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► To cite this version:

Patrick Ollivier, Stéphane Touzelet, Sébastien Bristeau, Christophe Mouvet. Transport of chlordecone and two of its derivatives through a saturated nitisol column (Martinique, France). *Science of the Total Environment*, 2020, 704, pp.135348. 10.1016/j.scitotenv.2019.135348 . hal-02734948

HAL Id: hal-02734948

<https://brgm.hal.science/hal-02734948>

Submitted on 7 Mar 2022

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Transport of chlordecone and two of its derivatives through a saturated nitisol column (Martinique, France)

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keywords : Chlordecone, derivatives, mobility, nitisol, pollution, French West Indies

1 **Abstract**

2 Soils, surface and groundwater in Martinique (French West Indies) are contaminated by
3 chlordecone (CLD), a highly persistent organochlorine pesticide. In Situ Chemical Reduction
4 (ISCR) using zero valent iron has been tested as a remediation technique to lower CLD levels
5 in soils but it produces derivatives whose fate in environment may differ from the parent
6 molecule. Here, the transfer of CLD and two of its main derivatives resulting from ISCR,
7 CLD5aH and a CLD-3Cl, have been investigated in untreated and treated nitisol from a
8 banana plantation using column experiments (20cm long and 2.5cm in diameter) under
9 saturated conditions. The circulation of CaCl_2 10^{-2}M solution, simulating the ionic strength of
10 soil water, in untreated nitisol results in CLD concentrations in solutions that remain for
11 decades above the threshold limit for drinking water. ISCR treatment lowers the CLD
12 concentration by ~50% in soil and by a factor 3 in waters but they remain above the threshold
13 values. CLD derivatives, CLD5aH and a CLD-3Cl and, to a lesser extent, a CLD-2Cl and a
14 CLD-5Cl, are found in waters after treatment. Dechlorination increases the mobility of the
15 derivatives with respect to the parent molecule, which is likely to induce their transfer to
16 deeper soil layers than those treated by ISCR: CLD-3Cl is more mobile than CLD5aH which
17 is more mobile than CLD. When the water is in contact with the contaminated soil, a period of
18 fast desorption kinetic of CLD and its derivatives, followed by a period of slow kinetics are
19 found. This attests the high risk for water contamination and the potential influence of rainfall
20 events on the concentrations likely to be encountered in soil waters or in waters accumulated
21 on the soil surface.

22

23 Introduction

24 Chlordecone (CLD; C₁₀Cl₁₀O; CAS number 143–50-0 - decachlorooctahydro-1,3,2-
25 metheno-2Hcyclobuta[c,d]pentalen-2-one) was extensively used (3kg/ha⁻¹/yr) in the French
26 West Indies, officially from 1972 to 1978 and from 1981 to 1993, to protect banana
27 plantations against the banana Weevil (*Cosmopolites sordidus*), resulting in a severe
28 contamination of soils, surface water and groundwater. CLD is a highly hydrophobic
29 organochlorine pesticide (Kow between 4.9 and 5.4), strongly sorbed to soil (log K_{oc} = 4.1-
30 4.2) and poorly soluble (0.020 mg L⁻¹ at 25°C) (US Environmental Protection Agency, 2012;
31 UNEP, 2007). It accumulates in food chains. Long-term exposure to CLD through food and
32 drinking water can have severe impacts on human health. Chlordecone is a potential
33 carcinogen and causes hepatic tumors in laboratory rats and mice (Reuber, 1979). It is a
34 reproductive and developmental toxicant, an endocrine disruptor and a neurotoxin (Dallaire et
35 al., 2012, Boucher et al., 2013, Costet et al., 2015). It is also suspected to increase the risk of
36 preterm birth and prostate cancer (Multigner et al., 2010, 2016; Kadhel et al., 2014; Cordier et
37 al., 2015; Emeville et al., 2015).

38 Chlordecone persists in the environment. It undergoes no significant or fast biotic or
39 abiotic degradation during conventional use of agricultural soils (Cabidoche et al., 2009 ;
40 Levillain et al., 2012). However, Devault et al. (2016) and Cattan et al. (2019) showed that
41 5b-hydroCLD/CLD ratios in surface and groundwater in Martinique were 25 times greater
42 than in commercial formulations and concluded that natural CLD transformation into 5b-
43 hydroCLD over the long term may occur. Recently, Chevalier et al. (2019) detected new
44 chlordecone transformation products in soil, sediment, and water samples from Martinique.
45 Most of them were not initially found in commercial CLD formulations suggesting that CLD
46 pollution extends beyond the parent CLD molecule. Fernandez-Bayo et al. (2013) showed the
47 existence of CLD-degrading microorganisms in andosols under aerobic conditions. However,

48 they confirmed that CLD long-term biodegradation was very low. Based on the calculation of
49 the Gibbs free energy of formation of CLD and potential degradation products, Dolfig et al
50 (2012) concluded that bioremediation of chlordecone hotspots will require at least
51 biostimulation, at best bioaugmentation. Currently, leaching is the main way to reduce
52 pollution, but the process is also very slow due to the affinity of CLD for soil organic matter
53 (Cabidoche et al., 2009). The persistence of CLD in agricultural soils in the French West
54 Indies has been estimated at several decades for nitisol, several centuries for ferralsol and
55 more than half a millennium for andosol (Cabidoche et al., 2009). CLD was banned in early
56 1993 and included in the Persistent Organic Pollutants (POPs) prohibition list of the
57 Stockholm Convention in May 2009 (UNEP, 2009; Stockholm Convention, 2011). But its
58 previous use has led to widespread contamination of agricultural soils in the French West
59 Indies. More than 45% of the agricultural soils in Martinique are contaminated by CLD. High
60 concentrations in the soils can lead to crop products exceeding the Maximum Residue Limit
61 (MRL, 20 mg/kg of fresh product) applied to tropical crops according to European Union
62 regulations No 149/2008 and 839/2008 (Dubuisson et al., 2007; Clostre et al. 2014, 2015).

63 Soils exposed to long-term CLD contamination represent extreme challenges to find
64 remediation solutions (Cabidoche and Lesueur-Jannoyer, 2011; Levillain et al., 2012). In situ
65 chemical reduction (ISCR) using zero valent iron has been proposed as a remediation
66 technique to reduce chlordecone levels in soils (Mouvet et al., 2017). It is based on treatment
67 cycles of alternated strongly reducing conditions with oxidizing conditions (Bryan and
68 Wilson, 2003). The efficiency of ISCR has already been proven for remediation of soils
69 contaminated by various pesticides (Phillips et al. 2004, 2006; Kim et al. 2010), including
70 CLD (Mouvet et al., 2016, 2017). Mouvet et al (2017) showed that, after a 6-month treatment
71 with ISCR in pilot-scale (80kg) laboratory experiments, CLD concentration in soil is
72 decreased by 74% in a nitisol. The chemical reduction induced by the ISCR process generates

73 dechlorinated transformation products, in particular a mono-dechlorinated CLD (CLD-1Cl),
74 the CLD5aH, and a tri-dechlorinated CLD (CLD-3Cl). The behavior of these neo-formed
75 molecules in the soil could significantly deviate from the parent molecule (Benoit et al.,
76 2017).

77 Here, we present a column study on the mobility of CLD and two of its derivatives, a
78 CLD-1Cl and a CLD-3Cl, in a nitisol sampled from a banana plantation in Martinique,
79 contaminated by CLD, before and after on-site ISCR treatment (i.e., zero valent iron). The
80 evolution of CLD, CLD5aH and CLD-3Cl concentrations in waters and the soils over the time
81 (~19 years of effective rainwater in the plain of Lamentin, Martinique) are fully discussed in
82 relation with the threshold values for drinking water and the soil.

83

84 **Materials and methods**

85 **Soils**

86 The soil used in this study is a nitisol from a banana plantation in the plain of Lamentin
87 (Martinique, France) that has been treated by In Situ Chemical Reduction (ISCR). ISCR
88 treatment is fully described in Mouvet et al. (2016). It consisted of the addition of zero valent
89 iron (ZVI) in soil (Bryant and Wilson, 2003). Briefly, the soil of the banana plantation was
90 plowed with a rotary harrow. 385 kg of ZVI (4.3% dry weight, coarse grain size, 30% with a
91 size <50 μm) were incorporated homogeneously in the soil on a plot of 30 m² and a depth of
92 30 cm. The soil was then compacted and irrigated for 15 days with a daily water supply of 5
93 to 24.1 mm, for a total of 142 mm (i.e., ~5-7 weeks of a conventional irrigation for banana
94 plantations). The redox potential was measured in field (readings were taken at a 10cm
95 depth). It was 635 ± 18 mV in untreated soil and dropped sharply to values ca. -357 ± 58 mV
96 after the addition of ZVI.

