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Status of Dieldrin in vegetable growing soils across a peri-urban agricultural area according to an adapted sampling strategy

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Abstract

Since the fifties, organochlorine pesticides (OCPs) had been used in agriculture to protect vegetables. Two decades after their ban by the Stockholm convention in 2001, OCPs are still present in agricultural soils inducing vegetable contamination with concentrations above Maximum Residue Level (MRL). This is a major concern for a 5 km² peri-urban vegetable growing valley located in the south west of France. In the present work, the sampling method was developed to clarify the spatial distribution of one OCP, Dieldrin, and its relationship with soil properties at the scale of study area. A total of 99 soil samples was collected for physicochemical analyses and Dieldrin concentrations. Results show Dieldrin concentrations in soils up to 204 µg.kg⁻¹. The horizontal distribution of this pesticide is heterogeneous at the study area scale but homogeneous in each reference plot studied. About 85% of the contamination was located in the top soil layers (0-40 cm depth), but Dieldrin may still be quantified at a depth of 80 cm. Among all soil physicochemical parameters analysed, SOM was the most significantly related ($P < 10^{-4}$) with Dieldrin concentrations, once different grain size fractions were considered. Moreover, results indicate a 33 times higher Dieldrin concentration and/or extractability for coarse sand than for other grain size fractions. These results show that the developed sampling method is adapted for the study area scale as it helps understanding the factors influencing the spatial distribution of Dieldrin. Historical amendments are the predominant factor for the horizontal contamination and deep ploughing for the vertical contamination. Also, the variations of coarse sand repartition in soils prevents identification of relationships between SOM and Dieldrin contamination in bulk soil. Further investigation is required to explain these relationships but these results highlight why no clear relationship between OCPs and SOM was previously identified.

Keywords: Dieldrin distribution, Agricultural soils, Dieldrin - SOM relationship, grain size fractions, sampling method

31 1. Introduction

32 Soil contamination by OrganoChlorine Pesticides (OCPs) is a major concern not only because of their
33 ubiquity and high toxicity but also their persistence in the environment (Gavrilescu, 2005). These types of
34 pesticides, including Dieldrin, were used in agriculture to protect vegetable cultures in many industrial
35 countries from the fifties until the end of the nineties (Hashimoto, 2005; Jorgenson, 2001; Meijer et al.,
36 2001; Wang et al., 2007). More specifically, in France, Dieldrin was banned in agriculture in 1972, but its
37 complete ban on marketing and use did not come until 1992 (INRS, 2007). However, two decades after its
38 worldwide ban by the Stockholm convention in 2001, and forty-five years after its ban in France, Dieldrin is
39 still present in soil and continue to be a potential source of contamination with, for example, vegetable
40 contamination at concentrations exceeding Maximum Residue Level (MRL) fixed by regulatory institutions
41 (Namiki et al., 2018, 2015; Saito et al., 2011; Tsiantas et al., 2021).

42 In order to characterise soil contamination with OCPs, several studies have been conducted: (i) at regional
43 scales with large surfaces of more than 1000 km² (Aichner et al., 2013; Gong et al., 2004; Jiang et al., 2009;
44 Mishra et al., 2012; Orton et al., 2013; Qu et al., 2016, 2019; Ribes et al., 2002; Sánchez-Osorio et al., 2017;
45 Shegunova et al., 2007; Tao et al., 2008; Wong et al., 2010; Yu et al., 2013; A. Zhang et al., 2011; H. Zhang et
46 al., 2009; Zhang et al., 2006) and (ii) on very small areas of approximately a few hundred square metres
47 corresponding to agricultural plot scale (Hashimoto, 2005; Mattina et al., 1999; Zhao et al., 2013). However,
48 few studies have been conducted on intermediate scales of several km², corresponding to urban or peri-
49 urban agricultural areas dimensions (Péron and Geoffriau, 2007; Piorr et al., 2018). These studies however,
50 only investigated areas divided into different zones in function of their use (i.e. agricultural, recreational,
51 and natural) and location (Miglioranza et al., 2003; Wenzel et al., 2002). This is irrelevant when
52 investigating the distribution of OCPs in soil in a context of peri-urban agricultural land use. It is thus
53 necessary to develop and adapt a sampling strategy suitable to the spatial characteristics of urban or peri-
54 urban agricultural areas.

