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Comparison of the Effectiveness, Kinetics and Costs of Three Remediation Techniques for Agricultural Soils Historically Contaminated with Dieldrin, Using Laboratory Experiments

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32 1. Introduction

33 Organochlorine Pesticides (OCPs), including Dieldrin, have been largely used in agriculture to protect
34 vegetable between 1950 to the end of 1970 (Hashimoto, 2005; Jorgenson, 2001; Morillo and Villaverde,
35 2017). In France, Dieldrin was banned in agriculture in 1972, but its complete ban on marketing and use
36 did not come until 1992 (INRS, 2007). However, fifty years after its prohibition, Dieldrin is still present
37 in soil and continue to be a potential source of contamination especially for vegetable, with
38 contamination at concentrations exceeding Maximum Residue Level (MRL) fixed by regulatory
39 institutions (Namiki et al., 2018, 2015; Saito et al., 2011; Tsiantas et al., 2021). There is thus a need of
40 soil remediation for these contaminated agricultural soils.

41 In the literature, a lot of physicochemical technologies for the remediation of OCPs contaminated soil
42 have been studied like immobilisation, separation or destruction (Castelo-Grande et al., 2010; Morillo
43 and Villaverde, 2017). However, some of these techniques are still in development at laboratory scale
44 and they were most of the time tested on artificially contaminated soil (Al-Marzouqi et al., 2019, 2007;
45 Bielská et al., 2013; Falciglia et al., 2011a) and rarely with Dieldrin. Although experiment with spiked
46 soil is an effective tool for testing various parameters of the remediation process, spiked samples are
47 barely suitable for aged contamination (Anitescu and Tavlarides, 2006; Bielská et al., 2013; Ling and
48 Liao, 1996; Saldaña et al., 2005). Indeed, it is well established now that the behaviour of freshly applied
49 OCPs on the soil is different from the one of historical contamination due to the higher sequestration
50 and OCP stronger binding to soil compounds such as SOM (Benner, 2015; Gonçalves et al., 2006).
51 OCPs are therefore more difficult to reach and eliminate, due to the ageing effect (Alexander, 2000;
52 Duan et al., 2015; Jones and De Voogt, 1999; Ncibi et al., 2007; Pignatello and Nason, 2020). It is
53 necessary to test these physicochemical remediation technologies on aged contaminated agricultural
54 soils in order to validate their effectiveness to reduce the bioavailability of OCPs.

55 In this study, three physicochemical remediation techniques were tested on agricultural soil presenting
56 historical contamination with Dieldrin: Zero-Valent Iron (ZVI) degradation, Very Low Temperature
57 Thermal Treatment (VLTTT) and Supercritical Fluid Extraction (SFE) with CO₂. The selection of these
58 remediation techniques was based on a compromise between an efficiency of at least 50% reduction of
59 the concentration of OCPs in soils and less disruption of the agronomic properties of the soils, according
60 to literature.

61 Degradation of OCPs using ZVI or ZVI combined with other reagent as acetic acid (AA), aluminium
62 sulphate (AS), or surfactant, was well studied in the literature on several OCPs (Cao et al., 2013; Comfort
63 et al., 2001; Li et al., 2006; Ševců et al., 2017; Shea et al., 2004; Wu et al., 2017; Yang et al., 2010).
64 This technique is based on the dechlorination of OCPs, thanks to the reducing capacity of ZVI
65 (Boussahel et al., 2007). In the literature, ZVI amount of 5% (w/w) has been found to be optimal
66 (Boparai et al., 2008; Comfort et al., 2001; Satapanajaru et al., 2003). However, in these studies, the

67 tests were mostly conducted in aqueous or soil solutions and not directly in soil. Furthermore, in the few
68 studies dealing with soil, the concentrations of OCPs were relatively high ($> 1 \text{ mg kg}^{-1}$), sometimes due
69 to point source contamination from accidental product spills (Comfort et al., 2001; Dahmer et al., 2017;
70 Shea et al., 2004; Yang et al., 2010). This technique also shows other limitations: low reactivity, narrow
71 working pH, reactivity loss with time due to the precipitation of metal hydroxides, low selectivity for
72 the target contaminant and limited efficacy for treatment of some refractory contaminants (Guan et al.,
73 2015). Thus, the ZVI degradation needs to be directly tested on soil to validate its efficiency to degrade
74 Dieldrin from historically contaminated soil.

75 In the literature, thermal remediation techniques, also called Thermal Desorption (TD) can be
76 discriminated into 2 groups depending on temperature range: Low-Temperature Thermal Desorption
77 (LTTD) from 100 to 350°C and High-Temperature Thermal Desorption (HTTD) from 350 to 650°C
78 (O'Brien et al., 2018; Pavel and Gavrilescu, 2008; Wang et al., 2021; Yi et al., 2016; Zhao et al., 2019).
79 This process targets Volatile and Semi-Volatile Organic Compounds (VOC and SVOC) in soil, passing
80 them into the gas phase with direct or indirect heating (Wang et al., 2021) before their extraction from
81 soil. However, above 100°C, TD can lead to an alteration of soil properties such as Soil Organic Matter
82 (SOM), pH, texture, Cation Exchange Capacity (CEC) and therefore affects soil fertility and agricultural
83 production (Ding et al., 2019; O'Brien et al., 2018). Since the present study deals with agricultural soils,
84 it is of main importance to not degrade their agronomic qualities. Thus, in order to preserve soil
85 agronomic properties, it is necessary to test the efficiency of such technique below 100°C, tipping the
86 process into a Very Low-Temperature Thermal Treatment (VLTTT). These tests are essential to assess
87 the efficiency on soils formerly contaminated with Dieldrin.

