the mechanism involved is physico-chemical rather than microbial, because even in optimised laboratory conditions with a highly favourable growth medium and anaerobic conditions, multiple enrichments over weeks (Orndorff & Colwell, 1980) or months (Chaussonnerie et al, 2015) are required before the microbial transformation of CLD becomes significant. The synchronicity of the formation of all degradates, from mono- up to hepta-hydroCLD, suggests formation pathways either in parallel or in quite rapid succession.

Another important and consistent result in studies on ZVI and CLD is the unequivocal absence of degradate accumulation over time, whatever the matrix studied and the degradate considered (Fig. 6, Belghit et al, 2015 ; fig. 3, Mouvet et al, 2016 a; tables 5 to 8 in this paper). Whether this results from leaching, further transformation or mineralisation is yet to be determined.

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

Agronomic effects of the different treatments applied

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

Radishes (Table 11)

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

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

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

Cucumbers (Table 12)

Transplanting of the cucumber seedlings was entirely successful, with 100 % of the 350 seedlings well established within 7 days after planting. Subsequently, fertiliser applied too close to the seedlings caused burns around the collar, which resulted in varying degrees of mortality in the different plots. A new batch of seedlings was then transplanted and successfully established in all the plots. Unfortunately, a high degree of mortality was subsequently observed in the ZVI plot, with only a single cucumber harvested from it. However, this seems to have been a temporary one-off problem. A subsequent experiment in greenhouse conditions and on a different soil treated with ZVI produced a perfectly normal cucumber harvest with an interval of just 1 month between ending the treatment and planting out the seedlings (Mouvet et al, 2016 a). A key factor in this respect seems to be finely controlled irrigation.

No significant differences were found (Wilcoxon test) between the trial plots in the average percentage of marketable cucumbers, their average unit mass and the average percentages of dry matter. No significant differences were found (Wilcoxon test) between the average commercial yields of the two control plots and the three treated trial plots, the only significant

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).

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

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16 Regarding the average unit mass measured on 50 marketable tubers, the Wilcoxon test
17 showed no significant difference between treatments, with coefficients of variation ranging from
18 24 to 64 %. Regarding the percentage of dry matter, the Fisher LSD test showed no significant
19 differences between treatments, with much lower variability in the results (coefficients of
20 variation from 5 to 13 %) than for the two parameters above.

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23 Concerning marketable yields, the averages for the plots treated with the Daramend® bagasse,
24 the regular Daramend® and coarse ZVI only were statistically no different to the averages for
25 the two control plots. Plot 6, treated with bagasse + ZVI, had by far the lowest yield, but this
26 was statistically different only from Control 2 and the ZVI-only plot (Wilcoxon test).

27 28 *CLD and degrade 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.

51 52 53 54 55 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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weight (Anses, 2018), which is a very important criterion given that plant consumption is a major factor in the population's exposure to chlordecone.

Radishes

The average concentration of chlordecone in the radishes from the two control plots were above the Maximum Residue Limit, 20 µg/kg. Therefore, none of these control radishes were marketable under the regulations in force.

Average chlordecone concentrations in the radishes from the bagasse + ZVI and ZVI -only plots were significantly below those from the two control plots ($P < 0.05$) and the MRL (Shapiro test, 0.1 %). The average chlordecone concentrations in the radishes from the regular Daramend® trial plot were also significantly below the 2 controls, but not below the MRL. The reason why the average value is not significantly lower than the MRL may be found in the highly variable values for this trial plot ($n = 5$; 1 outlier at 23.2 mg/kg; without the outlier, the average drops to 11.7 ± 3.0). The average concentration for the Daramend® bagasse trial is not significantly different to the control plots and significantly higher than the MRL (Shapiro test, 1% level). The majority of the treatments therefore reduced contamination in the radishes, with particularly outstanding results in the case of two trials, with which concentrations dropped not only below the values in the two control plots, but also below the MRL. The large reduction in contamination of the radishes is accounted for by the mechanism involved in CLD transfer, which occurs preferentially by contact (Woignier et al, 2012 b).

