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# Elucidating the Fate of the Organochlorine Pesticide Chlordecone under Abiotic Reductive and Oxidative Processes: Kinetics, Transformation Products, and C vs Cl Isotope Fractionation

Maria Prieto-Espinoza, Laure Malleret, Amandine Durand, Patrick Höhener

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1 **Elucidating the fate of the organochlorine pesticide chlordecone under abiotic reductive and oxidative**  
2 **processes: kinetics, transformation products and C vs Cl isotope fractionation**

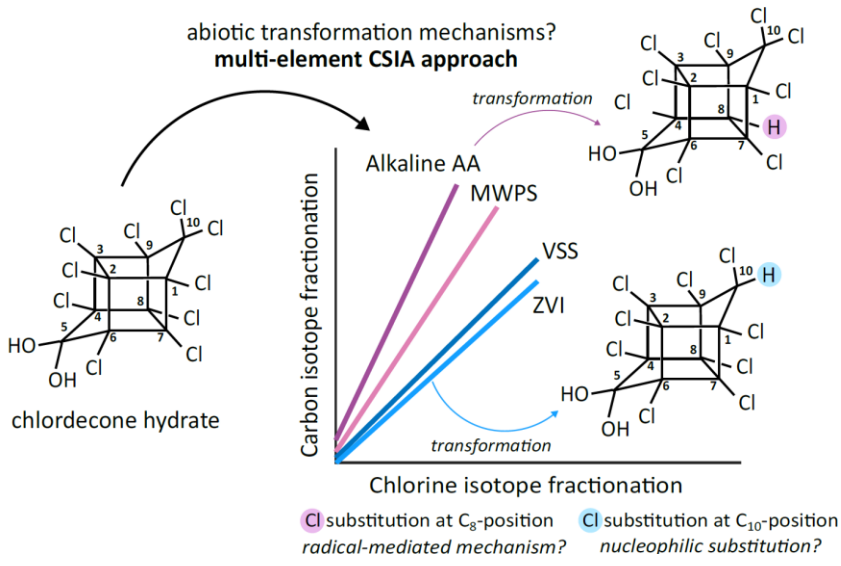
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4 Maria Prieto-Espinoza<sup>1,+</sup>, Laure Malleret<sup>1</sup>, Amandine Durand<sup>1</sup>, Patrick Höhener<sup>1,\*</sup>

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6 <sup>1</sup> Aix-Marseille Université, CNRS, Laboratoire Chimie Environnement (LCE), Marseille, France

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10  
11 \*Corresponding author: Patrick Höhener

12 \*Email address: [patrick.hohener@univ-amu.fr](mailto:patrick.hohener@univ-amu.fr)

19 **Graphical abstract**



20

## Abstract

Pollution of French West Indies (FWI) soils by the organochlorine pesticide chlordecone still poses environmental and societal concerns due to its low biodegradability and long-term persistence. Assessing chlordecone degradation remains challenging due to analytical constraints to identify transformation products (TPs). In this study, multi-element compound-specific isotope analysis (ME-CSIA) was used to identify changes in stable isotope signatures of chlordecone ( $^{13}\text{C}/^{12}\text{C}$  and  $^{37}\text{Cl}/^{35}\text{Cl}$ ) produced during abiotic transformation reactions under reducing and oxidative conditions. Effective chlordecone transformation was shown in reactions with zero-valent iron (ZVI), vitamin B<sub>12</sub> and sodium sulfide (VSS), alkaline ascorbic acid (AA), and sodium persulfate activated by microwave irradiation (MWPS). Significant enrichment of  $^{13}\text{C}$  and  $^{37}\text{Cl}$  was observed in all abiotic reactions, with  $\varepsilon_{\text{C,bulk}}$  and  $\varepsilon_{\text{Cl,bulk}}$  values ranging from  $-4.3 \pm 0.4\text{‰}$  to  $-2.3 \pm 0.2\text{‰}$  and from  $-2.6 \pm 0.4\text{‰}$  to  $-1.3 \pm 0.3\text{‰}$ , respectively. Distinct mechanisms were evidenced by correlating  $^{13}\text{C}$  and  $^{37}\text{Cl}$  signatures (dual plot), resulting in  $\Lambda$  values of  $1.17 \pm 0.28$  for ZVI,  $1.26 \pm 0.50$  for VSS,  $2.06 \pm 0.30$  for AA, and  $2.90 \pm 0.50$  for MWPS. Formation of two major TPs were also observed, 10-monohydrochlordecone and 8-monohydrochlordecone. Further, Cl-CSIA data suggested that first Cl substitution at the C<sub>10</sub>-position likely produced secondary Cl isotope effects (via nucleophilic substitution). Overall, results suggest that ME-CSIA can help quantifying *in-situ* chlordecone degradation, distinguishing between different ongoing degradation mechanisms and fingerprinting pollutant sources from chlordecone formulations (Curlone®).

**Keywords:** chlordecone, abiotic transformation, degradation, isotopes, ME-CSIA, remediation, soils

### Environmental relevance and significance (20 words)

ME-CSIA can improve the investigation of *in-situ* degradation processes of chlordecone and help fingerprinting pollutant sources from pesticide formulations.

## 47 Introduction

48 Chlordecone (C<sub>10</sub>Cl<sub>10</sub>O) is a legacy synthetic organochlorine insecticide that was used from 1960 to 1993  
49 across Africa, Europe, the U.S., Latin America and the Caribbeans.<sup>1</sup> Chlordecone (Kepone®) production and  
50 applications were first banned in 1976 in the U.S. after a poisoning incident.<sup>2</sup> Despite evidence of its toxicity,<sup>3</sup>  
51 the use of other chlordecone formulations (Curlone®) were permitted from 1981 to 1993 in the French West Indies  
52 (FWI), Guadalupe and Martinique, for the control of a banana weevil borer.<sup>4</sup> Numerous studies thereafter revealed  
53 severe contamination of soils,<sup>5,6</sup> surface waters,<sup>7,8</sup> groundwater,<sup>9,10</sup> and food products<sup>11-15</sup> of the FWI. Known  
54 adverse effects to chlordecone exposure include male infertility disorders after acute exposure,<sup>2</sup> cognitive and  
55 neuromotor development disorders,<sup>16,17</sup> and prostate cancer.<sup>17</sup> As a consequence, strong local regulations are put  
56 in place to reduce chlordecone exposure of FWI populations. However, chlordecone is expected to persist in soils  
57 for several more decades to centuries due to degradation resistance,<sup>5</sup> while significant concentrations continue to  
58 be recorded in contaminated FWI soils (> 1 mg kg<sup>-1</sup>).<sup>18</sup> The unprecedented soil contamination in the FWI is  
59 therefore an ongoing public concern for which effective remediation strategies are still required.

60 Chlordecone is highly recalcitrant in the environment due to the high steric hindrance of its bishomocubane  
61 structure containing 10 chlorine atoms (Fig. 1).<sup>19</sup> Chlordecone can be hydrated in the presence of water to a gem-  
62 diol form in place of the ketone moiety,<sup>20</sup> which makes it slightly soluble in acidic and neutral water (~2 mg L<sup>-1</sup>),  
63 while solubility increases with increasing pH (pH>10.9).<sup>21</sup> Chlordecone can also strongly adsorb/or sorb to soils  
64 (K<sub>oc</sub> value: 2,500-20,000 L kg<sup>-1</sup>),<sup>5</sup> although it may be remobilized during flood events and soil erosion, thus  
65 increasing its percolation to groundwater.<sup>22</sup>

66 Chlordecone *in-situ* degradation by soil microorganisms remains poorly documented and is presently limited  
67 to laboratory conditions. Chlordecone microbial transformation is a slow process known in few specialized  
68 anaerobic microorganisms,<sup>23-26</sup> and mixed cultures from soils and sludge from a wastewater treatment plant.<sup>27,28</sup>  
69 Resistance to microbial transformation of chlordecone in contaminated soils is likely linked to the low  
70 accessibility within soil aggregates, the absence of catabolic metabolisms in *indigenous* microorganisms, and the  
71 prevalent oxic conditions of FWI soils.<sup>19,29</sup> It is therefore necessary to propose other efficient remediation

72 strategies. Notably, the recent detection of numerous chlordecone transformation products (TPs) in FWI soils,  
73 including hydrochlordecones and indene derivatives,<sup>24,28,30</sup> opens questions regarding past and current *in-situ*  
74 mechanisms of chlordecone transformation.<sup>6,24</sup>