88 SFE is an alternative for conventional solid-liquid extraction of OCPs from soils (Al-Marzouqi et al.,
89 2019; Koinecke et al., 1997; Marr and Gamse, 2000; Van der Velde et al., 1994). This physicochemical
90 method uses the properties of supercritical fluid like CO_2 (i.e. liquid-like density, low viscosity, high
91 diffusivity, and no surface tension) to extract contaminants. Most of the time CO_2 is used because its
92 critical point (31°C, 74 bar) is quite low (Anitescu and Tavlarides, 2006) and it has a strong affinity for
93 hydrophobic contaminants like Dieldrin (Jorgenson, 2001) due to its low polarity (Benner, 2015). The
94 CO_2 also offers other advantages such as being non-toxic, non-flammability, chemically stable,
95 environmentally acceptable and low cost (Al-Marzouqi et al., 2019; Sunarso and Ismadji, 2009).
96 However, this remediation technology was mainly tested on spiked soil (Al-Marzouqi et al., 2007;
97 Meskar et al., 2019, 2018) to optimize the experimental conditions as temperature, pressure, and flow
98 rate (Anitescu and Tavlarides, 2006; Benner, 2015; Gonçalves et al., 2006) or compare recoveries of
99 different contaminants (Koinecke et al., 1997; Kreuzig et al., 2000). For these reasons, SFE with CO_2
100 needs to be tested on historically contaminated soil to validate its efficiency.

101 Considering the above discussion, the objectives of the present study are (i) to compare the effectiveness
102 of the three remediation techniques on a soil historically contaminated with Dieldrin, (ii) to characterise
103 their kinetic of reaction and (iii) to estimate their costs. To achieve these goals, batch experiments with
104 20 to 120 g of historically contaminated soil were conducted during a maximum of 70 days for
105 degradation, 96 h for VLTTT and 4 h for SFE with CO₂. First-order kinetic models were applied and
106 optimised using *Excel* solver (Non-linear GRG). In addition, the treatment cost of each technique was
107 estimated for one ton of soil, taking into account the reagents and energy required. To our knowledge,
108 this is the first study dealing with a fully comparison of different remediation techniques on soil
109 historically contaminated by Dieldrin, including an economical aspect.

110

111 2. Material and Methods

112 2.1. Soil sampling

113 In order to perform the different experimentations, a natural soil historically contaminated with Dieldrin
114 was sampled with a manual shovel in an agricultural field located near Bordeaux (France). The bulk soil
115 was sampled between 0–20 cm depth from an area of 4 m² at the centre of the contaminated plot.
116 Approximately 60 kg of soil was collected and stored in a 60 L plastic barrel until experimentations.
117 The soil texture was 80.6% of coarse sand (2000-200 µm), 4.6% of fine sand (200-50 µm) and 14.9%
118 of silt and clay (< 50 µm) with an initial Dieldrin concentration about 100 µg kg⁻¹.

119 2.2. Soil remediation experiments

120 The following paragraphs describe the protocols used to characterise the efficiency and kinetics of the
121 selected remediation techniques. For each one, a few kilograms aliquot of the historically contaminated
122 bulk soil was homogenised in order to minimize contamination heterogeneity and ease results
123 interpretations. On each aliquot, 3 sub-samples were analysed to measure initial contamination (t = 0 h).

124 2.2.1. ZVI degradation

125 In order to observe the efficiency of ZVI treatment, 3 sets of batch experiments were conducted in 50 mL
126 glass flask containing 20 g of aged contaminated soil mixed with 5% (w/w) ZVI (99%, powder
127 < 212 µm, Arcos Organics, UK). The first set did not contain other additional reagent than ZVI, while
128 the second and the third contained 2% (w/w) of AS (Al₂(SO₄)₃, > 94%, Hexadecahydrate, Fisher
129 Scientific, France) and 0.5% of AA (100%, NORMAPUR®, VWR Chemicals, USA), respectively. The
130 flasks were hermetically capped with a stopped equipped with PTFE seal, homogenised manually and
131 then stored at 22°C in the dark. Each set was conducted in triplicate for each of the following incubation
132 times: 10, 20 and 30 days. However, in order to observe a potential delayed effect of this treatment, one
133 of the flask dedicated to the 30 d experiment was kept until 70 d prior analysis. In order to adapt to real
134 field application conditions, no agitation was carried out during these experiments after incorporation
135 of the treatments into the soil.

136 2.2.2. Very low-temperature thermal treatment (VLTTT)

137 Concerning VLTTT, 3 temperatures were tested and for each one, aliquots of 20 g of contaminated soil
138 were placed in aluminium tray and heated in an oven (Venticell 55, MMM Medcenter, Germany) at 50,
139 70 or 90°C. Soils were heated during 0.5, 1, 3, 5, 7, 16, 24, and 96 h and the gas phase of the oven was
140 renewed 123 times per hour. For each time and temperature condition, triplicates were conducted. After
141 cooling, soil was stored in 50 mL glass flask at room temperature until analyses. No agitation was
142 conducted during these experiments.

143 2.2.3. Supercritical fluid extraction with CO₂

144 The experiments using SFE with CO₂ were conducted with the system described in Cario et al. (2022).
145 A high-pressure stainless steel reactor (Top Industrie, France) with a maximal internal volume of
146 300 mL was filled with approximately 120 g of contaminated soil. The system was heated to 50°C
147 thanks to the preheating coil and the ceramic heating ring. The pressure in the autoclave was increased
148 with a high-pressure pump (MiltonRoy, USA) allowing to set CO₂ (CO₂ 4.8, Messer, Switzerland)
149 pressure to 200 bar. About 30-40 min were needed to reach these conditions. The experiments were
150 conducted during 1, 2.25 and 4 h with a continuous flow of CO₂ of approximately 800 mL h⁻¹. After
151 soil treatment, the back-pressure regulator (BPR) allowed a fast depressurization at 5 bar min⁻¹. Once
152 depressurisation was completed, the treated soil was recovered, homogenised and stored in hermetic
153 glass flask until analysis. These experiments were conducted once for each treatment time.