Two CLD by-products originally present in the untreated soil were analysed in the radishes. Chlordecol (CLDOH) was not detected in any of the radishes, and 5b-hydroCLD was detected only in two of the 10 samples of radishes in the control plot. This absence of contamination should be considered relatively to the low concentrations of these compounds in the soil samples, with both 5b-hydroCLD and CLD-OH always below 0.05 mg/kg and 0.10 mg/kg respectively. The available literature unfortunately does not provide data to which our results can be compared. The only paper with data on 5b-hydroCLD in plants addresses its fate in soils (andosol and nitisol) and in different plants (cabbages, cucumbers, radishes, bell peppers, sugarcane, sweet potatoes and lettuces) and plant organs (fine roots, tubers, corms, leaves, stems and fruits), compared to CLD. The authors note that 5b-hydroCLD concentrations exceeded 10 µg/kg fresh weight only in dasheen and sweet potato (Clostre et al, 2015). Given the detection limit of 0.33 µg/kg for 5b-hydroCLD in our study, it is not surprising that it was never detected. As with CLDOH, we are not aware of any published data to which ours could be compared.

Cucumbers

Average chlordecone concentrations in cucumbers from all plots, including the control plots with untreated soil, were below the MRL. Control plot 1 and the Daramend® bagasse plot formed a group in which the average concentrations differed statistically from those in the other plots and included some samples > MRL: two from Control 1 (21.2 and 21.4 µg/kg) and 1 from the Daramend® Bagasse plot (22.3 µg/kg). All the other plots formed a homogeneous group with average concentrations in the range of 5 to 10 µg/kg, and no samples above the MRL.

The difference between the two control plots was striking and statistically significant (Dunnett test: $Pr > |t| = 0.000141$). At the time of writing, we had no evidence enabling us to account for the difference between the cucumbers harvested from the two control plots.

Two of the trials, with regular Daramend® and with bagasse + ZVI, produced cucumbers with significantly lower CLD concentrations than in one of the two control plots. The surprisingly low CLD concentrations in the cucumbers from Control 2 are the reason why the values for the two treated plots do not differ significantly from those for this second control plot. A field trial with the same soil type (nitisol) and the same level of CLD contamination (0.91 mg/kg) as control

plot 2 plot produced cucumbers with an average CLD concentration of 19 µg/kg (Clostre et al, 2014 b). In view of the CLD concentrations in the soil of control plot 2 in this study (0.77 mg/kg), values of around 20 µg/kg would have been expected in the cucumbers from that plot. The much lower average value measured, of 8.1 µg/kg, is yet to be explained.

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

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

Sweet potatoes

With an average of 21.0 µg/kg (standard deviation = 11.3), plot 4 (regular Daramend®) was close to the MRL and its average level of contamination was 2.3 to 3 times lower than in the control plots. However, these differences compared to the control plots were not statistically significant. Average chlordecone concentrations in the tubers from the other two plots (Daramend® bagasse and ZVI only) were in the range of 30 to 60 µg/kg, values that are similar and not significantly different to each other or from the values for the two control plots. The treatments applied to these three plots did not limit the transfer of chlordecone from the soil to the sweet potato tubers.

The lowest average concentration of chlordecone was observed in the bagasse + ZVI plot, at 9.2 µg/kg, which is below the MRL (20 µg/kg) and significantly lower (Dunnett test: $\Pr(>|t|) = < 0.001$) than in control plot 1, P2 (64.0 µg/kg) and control plot 2, P8 (47.9 µg/kg de MF). This is also the only plot in which all samples had concentrations below the MRL. The question arises as to whether it is indeed the beneficial effect of the ISCR treatment that produces values below the MRL, or whether other factors such as the effects of limited growth or, conversely, dilution, are involved. Given that in this bagasse + ZVI plot (Table 15), i) the yield was not significantly different to that from the two control plots, ii) the number of tubers was the smallest among all trial plots although the difference was not significant compared to the two control plots, and iii) the average unit mass was the smallest among all trial plots, it is most likely that the bagasse + ZVI treatment did indeed have an effect on CLD transfer.