97 Soil samples were collected in the top 30cm of soil before (« untreated soil ») and after
98 treatment (« treated soil ») by ISCR. About 20 kg of each soil, dried at 40 °C were sieved (2
99 mm). Concentrations in the treated soil are $1.51 \pm 0.22 \mu\text{mol CLD /kg}$, $0.58 \pm 0.06 \mu\text{mol}$
100 CLD5aH /kg and $< 0.08 \mu\text{mol CLD-3Cl /kg}$ while they are $3.1 \pm 0.24 \mu\text{mol CLD /kg}$, < 0.07
101 $\mu\text{mol CLD5aH /kg}$ and $< 0.08 \mu\text{mol CLD-3Cl /kg}$ in the untreated soil. ISCR led thus to a
102 reduction by a factor ~ 2 of CLD content in soil. About 20% of CLD was transformed into
103 CLD5aH. Though they were not quantified, other transformation products are probably
104 present in soil. Mouvet et al (2017) showed that ISCR treatment applied to a nitisol may
105 generate 11 CLD-dechlorinated transformation products, from mono- to penta-dechlorinated.

106 The main physico-chemical parameters of the untreated and treated soils are reported in Table
107 1. They were analyzed by an accredited laboratory (SAS, Ardon, France) using standardized
108 procedures (AFNOR or ISO). As expected, pH and Fe concentrations are higher in treated soil
109 due to the formation of OH^- after the oxidation of ZVI.

110

111 **Reagents**

112 The studied molecules are chlordecone (CLD) and the two main transformation products of
113 CLD formed by ISCR, i.e., CLD5aH (CLD-1Cl) and CLD-3Cl (the position on the carbon
114 skeleton of the 3 Cl replaced by H remains unknown).

115 Chlordecone (purity 93.5%) was purchased from Dr. Ehrenstorfer (reference C11220000).
116 CLD-5a-hydro or CLD-5-hydro (5a- or 5- according to CAS nomenclature; CLD-1Cl) and the
117 main tri-hydroCLD (CLD-3Cl) formed by ISCR were synthesized by Alpha-Chimica
118 (AlphaChimica, Châtenay-Malabry. FRANCE) with a purity of 92.6 and 88.6%, respectively.
119 GC/MS/MS show the impurities to be other CLD dechlorinated derivatives. The purity of the
120 tested compounds was taken into account for the preparation of each concentration
121 investigated.

122

123 **Column experiments**

124 The transport of CLD and its transformation products in top-soil (0-30cm) of the
125 untreated and treated soils were studied in the laboratory using column experiments (20cm-
126 long and 2.5cm in diameter; Figure S1) under saturated flow regime. Solutions were
127 introduced uniformly upward using a peristaltic pump.

128 The experimental set-up was designed to minimize interference related to the contact
129 between solutes and the constituent materials of the system. Because CLD hydrophobicity is
130 high, with a strong affinity for all organic materials (e.g., plastics), the entire system consists
131 of glass (e.g., column, tubes used to collect the solutions) and Teflon (e.g., tubing) materials.
132 The column effluent fractions (10 mL ; ~1/3 Pore Volume (PV) each; or 20mL) were
133 continuously collected using an autosampler. Water samples were kept in the dark at 4°C
134 before analysis.

135

136 **Untreated nitisol**

137 A mass of 110.7g of untreated nitisol, corresponding to a total amount of 0.34 ± 0.02
138 μmol CLD, was dried and crushed < 2 mm, and then placed into the glass column (20cm long
139 and 2.5cm in diameter). Soil density in the column was 1.12 g/cm^3 . The effective porosity of
140 the porous media was determined using a nonreactive tracer (NaBr, at a concentration of
141 50mg/L). It was 39.6%.

142 A synthetic solution (deionized water with CaCl_2 10^{-2}M), simulating the ionic strength
143 of soil water, was injected into the column at a seepage velocity of $\sim 3\text{m/d}$, during 85 pore
144 volumes (PV), corresponding to 6082 mm of water. Using an average value of 1670 mm/yr
145 for the annual effective rainfall in Lamentin plain (Martinique; Vittecoq et al., 2010), the

146 volume of CaCl_2 10^{-2}M solution injected into the soil column corresponds to ~ 3.6 years of
147 effective rainfall.

148 In a second step, the retention of CLD, CLD5aH and CLD-3Cl by nitisol was studied by
149 injecting, in the same soil column, at a seepage velocity of $\sim 3\text{m/d}$, a solution of CaCl_2 10^{-2}M
150 containing CLD (12 nmol/L), CLD5aH (28.3 nmol/L) and CLD-3Cl (41.8 nmol/L), during 45
151 PV (from PV85 to PV130). The total amount of CLD, CLD5aH and CLD-3Cl injected into
152 the soil were 19 nmols (i.e., about 5% of CLD contained in the soil column at t_0 , i.e., before
153 the experiment), 44.7 nmols and 66 nmols, respectively.

154 The influence of the interaction time between the solutions (CaCl_2 10^{-2}M or CaCl_2 10^{-2}M
155 $+ \text{CLD} + \text{CLD5aH} + \text{CLD-3Cl}$) and the nitisol on the release or sorption of CLD,
156 CLD5aH and CLD-3Cl from or by the soil was also studied by stopping the circulation of
157 injected solutions, from a few days to several weeks, while maintaining saturated conditions.
158 The objective is to better understand both their transfer from contaminated solutions to
159 uncontaminated soil and their release from contaminated soil to uncontaminated solutions in a
160 static system simulating realistic environmental conditions such as the accumulation of water
161 on the surface of a soil after a rain event or a soil with a low permeability, saturated with
162 water. The influence of the flow rate on the desorption of CLD and its transformation
163 products was also assessed by increasing the seepage velocity, from 3 to 15 m/d, after PV318
164 (i.e., ~ 13.5 years of effective rainfall).

165

166 In detail, the column experiment procedure was composed of 11 steps (Fig. S2):

167 1. Circulation of CaCl_2 10^{-2}M solution during ~ 28 PV

168 2. Stop 1: CaCl_2 10^{-2}M solution is kept in the soil column for 48 h

169 3. Circulation of CaCl_2 10^{-2}M solution during ~ 57 PV

- 170 4. Circulation of the solution containing CaCl_2 10^{-2}M + CLD + CLD5aH + CLD-3Cl during
171 ~45 PV
- 172 5. Stop 2: The solution containing CaCl_2 10^{-2}M + CLD + CLD5aH + CLD-3Cl is kept in the
173 soil column for 66 h.
- 174 6. Circulation of CaCl_2 10^{-2}M solution during ~47 PV
- 175 7. Stop 3: CaCl_2 10^{-2}M solution is kept in the soil column for 2 months
- 176 8. Circulation of CaCl_2 10^{-2}M solution during ~42 PV
- 177 9. Stop 4: CaCl_2 10^{-2}M solution is kept in the soil column for 64 h
- 178 10. Circulation of CaCl_2 10^{-2}M solution during ~98 PV
- 179 11. Circulation of CaCl_2 10^{-2}M solution during ~128 PV at a seepage velocity of 15m/d

180

181 At the end of the experiment, a total of ~19 years of effective rainfall was thus injected
182 in the soil column.

183

184 **Nitisol treated by ISCR**

185 A mass of 117.5g of treated nitisol, corresponding to a total amount of 177.4 ± 25.8
186 nmol CLD and 68.2 ± 7 nmol CLD5aH, was dried and crushed (< 2 mm) and then placed into
187 a glass column (20cm long and 2.5cm in diameter). Soil density in the column was 1.2 g/cm^3 .
188 The effective porosity of the porous media, 39%, was also determined using NaBr (50mg/L).
189 CaCl_2 10^{-2}M solution was injected into the column at a seepage velocity of ~3m/d, during 138
190 PV, i.e., ~6.4 years of effective rainfall.