154 2.3. Analysis of Dieldrin in soil

155 The analyses of Dieldrin in treated soil were carried out on the whole soil contained in each batch (20 g
156 of bulk soil and eventual reagents) for ZVI and VLTTT experiments, while a sub-aliquot of 20 g of
157 treated soil was analysed after homogenisation for the CO₂ treatment. Dieldrin quantification in soil
158 before and after treatment was conducted following the procedure presented in Colin et al. (2022).

159 2.4. Kinetic model

160 In order to characterise and compare the kinetic of the tested remediation techniques, first order model
161 is typically used (Alonso et al., 2002; Falciglia et al., 2011a; La Mori et al., 2010; Wang et al., 2011).
162 Since the heterogeneity of the concentration of Dieldrin in the soil could be considered up to 20%, the
163 models were only applied to treatments showing an efficiency of at least 40%. The following equation
164 (1.0) adapted from Northcott and Jones, (2001) was used to account for the thermodynamic thresholds
165 achieved for each of the techniques.

$$166 R_t = (1 - R_\infty) \times e^{-kt} + R_\infty \quad (1.0)$$

167 Where R_t is the ratio of Dieldrin concentration in soil at t time and $t = 0$ ($R_t = [Dieldrin]_t/[Dieldrin]_0$
168 , dimensionless), R_∞ is the ratio of the residual Dieldrin concentration in soil and the initial
169 concentration at $t = 0$ ($R_\infty = [Dieldrin]_\infty/[Dieldrin]_0$, dimensionless), k is the first order kinetic
170 constant (h⁻¹) and t the time (h).

171 Models were optimised using *Excel* solver (Non-linear GRG) and compared with the null model
172 according to the Modelling Efficiency (ME) defined in equation (2.0) (Mayer and Butler, 1993).

$$173 ME = 1 - \frac{\sum (y_i - \hat{y}_i)^2}{\sum (y_i - \bar{y})^2} \quad (2.0)$$

174 Where \bar{y} is the mean of the observed variable, \hat{y}_i is the predicted variable (from the model) and y_i is the
175 observed variables. ME range from 0 (model not better than the null model \bar{y}) to 1 (perfect relationship).

176 2.5. Costs of remediation techniques

177 In order to financially evaluate and compare the remediation techniques investigated in this study, the
178 costs of each technique were estimated considering 1 ton of contaminated soil and taking into account
179 reagent prices as well as the energy/electricity required, depending on the technique. Thus, the following
180 general equation (3.0) was considered:

$$181 \quad \text{Costs} = P_{\text{Reagents}} + P_{\text{Energy}} \quad (3.0)$$

182 The first term in equation (3.0), P_{Reagents} is the price of the different reagents used in the degradation
183 technique as ZVI, AS or AA, depending on the reagent price (P_i , € kg⁻¹, Table S1) and the mass
184 percentage (x_i) considered to treat a mass of contaminated soil (m_{soil}). P_{Reagents} is described in the
185 equation (3.1):

$$186 \quad P_{\text{Reagents}} = m_{\text{soil}} \times \sum_i (P_i \times x_i) \quad (3.1)$$

187 The second term in equation (3.0), P_{Energy} , represents the energy costs for heating and keeping the
188 defined temperature. For VLTTT and SFE, as systems are not perfectly insulated heat loss are
189 considered. Thus, this term takes into account the energy needed to heat the soil to a certain temperature
190 (Energy_1) and the energy to maintain the treatment temperature (Energy_2) while the soil is flushed by
191 a fluid (air or CO₂). The term $P_{\text{Electricity}}$ represents the price of electricity (€ kWh⁻¹), P_{Energy} is
192 described in the equation (3.2):

$$193 \quad P_{\text{Energy}} = (\text{Energy}_1 + \text{Energy}_2) \times P_{\text{Electricity}} \quad (3.2)$$

194 The two terms Energy_1 and Energy_2 are calculated with the equation (3.2.0) as described by Schön
195 (2015):

$$196 \quad \text{Energy} = C \times (T_f - T_i) \times m \quad (3.2.0)$$

197 Where C is the thermal capacity (J °C⁻¹ kg⁻¹) of soil or carrier fluid, T_i and T_f are respectively the initial
198 and final temperature of the experiment (°C) and m is the mass (kg) of matter.

199 According to equation (3.0), the costs for ZVI degradation techniques are only calculated with the factor
200 P_{Reagents} since no energy is supplied to the system ($P_{\text{Energy}} = 0$). The cost for VLTTT was estimated
201 with the P_{Energy} only and for SFE with CO₂ the cost estimation is conducted with the complete equation
202 (3.0) since the purchase of CO₂ is considered.

203 The conversion rate of \$1 = €0.88 has been used to compare present costs with those found in the
204 literature. Apparent density of 1.49 ton m⁻³ (Bruand et al., 2004) was used to convert volume cost (€ m⁻³)

205 from literature into mass cost (€ ton⁻¹) and the mass cost was also convert into a surface cost (€ ha⁻¹) for
206 the treatment of the first 40 cm of soil, since 85% of the contamination is found in this layer (Colin et
207 al., 2022). At this depth, the treatment of an area of 1 ha is equivalent to the treatment of 5960 tons of
208 soil.