Neither chlordecol nor 5bhydroCLD was detected in any sample. The study by Clostre et al, 2015, does not have any data on 5b-hydroCLD in sweet potatoes grown on nitisol. Our results can therefore not be compared to any other similar dataset.

CONCLUSIONS AND OUTLOOK

The first aim of this study was to test the effectiveness of the In Situ Chemical Reduction (ISCR) process to lower chlordecone (CLD) concentrations in a nitisol in a French Caribbean banana plantation. Five soil amendments capable of triggering the mechanisms involved in chemical CLD reduction were tested using facilities and operating procedures that could be readily implemented locally. The best results were obtained with the addition of Zero Valent

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 ± 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® 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 ± 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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effects were less marked in the cucumbers and sweet potatoes due to the high variability of the results (both crops) and the generally low level of contamination (cucumbers). For the cucumbers, however, two ISCR trials produced fruits with CLD concentrations below the MRL and also below those in one of the two control plots. As for the sweet potatoes, one of the four ISCR trials, with a bagasse-ZVI amendment, produced a significant positive effect by decreasing contamination to below the levels in the two control plots and below the MRL.

Obviously, the question of implementation costs has to be considered. On the scale of the 100 m² trial with a 4 % dose of coarse ZVI applied to a 40 cm layer of nitisol, the cost price amounted to 19 €/m². This includes purchase of the ZVI, customs duties, delivery to the site, hours of use and fuel for the agricultural machinery and the cost of the labour required to plough in the amendment, compact the soil and irrigate the crops. With application on a larger scale, a reduction of around 20 % can be expected in the cost of raw materials and overheads such as bringing agricultural machinery in and out. The unit cost could therefore drop to 17 €/m², even 12 €/m² if the dosage is reduced to 2.8 %, which was the dose applied in the 2nd nitisol plot that produced good results both in terms of lowering CLD concentrations in the soil and for the various crop criteria. With a unit cost of this order, it would not be possible to consider applying the treatment to the entire area affected by CLD contamination of the soils. Targeting treatment to zones where the issue is of particular concern, such as household gardens and catchments around water abstraction points, should therefore be considered to back up the current crisis management approach that relies on regulatory constraints and informing the population about good practices to be applied. A study on the social acceptability of implementing soil decontamination, of whatever kind, would however be required in the first place.

Over and above these socio-economic perspectives, several additional lines of research can already be identified. One of these concerns the transfer into plants of CLD degradates produced by the ISCR process. Unfortunately, this question can only be addressed for the degradates for which analytical standards are available. The analyses conducted in a later study showed that one CLD-1CL, one CLD -3Cl and one CLD-4Cl were present in the plants but that the sum of the molar concentrations of all the quantifiable substances, obviously including CLD itself, was lower in the plants grown on ISCR-treated soil than on the control soil (Mouvet et Bristeau, 2016). More detailed and exhaustive studies are still needed on this subject. Combining the ISCR approach with simultaneous or subsequent activation of microbiological activity could also be considered, as there is a possibility that with the partial dechlorination observed, the resulting molecules could biodegrade more efficiently than the parent molecules. To undertake these studies, analytical standards for the main CLD transformation products would again be required, but obtaining the mass and purity needed for these standards would be a project in itself.