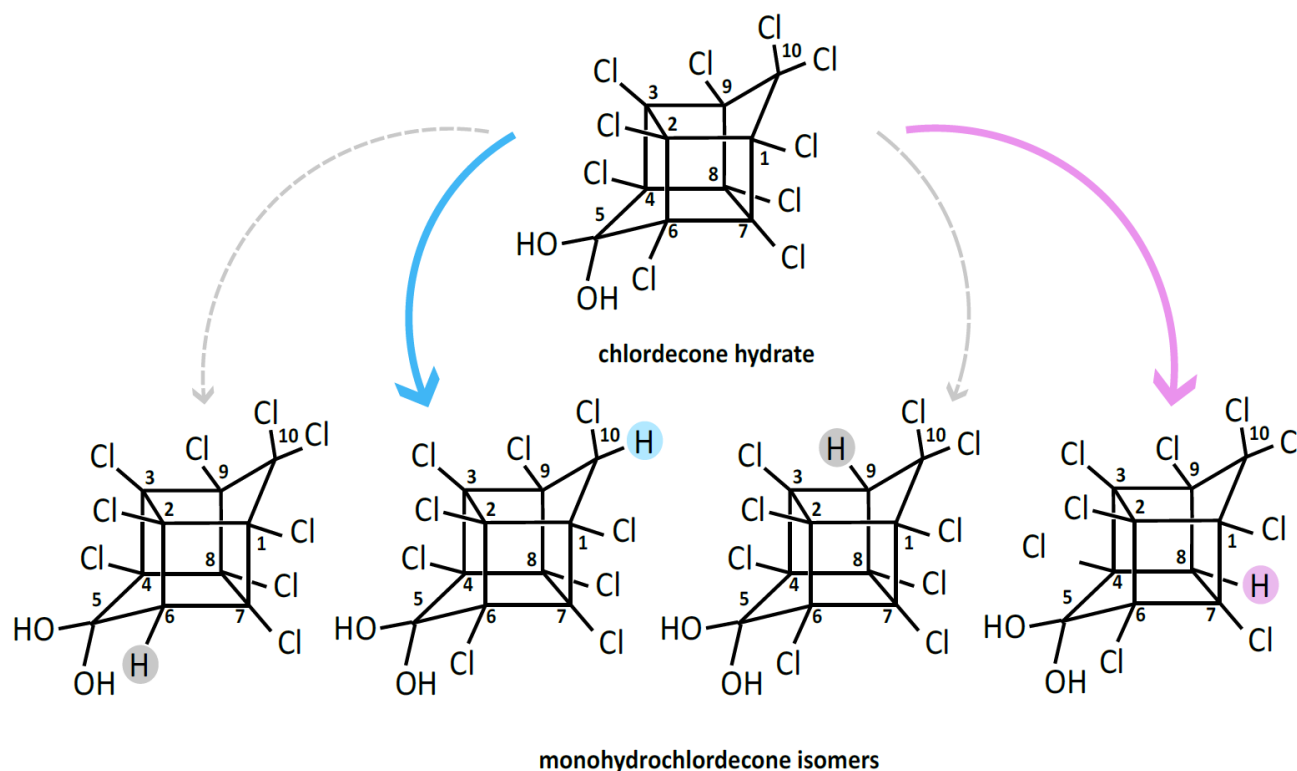
75 Chlordecone degradation mechanisms are partly understood and mostly reported for reducing conditions. For  
76 instance, zero-valent iron (ZVI) can reductively dechlorinate chlordecone resulting in the sequential formation of  
77 hydrochlordecone TPs (Family A;  $C_{10}Cl_{10-n}H_{n+2}O_2$ ,  $1 \leq n \leq 5$ ).<sup>31</sup> Vitamin B<sub>12</sub> also showed potential to transform  
78 chlordecone in the presence of different reductants, such as sodium sulfide, titanium (III) citrate and alkaline  
79 acetoin, forming hydrochlordecones and indene derivatives (Family B;  $C_9Cl_{6-n}H_{2+n}$ ,  $1 \leq n \leq 3$ ) depending on the  
80 type of reducing agent used.<sup>24,32</sup> Notably, indene derivatives were also observed during anaerobic microbial  
81 transformation reactions,<sup>24,25,27,28,30</sup> which suggests that a cobalamin is likely involved in the ring opening of the  
82 bishomocubane cage.<sup>33</sup> In contrast, few studies have shown chlordecone transformation under oxidative  
83 conditions, including chlordecone transformation by photolysis which was suggested to form a hydrochlordecone  
84 during photo-Fenton oxidation although no clear analytical evidence was provided.<sup>34</sup> With the advances in  
85 suspected or untargeted analytical strategies, seven families of chlordecone TPs have been identified so far,  
86 enabling a better understanding of chlordecone transformation processes.<sup>24,25,27,28,30</sup> However, the quantification  
87 of chlordecone TPs is currently limited by the lack of available pure chemical standards of most known TPs,  
88 which hampers their use to evidence the extent of chlordecone degradation in environmental samples.

89 Compound-specific isotope analysis (CSIA) is a well-recognized tool that allows direct identification and  
90 quantification of transformation processes of organic pollutants, such as pesticides.<sup>35,36</sup> CSIA enables the  
91 quantification of the extent of pesticide degradation by following up the stable isotope composition of the given  
92 pesticide. The CSIA approach is based on the preferential cleavage of bonds containing light isotopes compared  
93 to those bearing one or more heavy isotopes (kinetic isotope effect), leading to a progressive enrichment of heavy  
94 isotopes in the non-degraded pesticide fraction. Such isotopic enrichment ( $\epsilon$ ) can be measured based on changes  
95 in the isotope ratio of a target element in the pesticide fraction, e.g.,  $^{13}C/^{12}C$  or  $^{37}Cl/^{35}Cl$  (see review of Hofstetter  
96 et al.<sup>36</sup>). Observable isotope fractionation of an organic molecule can however be restricted by the total number

97 of atoms of the target element present in the molecule, creating a ‘dilution’ effect by the presence of non-reactive  
98 atoms of the same element.<sup>36</sup> Typically, C isotope fractionation of > 2‰ is considered a good indicator that a  
99 transformation process is occurring, often after extensive degradation has occurred.<sup>37</sup> Recently, Chevallier et al.<sup>38</sup>  
100 showed distinct carbon (C) isotope fractionation during microbial and abiotic reductive transformation of  
101 chlordecone, demonstrating the feasibility of the C-CSIA approach for bis-homocubane C<sub>10</sub>-molecules. Multi-  
102 element CSIA (ME-CSIA) may also provide significant insights into underlying mechanisms that act upon  
103 chlordecone degradation (e.g., nature of the bond-cleavage mechanism) based on C and chlorine (Cl) isotope-  
104 specific fractionation, as demonstrated for other chlorinated pesticides.<sup>39,40</sup> In particular, C-Cl CSIA (dual plot)  
105 of chlordecone from laboratory batch reactions can provide a quantitative parameter of the corresponding  
106 transformation mechanism ( $\Delta$ ), which can then be used to monitor and assess *in-situ* chlordecone degradation.  
107 Moreover, ME-CSIA can help fingerprinting pollutant sources of chlordecone formulations in contaminated soils,  
108 each of which may exhibit a unique initial isotopic signature. To date, the implementation of a ME-CSIA approach  
109 for chlordecone is still lacking. However, the recent method development for stable Cl isotope ratios of  
110 chlordecone by liquid chromatography quadrupole time-of-flight mass spectrometry (LC-QTOF-MS) could help  
111 to fill this gap.<sup>41</sup>

112 This study aims to gain insights into chlordecone transformation mechanisms during abiotic reactions and  
113 associated C and Cl isotope fractionation. For different reactive conditions, Cl-CSIA of chlordecone was  
114 established following a novel in-house method performed by LC-QTOF-MS.<sup>41</sup> Reductive and oxidative  
115 conditions were tested to investigate the feasibility of *in-situ* chemical reduction (ISCR) or oxidation (ISCO) of  
116 chlordecone. This includes reactions with ZVI and vitamin B<sub>12</sub> from which C-CSIA has been established.<sup>38</sup> Two  
117 new reactions were here investigated by alkaline ascorbic acid (AA) and sodium persulfate activated by  
118 microwave irradiation (MWPS). Alkaline AA (vitamin C) was tested based on its ability to induce reductive  
119 dechlorination of other chlorinated compounds, such as carbon tetrachloride and tetrachloroethylene (PCE).<sup>42,43</sup>  
120 Under oxidative conditions, MWPS was tested based on its potential to transform other pesticides, such as atrazine  
121 and parathion,<sup>44,45</sup> and recent evidence of chlordecone attenuation in soils upon microwave irradiation.<sup>46</sup>

122 Hydrolysis experiments of chlordecone at distinct pH conditions (pH = 1, 7 and 13) was also performed and  
123 further served as control experiments.



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125 Figure 1. Chlordecone hydrate and plausible monohydrochlordecone isomers forming upon first chlorine  
126 substitution.<sup>47</sup> Monohydrochlordecone isomers from left to right: 6-monohydrochlordecone (= 4-  
127 monohydrochlordecone), 10-monohydrochlordecone, 9-monohydrochlordecone (= 1-monohydrochlordecone),  
128 and 8-monohydrochlordecone (= 2-, 3-, and 7-monohydrochlordecones). Numbers indicate the position of Cl  
129 atoms following IUPAC nomenclature. First Cl substitution is highlighted in colored circles. 10-  
130 monohydrochlordecone (blue arrow) and 8-monohydrochlordecone (pink arrow) were identified in this study as  
131 major TPs. Two other monohydrochlordecone isomers were detected in minor amounts. 6- and 9-  
132 monohydrochlordecone (gray dashed arrows) are suspected isomers.