209

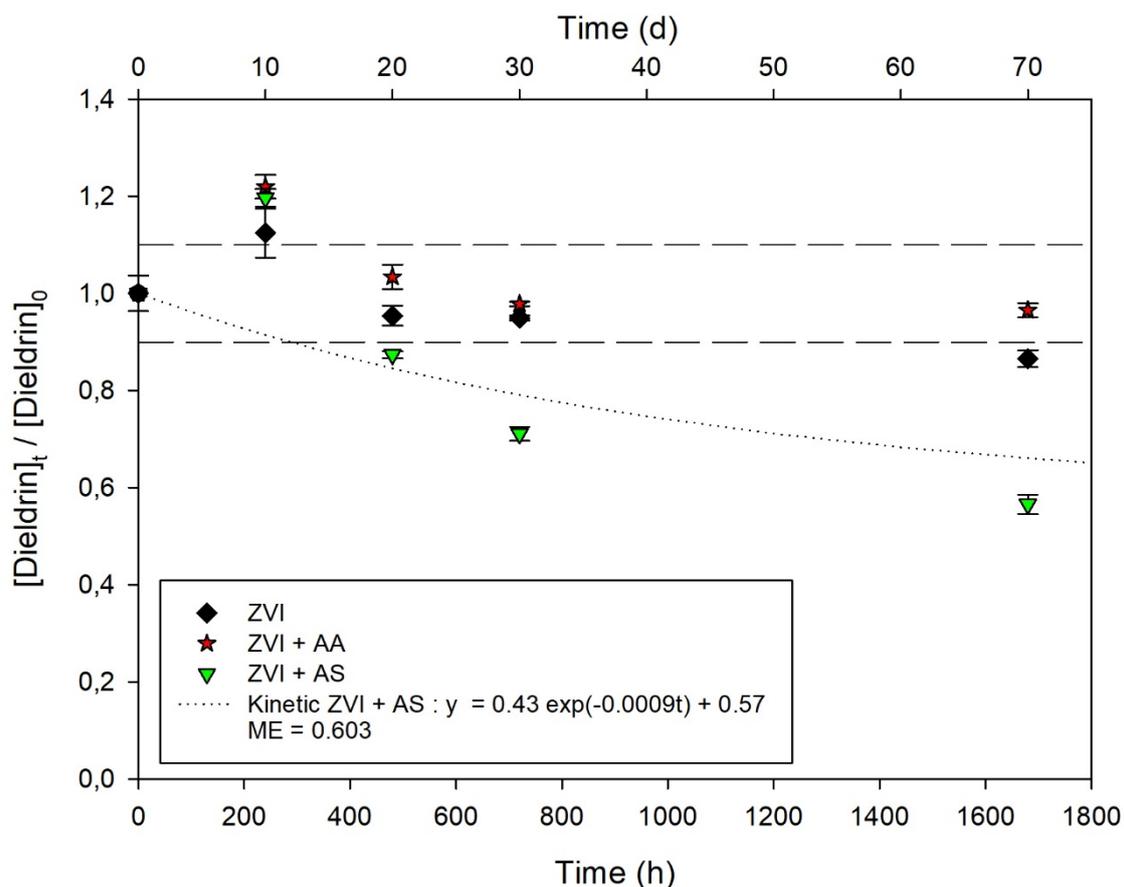
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211 3. Results and discussion

212 The following paragraphs detail the results regarding efficiency, kinetic and cost for the 3 techniques
213 tested and discuss them according to the literature.

214 3.1. ZVI degradation

215 The Figure 1 presents the ratios of Dieldrin concentration in soil for degradation with ZVI and others
216 reagents after 10, 20, 30 and 70 d. For the three treatments, a slight increase in the ratio from 1 to 1.2 is
217 noted after 10 d of experiments, but this remains the 20% heterogeneity of the initial soil. For ZVI and
218 ZVI + AA treatments, the ratio R_t stay close to 1, showing no significant change in the concentration of
219 Dieldrin in the soil, even after 70 d of treatment. Regarding the treatment ZVI + AS, the results show a
220 decrease in Dieldrin concentration with a maximum decline of 40% after 70 d. This decrease can be
221 approximated by a first-order kinetic model which is classically used for the degradation of organic
222 compounds with ZVI in aqueous solution (Boparai et al., 2008; Boussahel et al., 2007; Cao et al., 2013;
223 Satapanajaru et al., 2003; Wang et al., 2011), with a constant k of $9.3 \times 10^{-4} \text{ h}^{-1}$ and the model fitted the
224 data at 60.3% according to the ME calculation.



225
226 *Figure 1 : Effect of ZVI, ZVI + AA and ZVI + AS treatments on Dieldrin concentration in the soil against time (h). The long*
227 *dashed line indicates the soil heterogeneity interval.*

228 There are still uncertainties about ZVI dechlorination effect on chlorine compounds, with contradictory
229 studies. Indeed, Comfort et al. (2001) and Shea et al. (2004) observed a decrease in metolachlor
230 concentration of 70 and 98% in the soil directly after 90 days with ZVI, ZVI + AA or ZVI + AS. In
231 contrast, the results of Dahmer et al. (2017) showing that the *in situ* application of DARAMEND®
232 (commercial product composed of 40-50% ZVI and 50-60% Organic Matter) at 2% (w/w) had no effect
233 on Dieldrin and DDT concentrations, and the same observations were reported by Ševců et al. (2017)
234 indicating that ZVI was ineffective in treating PCBs in the soil

235 The physicochemical properties of the contaminants could explain these differences, the accessibilities
236 to the reduction of chlorine atoms must depend on the molecules. Indeed, Yang et al. (2010) showed a
237 slight effect of ZVI to degrade some DDx and HCx, only β -HCH, DDT and DDE were affected, as well
238 as the capacity of ZVI to degrade Dieldrin in soil seems to be limited. The application conditions and
239 the properties of the soil (moisture, pH, SOM content) could also be taken into account regarding the
240 efficiency of this technique. Indeed, in the present work no agitation of the batches was carried out
241 during the 70 d of experimentation in order to preserve real application conditions, but this limits the
242 contact between the soil and the ZVI. Even if this technic had limited effect in the present case, better
243 incorporation of solid particles (ZVI and AS) into soils by regular mixing with mechanical tools and the
244 addition of a desorption agent (Wu et al., 2017) could enhance the efficiency of the technique.