Finally, decontaminating soils to eliminate CLD is not the only way of preventing CLD from being washed away by rainwater and thus contaminating aquatic environments, or of reducing contamination in plants grown on polluted soil. An alternative is CLD sequestration by adding organic matter. A 10 % dose of compost (dw/dw) added to the soil of one plot in this study reduced CLD concentrations in radishes to below the MRL, as also observed in several of the ISCR trials implemented. For two of the three crop plants tested, the addition of compost also improved yields and accelerated the harvest compared to the control and ISCR plots (Mouvet et al, 2016 a). The dosage was 10 times higher than that recommended by the compost manufacturer, but positive results have been obtained in some soils and some crops with a 5 % dose (Woignier et al, 2012, 2013) and even with 1 % (Clostre et al, 2014 b). The 10 % dose may therefore not be necessary. However, the question arises as to how long the effect of the added compost would last, as it results on the one hand from CLD sorption onto the organic matter, and on the other hand from a physical restriction of porosity (Woignier et al, 2013). The physical effect is active in andosols but not in nitisols (Woignier et al, 2013). As for

the chemical sorption phenomenon, there is every reason to expect that it would weaken as the added compost becomes mineralised, which would occur rapidly in a tropical climate. Repeated inputs would therefore be required, with the costs of treatment rising accordingly and a possibly negative effect on soil properties in the medium term. *A contrario*, the lasting positive effect of just a single ISCR treatment is not open to question.

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

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Figure captions

Fig 1 Change over time in the mean Eh values in the 0 – 20 cm soil layer. Only 1 standard deviation (+ or -) is presented in order to clearly distinguish the range of values for each treatment. Blue arrows: irrigation. Red arrows: analysis of CLD and degradates

Fig 2 Box and whisker plot of Eh values in the 0 - 20 cm layer for each trial plot at T0 before the experiment started. Plots identified by the same letter are not different at the 0.05 level (Post hoc Tukey HSD test)

Fig 3 Box and whisker plot of Eh values in the 0 - 20 cm layer for each trial plot at T1, two days after the experiment started. Plots identified by the same letter are not different at the 0.05 level (Post hoc Tukey HSD test)

Fig 4 Box and whisker plot of Eh values in the 0 - 20 cm layer for each trial plot at T2, seven days after the experiment started. Plots identified by the same letter are not different at the 0.05 level (Post hoc Tukey HSD test)

Fig 5 Box and whisker plot of Eh values in the 0 - 20 cm layer for each trial plot at T3, twenty-one days after the experiment started. Plots identified by the same letter are not different at the 0.05 level (Post hoc Tukey HSD test)

Fig 6 Box and whisker plot of Eh values in the 0 - 20 cm layer for each trial plot at T4, thirty-five days after the experiment started. Plots identified by the same letter are not different at the 0.05 level (Post hoc Tukey HSD test)

Fig 7 Box and whisker plot of Eh values in the 0 - 20 cm layer for each trial plot at T7, ninety-four days after the experiment started. Plots identified by the same letter are not different at the 0.05 level (Post hoc Tukey HSD test)

Fig 8 Box and whisker plot of Eh values in the 0 - 20 cm soil layer throughout the duration of the treatment in each trial plot. Plots identified by the same letter are not different at the 0.05 level (Post hoc Tukey HSD test)

Fig 9 Box and whisker plot of Eh values in the 0 - 20 cm layer for each measuring campaign in the coarse ZVI trial P1. Plots identified by the same letter are not different at the 0.05 level (Post hoc Tukey HSD test)

Fig 10 Box and whisker plot of Eh values in the 0 - 20 cm layer for each measuring campaign in the control trial P2. Plots identified by the same letter are not different at the 0.05 level (Post hoc Tukey HSD test)

Fig 11 Box and whisker plot of Eh values in the 0 - 20 cm layer for each measuring campaign in the regular Daramend trial P4. Plots identified by the same letter are not different at the 0.05 level (Post hoc Tukey HSD test)

Fig 12 Change over time in the mean Eh values in the 20 – 40 cm soil layer. Only 1 standard deviation (+ or -) is presented in order to clearly distinguish the range of values for each treatment. Blue arrows: irrigation. Red arrows: analysis of CLD and degradates