## 133 **Material and Methods**

### 134 **Chemicals**

135 A detailed description of chemical reagents and preparation of standard and buffered solutions is given as  
136 Supporting Information (SI, Chemicals). Briefly, two chlordecone (CLD) analytical standards, CLD<sub>CLUZEAU</sub> and  
137 CLD<sub>SIGMA</sub>, were purchased from Cluzeau Info Labo (Dr. Ehrenstorfer, purity 96.7%) and Sigma Aldrich (Supelco,  
138 purity 99.9%), respectively. Available TPs were also purchased: 8-monohydrochlordecone (IUPAC  
139 nomenclature) (C<sub>10</sub>HCl<sub>9</sub>O; HPC Standards GmbH) and chlordecone-alcohol (C<sub>10</sub>H<sub>2</sub>Cl<sub>10</sub>O, Cluzeau Info Labo).  
140 In addition, a sample of the Curlone<sup>®</sup> formulation was analyzed to retrieve C and Cl isotope signatures.

### 141 **Experimental setup**

142 A detailed description of the experimental setup is given in the SI (SI, Setup).

143 *Hydrolysis.* Chlordecone hydrolysis was carried out in buffered solutions at pH 1, pH 7 and pH 13 and  
144 incubated at 60° C for 45 days, as suggested elsewhere.<sup>48</sup> Hydrolysis experiments were carried out in sterile 500  
145 mL Schott glass bottles containing 400 mL solutions and under dark conditions. Buffered solutions were spiked  
146 with chlordecone and stirred for 15 min to reach concentrations of 2 mg L<sup>-1</sup>. Samples were collected for  
147 chlordecone quantification and stable isotope analysis (48 mL). Blanks were prepared similarly and did not  
148 contain chlordecone.

149 *Zero-Valent Iron (ZVI).* Chlordecone transformation by ZVI was tested using two types of ZVI powders (ZVI<sub>f</sub>  
150 and ZVI<sub>s</sub>) and performed each in duplicate, in sacrificial mode and in buffered solutions at pH 7. The morphology  
151 of the ZVI powders was characterized at the Center of Nanoscience of Marseille (CINAM) by scanning electron  
152 microscopy (SEM). Experiments were carried out in sterile 20 mL serum vials containing 12 mL of an  
153 acetone/water mixture (20:80 v/v) to increase chlordecone solubility.<sup>38</sup> Aqueous solutions contained 90 mg of the  
154 corresponding ZVI powder and chlordecone was spiked to reach final concentrations of 170 mg L<sup>-1</sup>. Solutions  
155 were flushed with N<sub>2</sub> and vials were crimped with Teflon crimp caps. Experiments were carried out under constant  
156 stirring and dark conditions and lasted 239 h and 724 h for ZVI<sub>f</sub> and ZVI<sub>s</sub> reactions, respectively. Samples were

157 collected for chlordecone quantification and stable isotope analysis (10 mL), and chloride analysis (2 mL).  
158 Negative controls did not contain ZVI. Two blanks were prepared containing only ZVI.

159 *Vitamin B<sub>12</sub> with sodium sulfide (VSS)*. Chlordecone transformation by VSS was performed in duplicate in  
160 sterile 100 mL serum bottles containing a 50 mL aqueous solution buffered to pH 12.7. Solutions were flushed  
161 with N<sub>2</sub> and bottles were closed with a PTFE valve cap (Mininert®, Sigma Aldrich). Solutions contained vitamin  
162 B<sub>12</sub> (6.5 mg L<sup>-1</sup>), sodium sulfide (336 mg L<sup>-1</sup>) and chlordecone (170 mg L<sup>-1</sup>).<sup>38</sup> Negative controls were prepared  
163 similarly but did not contain vitamin B<sub>12</sub>. Blanks were prepared containing vitamin B<sub>12</sub> and sodium sulfide only.  
164 Experiments were carried out under dark conditions and constant stirring and lasted 6.5 h. Two 2 mL aliquots  
165 were collected for chloride analysis and for chlordecone quantification and stable isotope analysis at each  
166 sampling time.

167 *Alkaline ascorbic acid (AA)*. Chlordecone transformation by alkaline AA was performed in a sterile 1 L  
168 Schott glass bottle containing a 1 L solution buffered to pH 12.78. Solution contained 1 mM of AA and  
169 chlordecone was spiked to 2 mg L<sup>-1</sup>. Experiments were carried out under dark conditions and constant stirring  
170 and lasted 10 days. Samples were collected for chlordecone quantification and stable isotope analysis (48 mL),  
171 and chloride analysis (2 mL). Negative controls did not contain AA and blanks were prepared with AA only.

172 *Sodium persulfate activated by microwave irradiation (MWPS)*. Chlordecone transformation by MWPS  
173 was performed in sterile 250 mL glass bottles, in duplicate and in sacrificial mode. Aqueous solutions were  
174 buffered to pH 7. Each bottle contained a 100 mL solution with 1 mM of sodium persulfate (PS) and 2 mg L<sup>-1</sup>  
175 of chlordecone. Experiments were carried out using a conventional microwave oven (Samsung RE 576D) at  
176 medium power (500 W). Experiments were performed in sacrificial mode and lasted 15 min. Samples were  
177 collected for chlordecone quantification and stable isotope analysis (98 mL), and chloride analysis (2 mL).  
178 Negative controls consisted of bottles containing (i) PS and chlordecone at room temperature, (ii) PS and  
179 chlordecone incubated at 105° C for 15 min, and (iii) chlordecone solutions microwaved for 15 min. Temperature  
180 was recorded in negative controls. Blanks were prepared with PS only. Neither PS consumption nor sulfate  
181 production were monitored along the experiments.

## 182 **Chemical extraction procedure**

183 Chlordecone from abiotic batch experiments was extracted following methods adapted from the literature  
184 (SI, Methods).<sup>38,49</sup> Briefly, extractions were carried out by adding dichloromethane (DCM) as organic solvent at  
185 a volume adapted according to the volume of available sample (Fig. S2). Before extraction, samples were  
186 acidified to pH 3, and then mixed with DCM by vortex (1 min) and horizontally shaken (300 rpm) for 10 min.  
187 DCM was recovered and the extraction procedure was repeated three times until pooling all DCM extracts. The  
188 extraction procedure was further adapted for MWPS and ZVI reactions due to volume and fine particle  
189 constraints (Fig. S2). Collected solvent extracts were evaporated until dryness, assisted by a gentle N<sub>2</sub> stream in  
190 a water bath (40 °C), and resuspended in a 1 mL hexane/acetone (3:1 v/v) mixture and stored at -20° C until  
191 further analyses. Due to elevated C mass required for C-CSIA of pesticides,<sup>49</sup> chlordecone extractions were  
192 validated based on satisfactory recoveries ( $\geq 94\%$ ) and absence of C isotope fractionation ( $\Delta\delta^{13}\leq 0.47\%$ ) (SI,  
193 Table S3).

## 194 **Chlordecone quantification and identification of TPs**

195 A detailed description of analytical methods is described in the SI (SI, Methods). Briefly, chlordecone and  
196 available TPs were quantified using a gas chromatograph (GC, Trace 1300, Thermo Scientific) equipped with a  
197 TG-5MS column (30 m  $\times$  0.25 mm ID, 0.25  $\mu$ m film thickness, Thermo Scientific), coupled to a quadrupole mass  
198 spectrometer (MS, ISQ<sup>TM</sup> 7000, Thermo Scientific) and in electron impact ionization mode (70 eV). Suspected  
199 TPs without available standards were searched with adapted methods by GC-qMS in full scan and SIM mode,<sup>24</sup>  
200 and using ultra-high performance liquid chromatography (UPLC, Waters) coupled to a hybrid quadrupole time-  
201 of-flight (QTOF) mass spectrometer (SynaptG2 HDMS, Waters), fitted with an electrospray ionization source  
202 (ESI) operated in negative mode.

## 203 **Compound-specific isotope analysis (CSIA) of chlordecone**

204 A detailed description of the analytical methods for C- and Cl-CSIA is provided in the SI (SI, Methods).  
205 Calculations of Cl isotope ratios are also provided as a supporting MS Excel spreadsheet. C isotope composition

of chlordecone was determined by gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS), with a gas chromatograph (Trace 1310) coupled via a GC/Conflow IV interface to an isotope ratio mass spectrometer (Delta V advantage, Thermo Fisher). Chlordecone standards (CLD<sub>CLUZEAU</sub> and CLD<sub>SIGMA</sub>) were prepared daily and analyzed prior to sample measurements, and caffeine was used as external standard. Instrument linearity was determined between 25-250 mg L<sup>-1</sup> (Fig. S4).