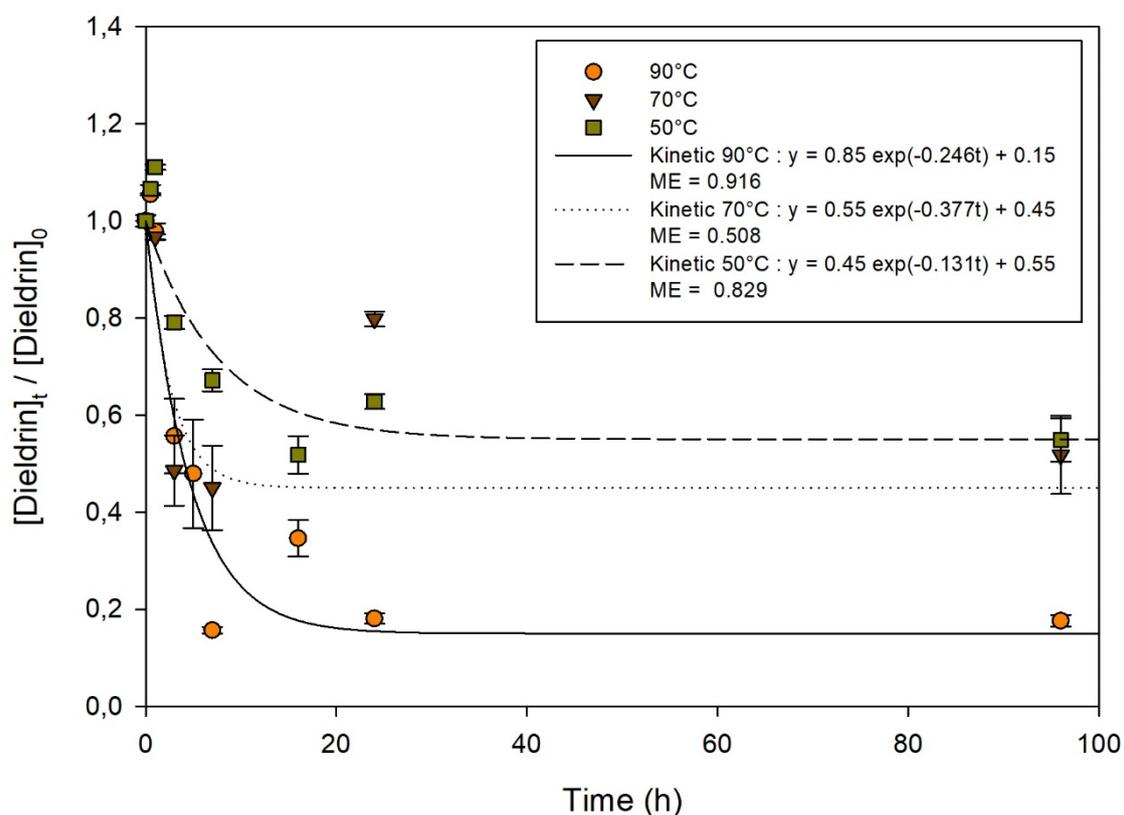
245 The initial concentration of the contaminant could also explain the differences in effectiveness. In
246 Comfort et al. (2001) study, the concentration of metolachlor was very high (1700 mg kg^{-1}), probably
247 making the contaminant more available for ZVI treatment than at low concentration. However, even
248 with high efficiencies (75-95%) in reducing metolachlor concentrations, these were still between 40 and
249 500 mg kg^{-1} after 90 d, thus 400 or 5000 times higher than the initial concentration of Dieldrin found in
250 the present work (0.1 mg kg^{-1}). Since, this very low concentration of Dieldrin is always a problem for
251 agricultural field, the ZVI degradation could be suitable only for highly contaminated sites.

252 Furthermore, in the study of Yang et al. (2010), the total amount DDx did not changed because DDT
253 was degraded to DDD. As DDD is more toxic than DDT (Cao et al., 2013), the ZVI remediation
254 technique seems barely suitable for agricultural soils. Thus, in the present case, even with the moderate
255 decrease (40%) in Dieldrin concentration after 70 days with ZVI + SA application, more toxic Dieldrin
256 by-products could potentially be formed. Their determination and quantification, as well as the fate of
257 iron and sulphate in the soil must be investigated prior application on agricultural field.

258

259 **3.2. Very low-temperature thermal treatment**

260 Results of the thermal experimentation are presented in Figure 2, showing the Dieldrin ratio against
 261 incubation times. Before 1 h of treatment, the VLTTT at each temperature does not seem to have any
 262 effect on the concentration of Dieldrin, which remains within the initial soil heterogeneity. When the
 263 soil is heated to 50°C, the concentration of Dieldrin decreases during 40 h and stabilises at 45%
 264 efficiency thereafter. This decrease can be modelled by a first order kinetic model, with a constant k of
 265 $1.3 \times 10^{-1} \text{ h}^{-1}$ and an ME of 82.9%. At 70°C, the decrease is faster with a constant k of $3.8 \times 10^{-1} \text{ h}^{-1}$ but
 266 also reaches a stabilisation after 20 h, showing an efficiency of 55% and a ME of 50.8%. This low ME
 267 is due to the 24 h value which seems very high compared to the general trend. For heating to 90°C, the
 268 associated k constant is $2.5 \times 10^{-1} \text{ h}^{-1}$ but shows a greater decrease in Dieldrin concentration with a
 269 stabilisation at 85% efficiency after 24 h and a ME of 91.6%.