Fig 13 : Box and whisker plot of Eh values in the 20 - 40 cm soil layer throughout the duration of the treatment in each trial plot. Plots identified by the same letter are not different at the 0.05 level (Post hoc Tukey HSD test)

Figure 14: Box and whisker plot of chlordecone concentrations (mg/kg dw) in the 0 - 40 cm soil layer. Data for each plot covers the 3 sampling campaigns, i.e. 24, 64 and 94 days following the beginning of the experiment. Plots identified by at least one letter in common are not different at the 0.05 level (Kruskal-wallis test)

Figure 15: Box and whisker plot of chlordecol concentrations (mg/kg dw) in the 0 - 40 cm soil layer. Data for each plot covers the 3 sampling campaigns, i.e. 24, 64 and 94 days following the beginning of the experiment. Plots identified by at least one letter in common are not different at the 0.05 level (Kruskal-wallis test)

Figure 16: Box and whisker plot of 5a-chlordecone concentrations (mg/kg dw) in the 0 - 40 cm soil layer. Data for each plot covers the 3 sampling campaigns, i.e. 24, 64 and 94 days following the beginning of the experiment. Plots identified by at least one letter in common are not different at the 0.05 level (Kruskal-wallis test)

Figure 17: Box and whisker plot of 5,6- or 5a,6-dihydrochlordecone relative peak area in the 0 – 40 cm soil layer. Data for each plot covers the 3 sampling campaigns, i.e. 24, 64 and 94 days following the beginning of the experiment. Plots identified by at least one letter in common are not different at the 0.05 level (Kruskal-wallis test)

Figure 18: Box and whisker plot of the second identified dihydrochlordecone relative peak area in the 0 - 40 cm soil layer. Data for each plot covers the 3 sampling campaigns, i.e. 24, 64 and 94 days following the beginning of the experiment. Plots identified by at least one letter in common are not different at the 0.05 level (Kruskal-wallis test)

Figure 19: Box and whisker plot of the tetrahydrochlordecone relative peak area in the 0 - 40 cm soil layer. Data for each plot covers the 3 sampling campaigns, i.e. 24, 64 and 94 days following the beginning of the experiment. Plots identified by at least one letter in common are not different at the 0.05 level (Kruskal-wallis test)

Figure 20: Box and whisker plot of the trihydrochlordecone relative peak area in the 0 - 40 cm soil layer. Data for each plot covers the 3 sampling campaigns, i.e. 24, 64 and 94 days following the beginning of the experiment. Plots identified by at least one letter in common are not different at the 0.05 level (Kruskal-wallis test)

Fig 21 Relationship between the % decrease in CLD concentration at the end of the treatment period and the % of Eh values < - 250 mV measured during the whole duration of the treatment

Fig 22 Relationship between the % decrease in CLD concentration at the end of the treatment period and the lowest mean Eh values measured during the treatment

Table captions

Table 1 Fertiliser quantities (in kg/100 m²) applied to each crop

Table 2 Physico-chemical characteristics of the nitisol studied

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

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

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

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

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

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

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

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

Table 11 Values (mean $\pm$ standard deviation) of three agronomic parameters determined for radishes in the 6 trial plots

Table 12: Agronomic parameters measured for each treatment applied to the cucumbers. For the yield (g/metre), which is considered the most important parameter, the Wilcoxon test was applied. Mean values followed by at least 1 letter in common are not statistically different to each other at the 5 % level

Table 13: Agronomic parameters measured for the sweet potatoes after each treatment. Mean values followed by at least 1 letter in common are not statistically different to each other at the 5 % level. The Wilcoxon test was applied for the yield (kg/plant), and the LSD test for the other parameters

Table 14 Concentrations (mean $\pm$ standard deviation, $n = 3$) of CLD and degradates quantified in the soil water sampled with the suction cups during growth of the sweet potatoes. Values followed by same letter are not statistically different from each other (Wilcoxon test, $\alpha = 20 \%$)

Table 15 Chlordecone concentrations ($\mu\text{g/kg}$ fresh weight, mean $\pm$ standard deviation, $n = 5$) in the three plants studied in the six different trial plots. Mean values followed by at least 1 letter in common are not statistically different to each other at the 5 % level.