Cl isotope composition of chlordecone was determined by LC-QTOF-MS.<sup>41</sup> Samples were measured following a bracketing and two-point calibration approach.<sup>41</sup> CLD<sub>SIGMA</sub> and CLD<sub>CLUZEAU</sub> standards were characterized by dual-inlet IRMS at the University of Delaware ( $\delta^{37}\text{Cl}$  values of  $-0.11 \pm 0.17\text{‰}$  and  $+0.52 \pm 0.17\text{‰}$ , respectively). The evaluation scheme for the calculation of Cl isotope ratios of chlordecone was based on the five most abundant ion peaks of the molecular ion (502 m/z) and correction factors were added to account for the presence of other heavy isotopes (i.e., <sup>13</sup>C, <sup>16</sup>O, <sup>17</sup>O, <sup>18</sup>O, <sup>2</sup>H) and instrument nonlinearity.<sup>41</sup> Instrument linearity was determined between 100-1000  $\mu\text{g L}^{-1}$  (Fig. S6).

For a quantitative evaluation of chlordecone transformation, isotope enrichment factors ( $\epsilon_{E,\text{bulk}}$ ), which express the difference in transformation rates of light and heavy isotopologues, were derived according to the Rayleigh equation:<sup>50</sup>

$$\ln\left(\frac{\delta^h E_t + 1}{\delta^h E_0 + 1}\right) = \ln\left(\frac{c_{t,E}}{c_{0,E}}\right) \cdot \frac{\epsilon_{E,\text{bulk}}}{1000} \quad (1)$$

where  $\delta^h E_t$  and  $\delta^h E_0$  (in ‰) are the isotope signatures of element  $E$  (i.e., <sup>13</sup>C and <sup>37</sup>Cl), and  $c_{t,E}$  and  $c_{0,E}$  are chlordecone concentrations at a given ( $t$ ) and initial time ( $0$ ), respectively. C and Cl isotope signatures were reported based on measured C and Cl isotope ratios relative to international reference materials (V-PDB and SMOC, respectively), following  $\delta^h E = [(R_{\text{sample}}/R_{\text{standard}}) - 1]$ .<sup>51,52</sup> Standard errors were reported as  $\sigma_m = s/\sqrt{n}$ , where  $s$  is the sample standard deviation and  $n$  is the number of injections performed. The total analytical uncertainty ( $1\sigma_m$ ) of measurements was  $\leq 0.5\text{‰}$  and  $\leq 0.9\text{‰}$  for  $\delta^{13}\text{C}$  and  $\delta^{37}\text{Cl}$ , respectively.  $\epsilon_{E,\text{bulk}}$  values were obtained from the slope of the linear regression and are reported with a 95% confidence interval (CI).

C and Cl isotope signatures were correlated in a dual-element isotope plot.  $\Lambda^{\text{C/Cl}}$  values were obtained from the slopes using the ratio of  $\epsilon_{E,\text{bulk}}$  values, i.e., second term of Eq. 2, and following error propagation.

$$\Lambda^{C/Cl} = \frac{\Delta\delta^{13}C}{\Delta\delta^{37}Cl} \approx \frac{\varepsilon_{C,bulk}}{\varepsilon_{Cl,bulk}} \quad (2)$$

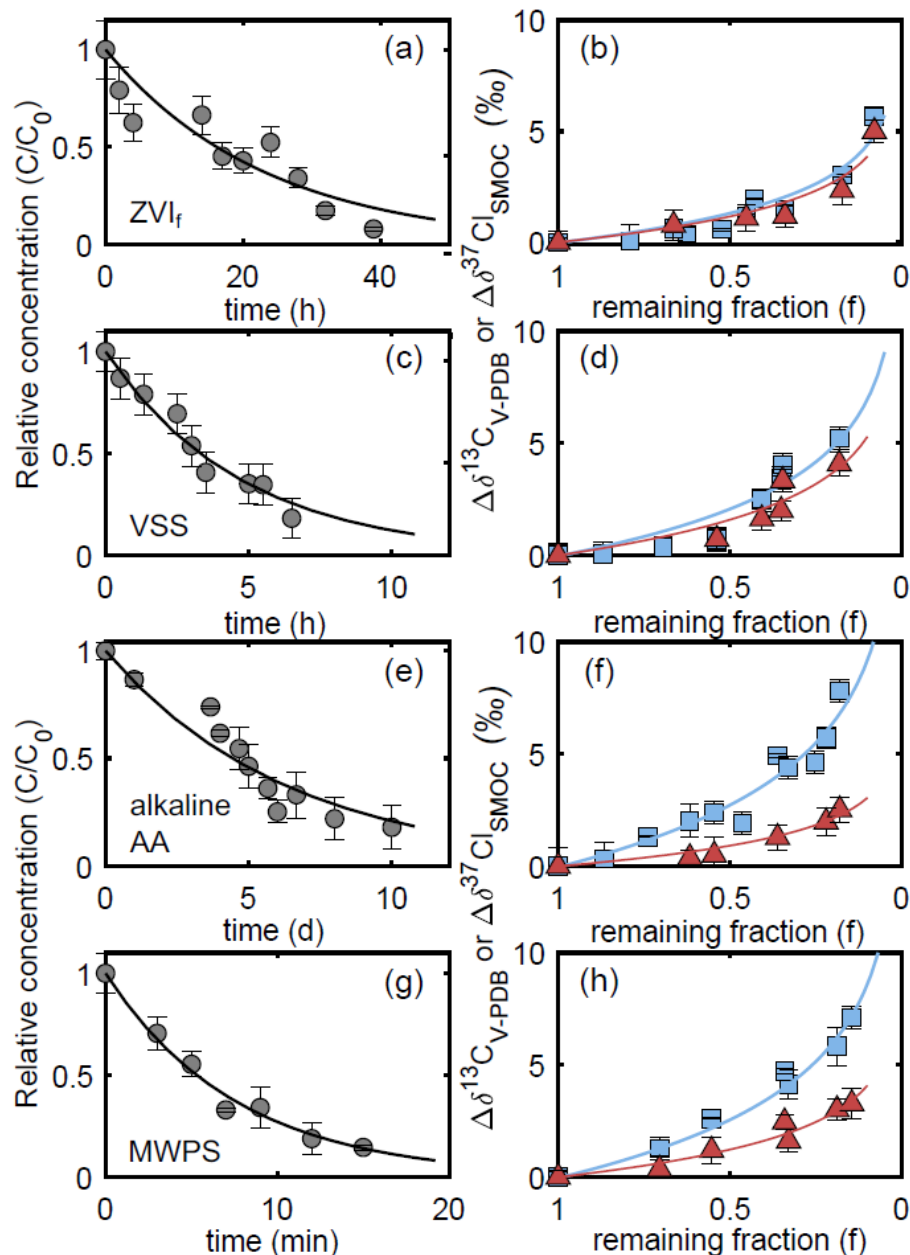
## Results and discussion

### Recalcitrance of chlordecone

Hydrolysis experiments at pH 1, 7 and 13 and incubated at 60 °C did not evidence chlordecone transformation during the 45-day period (Figs. S7-S10). Hydrolysis experiments thus confirmed the high recalcitrance of chlordecone under acidic, neutral and alkaline aqueous conditions even at elevated temperatures (60 °C). This is consistent with reported absence of chlordecone hydrolysis at room temperature under neutral and alkaline conditions,<sup>38</sup> and with our ZVI and alkaline AA controls (Figs. S13-S14). Hydrolysis experiments also served as controls for the remaining abiotic reactions which showed efficient transformation of chlordecone following pseudo-first order kinetics (Fig. 2). The absence of C isotope fractionation with time during chlordecone hydrolysis further indicated that our proposed extraction procedure for C-CSIA of chlordecone does not produce isotope fractionation (Fig. S7).<sup>49</sup>

### Efficient abiotic reductive dechlorination of chlordecone

ZVI<sub>f</sub> and ZVI<sub>s</sub> powders showed efficient chlordecone removal within 39 h (92%;  $k_{obs} = 0.043 \text{ h}^{-1}$ ) and 104 h (88 %;  $k_{obs} = 0.014 \text{ h}^{-1}$ ) of the reactions, respectively (Figs. 2a and S12). No chlordecone transformation was observed in negative controls (Fig. S13). Chlordecone reduction via ZVI was previously reported in the range of 7 d (97%) to 5 weeks (93%).<sup>31,38</sup> Discrepancies in chlordecone transformation efficiency by distinct ZVI powders may be attributed to differences in their initial surface properties and porous structure.<sup>53</sup> Indeed, ZVI<sub>f</sub> showed a more complex porous morphology and higher surface area than ZVI<sub>s</sub> powders (Fig. S11), which explains the observed faster chlordecone transformation in ZVI<sub>f</sub> reactions. These results indicate the high capacity of different iron types to induce efficient reductive dechlorination of chlordecone. Moreover, chlordecone reduction via ZVI in contaminated soils of the FWI was evidenced in laboratory soil pilot experiments alternating reducing and oxidizing periods (22%–74% removal),<sup>54</sup> which further highlights the promising use of ZVI for the *in-situ* remediation of chlordecone in contaminated soils.