270

271 *Figure 2 : Effect of VLTTT on Dieldrin concentration in soil against time (h)*

272 These decreases in Dieldrin concentration can be modelled by first-order kinetics that were previously
 273 observed by (Falciglia et al., 2011a) with spiked hydrocarbons on soil for temperatures between 100 and
 274 300°C. Gao et al. (2013) described the same kinetics on soil contaminated with aged DDx with k -
 275 constants of 8.0×10^{-1} and $1.8 \times 10^1 \text{ h}^{-1}$ at 225 and 500°C, respectively. These results show greater k -
 276 constants than in the present study, probably due to the higher treatment temperature and the properties
 277 of the contaminants.

278 In addition, the initial concentration of contaminants can also have a slight influence (10-20%) on the
279 efficiency of TD: a lower concentration in soil leads to a lower efficiency (Risoul et al., 2002). Zhao et
280 al. (2019) gave some explanations (i) at high initial concentration as for spiking, a larger amount of
281 contaminants is directly exposed to the soil surface and can therefore be easily removed from the soil
282 and (ii) at low initial concentration as for an historical contamination, contaminants are strongly
283 adsorbed to high-energy sites and are then more difficult to desorb from soil particles. In the present
284 case, the low concentration of Dieldrin ($100 \mu\text{g kg}^{-1}$) could limit the effectiveness of the method and the
285 remaining 15% of Dieldrin were adsorbed more strongly to the soil particles and thus not affected by
286 thermal treatment.

287 The mechanisms implied in this decline could be: desorption and volatilisation, irreversible sorption of
288 contaminant on soil particles or degradation (Ding et al., 2019; Kuppusamy et al., 2017; Vidonish et al.,
289 2016). At these temperatures ($< 100^\circ\text{C}$), it is unlikely that degradation was involved since low
290 contaminant degradation rates were observed with conventional TD at temperatures between 100 and
291 600°C (Zhao et al., 2019). There are two mechanisms left, irreversible sorption of Dieldrin onto the
292 SOM during heating, making it impossible of extract with the solvent used, or to Dieldrin volatilisation
293 and evacuation through the air stream. The second option might be preferred as this is what happens in
294 classical TD, according to Wang et al. (2021) there are 2 steps for the removal of contaminant by TD,
295 (i) volatilization and evaporation of contaminants on the soil particle surface and (ii) the diffusion and
296 migration in the soil pores and particles surfaces. Further experiments would be needed to complete the
297 understanding of the mechanism involved, such as measuring the concentration of Dieldrin in the soil
298 without air flow or measuring directly the Dieldrin concentration in the air flow out of the system.

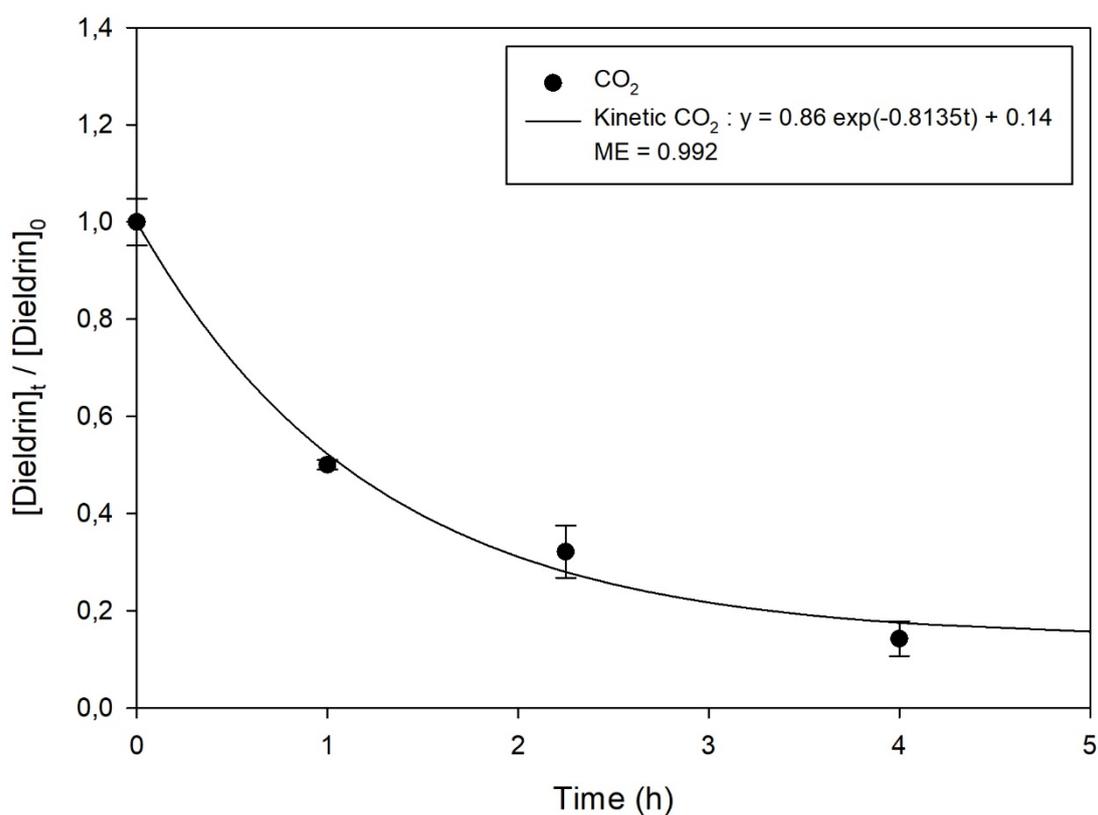
299 The results of Falciglia et al. (2011b) showed that an optimal flow of helium, as carrier gas, exists to
300 decrease the diesel concentration in the soil and other similar results have been described by Wang et
301 al. (2021). In the present case, the air flow was estimated globally in the oven but the exact volumes
302 passing through the soil batches were not precisely quantified. More experiments with different air flows
303 could be conducted to verify these results on formerly contaminated soils and improve efficiency of the
304 VLTTT.