191

192 **Analytical method**

193 The extraction and analytical methods for CLD and its derivatives are fully described
194 in Bristeau et al. (2014) and Mouvet et al (2017). Briefly, the soil samples (5g) were dried at

195 38°C for a period of 72 h and then reduced by crushing followed by grinding to a particle size
196 of less than 80 µm. Extraction was performed using Pressurized Liquid Extraction with a
197 mixture acetone/hexane 50:50 v/v at 100°C and 110 bars pressure.

198 Trans-nonachlor was used before extraction as surrogate to correct the results for extraction
199 efficiency. Two internal standards were added before analysis, CB53 for the trans-nonachlor
200 calibration and ¹³C-CLD for CLD calibration. The extract was reduced to a volume of
201 approximately 10 mL by means of a nitrogen stream. An aliquot of 1mL was taken
202 (fractionated to 1/10), reduced by nitrogen stream and extracted with cyclohexane three times.
203 The final extract was obtained using 1ml of cyclohexane.

204 GC/MS/MS was achieved with a Bruker GC450 gas chromatograph, 1177 injector, automated
205 sampler Combi Pal (CTC) and a triple quadrupole mass spectrometer 300MS. The
206 quantification limit is 0.03 mg kg⁻¹. (i.e., 0.061, 0.066 and 0.077 µmol/kg for CLD, CLD5aH
207 and CLD-3Cl, respectively).

208 For aqueous samples (i.e., solutions injected into the column and solutions collected at the
209 outlet of the columns), the concentrations of CLD and its derivatives were measured in small
210 volumes, 10mL or 20mL according to the seepage velocity (3 or 15m/d). Samples analyses
211 were carried out by liquid/liquid extraction (dichloromethane). The final extract was obtained
212 using 0.05 ml of cyclohexane followed by GC/MS/MS. ¹³C-CLD was added as an internal
213 standard before analysis. The limits of quantification were 0.1 µg/L (i.e., 0.2, 0.22 and 0.258
214 nmol/L for CLD, CLD5aH and CLD-3Cl, respectively) in the 10 mL samples and 0.05 µg/L
215 (i.e., 0.1, 0.11 and 0.129 nmol/L for CLD, CLD5aH and CLD-3Cl, respectively) in the 20 mL
216 samples.

217

218 **Results and discussion**

219 **Release of CLD, CLD5aH and CLD-3Cl from the untreated and treated nitisols**

220 The circulation of CaCl_2 10^{-2}M in the untreated nitisol column released CLD from soil
221 with CLD concentrations between 12 and 15 nmol/L in the outlet waters (Figure 1). CLD5aH
222 and CLD-3Cl concentrations were below the limit of quantification (i.e., 0.2 and 0.22 nmol/L,
223 respectively). No other CLD transformation products were detected in outlet waters or in the
224 soil. This result is consistent with the literature which indicates that CLD (bio)degradation is
225 low under environmental conditions (Cabidoche et al., 2009; Dolfing et al., 2012).

226 By contrast, the circulation of CaCl_2 10^{-2}M in the soil treated by ISCR released CLD,
227 CLD5aH and to a lesser extent CLD-3Cl in waters that pass through the soil column (Figure
228 1). A dihydroCLD (CLD-2Cl), a CLD-5Cl, and an unidentified molecule were also found
229 (Figure 2). The CLD concentrations were lower by a factor of 3 than those measured during
230 the circulation of the CaCl_2 10^{-2}M solution in the untreated nitisol column. These lower
231 concentrations in waters associated with the presence of CLD transformation products show
232 the effectiveness of the ISCR process on CLD degradation. During the first 16 PV (i.e., ~8
233 months of effective rainfall in the plain of Lamentin), CLD concentrations increased from 3.5
234 nmol/L to 5.4 nmol/L. Then they were stable (or decreased very slowly over time). They were
235 ~4.2 nmol/L after ~6 years of effective rainfall (137 PV). CLD5aH concentrations were
236 between 4.3 and 4.9 nmol/L during the first PV, i.e., similar to those measured for CLD. But
237 they decreased regularly, to only 0.88 nmol/L (i.e., ~18% of the maximum value) at the end of
238 the experiment. CLD-3Cl concentrations were much lower than those of CLD and CLD5aH,
239 with a maximum value of ~0.86 nmol/L. They decreased rapidly and were below the limit of
240 quantification (0.22 nmol/L) after ~1.6 years of effective rainfall (35 PV). Because the lack of
241 analytical standards for CLD-2Cl, CLD-5Cl, and the unidentified molecule, the relative peak
242 area of each of those substances are used as a proxy for their semi-quantification (see Mouvet
243 et al. (2017) for details). They also decreased rapidly (Figure 2). The curves of the figures 1
244 and 2 can be compared. The decrease in concentrations/peak areas in solutions over time are

245 dependent on the molecules. The decrease rate is in the order: CLD-5Cl > CLD-3Cl >
246 unidentified molecule > CLD-2Cl > CLD5aH > CLD. The general trend is, therefore, an
247 increase in mobility of molecules with increasing degree of dechlorination. This is consistent
248 with predictive thermodynamic calculations showing that the solubility of chlordecone
249 congeners increases with decreasing degree of chlorination (Dolfing et al., 2012). The authors
250 concluded that dechlorination products of chlordecone are thus likely to be more mobile in the
251 environment than their parent compound. Other works showed a higher mobility of CLD5bH
252 compared to CLD (Devault et al., 2016; Cattani et al., 2019).

253

254 **Behavior of CLD, CLD5aH and CLD-3Cl in the untreated nitisol column**

255 The circulation of a CaCl_2 10^{-2}M solution containing CLD (12 nmol/L), CLD5aH
256 (28.3 nmol/L) and CLD-3Cl (41.8 nmol/L) resulted in a small increase in CLD
257 concentrations, from 14.8 to 16.8 nmol/L, in solutions at the outlet of the column (Figure 3).
258 However, the increase was over a short period of time. After 5 PV, CLD concentrations
259 gradually decreased while the solution was still injected in the column. This trend can be
260 explained by i) a CLD concentration in the injected solution similar to those measured in
261 outlet solutions before the injection, ii) the small amount of CLD injected (19 nmols) into the
262 column compared to the amount already present (343 nmols) in the soil and iii) the high
263 reactivity of CLD to the soil. On the contrary, the CLD5aH and CLD-3Cl concentrations
264 increased in the outlet waters during the entire duration of the injection of the solution. A
265 delay is found for the 2 molecules compared to the conservative tracer (Br) attesting of their
266 interactions with the soil. Differences in the behavior of CLD5aH and CLD-3Cl are however
267 observed. The delay was less pronounced for CLD-3Cl and the concentrations increased more
268 rapidly, reaching a relative plateau after 25 PV (i.e., PV110) at a normalized concentration
269 (C/C_0) of 0.62-0.66 ($C \sim 26$ nmol/L) while CLD5aH concentrations did not reach a plateau.

270 When the circulation of the solution containing CLD, CLD5aH and CLD-3Cl was stopped
271 (PV130), CLD5aH concentrations were still increasing, with a maximum concentration of
272 10.6 nmol/L, i.e., $C/C_0 = 0.37$. This confirms the difference in reactivity of CLD5aH and
273 CLD-3Cl towards the nitisol: CLD-3Cl being more mobile than CLD5aH.