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Figure 2. Chlordecone relative concentrations (gray circles) vs. time (a, c, e, g) and associated stable C (blue squares) and Cl (red triangles) isotope fractionation in  $\Delta\delta^{13}C_{V-PDB}$  (‰) and  $\Delta\delta^{37}Cl_{SMOC}$  (‰), respectively (b, d, f, h). Symbols correspond to observed chlordecone transformation by (a, b) zero-valent iron (ZVI<sub>f</sub>), (c, d) vitamin B<sub>12</sub> and sodium sulfide (VSS), (e, f) alkaline ascorbic acid (AA), and (g, h) sodium persulfate activated by microwave irradiation (MWPS) reactions. Colored curves are fitted to the observed concentration data following pseudo-first order kinetics ( $k_{obs}$ ) and isotope data following the logarithmic expression of the Rayleigh equation (Eq. 1).

Sodium sulfide was also able to reductively dechlorinate chlordecone in the presence of vitamin B<sub>12</sub> as catalyst (VSS), resulting in chlordecone mass removal of 82% after 6.5 h ( $k_{obs} = 0.206 \text{ h}^{-1}$ ) (Fig. 2c). Negative controls did not show chlordecone transformation with time (Fig. S14), suggesting that a catalyst is necessary for the reaction to occur. Vitamin B<sub>12</sub> is a cobalt corrinoid which can undergo reduction from the Co(III) to the

268 Co(II) or Co(I) states.<sup>55</sup> In presence of vitamin B<sub>12</sub>, different reducing agents are known to determine the rate  
269 and efficiency of chlordecone transformation.<sup>32,38,56</sup> For instance, titanium(III) citrate can reduce vitamin B<sub>12</sub> to  
270 the Co(I) state, resulting in a supernucleophile involved in the reductive dechlorination of chlordecone,<sup>32,38</sup> and  
271 other chlorinated compounds.<sup>57</sup> Moreover, strong reducing conditions are required for the reduction of vitamin  
272 B<sub>12</sub> to the Co(I) state ( $E_h < -0.61$  V, normal hydrogen electrode (NHE)),<sup>55</sup> which are likely more difficult to  
273 control in large-scale contaminated soils. On the other hand, sodium sulfide is a weaker reducing agent that can  
274 reduce vitamin B<sub>12</sub> to the Co(II) state only via an one-electron transfer from S<sup>2-</sup>.<sup>58</sup> The redox experimental  
275 conditions measured ( $-0.37$  V, Table S2) are indeed consistent with the stability range associated with a Co(II)  
276 state for vitamin B<sub>12</sub> at alkaline pH ( $E_h$  range:  $-0.61$  to  $-0.06$  V, NHE).<sup>55</sup> Moreover, sodium sulfide in the  
277 presence of vitamin B<sub>12</sub> was proven successful in transforming highly recalcitrant pollutants such as  
278 perfluoroalkyl substances (PFAS).<sup>58</sup> Thus, in reactions with vitamin B<sub>12</sub>, sulfide may prove adequate for the  
279 remediation of chlordecone contaminated soils. In addition, sulfide may naturally be present in deep oxygen-  
280 depleted soils or aquifers of the FWI where microbial organic matter decomposition and sulfate reduction likely  
281 occur.<sup>59,60</sup> Although chlordecone transformation may be successful with VSS, knowledge on the fate of the  
282 formed hydrochlordecones is still limited, including the possible formation of sulfur-containing TPs, such as the  
283 recently proposed chlordecone thiol derivative,<sup>61</sup> which warrants further studies.

284 Chlordecone transformation by alkaline ascorbic acid (AA) was for the first time tested and showed mass  
285 removal of 82% after 10 d ( $k_{obs} = 0.007$  h<sup>-1</sup>) (Fig. 2e). Negative controls did not show chlordecone transformation  
286 with time (Fig. S15), indicating the potential of AA to induce chlordecone transformation. Moreover, the  
287 measured low redox potential in reactions with alkaline AA ( $E_h = -0.22$  V; Table S2) was in good agreement with  
288 reductive dechlorination conditions and dissociation of AA to dehydroascorbic acid (bicyclic hydrated structure;  
289  $E_h = -0.18$  V).<sup>62</sup> Indeed, AA is a naturally organic reductant that can dissociate in aqueous solutions as a function  
290 of pH to form ascorbic anion (C<sub>6</sub>H<sub>7</sub>O<sub>6</sub><sup>-</sup>, pK<sub>a1</sub> = 4.25) and dianionic ascorbic acid (C<sub>6</sub>H<sub>6</sub>O<sub>6</sub><sup>2-</sup>, pK<sub>a2</sub> = 11.79).<sup>62</sup> At  
291 alkaline pH, AA can lose electrons in two one-electron steps or one two-electron step, involving ascorbate radical  
292 intermediates, which provides C<sub>6</sub>H<sub>6</sub>O<sub>6</sub><sup>2-</sup> reductive abilities for pollutant removal, such as carbon tetrachloride or  
293 chlorinated ethenes,<sup>42,43</sup> pesticides,<sup>63</sup> and nitrobenzenes.<sup>64</sup> Results thus indicate that AA holds promising abilities

294 for ISCR of chlordecone contaminated soils. In addition, AA is a water soluble vitamin (vitamin C) present in  
295 many fruits and vegetables, and in solution may easily permeate agricultural soils.<sup>65</sup> AA may thus be applied as  
296 part of nature-based solutions.

### 297 **Advanced oxidation processes (AOPs) for chlordecone removal**

298 Transformation of chlordecone under AOPs was performed with PS activated by MW irradiation.  
299 Efficient chlordecone removal was observed within 15 min of the reaction (98%,  $k_{obs} = 7.88 \text{ h}^{-1}$ ) (Fig. 2g).  
300 Negative controls did not evidence chlordecone removal (Fig. S16), which is in line with previous studies  
301 demonstrating that MW irradiation or PS alone do not induce significant pollutant transformation.<sup>44,45,66</sup>  
302 Moreover, thermal destruction is only expected to be a significant removal mechanism of chlordecone at  
303 temperatures exceeding 200°C,<sup>67</sup> which were not reached in this study (up to 105°C; Fig. S17). Results thus  
304 suggest that heat activated PS by MW was the main mechanism controlling chlordecone transformation (Fig. 2g).

305 PS ( $\text{S}_2\text{O}_8^{2-}$ ) can be activated by the increase in solution temperature via MW irradiation, generating sulfate  
306 ( $\text{SO}_4^{\cdot-}$ ,  $E^\circ = 2.6\text{-}3.2 \text{ V}$ ) and hydroxyl ( $\cdot\text{OH}$ ,  $E^\circ = 2.4\text{-}3.0 \text{ V}$ ) radicals.<sup>44</sup> It is thus likely that a radical-mediated  
307 mechanism is involved in MWPS reactions of chlordecone, similarly as in chlordecone photolysis and photo-  
308 Fenton reactions.<sup>34,68</sup> This is also consistent with the formation of similar chlordecone TPs between MWPS and  
309 photolysis reactions (8-monohydrochlordecone, see below). Further quenching experiments on the effect of  $\text{SO}_4^{\cdot-}$   
310 radicals in MWPS reactions of chlordecone are needed to provide additional insights into chlordecone  
311 dechlorination mechanisms under such oxidative conditions.

312 Efficient removal of other banned pesticides such as parathion<sup>44</sup> and atrazine<sup>45</sup> was also demonstrated in  
313 soil experiments under a MWPS system with similar temperature ranges as in this study (80-100 °C). Notably, a  
314 recent study showed that MW irradiation of chlordecone-containing dehydrated soils can reduce chlordecone by  
315 50% to 90%, depending on soil type and moisture content (0-20% wt.), and after 10 min of treatment.<sup>46</sup> However,  
316 in the same study, soil temperatures reached >200 °C, indicating that thermal destruction was likely a controlling  
317 mechanism for chlordecone removal while formation of hydrochlordecones was not evidenced,<sup>46</sup> contrasting with  
318 our study. Overall, results suggest that activation of PS by MW irradiation may be a suitable ISCO remediation