305 Finally, heating the soil to 90°C provided a solution to decrease by 85% the Dieldrin concentration in
306 soil formerly contaminated, which is a lower temperature than the one O'Brien et al. (2018) stated,
307 showing that pesticides in soil are thermally impacted before 300°C . If agronomic soil parameters are
308 not negatively impacted by VLTTT, this would be a feasible solution for agricultural soils remediation.

309

310 3.3. Supercritical fluid extraction with CO₂

311 The Figure 3 presents the Dieldrin ratio against extraction time of SFE with CO₂. A very fast decrease
312 of about 50% of the initial Dieldrin concentration in soil is observed after 1 h and 86% after 4 h. The
313 diminution of Dieldrin concentration in soil follows a first-order kinetic model with an associated k -
314 constant of $8.1 \times 10^{-1} \text{ h}^{-1}$. This model fitted with data at 99.2% according to ME. This first-order kinetic
315 was observed by Alonso et al. (2002) with k -constant between 3.8×10^0 and $2.2 \times 10^1 \text{ h}^{-1}$, for experiments
316 at 260 bar, 40°C and different CO₂ flow rate on soil contaminated with gasoil. The higher k value could
317 be explained by the properties of the hydrocarbons compared to Dieldrin as vapour pressure (Saldaña et
318 al., 2005). These results are also in accordance with literature showing a great efficiency (> 70%) of this
319 technique to remove organic compound from soil (Al-Marzouqi et al., 2019; Meskar et al., 2019).



320

321 *Figure 3 : Effect of SFE CO₂ on Dieldrin concentration in soil against time (h)*

322 The conditions of experimentation could play a role, indeed pressure and temperature are the main
323 parameters influencing the efficiency of the technic but CO₂ flow rate and its density are important too
324 (Alonso et al., 2002; Ling and Liao, 1996; Saldaña et al., 2005). Several studies have varied the pressure
325 and temperature conditions on soils spiked with different organic contaminants (Al-Marzouqi et al.,
326 2007; Meskar et al., 2019, 2018). and have shown removal percentages between 70 and 99% after a few
327 hours (between 1 and 15 h) of treatment. According to Al-Marzouqi et al. (2007), increasing the pressure
328 at the same temperature improves the extractability of contaminants because the density and solvation
329 power of CO₂ increased. Conversely, Meskar et al. (2019) showed an optimum of pressure and

330 temperature conditions to reach maximum extraction rate of petroleum hydrocarbons. In the present
331 study, the chosen conditions of 200 bar and 50°C achieved a decrease in Dieldrin concentration of 86%,
332 but tests with other temperatures and pressures would be required to determine potential optimal
333 conditions. Furthermore, the SFE process depends on other factors specific to the characteristics of the
334 solid matrix such as particle size, shape, surface area, moisture and porosity (Anitescu and Tavlarides,
335 2006; Ling and Liao, 1996; Sunarso and Ismadji, 2009).

336 The decrease in Dieldrin concentration observed in the soil is probably due to the solubilisation of
337 Dieldrin from the soil in CO₂, as no degradation of Dieldrin occurs with SFE (Khan, 1995). The
338 extraction of organic contaminants from solid matrices was summarise into 4 steps: (i) desorption of
339 contaminant form soil particles, (ii) CO₂ diffusion through the solid, (iii) contaminants solubilisation in
340 CO₂ and (iv) transport of solubilised contaminant to the system outlet (Al-Marzouqi et al., 2007). In the
341 present work, since it was an old contamination, Dieldrin is deeper sequestered in the soil matrix
342 (Benner, 2015) and step (i) might be the crucial step that mainly controls the efficiency of the SFE. At
343 the opposite, the spiked or heavily contaminated samples should be governed primarily by step (iii) and
344 the solubility of the contaminant in CO₂ (Hawthorne et al., 1995). Step (ii) could be relevant, as the CO₂
345 flow of 800 mL h⁻¹ used here could be adjusted to modify the residence time of CO₂ in the soil and
346 favours its diffusion through the whole sample. Although the results of Al-Marzouqi et al. (2019) do not
347 show a significant effect of CO₂ flow rate on the efficiency of hydrocarbon decontamination by SFE,
348 future experiments with different flow rates should be conducted to provide answers regarding aged
349 Dieldrin contamination. These future experiments could also validate the capacity of CO₂ to solubilise
350 Dieldrin, analysing the CO₂ at the output of the system, which has not been done in the present work.

351 As with VLTTT, the ratio of Dieldrin seems to stabilise at 15% in the long term, showing a limit of
352 these techniques to reach a Dieldrin fraction that is difficult to extract from the soil. However, SFE
353 follows more closely the first order kinetics unlike VLTTT which shows variability, possibly due to
354 better diffusion of CO₂ through the soil than from the oven airflow. In order to further optimise the
355 process, various parameters such as temperature, heating rate, pressure, CO₂ flow rate, CO₂ recycling,
356 reactor configuration, initial soil moisture or grain size could be better adjusted (Al-Marzouqi et al.,
357 2007; Anitescu and Tavlarides, 2006; Cocero et al., 2000; Ding et al., 2019; Saldaña et al., 2005; Zhao
358 et al., 2019).

359 Finally, the present results show that SFE is 85% effective in remediating soils contaminated with aged
360 Dieldrin, but all the mechanisms involved are not yet fully understood and optimisation of the technique
361 have yet to be found. Once these parameters will be adjusted, it must be ensured that the technique does
362 not have negative effects on the agronomic properties of the soil.