274 CLD, CLD5aH and CLD-3Cl also showed different behaviors when the interaction
275 time between the solution that contains these molecules and the soil was increased by
276 stopping the circulation of the solution for 66 hours (maintaining saturated conditions in the
277 column; stop 2, PV129; Figure 3), followed by the circulation of the CaCl_2 10^{-2}M only
278 solution. No significant differences were observed for CLD concentrations in outlet waters
279 before and immediately after the interruption. They were around 12.5 ± 0.2 nmol/L, i.e., close
280 to the concentration in the injected solution. Then they decreased over time due to the
281 circulation of the CaCl_2 10^{-2}M solution. As indicated above, CLD strongly interacts with the
282 soil but the experimental conditions were not favorable to show its sorption on the soil. In
283 contrast, CLD5aH and CLD-3Cl were absent from the soil. Concentrations measured in the
284 outlet waters just after the interruption were significantly lower than those measured before
285 the interruption: 8.9 vs 10.6 nmol/L, respectively, for CLD5aH and 23.8 vs 26 nmol/L,
286 respectively, for CLD-3Cl. A part of CLD5aH and CLD-3Cl were, therefore, transferred from
287 the solution to the soil while the solution was maintained in the column. The CLD-3Cl
288 concentrations then decreased very strongly to reach 1.5 nmol/L at PV178 due to the
289 circulation of the CaCl_2 10^{-2}M solution. The fate of CLD5aH is slightly different. Before
290 decreasing, its concentrations increased to reach 13 nmol/L (i.e., $C/C_0 = 0.46$) at PV140. As
291 discussed above, CLD5aH interacts strongly with the soil and is less mobile than CLD-3Cl in
292 the nitisol. Unlike CLD-3Cl, CLD5aH concentrations did not reach a plateau before the
293 interruption of the circulation of the solution. That's why, after the interruption,
294 concentrations still increased. Note that CLD5aH concentrations higher than 13 nmol/L could

295 probably have been measured in the outlet waters if the circulation of the CLD5aH-containing
296 solution had not been stopped for 66 hours and replaced by the CaCl_2 10^{-2}M solution.
297 CLD5aH is the main CLD transformation product after ISCR treatment. CLD5aH
298 concentration in the inlet solution used in this study is likely to be encountered in the waters
299 of a nitisol treated by ISCR. Though CLD5aH interacted with the soil, results show that a
300 large proportion (~48% after 4 years of effective rainfall and up to 75% after 15 years of
301 effective rainfall) of CLD5aH injected in the column was not retained and passed through the
302 20 cm of nitisol. The possibility of its transfer at depths greater than 20cm is therefore real.

303

304 **Desorption of CLD, CLD5aH and CLD-3Cl from a nitisol column**

305 CLD, CLD5aH and CLD-3Cl accumulated in soil were gradually released by leaching
306 during the circulation of the CaCl_2 10^{-2}M solution. The rate of decrease in concentrations,
307 between PV 129 (end of the injection of the CaCl_2 solution spiked with the 3 contaminants)
308 and PV 178 (stop #3), followed the order $\text{CLD-3Cl} > \text{CLD5aH} > \text{CLD}$, reflecting their
309 respective mobility in nitisol. After 93 PV (i.e., ~4 years of effective rainfall; at PV 178),
310 however, CLD, CLD5aH and CLD-3Cl concentrations were still high: 11.5, 6.4 and 1.5
311 nmol/L respectively.

312 A two-month interaction period (stop 3, PV178, Figure 3) between the soil containing CLD,
313 CLD5aH and CLD-3Cl and the CaCl_2 10^{-2}M solution resulted in a significant increase in
314 CLD, CLD5aH and CLD-3Cl concentrations in outlet waters when restarting the circulation
315 of the CaCl_2 10^{-2}M solution. This trend was very pronounced for CLD and CLD-3Cl with
316 concentrations reaching 15.9 nmol/L (against 11.5 nmol/L before the two-month interaction
317 period) and 6.8 nmol/L (vs 1.5 nmol/L) respectively, corresponding to an increase of ~39%
318 for CLD and ~350% for CLD-3Cl. CLD concentrations were thus close to the highest values
319 measured during the experiment. Although less pronounced, CLD5aH was also desorbed from

320 the soil during the two-month interaction period, with a concentration of 6.6 nmol/L vs 6.1
321 nmol/L before the interaction period (i.e., an increase of ~8%).

322 For short interaction periods (48 h or 64 h), the increase in CLD concentrations in the CaCl₂
323 10⁻²M solution was, however, not obvious (stops #1 and #4, at PV 28 and 219, Figures 1 and
324 4). The consequences on CLD5aH were also low, with a short stabilization of concentrations,
325 around 1.9 nmol/L, during ~6 PV (i.e., 3 months of effective rainfall) after stop #4 (64 h;
326 Figure 4). In contrast, the increase in CLD-5Cl concentrations was obvious: 0.46 nmol/L vs
327 0.27 nmol/L before the interaction period, probably due to both its low concentrations in
328 solutions that allow to observe a low input from the soil and its higher mobility compared to
329 CLD and CLD5aH (Figure 4). Increasing the seepage velocity of the solution in the soil
330 column, from 3 to 15 m/d, had no noticeable effect on the desorption of CLD and its
331 derivatives (Figure 3, from PV321). CLD concentrations in outlet waters continued to
332 decrease regularly with a rate of -21.6 pmol/L/PV between PV 321 and PV 446 against -28.6
333 pmol/L/PV with a seepage velocity of ~ 3m/d, to reach ~4.42 ± 0.05 nmol/L at the end of
334 experiment. CLD5aH concentrations also continued to decrease. They were ~0.61 nmol/L and
335 decreased with a rate of -3.5 pmol/L/PV to reach 0.18 nmol/L at the end of the experiment.

336 CLD-3Cl concentrations were below the limit of quantification (i.e., 0.13 nmol/L) before and
337 after increasing the flow rate. Therefore, a reduction from 1.6 hours (with a seepage velocity
338 of 3m/d) to 19 minutes (15 m/d) of the time allowed for the interactions between the CaCl₂
339 10⁻²M solution and the soil did not change the contaminants concentrations in the water
340 exiting the soil column. This shows that a part of CLD and derivatives contained in the soil
341 was rapidly released in solutions when it was in contact with soil and then a slow and
342 progressive desorption occurred. These results are also consistent with the literature that
343 indicates for organic compounds a period of fast desorption kinetics followed by a period of
344 slow kinetics (Culver et al., 1997).

345

346 **Environmental relevance**

347 In Martinique, soils, surface and groundwater are contaminated by CLD. According to
348 the EU “Water Framework” and “Quality of drinking water” Directives (European Union,
349 1998, 2000) and their transposition into French law (French government, 2001), a common
350 and precautionary limit value of 0.1µg/L (i.e., 0.204, 0.219 and 0.258 nmol/L for CLD,
351 CLD5aH and CLD-3Cl, respectively) is applied for each pesticide (including CLD) in
352 drinking water. The threshold value for freshwater organisms is 0.001 µg/L (i.e., 2.04, 2.19
353 and 2.58 pmol/L for CLD, CLD5aH and CLD-3Cl, respectively). In Martinique, groundwater
354 drainage is a major process of river contamination (Arnaud et al., 2017; Charlier et al., 2009;
355 Mottes et al., 2015). Accordingly, CLD concentrations in the outlet waters of the untreated
356 and treated column are discussed below in relation to the threshold values for drinking water
357 and freshwater organisms.

358 The circulation of CaCl_2 10^{-2}M solution in a 20cm-long column containing untreated
359 nitisol led to CLD concentrations in the outlet waters above the two threshold values. CLD
360 concentrations exponentially decreased with time. This trend may be explained by both a
361 reduction of CLD mass in the soil over time due to leaching and its strong interaction with the
362 soil. However, at the end of the experiment (i.e., ~19 years of effective rainfall),
363 concentrations in water were 4.42 nmol/L, i.e., still above the threshold values mentioned
364 above. Assuming that the decrease in CLD concentrations in the outlet waters of the nitisol
365 column remains exponential beyond the 19 years of effective rainfall, CLD concentrations in
366 waters would be < 204 pmol/L and < 2.04 pmol/L after a total of 48 and 93 years of effective
367 rainfall, respectively (Figure 5). These time periods are probably underestimated. Indeed, the
368 fields in Martinique have been tilled at 60 or 70 cm depth since CLD spreading and the
369 thickness of CLD-contaminated soil is greater than 20cm (Cabidoche et al., 2009).

370 After the ISCR treatment, CLD aqueous concentrations at the outlet of the column are
371 lower, by a factor of 3, than those measured for the untreated soil. However, they are still
372 above the threshold values. CLD concentrations seem to decrease after 0.5 years of effective
373 rainfall. The number of data, however, is not sufficient to define a long-term trend. Based on
374 results obtained in the untreated nitisol column and assuming an exponential decrease of CLD
375 concentrations in the outlet waters over time, 31 and 76 years of effective rainfall would be
376 necessary to decrease CLD concentrations in outlet waters from 5 nmol/L to 0.204 nmol/L
377 and from 5 nmol/L to 2.04 pmol/L, respectively. CLD5aH and CLD-3Cl were also present in
378 the waters that pass through the treated nitisol column with concentrations exceeding the
379 threshold values but they strongly decreased with time due to their lower affinity for the soil
380 compared to CLD. CLD5aH and CLD-3Cl concentrations would be below the threshold value
381 for drinking water after 11 years and 8 months of effective rainfall, respectively. They would
382 be below the threshold value for freshwater organisms after 25 and 5 years of effective
383 rainfall, respectively.