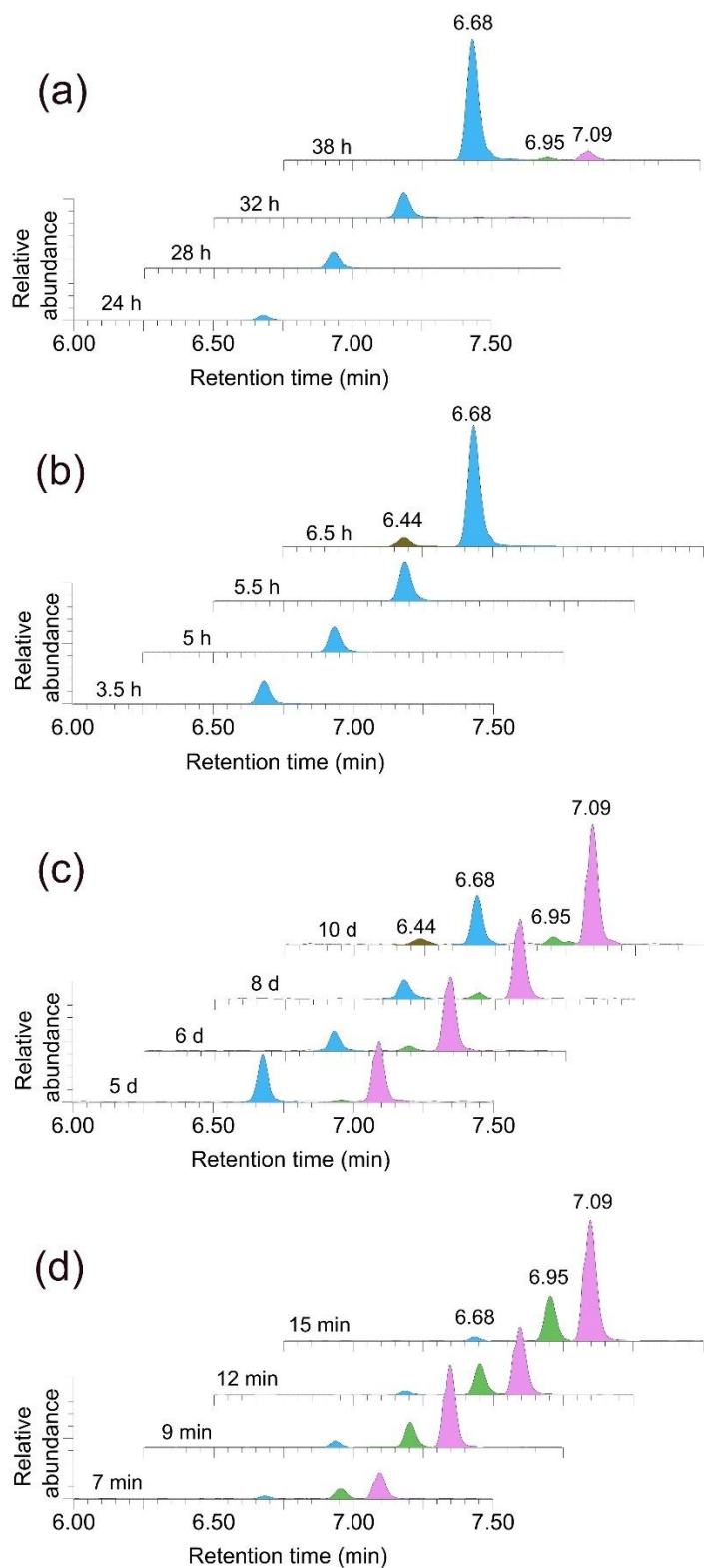
319 technique for efficient chlordecone removal in contaminated soils. In addition, low soil temperatures (<100 °C)  
320 and short MW periods may help in reducing the impact on soil properties and bacterial communities after soil  
321 restoration.<sup>69</sup>

### 322 **Formation of distinct monohydrochlordecone isomers during chlordecone dechlorination**

323 Hydrochlordecones (Family A) were the only TPs identified during all abiotic chlordecone transformation  
324 reactions. No other families of TPs were identified with our searching methodology by GC-qMS or LC-QTOF-  
325 MS (SI, Results). Upon the first Cl substitution, four monohydrochlordecone isomers were observed in abiotic  
326 reactions at (LC-QTOF-MS) chromatographic retention times of 6.44 min (Peak 1), 6.69 min (Peak 2), 6.95 min  
327 (Peak 3), and 7.09 min (Peak 4) (Fig. 3). These isomers were also the major TPs observed in all reactions and  
328 were accompanied by other family A hydrochlordecones (removal of up to 5 Cl atoms) (Figs. S21-S25). The  
329 position of first Cl substitutions of chlordecone are depicted in Fig. 1. Peak 2 was attributed as 10-  
330 monohydrochlordecone based on reported LC-QTOF-MS and GC-qMS mass spectra (Figs. S26 and S34).<sup>24,31</sup>  
331 Peak 4 was identified as 8-monohydrochlordecone based on standard compound injection (Figs. S26 and S30).  
332 Thus, peaks 1 and 3 were suspected as either 6- or 9-monohydrochlordecones (Fig. S26), supported by the  
333 expected four monohydrochlordecone isomers of chlordecone upon first Cl substitution (Fig. 1).<sup>19,47</sup> Because no  
334 available chemical standards exist for these two suspected isomers, the full identification of peaks 1 and 3 as  
335 either 6- or 9 monohydrochlordecones was not possible.

336 Chlordecone transformation by ZVI<sub>f</sub> produced the 10-monohydrochlordecone isomer as the major TP,  
337 followed by 8-monohydrochlordecone in minor amounts after 39 h of reaction (Fig. 3a). Based on the ratio  
338 between peak areas of TPs and chlordecone by GC-qMS (i.e., Area TP/Area CLD<sub>initial</sub>), 10-  
339 monohydrochlordecone accounted for 54% of the degraded chlordecone (Fig. S48). Five dihydrochlordecone  
340 isomers (i.e., substitution of 2 Cl atoms) were also identified after 39 h (Fig. S21), while the number of  
341 hydrochlordecone TPs increased upon complete removal of chlordecone. Up to 15 hydrochlordecones were  
342 detected at the end of the monitoring period (239 h), indicating removal of up to 5 Cl atoms (Figs. S21 and S31).  
343 This is also consistent with measured increase in chloride concentrations (Fig. S18). Overall, results are in good

344 agreement with Belghit et al.<sup>31</sup> who identified 14 hydrochlordecones during chlordecone reduction via ZVI.  
345 Moreover, the similar formation of hydrochlordecones observed in reactions with ZVI<sub>f</sub> and ZVI<sub>s</sub> powders (Figs.  
346 S21-S22 and S31-S32) confirms that different iron types result in a large number of chlordecone dechlorination  
347 products. This raises questions about their mobility and long-term persistence in chlordecone contaminated soils.



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349 Figure 3. LC-QTOF-MS chromatograms of four monohydrochlordecone isomers observed in (a) ZVI<sub>r</sub>, (b) VSS,  
 350 (c) alkaline AA, and (d) MWPS reactions with time (reaction time indicated on the left of the x-axis). Four  
 351 monohydrochlordecone isomers are shown in colored chromatographic peaks eluting at 6.44 min (peak 1, brown),  
 352 6.68 min (peak 2, blue), 6.95 min (peak 3, green), and 7.09 min (peak 4, pink). Peaks 2 and 4 were attributed to  
 353 10-monohydrochlordecone and 8-monohydrochlordecone, respectively. Peaks 1 and 3 were suspected as either  
 354 6- or 9-monohydrochlordecone. Relative abundance is shown relative to the highest peak.

355 On the other hand, only four hydrochlordecones were identified during chlordecone transformation by  
356 VSS (Fig. S23), with a maximal removal of 2 Cl atoms. This enlarges previous findings only reporting 10-  
357 monohydrochlordecone during reactions by VSS.<sup>24,38</sup> In agreement and similarly as ZVI reactions, the 10-  
358 monohydrochlordecone isomer was the major TP and accounted for 46% of the degraded chlordecone (Fig. S48).  
359 Traces of a second monohydrochlordecone isomer (peak 1) appeared only after 6.5 h (Figs. 3b and S23). Results  
360 suggest that degradation mechanisms acting upon chlordecone reactions by ZVI and VSS produce a first Cl  
361 substitution at the C<sub>10</sub>-position, although the number of total hydrochlordecone TPs formed largely differs  
362 between these two reactions (Figs. S21-S23).

363 Chlordecone transformation by alkaline AA resulted in the formation of four monohydrochlordecone  
364 isomers (Fig. 3c). Contrastingly, 8-monohydrochlordecone was the main TP and accounted for 27% of the  
365 degraded chlordecone (Fig. S48), followed by 10-monohydrochlordecone and traces of peaks 1 (RT: 6.44 min)  
366 and 3 (RT: 6.95 min). In addition, one dihydrochlordecone and one trihydrochlordecone isomers were observed  
367 at the end of the reaction (Fig. S24). The prevalence of 8-monohydrochlordecone (peak 4, pink) differs from ZVI  
368 and VSS reactions, which consistently showed 10-monohydrochlordecone (peak 2, blue) as the major TP (Figs.  
369 3a and 3b). This suggests a mechanism by alkaline AA in which the first Cl substitution of chlordecone occurs at  
370 the C<sub>8</sub>-position. Indeed, the 8-monohydrochlordecone isomer (5b-hydrochlordecone, CAS nomenclature) was  
371 previously suggested as an impurity in chlordecone formulations. However, detected high amounts of 8-  
372 monohydrochlordecone in FWI soils are better explained by chlordecone transformation processes of rather  
373 natural origin which have not yet been identified.<sup>6,9,11</sup> Notably, transformation of the pesticide atrazine by AA  
374 was demonstrated at neutral pH.<sup>63</sup> Although the association between AA (vitamin C) and chlordecone  
375 transformation in FWI soils has not been studied to date, agricultural soils containing natural occurring vitamin  
376 C could trigger abiotic chlordecone transformation processes. Complementary studies of chlordecone  
377 transformation by vitamin C in neutral soils are needed to explore this hypothesis.