Fig 1

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Fig 12

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Fig 20

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 ₂ O ₅ Olsen (mg/kg)	49 $\pm$ 9	17
K ₂ 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 ₃ total (%)	< 0.1	0
Fe Total (%)	8.4 $\pm$ 0.3	3
% Coarse sand (200 - 2000 μ m)	5.9 $\pm$ 0.7	12
% Fine sand (50 - 200 μ m)	8.4 $\pm$ 0.5	6
% Coarse silt (20 - 50 μ m)	13.2 $\pm$ 1.8	13
% Fine silt (2 - 20 μ m)	8.6 $\pm$ 1.3	15
% Clay (< 2 μ m)	61.5 $\pm$ 1.8	3

Table 3

Treatment	% of Eh values < - 350 mV	% of Eh values < - 300 mV	% of Eh values < - 250 mV	% of Eh values < 0 mV
P1, fine ZVI	4.0	6.3	15.3	30
P2, control	0.0	0.0	0.0	0.0
P3, Daramend® bagasse	0.0	0.4	1.5	5
P4 regular Daramend®	4.7	10.4	18.5	49
P5, fine ZVI	8.4	16.0	23.8	42
P6, mix bagasse – coarse ZVI	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 ^b	< 0.05	0.13 ± 0.03 ^{ab}	0.07 ± 0.01 ^{ab}	209 ± 67 ^a	73 ± 25 ^{ab}	60 ± 53 ^a	205 ± 78 ^a
P2	0.92 ± 0.23 ^a	< 0.05	< 0.03 ^c	0.09 ± 0.03 ^a	0 ^c	0 ^c	0 ^b	0 ^b
P3	0.82 ± 0.18 ^a	< 0.05	0.08 ± 0.02 ^b	0.09 ± 0.01 ^a	31 ± 25 ^{bc}	27 ± 26 ^{bc}	0 ^b	0 ^b
P4	0.80 ± 0.18 ^a	< 0.05	0.09 ± 0.02 ^{ab}	0.08 ± 0.01 ^{ab}	50 ± 14 ^{ab}	12 ± 23 ^c	0 ^b	7 ± 11 ^b
P5	0.34 ± 0.00 ^b	< 0.05	0.23 ± 0.03 ^a	0.04 ± 0.00 ^b	23 ± 14 ^a	125 ± 21 ^a	0 ^b	236 ± 65 ^b
P6	0.57 ± 0.08 ^b	< 0.05	0.08 ± 0.02 ^b	0.07 ± 0.01 ^{ab}	52 ± 45 ^{bc}	12 ± 20 ^c	0 ^b	44 ± 43 ^b

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>			
P1	0.51 ± 0.07 ^{cd}	< 0.05	0.09 ± 0.03 ^{abc}	0.06 ± 0.00 ^{ab}	138 ± 27 ^a	12 ± 22 ^b	0	99 ± 10 ^a
P2	1.03 ± 0.23 ^a	< 0.05	< 0.03 ^d	0.08 ± 0.01 ^a	0 ^c	0 ^b	0	0 ^c
P3	0.75 ± 0.14 ^{ab}	< 0.05	0.07 ± 0.03 ^{cd}	0.07 ± 0.02 ^{ab}	9 ± 22 ^c	0 ^b	0	0 ^c
P4	0.67 ± 0.06 ^{bc}	< 0.05	0.15 ± 0.05 ^{ab}	0.08 ± 0.01 ^a	71 ± 31 ^{ab}	2 ± 5 ^b	0	3 ± 7 ^c
P5	0.33 ± 0.03 ^d	< 0.05	0.18 ± 0.01 ^a	0.04 ± 0.01 ^b	74 ± 34 ^{ab}	47 ± 29 ^a	0	62 ± 48 ^{ab}
P6	0.56 ± 0.07 ^{cd}	< 0.05	0.07 ± 0.01 ^{bc}	0.08 ± 0.01 ^a	53 ± 32 ^b	0 ^b	0	18 ± 24 ^{bc}