384 Our data show that a few minutes interaction period between the CaCl_2 10^{-2}M solution
385 and the soil was sufficient to obtain CLD, CLD5aH and CLD-3Cl concentrations in waters
386 exiting the column above the threshold value for drinking water due to a fast desorption
387 kinetic of CLD and its derivatives. This suggests that waters accumulated on the surface of a
388 contaminated soil may rapidly be contaminated and thereby expose human and animals to
389 contaminants. In addition, the duration of interaction between the solution and the soil can
390 strongly modify the concentrations in CLD and its derivatives in solutions. For instance, we
391 show that CLD-3Cl concentrations in solutions circulating in a low-contaminated soil (~ 0.175
392 $\mu\text{mol/kg}$, i.e., $67.2 \mu\text{g/kg}$) were 0.27 nmol/L, i.e., close to the threshold value for drinking
393 water, but after a 64h-interaction period between the solution and the soil, they were 0.46
394 nmol/L, i.e., well above the threshold value (stop #4; Figure 4). And, 6 months of effective

395 rainfall were then needed to reach a concentration in the outlet waters similar to those
396 measured before the interaction period. Waters that pass through the soil or accumulate on the
397 soil surface may thus be easily contaminated by soil. Furthermore, CLD-3Cl concentrations
398 increased from 1.5 to 6.8 nmol/L after a 2-month interaction period between the solution and
399 the soil (stop #3, Figure 3). The degree of contamination depends on the concentration in soil
400 but also on the duration of the interaction.

401 Soil contamination is a major concern. Several studies show that crops grown in
402 polluted soils can be contaminated by CLD to levels above the maximum residue limit
403 (MRL), the European regulatory threshold (Cabidoche and Lesueur-Jannoyer, 2012; Clostre
404 et al., 2014, 2015; Dubuisson et al., 2007). Also, farm animals (e.g., ruminants, free-range
405 poultry) may be exposed to CLD through polluted soil ingestion (Jondreville et al., 2014;
406 Fournier et al., 2017). The consumption of contaminated foodstuffs is the main source of
407 human exposure to CLD (Mutigner et al., 2016). Thresholds of soil contamination by
408 historical organochlorine pollutants are rarely available for agricultural use of the soil. Clostre
409 et al (2017) studied the relationship between contamination of the soil and contamination of
410 crops classified into three categories according to their contamination potential: “non-uptakers
411 and low-uptakers”, “medium-uptakers”, and “high-uptakers”. They propose a simple decision
412 tool based on two threshold values for soils: 0.1 mg/kg (i.e., 0.204, 0.219 and 0.258 $\mu\text{mol/kg}$
413 for CLD, CLD5aH and CLD-3Cl, respectively) for high-uptakers and 1 mg/kg (i.e., 2.04, 2.19
414 and 2.58 $\mu\text{mol/kg}$ for CLD, CLD5aH and CLD-3Cl, respectively) for medium-uptakers. In the
415 untreated nitisol used in our study, CLD concentration was 3.1 $\mu\text{mol/kg}$, i.e., above the
416 threshold values. At the end of our experiment (i.e., ~19 years of effective rainfall), ~42%
417 (154 nmols) of the amount of CLD initially contained in the untreated nitisol (362 nmols) left
418 the soil column due to the water circulation. The resulting soil concentration was 1.88
419 $\mu\text{mol/kg}$, i.e., still above the threshold for high-uptakers but below the soil threshold for

420 medium-uptakers. Assuming that the decrease in CLD concentrations in the waters exiting the
421 nitisol column is still exponential beyond the 19 years of effective rainfall, a maximum
422 additional amount of 32.3 nmols of CLD would be removed from soil, leading to a minimum
423 CLD concentration of 1.58 $\mu\text{mol}/\text{kg}$ in the untreated nitisol. In this case, in the absence of any
424 attenuation mechanisms other than leaching, e.g., no significant (bio)degradation, CLD would
425 persist in soil at level higher than the soil threshold for high-uptakers. A more optimistic
426 scenario would be to assume that the CLD concentration in the outlet waters remains stable at
427 4.42 nmol/L beyond the 19 years of effective rainfall (Figure 3). In this case, CLD
428 concentrations in soil would be $< 0.204 \mu\text{mol}/\text{kg}$ after 51 additional years of effective rainfall.
429 Thus, it would take at least in total 70 years to reach such a concentration in the soil. This
430 period of time is in good agreement with the 6–10 decades calculated by the leaching model
431 WISORCH, based on first-order desorption kinetics, as the duration required for a typical
432 nitisol in the French West Indies to be decontaminated (Cabidoche et al., 2009).

433 The trial of ISCR treatment that was applied to the soil sample used here succeeded in
434 reducing CLD concentrations in soil to values below the threshold value for medium-
435 uptakers. The residual CLD soil concentration was however still above the threshold value for
436 high-uptakers. Assuming an exponential decrease in CLD concentrations in the waters exiting
437 the nitisol column over time, a maximum additional amount of 112 nmol of CLD would be
438 removed by leaching, leading to a minimal CLD concentration in the soil of 0.56 $\mu\text{mol}/\text{kg}$. If
439 they remain stable at 4 nmol/L beyond the 6 years of effective rainfall, the threshold value for
440 high-uptakers would be reached ~46 years after the ISCR treatment. Although there are large
441 uncertainties about the evolution in CLD concentrations over time in the outlet waters of the
442 treated soil column, these results indicate that CLD would be persistent in the soil at
443 concentrations above the threshold for high-uptakers at least for decades. However, ISCR
444 treatment probably degrades the most easily accessible CLD in the soil, which are also the

445 most available for plants/crops. Mouvet et al. (2016) showed that ISCR treatment applied to a
446 nitisol significantly lowered CLD concentrations in radishes compared to controls (untreated
447 soil). Concentrations in radishes were below the maximum residue limit after treatment,
448 whereas they exceeded it in the untreated soil. ISCR treatment could thus significantly reduce
449 the risk of crop contamination.

450 ISCR treatment applied here lowered the CLD concentration by ~50% in soil and by a
451 factor 3 in waters that passed through a 20cm long nitisol column. However, concentrations in
452 the soil solutions at 20cm depth would still be above the threshold for drinking water for
453 decades. CLD soil concentrations would also remain for decades above the threshold value
454 for high-uptakers plants. The efficiency of the ISCR treatment, albeit greater for CLD
455 contaminated-soils than any other remediation technique so far, remains therefore to be
456 improved through changes such as the amounts of iron injected, the shape/size of iron, the
457 mixing of iron with other reactive compounds. Furthermore, previous studies showed that the
458 persistence of chlordecone differs between soil types, nitisol, ferralsol or andosol (Cattan et
459 al., 2019; Cabidoche et al., 2009; Levillain et al., 2012). CLD retention is notably governed
460 by a chemical interaction with soil organic carbon. Carbon contents are highest in andosols.
461 Nitisol has a low capacity to retain CLD suggesting higher losses by leaching in nitisols,
462 hence a higher risk of aquifer contamination (Cabidoche et al., 2009). By contrast, soil
463 decontamination by leaching will take centuries for ferralsol and more than half a millennium
464 for andosol (Cabidoche et al., 2009). Woignier et al (2012 and 2018) showed that CLD
465 retention in soil may also be explained by a physical interaction with allophane clay
466 microstructure: allophane soils (andosol) retained more CLD than non-allophanic soils (nitisol
467 and ferralsol) containing crystalline clays. They concluded that the allophane structure needs
468 to be taken into account for soil remediation processes. ISCR treatment must therefore be
469 tested on andosols and ferralsols.

470 The experimental conditions used in this study (e.g., sieved and unstructured soil,
471 saturated condition) are not fully representative of environmental conditions, and therefore the
472 results cannot be directly transposed to the natural environment. An experimental approach
473 with lysimeters containing undisturbed soil, treated or not by ISCR, would provide very
474 valuable information.

475

476 **Conclusion**

477 The mobility and the transfer of CLD and two of its main derivatives, CLD5aH and a
478 CLD-3Cl, in a nitisol from a banana plantation in Martinique, before and after treatment by
479 ISCR, have been investigated in laboratory using column experiments (20cm long and 2.5cm
480 in diameter).