378 Similarly, the 8-monohydrochlordecone isomer was observed as the main TP during chlordecone  
379 transformation in MWPS reactions and accounted for 25% of the degraded chlordecone (Fig. S48). Peak 3 and

traces of 10-monohydrochlordecone were also observed (Fig. 3d). In addition, traces of a dihydrochlordecone isomer were observed only after 15 min of the reaction (Fig. S25). Notably, 8-monohydrochlordecone and few dihydrochlordecone isomers were also identified during photolysis,<sup>20</sup> and aerobic microbial transformation reactions.<sup>70</sup> These results strongly suggest that radical-mediated mechanisms, such as those also involved in MWPS, likely trigger the first Cl substitution at the C<sub>8</sub>-position. Overall, results from these abiotic transformation reactions are consistent with Dolfing et al.<sup>47</sup> who showed that four monohydrochlordecone isomers (Fig. 1) are expected during chlordecone transformation reactions upon first Cl substitution, and proposed 8-monohydrochlordecone as the most thermodynamically stable isomer based on standard Gibbs free energy. Further, authors suggested that different mechanisms may trigger the formation of distinct monohydrochlordecone isomers, in agreement with this study (Fig. 3). The fact that some monohydrochlordecone isomers (peaks 1 and 3) could not be fully assigned with our methods highlights the hitherto analytical challenges in identifying chlordecone TPs, although recent studies have considerably improved the discovery of new TPs.<sup>24,28</sup>

### **C and Cl isotope analyses confirm distinct chlordecone degradation mechanisms**

Significant C and Cl isotope fractionation was observed among abiotic transformation reactions of chlordecone (>2‰) (Figs. 2 and S12). Reactions with ZVI<sub>f</sub> showed an enrichment of <sup>13</sup>C with δ<sup>13</sup>C values increasing from -29.4 ± 0.2‰ to -23.7 ± 0.4‰, which resulted in an ε<sub>C,bulk</sub> value of -2.3 ± 0.2‰ (Table 1, Fig. S49). In other words, chlordecone molecules containing one <sup>13</sup>C atom reacted 2.3‰ slower than those containing only <sup>12</sup>C atoms. Similarly, reactions with ZVI<sub>s</sub> resulted in an ε<sub>C,bulk</sub> value of -2.7 ± 0.9‰. These results differ somewhat from previously reported for reductive dechlorination of chlordecone by ZVI (ε<sub>C,bulk</sub> = -4.1 ± 0.8‰).<sup>38</sup> However, VanStone et al.<sup>71</sup> showed differences in reaction rates and C isotope fractionation of PCE and vinyl chloride depending on the iron type used. The selection of ε<sub>C,bulk</sub> values for pollutant transformation assessment during remediation via ZVI should thus be in accordance with the iron type used. On the other hand, an ε<sub>C,bulk</sub> value of -3.5 ± 0.3‰ was observed in VSS reactions, slightly different from previously reported (-2.6 ± 0.4‰).<sup>38</sup> A similar ε<sub>C,bulk</sub> value of -3.7 ± 0.2‰ was also observed for MWPS reactions, while reactions with alkaline AA

404 resulted in larger C isotope fractionation ( $\epsilon_{C,bulk} = -4.3 \pm 0.4\%$ ). Notably, large  $\epsilon_{C,bulk}$  values were so far reported  
 405 for biotic transformation reactions by a pure *Citrobacter* strain and a mixed consortium culture (Table 1).<sup>38</sup>

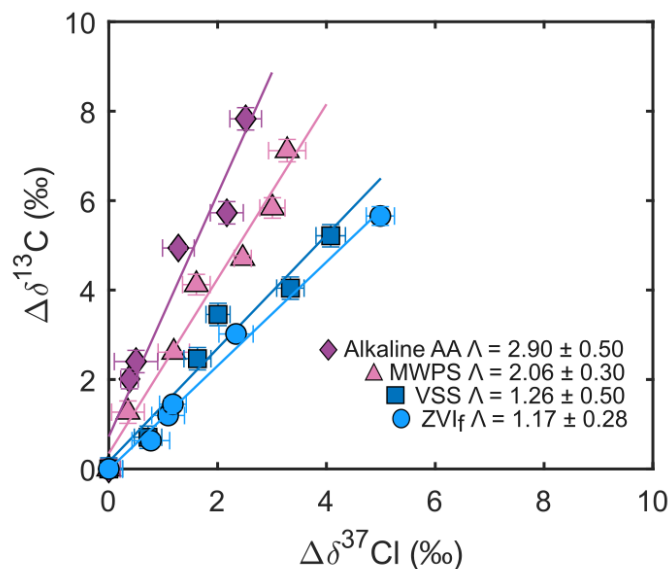
406 Cl-CSIA of chlordecone was developed using a novel method by LC-QTOF-MS,<sup>41</sup> offering new insights  
 407 into chlordecone degradation mechanisms. Abiotic chlordecone transformation reactions showed an enrichment  
 408 of <sup>37</sup>Cl upon C-Cl bond cleavage. Reactions with ZVI<sub>f</sub> and VSS consistently showed larger <sup>37</sup>Cl enrichment with  
 409  $\Delta\delta^{37}\text{Cl}$  ranging between 4.1‰ and 5.0‰ (Figs. 2b and 2d). Contrastingly, lower <sup>37</sup>Cl enrichment was observed  
 410 in reactions with alkaline AA and MWSP ( $\Delta\delta^{37}\text{Cl}$  ranging between 2.5‰ and 3.3‰) (Figs. 2f and 2h). Cl isotope  
 411 fractionation values ( $\epsilon_{Cl,bulk}$ ) ranged from  $-1.8 \pm 0.2\%$  to  $-2.6 \pm 0.4\%$  (Table 1).

412 Table 1. Available data of C and Cl isotope fractionation of chlordecone during abiotic and biotic transformation  
 413 reactions. Reactions were performed under neutral or (‡) alkaline (pH>12) conditions. n.a. = not analyzed, n.d.=  
 414 not determined.

Experiment	Condition	$\Delta\delta^{13}\text{C}$ (‰)	$\Delta\delta^{37}\text{Cl}$ (‰)	$\epsilon_{C,bulk}$ (‰)	$\epsilon_{Cl,bulk}$ (‰)	$\Lambda$	Reference
<b>Abiotic transformation</b>							
Zero-valent iron (ZVI <sub>f</sub> powder)	anoxic	5.6	5.0	$-2.3 \pm 0.2\%$	$-1.8 \pm 0.2\%$	$1.17 \pm 0.28$	This study
Zero-valent iron (ZVI <sub>s</sub> powder)	anoxic	2.5	n.a.	$-2.7 \pm 0.9\%$	n.d.	n.d.	This study
Zero-valent iron	anoxic	7.8	n.a.	$-4.1 \pm 0.8$	n.d.	n.d.	Chevallier et al. <sup>38</sup>
Vitamin B <sub>12</sub> and sodium sulfide † (VSS)	anoxic	5.2	4.1	$-3.5 \pm 0.3\%$	$-2.6 \pm 0.4\%$	$1.26 \pm 0.50$	This study
Vitamin B <sub>12</sub> and sodium sulfide †	anoxic	4.0	n.a.	$-2.6 \pm 0.4$	n.d.	n.d.	Chevallier et al. <sup>38</sup>
Vitamin B <sub>12</sub> and titanium (III) citrate †	anoxic	1.5	n.a.	$-0.8 \pm 0.4$	n.d.	n.d.	Chevallier et al. <sup>38</sup>
Alkaline ascorbic acid (AA)	oxic	7.8	2.5	$-4.3 \pm 0.4\%$	$-1.3 \pm 0.3\%$	$2.06 \pm 0.30$	This study
Sodium persulfate and microwave irradiation (MWSP) †	oxic	7.1	3.3	$-3.7 \pm 0.2\%$	$-1.8 \pm 0.2\%$	$2.90 \pm 0.50$	This study
<b>Biotic transformation</b>							
Pure <i>Citrobacter</i> strain	Anoxic	5.0	n.a.	$-6.8 \pm 2.2$	n.d.	n.d.	Chevallier et al. <sup>38</sup>
Mixed Consortium 86_1	Anoxic	7.7	n.a.	$-4.6 \pm 1.4$	n.d.	n.d.	Chevallier et al. <sup>38</sup>