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>		
P1	0.38 ± 0.05 ^{bc}	< 0.05	0.07 ± 0.01 ^b	0.06 ± 0.01 ^{bc}	83 ± 15 ^a	0 ^b	0	24 ± 21 ^b
P2	0.82 ± 0.29 ^a	< 0.05	< 0.03 ^c	0.08 ± 0.03 ^{ab}	0 ^b	0 ^b	0	0 ^b
P3	0.73 ± 0.11 ^a	< 0.05	0.07 ± 0.04 ^b	0.08 ± 0.02 ^a	7 ± 11 ^b	0 ^b	0	0 ^b
P4	0.54 ± 0.10 ^b	< 0.05	0.16 ± 0.02 ^a	0.07 ± 0.01 ^{abc}	62 ± 30 ^a	3 ± 7 ^b	0	0 ^b
P5	0.25 ± 0.01 ^c	< 0.05	0.18 ± 0.00 ^a	0.04 ± 0.01 ^c	89 ± 9 ^a	0 ^b	0	25 ± 22 ^b
P6	0.47 ± 0.03 ^{bc}	< 0.05	0.09 ± 0.01 ^b	0.07 ± 0.01 ^{abc}	37 ± 21 ^a	0 ^b	0	8 ± 19 ^b

Table 7

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

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

Table 9

Sampling point	Sampling date	Concentration (µg/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 (µg/L)			Dihydro-CLD (2)	Tetrahydro-CLD	Relative peak areas			-5Cl (2)	-7Cl?	Unknown 5
		CLD	5- or 5a-hydroCLD	5,6- or 5a,6-hydroCLD			Trihydro-CLD	Pentahydro-CLD				
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 ^{bc}	80 ± 49 ^d	312 ± 37 ^b	105 ± 16 ^d	243 ± 36 ^c	223 ± 51 ^c

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 ^{bc}	1.3 ± 0.2 ^b	1.1 ± 0.2 ^c	1.3 ± 0.7 ^{bc}	1.2 ± 0.5 ^{bc}	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 ^{abc}	3.4 ± 0.7 ^{bc}	5.7 ± 1.3 ^{ab}	2.8 ± 0.8 ^c	4.7 ± 2.0 ^{abc}	4.2 ± 1.2 ^{abc}
Marketable tubers (%)	66 ± 31 ^a	58 ± 32 ^a	61 ± 20 ^a	50 ± 17 ^a	64 ± 23 ^a	48 ± 20 ^a
Marketable tuber unit mass (kg)	0.50 ± 0.17 ^a	0.63 ± 0.31 ^a	0.43 ± 0.16 ^a	0.34 ± 0.08 ^a	0.48 ± 0.16 ^a	0.47 ± 0.30 ^a
Dry matter (%)	26.0 ± 1.0 ^a	24.9 ± 2.1 ^a	25.1 ± 2.0 ^a	25.0 ± 3.2 ^a	26.6 ± 2.9 ^a	26.1 ± 1.2 ^a
Marketable yield (kg/plant)	1.7 ± 0.9 ^{ab}	1.3 ± 0.9 ^{ab}	1.7 ± 1.0 ^{ab}	0.4 ± 0.1 ^b	1.3 ± 0.6 ^a	0.9 ± 0.7 ^a

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 ^a	< 0.10 ^a	< 0.10 ^a
Regular Daramend®	1.0 ± 0.6 ^b	1.7 ± 0.6 ^b	0.1 ± 0.1 ^b
Coarse ZVI only	1.3 ± 0.4 ^b	1.7 ± 0.4 ^b	0.4 ± 0.2 ^c

Table 15

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

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Supplementary Material

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