481 The circulation of a CaCl_2 10^{-2}M solution in deionized water, simulating the ionic
482 strength of soil water, in the unstructured nitisol contaminated by CLD ($3.1 \mu\text{mol/kg}$),
483 releases CLD in the solution at concentrations above the threshold limit for drinking water.
484 None of the 11 dechlorinated CLD derivative analysed was detected in solutions exiting the
485 untreated soil column, confirming that CLD is not or only slightly degraded in soil despite its
486 presence in the soil for several decades.

487 Soil treatment by ISCR resulted in both a significant reduction in CLD concentrations
488 and the appearance of CLD derivatives, CLD5aH and a CLD-3Cl and, to a lesser extent, a
489 CLD-2Cl and a CLD-5Cl, in waters that pass through the soil column. However, CLD
490 concentrations in solutions would remain above the threshold limit for drinking water for
491 decades. Also, ISCR treatment allowed to lower CLD concentrations in soil to values below
492 the threshold for medium-uptakers but they were still above the threshold for high-uptakers.

493 Significant differences in the fate of CLD, CLD5aH and CLD-3Cl are observed.
494 Dechlorination of the molecule leads to increased mobility of the derivatives with respect to

495 the parent molecule. CLD-3Cl is more mobile than CLD5aH which is more mobile than CLD.
496 Though the retention capacity of nitisol for these molecules is not negligible, the greater
497 mobility of derivatives compared to the parent molecule is likely to induce their transfer to
498 deeper soil layers than those treated by ISCR.

499 Finally, the increase in the concentrations of CLD and its derivatives in waters during
500 the interruption of the water circulation, while saturation conditions were maintained, shows
501 the potential influence of rainfall on the concentrations likely to be encountered in soil waters
502 or accumulated on the surface.

503

504 **Acknowledgments**

505 This work was supported by the French Ministry for the Ecological and Inclusive Transition
506 and the BRGM. J. Hellal of the BRGM is thanked for fruitful discussions.

507

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664

Figures

665 **Figure 1.** CLD, CLD5aH and CLD-3Cl concentrations in waters at the outlet of the untreated
666 (a) and treated (b) nitisol column as a function of the volume of the CaCl_2 10^{-2}M solution
667 injected (expressed as “pore volume” and “years of effective rainfall” in Lamentin; see text
668 for details). The 48h-interaction period between the CaCl_2 10^{-2}M solution and the soil is also
669 reported (stop #1; PV 28). It corresponds to an interruption of the circulation of the CaCl_2 10^{-2}M
670 solution in the column while solution was maintaining in the soil.

671 **Figure 2.** CLD-2Cl, an unidentified molecule and CLD-5Cl levels (expressed as relative peak
672 area) in waters at the outlet of the treated nitisol column as a function of the volume of the
673 CaCl_2 10^{-2}M solution injected (expressed as “pore volume” and “years of effective rainfall” in
674 Lamentin; see text for details).

675 **Figure 3.** CLD, CLD5aH and CLD-3Cl concentrations in the outlet waters of the untreated
676 nitisol column as a function of the volume of the solution injected in the column, expressed as
677 “pore volume” and “years of effective rainfall” in Lamentin (Martinique; see text for details)
678 from PV 85. C/C_0 ratios (where C_0 is the concentration of CLD, CLD5aH and CLD-3Cl
679 injected; i.e., in solution B) are also indicated. Two different solutions (solution A: CaCl_2 10^{-2}M ,
680 and solution B: CaCl_2 10^{-2}M + CLD (12 nmol/L) + CLD5aH (28.3 nmol/L) + CLD-3Cl
681 (41.8 nmol/L)) were injected into the column according to the experimental procedure as
682 indicated in the illustration on the top. The interaction periods (stop #2, #3 and #4) between
683 the solutions and the soil are also reported. They correspond to an interruption (64 h, 66 h or 2
684 months) of the circulation of the solution in the column while solution was maintaining in the
685 soil.

686 **Figure 4.** Variation of the CLD, CLD5aH and CLD-3Cl concentrations in waters that pass
687 through the untreated nitisol as a function of the volume of CaCl_2 10^{-2}M solution injected into
688 the column (expressed as “pore volume”) between PV 170 and PV 295.

689 **Figure 5.** CLD concentrations in the outlet waters of the untreated nitisol column as a
690 function of the volume of CaCl_2 10^{-2}M solution injected in the column, expressed as “years of
691 effective rainfall” in Lamentin (Martinique; see text for details). The dotted line represents the
692 modeled exponential decrease in CLD concentrations. 0.204 and 0.2 nmol/L are the threshold
693 values for the drinking water and for the freshwater organisms.

694

695

Table

696 **Table 1.** Physico-chemical characteristics of the untreated and treated (by ISCR) nitisol
697 studied (mean \pm standard deviation, $n = 3$; see text for details)