415  
 416 Dual isotope plots showed distinct  $\Lambda$  values among the four chlordecone transformation reactions (Fig.  
 417 4). Slopes were not significantly different between ZVI<sub>f</sub> and VSS reactions, with  $\Lambda$  values of  $1.17 \pm 0.28$  and  $1.26$   
 418  $\pm 0.50$ , respectively (Table 1). Contrastingly, larger  $\Lambda$  values were observed for MWPS and alkaline AA reactions  
 419 of  $2.06 \pm 0.30$  and  $2.90 \pm 0.50$ , respectively. Such differences in  $\Lambda$  values reflect the occurrence of different  
 420 reaction mechanisms acting upon chlordecone degradation. Fig. 4 also shows abiotic reactions from which

421 different monohydrochlordecone isomers were observed. Main TPs were 8-monohydrochlordecone (in pink) and  
422 10-monohydrochlordecone (in blue), with Cl substitution at C<sub>8</sub>- and C<sub>10</sub>-positions, respectively (Figs. 1 and 3).  
423 Isotope fractionation upon bond-cleavage reactions is linked to primary isotope effects affecting reacting bonds  
424 (i.e., C-Cl). However, adjacent bonds may also be slightly affected (secondary isotope effects) by the proximity  
425 to the reaction center, which may arise from changes in coordination geometry.<sup>50</sup> In the case of chlordecone, a  
426 second Cl atom is in the geminal position relative to the reactive center at the C<sub>10</sub>-position (Fig. 1), which is not  
427 the case at the C<sub>8</sub>-position (Fig. 1). On this basis, it seems reasonable to speculate that the observed larger <sup>37</sup>Cl  
428 enrichment in reaction mechanisms forming 10-monohydrochlordecone as the main TP may arise from secondary  
429 Cl isotope effects (Fig. 4 and Table 1). Such differences in Cl isotope effects were also observed for other  
430 chlorinated compounds such as  $\alpha$ - and  $\gamma$ -hexachlorocyclohexane showing different orientations of Cl atoms in the  
431 adjacent non-reactive bond.<sup>72</sup> Hence, the position at which Cl substitution occurs upon chlordecone  
432 transformation likely affects Cl isotope signatures, and may reflect the occurrence of secondary effects or  
433 intramolecular competition. Particularly, the C<sub>10</sub>-position in chlordecone presents less steric hindrance due to the  
434 relatively strain-free five-membered ring,<sup>47</sup> making this position more prone to nucleophilic substitution by ZVI  
435 and vitamin B<sub>12</sub> (with sodium sulfide) than the C<sub>8</sub>-position (Fig. 1). Further, the formation of 8-  
436 monohydrochlordecone in MWPS and alkaline AA reactions, resulting in the largest  $\Delta$  values reported so far,  
437 also points out to the possibility of chlordecone transformation by alkaline AA involving a radical-mediated  
438 mechanism. However, monitoring AA dissociation products and quenching experiments would be required to  
439 confirm the possible effect of ascorbate radical intermediates in chlordecone transformation. A validation of ME-  
440 CSIA of chlordecone from field samples, and in combination with chlordecone TP searching methodologies, may  
441 provide a reliable line of evidence of *in-situ* chlordecone degradation mechanisms and assist in the remediation  
442 of chlordecone contaminated soils.



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Figure 4. Dual plot of C and Cl isotope fractionation during abiotic chlordecone transformation reactions: ZVI<sub>x</sub> (circles), VSS (squares), MWPS (triangles), and alkaline AA (diamonds). Dark and light pink colors (diamonds and triangles, respectively) indicate reactions producing 8-monohydrochlordecone as the main TP. Dark and light blue colors (squares and circles, respectively) indicate reactions producing 10-monohydrochlordecone as the main TP.

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ME-CSIA of chlordecone also offers the opportunity to fingerprint sources of chlordecone pollution from pesticide formulations. C and Cl isotope signatures of a Curlone<sup>®</sup> formulation sample were also obtained. Curlone<sup>®</sup> samples showed a  $\delta^{13}\text{C}$  signature of  $-30.36 \pm 0.45\text{‰}$  ( $n = 3$ ). These  $\delta^{13}\text{C}$  values are similar to previously reported for other Curlone<sup>®</sup> formulations ( $-34.2 \pm 0.2\text{‰}$  to  $-31.1 \pm 0.2\text{‰}$ ).<sup>38</sup> On the other hand, Cl isotope analysis of Curlone<sup>®</sup> samples resulted in a  $\delta^{37}\text{Cl}$  signature of  $-0.82 \pm 0.53\text{‰}$  ( $n = 14$ ). No  $\delta^{37}\text{Cl}$  signatures of other chlordecone formulations have been reported so far. Both C and Cl isotope signatures of Curlone<sup>®</sup> samples are close to available chlordecone chemical standards (Table S5), which is consistent with isotope signatures reported for other pesticides formulations and their respective chemical standards.<sup>73</sup> This suggests that tracking chlordecone transformation in soils with a ME-CSIA approach is feasible, which may help identifying contaminant sources of chlordecone and quantitatively evidencing the extent of chlordecone transformation in contaminated soils.

## Environmental implications of ME-CSIA for the remediation of chlordecone-contaminated soils

Chlordecone pollution of FWI soils is a challenging environmental issue that warrants continuous attention. Evidence of the high recalcitrance of chlordecone over the last decades highlights the need for efficient remediation strategies of FWI soils. This study shows that abiotic transformation of chlordecone under reducing and oxidative conditions can effectively take place and could be a strategy for soil remediation. Notably, this study explores two alternatives involving alkaline AA and PS activated by MW irradiation, which can complement current remediation techniques for chlordecone requiring the establishment of strong reducing conditions in soils, such as ZVI. The formation of different monohydrochlordecone isomers, along with the lack of available standards for their quantification and identification, also highlights the difficulty in solely relying on TPs to track chlordecone degradation in environmental samples. Moreover, while chlordecone transformation was evidenced under both reducing and oxidative conditions, no complete mineralization of chlordecone was observed in this study, which highlights the difficulty in assessing chlordecone remediation without addressing the fate of chlordecone TPs, such as the numerous hydrochlordecones identified in this study.

Complementary, ME-CSIA of chlordecone proves feasible as another line of evidence of chlordecone transformation in soils, supported by C and Cl isotope fractionation observed during abiotic transformation reactions.  $\epsilon_{C,bulk}$  values of chlordecone could thus be implemented with confidence to quantitatively evidence the extent of chlordecone transformation in soils, provided that sufficient chlordecone transformation has occurred. Further, correlations between C and Cl isotope signatures also suggests the occurrence of distinct degradation mechanisms of chlordecone, and points out to mechanisms triggering first Cl substitutions at the C<sub>10</sub>-position (forming 10-monohydrochlordecone) and C<sub>8</sub>-position (forming 8-monohydrochlordecone) during abiotic reactions, possibly reflecting nucleophilic substitution or radical-mediated mechanisms, respectively. ME-CSIA of chlordecone during biotic transformation reactions has not yet been established. However, if distinct C and Cl isotope signatures were observed during microbial-mediated reactions of chlordecone, the occurrence of biotic or abiotic reaction mechanisms could in principle be distinguished based on C and Cl isotope signatures in chlordecone contaminated soils. Overall, our study shows that ME-CSIA of chlordecone can assist in conducting appropriate monitoring of soil remediation and reduce current challenges of monitoring chlordecone

488 transformation in FWI soils. Future large-scale pilot experiments of chlordecone degradation in soils are  
489 necessary to validate our proposed ME-CSIA approach of chlordecone at environmentally relevant concentrations  
490 from field soil samples.

491

## 492 **Associated content**

493 Technical details of experimental setups, analytical methods, extraction efficiencies, control experiments, mass  
494 spectra, chromatograms of detected TPs, and Rayleigh plots (PDF).

495 Calculations of chlorine isotope ratios of chlordecone (XLSX).

## 496 **Author Information**

### 497 **Corresponding Author**

498 Patrick Höhener – Aix-Marseille Université, CNRS, Laboratoire Chimie Environnement (LCE), Marseille,  
499 France; Email: patrick.hohener@univ-amu.fr

## 500 **Authors**

501 Maria Prieto-Espinoza – Aix-Marseille Université, CNRS, Laboratoire Chimie Environnement (LCE),  
502 Marseille, France; <sup>+</sup>Present Address: Department of Earth and Environmental Sciences, University of Waterloo,  
503 Waterloo, Ontario N2L 3G1, Canada; orcid.org/0009-0001-4243-4574

504 Laure Malleret – Aix-Marseille Université, CNRS, Laboratoire Chimie Environnement (LCE), Marseille,  
505 France; orcid.org/0000-0001-7146-8303

506 Amandine Durand – Aix-Marseille Université, CNRS, Laboratoire Chimie Environnement (LCE), Marseille,  
507 France

## 508 **Notes**

509 The authors declare no competing financial interest.

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