363

364 3.4. Financial costs

365 In this section, the costs of the three techniques were calculated with the shortest time to reach the
 366 maximum efficiency of each technique, once the decrease of Dieldrin concentration is stabilised. The
 367 conversion of the price per hectare to 40 cm depth is calculated by multiplying the price per ton by 5960
 368 (see section 2.5). The calculations are provided in SI and the results are summarised in the Table 1.

369 *Table 1 : Summary of efficiency, k-constant, and costs of each technic*

Treatment	Maximum Efficiency (%)	k (h ⁻¹)	Cost (€ per ton)	Cost (per ha)
ZVI (5%)	0	/	/	/
ZVI (5%) + AA (0.5%)	0	/	/	/
ZVI (5%) + AS (2%)	40	9.3×10^{-4}	191	M€1.1
VLTTT (50°C)	45	1.3×10^{-1}	1	k€7
VLTTT (70°C)	55	3.8×10^{-1}	2	k€12
VLTTT (90°C)	85	2.5×10^{-1}	3	k€18
SFE CO ₂	86	8.1×10^{-1}	68	k€405

370

371 For the degradation technique, the cost for ZVI + AS was estimated at €191 per ton of soil after 70 d of
 372 treatment. As a result, the treatment of one hectare on the first 40 cm cost M€1.1 to reduce Dieldrin
 373 concentration of 40% only and it will be too expensive for farmers. In comparison, Comfort et al. (2001)
 374 and Guan et al. (2015) estimated the cost of degradation with ZVI at 5% (w/w) for 1 ton of soil between
 375 €30 and €500 depending on the prices of ZVI (based on its particle size) and other reagents. These
 376 differences are mainly due to the cost of reagents used from various suppliers and the inflation of reagent
 377 prices in recent years. Thus, ZVI degradation, based on costs and poor efficiency, does not seem to be
 378 a suitable method for the problem of historical Dieldrin contamination in soil.

379 The costs of VLTTT were calculated at €1, €2 and €3 per ton of soil after 24 h, for the temperature of
 380 50, 70 and 90°C, respectively. This implies treatment costs for 1 ha on the first 40 cm of 7, 12 and k€18,
 381 which are more suitable for farmers than degradation but still expensive. In the literature, the cost of *in*
 382 *situ* TD (> 100°C) was estimated between €53 and €224 per ton of soil, depending on the technology
 383 used for heating and the targeted contaminant (Anitescu and Tavlarides, 2006; Ding et al., 2019).
 384 Contrary to the present work, they take other parameters into account as equipment and labour, not only
 385 the electrical cost. For example, Truex et al. (2009) estimated that the electrical cost was only 8% of the
 386 total cost of *in situ* TT, which would imply total costs around €12 and €38 in the present case. The cost
 387 per hectare would therefore be between k€70 and k€200 to reduce old Dieldrin contamination by 85%.

388 The energy cost for SFE with CO₂ was estimated at €68 per ton of soil after 4 h of treatment. The reagent
389 cost (CO₂) was estimated at k€300 per ton of soil, which is very expensive, but as presented by Zhou et
390 al. (2004) CO₂ could be recycling and this reagent cost would become negligible. The treatment of an
391 area of 1 ha on the first 40 cm depth, taking into account the recycling of CO₂, would still cost k€405
392 which is very expensive for farmers. In their review, Saldaña et al. (2005) gave a cost of SFE between
393 €140 and €300 per ton of soil, and Zhou et al. (2004) calculated the cost for PCB remediation in soil
394 and sediment between €70 and €90 per ton as in the present study. This technic gives the same results a
395 VLTTT for old Dieldrin contamination, but is at least twice as expensive.

396 However, care should be taken with the prices quoted here, as scaling up and using larger equipment
397 can significantly alter the costs calculated for each technique. Thus, the costs of techniques such as
398 VLTTT and SFE will need to be recalculated in future tests with metric scale pilots.

399

400 Conclusion

401 In the present work, three physicochemical remediation techniques (ZVI degradation, VLTTT and SFE
402 with CO₂) were tested on agricultural soil formerly contaminated with Dieldrin. Batches experiment
403 were conducted up to 70 days to observe the effectiveness, kinetics and financial cost of each technique.
404 Estimations for one ton of soil have also been carried out.

405 From a global point of view, it is clear that with these experimental conditions, degradation using ZVI
406 is ineffective or not sufficiently effective (< 40% for ZVI + AS) to reduce aged Dieldrin contamination
407 in agricultural soil even after 70 d. At the opposite, VLTTT at 90°C and SFE using CO₂ are the most
408 efficient techniques showing a decrease of Dieldrin concentration in the soil of 85% after 24 and 4 h,
409 respectively. Depending on the *k*-constants ranging from 9.0×10^{-4} to $8.1 \times 10^{-1} \text{ h}^{-1}$ associated with each
410 first-order kinetic, the speed of the remediation techniques can be classified as follows:
411 $\text{ZVI} < \text{VLTTT} < \text{SFE}$. This work therefore validates the effectiveness of VLTTT and SFE with CO₂ on
412 a soil formerly contaminated with Dieldrin.

413 Moreover, among the three techniques, VLTTT and SFE have the lowest treatment costs, €3 and €68
414 per ton of soil, respectively, while ZVI degradation costs €191 per ton. As VLTTT and SFE were equally
415 effective, the VLTTT technique would seem to be more suitable for farmers since it is less expensive.
416 However, these costs do not take into account the purchase of equipment, process optimisation and
417 scaling up will impact on the actual costs.

418 Finally, once the techniques will be optimised, futures research should be ensured that the
419 decontamination rates achieved are sufficient and that the agronomic qualities of the soils are not altered
420 by the decontamination processes tested.

421

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426

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