698

Figures

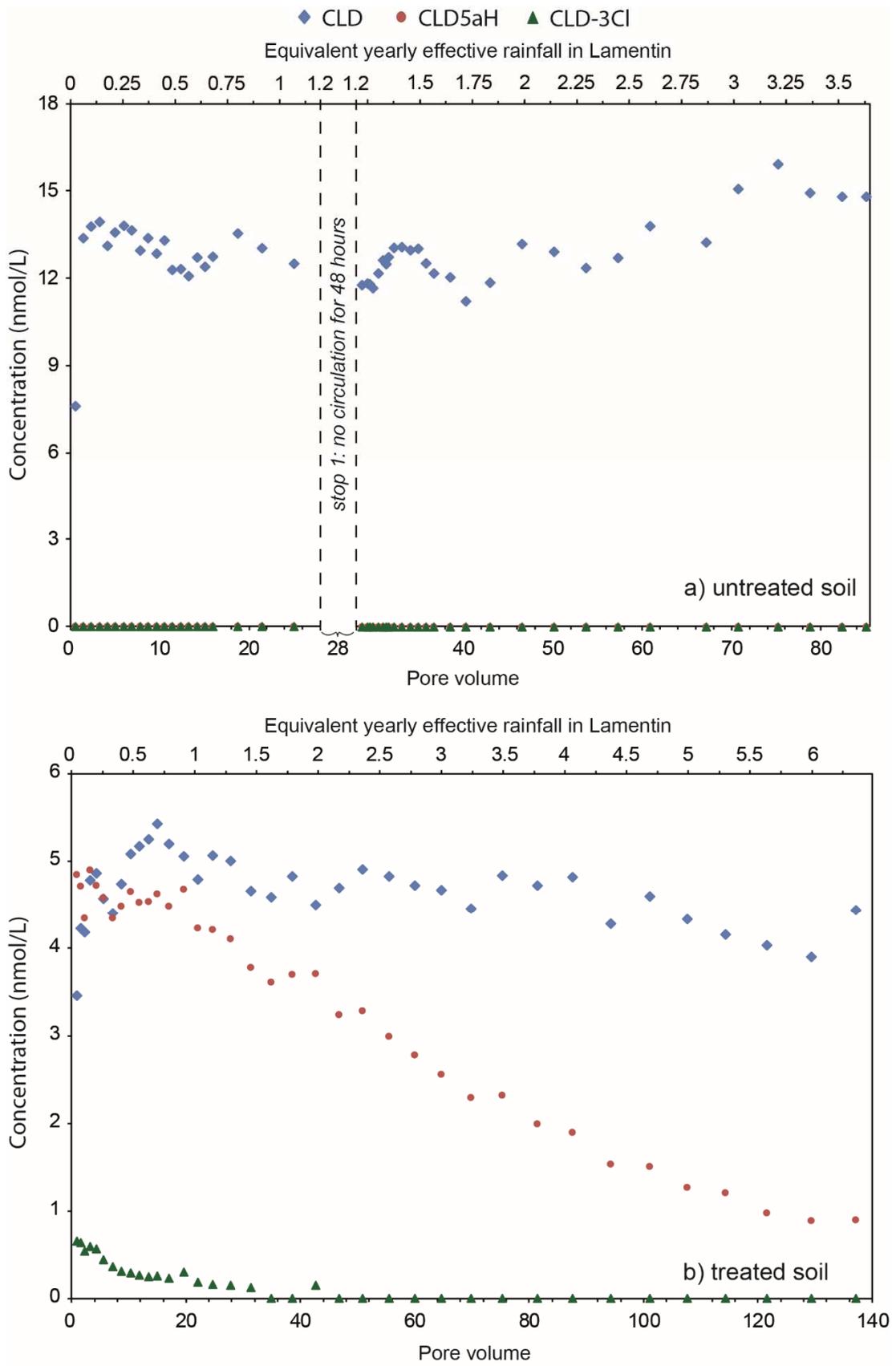


Figure 1

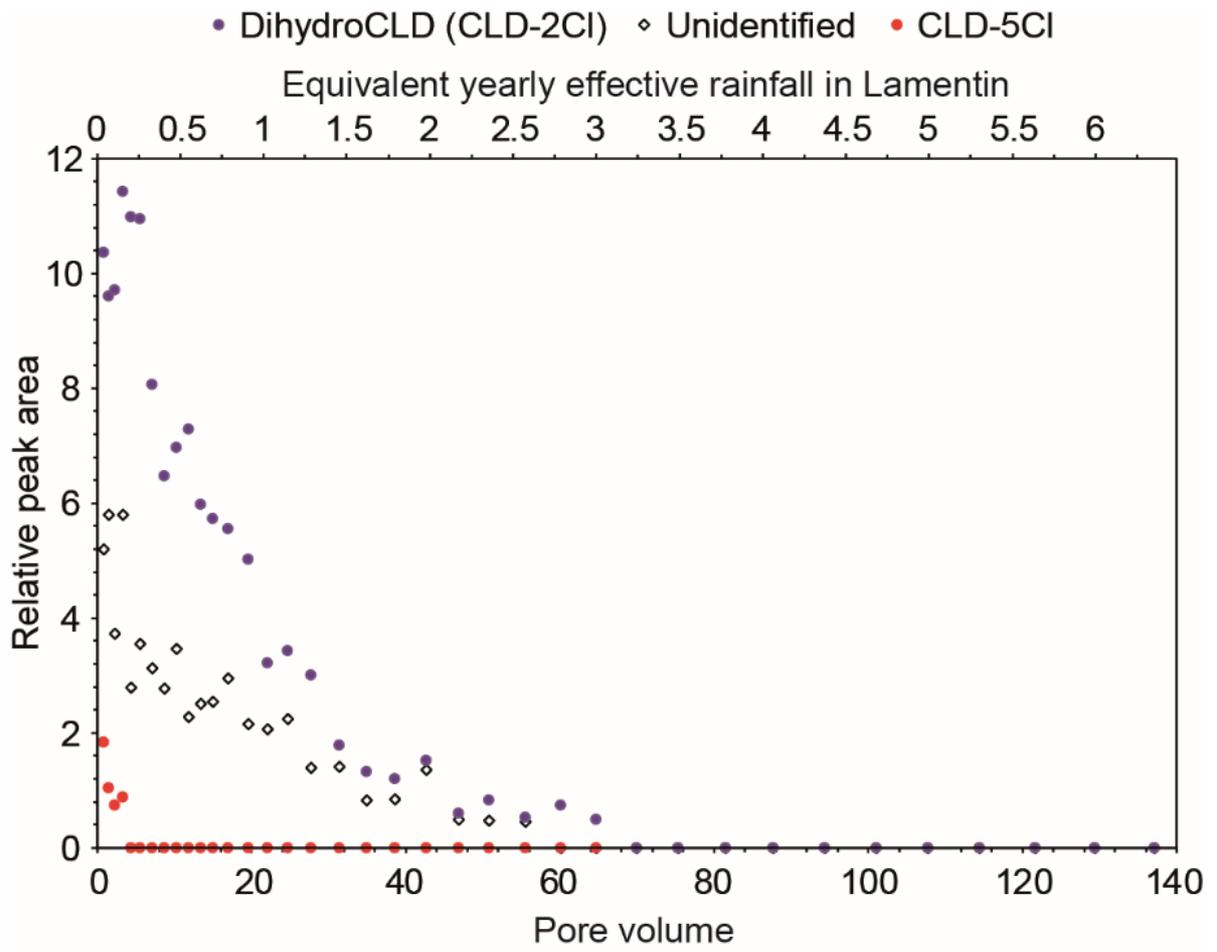


Figure 2

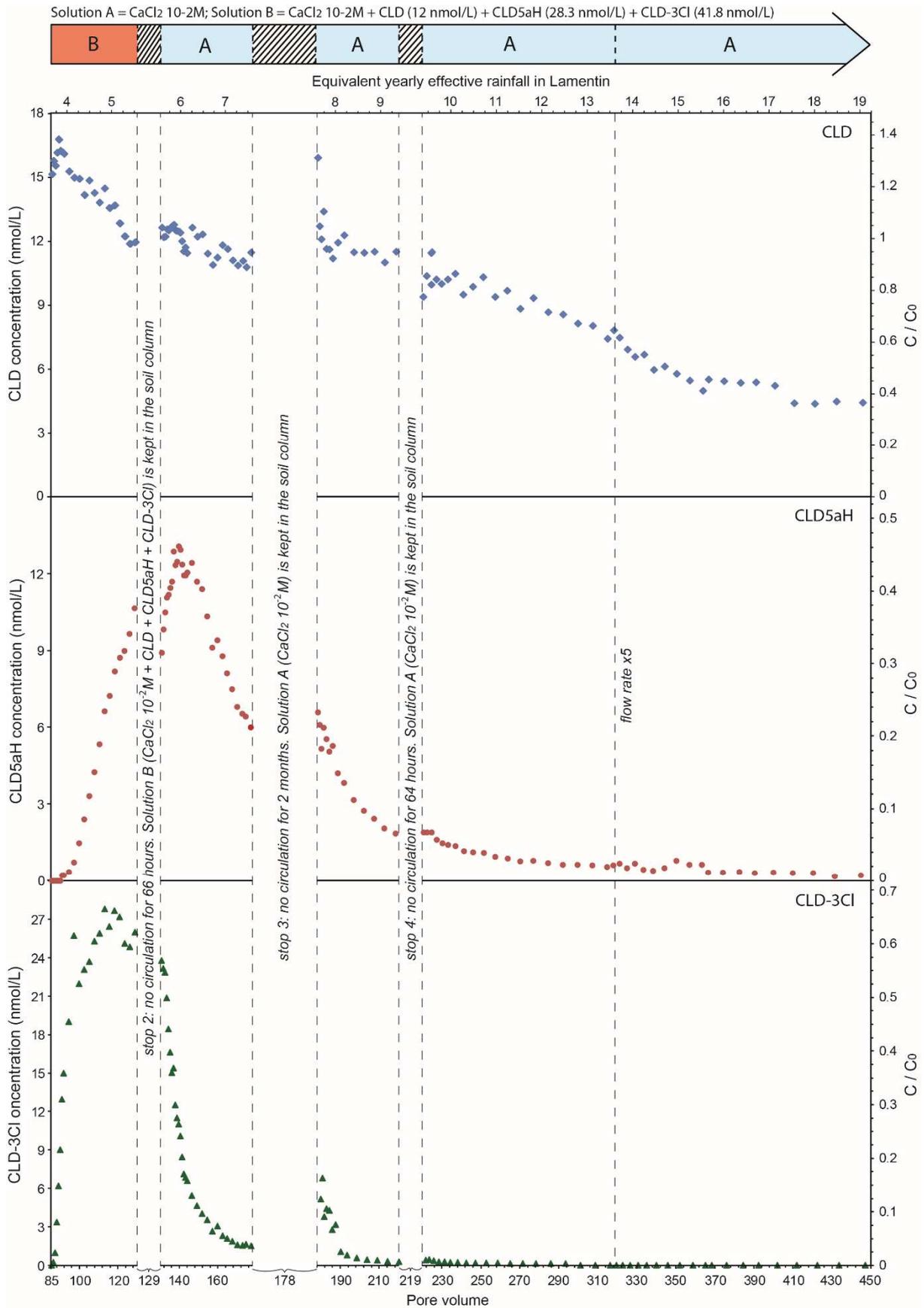


Figure 3

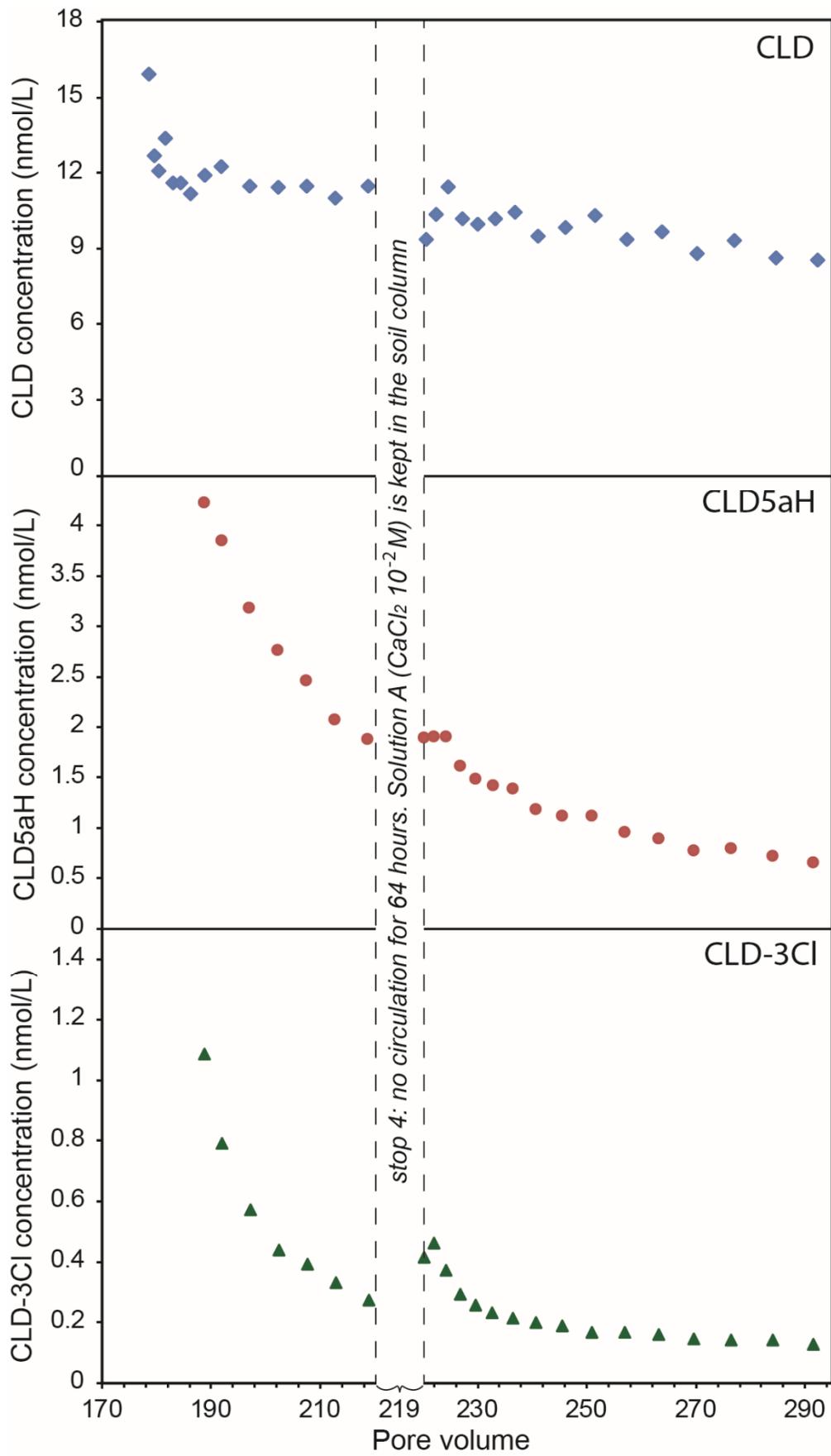


Figure 4

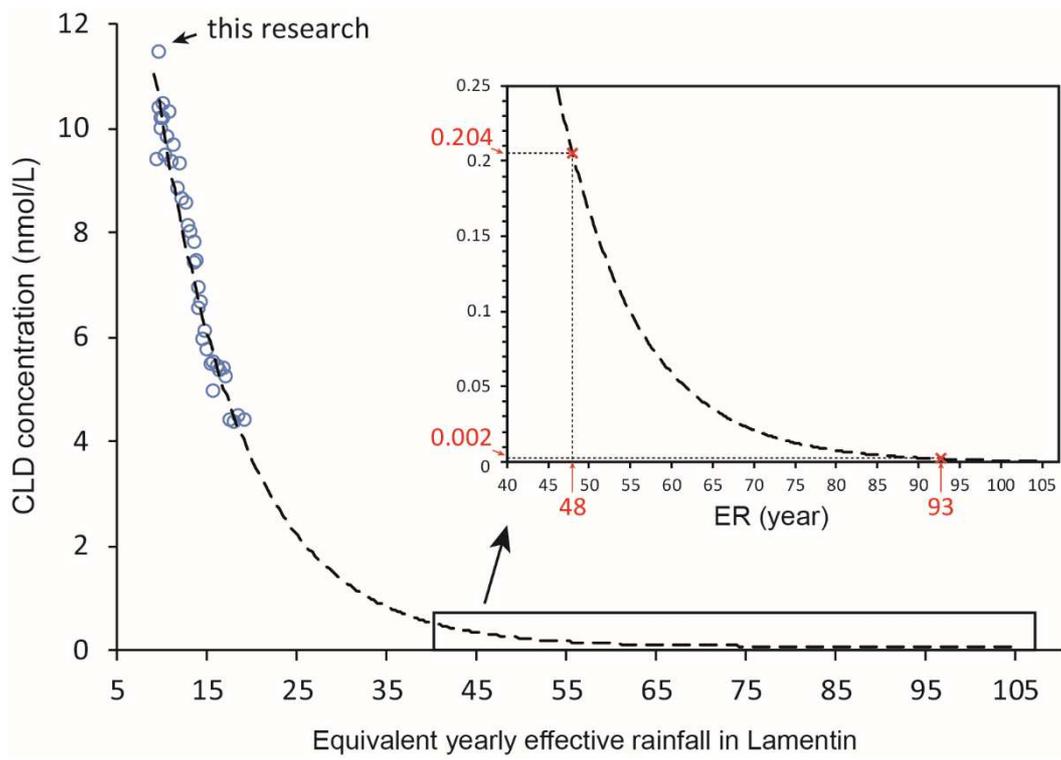
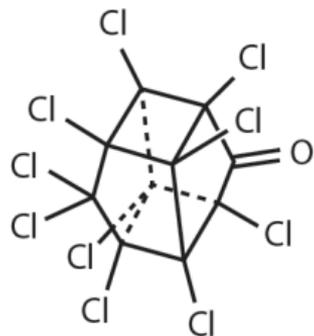


Figure 5

Table

parameter	Untreated soil	Treated soil
C/N ratio	11.6 ± 3.0	9.1 ± 0.7
P ₂ O ₅ Olsen (mg/kg)	87.7 ± 8.4	40.7 ± 0.6
Exchangeable K ₂ O (mg/kg)	1133 ± 47	892 ± 12
pH water	5.6 ± 0.1	6.1 ± 0.2
pH KCl	4.5 ± 0.1	5.1 ± 0.2
CEC (meq/100g)	25.1 ± 1.4	23.1 ± 0.7
Nitrogen (Dumas)	0.13 ± 0.03	0.14 ± 0.01
Total Fe (%)	6.8 ± 0.3	8.8 ± 0.3
Organic carbon (%)	1.4 ± 0.1	1.2 ± 0.1
Total nitrogen (%)	0.13 ± 0.03	0.14 ± 0.01
Exchangeable MgO (mg/kg)	748 ± 12	819 ± 6
Exchangeable CaO (mg/kg)	2449 ± 30	2785 ± 109
Total carboneous	< 0.1	< 0.1
Coarse sand (%; 0.2 – 2 mm)	5.9 ± 0.4	5.4 ± 0.4
Fine sand (%; 0.05 – 0.2 mm)	5.7 ± 0.8	6.4 ± 0.4
Coarse silt (%; 0.02 – 0.05 mm)	19.0 ± 2.1	18.4 ± 1.8
Fine silt (%; 0.002 – 0.02 mm)	23.6 ± 0.2	24.8 ± 0.6
Clay (%; < 0.002 mm)	43.1 ± 2.1	42.9 ± 1.6
CLD concentration (μmol/kg)	3.1 ± 0.24	1.51 ± 0.22
CLD5aH concentration (μmol/kg)	< 0.08	0.58 ± 0.06
CLD-3Cl concentration (μmol/kg)	< 0.08	< 0.08

Table 1



Chlordecone (CLD)

ISCR
treated soil



$\text{CaCl}_2 \cdot 10^{-2}\text{M}$

Release of CLD and its derivatives from soil