55 All previous studies highlighted three important factors that must be considered in order to characterise
56 OCPs contamination. Firstly, the historical application of OCPs in a given area is often correlated with their
57 actual concentration in soils (Arias-Estévez et al., 2008; Harner et al., 1999; Hashimoto, 2005; Mattina et al.,
58 1999; Qu et al., 2016). Thus, historical application of OCPs is an important source of heterogeneity in their
59 distribution pattern (Hashimoto, 2005; Mattina et al., 1999). Moreover, after the initial application,
60 secondary natural dispersion of OCPs can also occur with long range distance travel by atmospheric
61 transport and deposition (Jiang et al., 2009; Shegunova et al., 2007; A. Zhang et al., 2011). Secondly, soil
62 physicochemical properties can affect OCPs retention (Aichner et al., 2013; Gevao et al., 2000; Jiang et al.,
63 2009; Miglioranza et al., 2003; Wang et al., 2018), especially the Soil Organic Matter (SOM) content which is
64 often highlighted as the principal parameter influencing OCPs retention in soils (Gong et al., 2004; Krohn et
65 al., 2019; Miglioranza et al., 2003; Nam et al., 2008; Ribes et al., 2002; Wang et al., 2018; Yu et al., 2013;

66 Zhang et al., 2006; N. Zhang et al., 2011), but some studies did not observe this relationship between SOM
67 and OCPs (Harner et al., 1999; Mattina et al., 1999). Therefore, the relation between OCPs and soils
68 properties needs to be deeper investigated. Thirdly, the vertical distribution of OCPs contamination
69 indicates that the majority of OCPs are found at shallow depth (< 40 cm) (Wang et al., 2006; L. Zhang et al.,
70 2009). However, it is possible to identify a correlation between contamination at deeper depth and
71 ploughing practices (Hashimoto, 2005). As ploughing depth depends on farmer practices, it is of main
72 importance to characterise the vertical distribution as well.

73 Dieldrin (CAS: 60-57-1) is one of the most encountered OCPs in agricultural soils and also in vegetables
74 production (Namiki et al., 2018, 2015; Tsiantas et al., 2021). It was mainly used as an insecticide in crops
75 and also to protect wood structures from termites. With a molar mass of about 381 g.mol⁻¹, it is considered
76 as barely soluble in water (0.186 mg.L⁻¹, INRS, 2007) and non-volatile at normal temperature and pressure
77 conditions ($P_{\text{vap}} = 1.03 \times 10^{-4}$ Pa, INRS, 2007). As most OCPs, Dieldrin presents high affinity for organic carbon
78 with a Log(K_{ow}) estimated at 6.2 (INRS, 2007) and its Henry's law constant (H, dimensionless, air/water) is
79 4.1×10^{-4} (Altschuh et al., 1999). This pollutant was quantified at concentrations higher than MRL authorized
80 in the flesh of some *Cucurbita pepo* produced on the study, leading to reduced production and economic
81 issues for the farmers of the area concerned.

82 Considering the above discussion, the objectives of this study are (i) to investigate the horizontal and
83 vertical distribution of Dieldrin at the scale of the peri-urban agricultural area, (ii) to evaluate the influence
84 of soil properties (SOM content, humidity, grain sizes, pH and CEC) on Dieldrin distribution, and (iii) to
85 estimate the benefits of the sampling method used at the studied area scale. To reach these goals, a semi-
86 random nested sampling strategy was designed in order to characterise the horizontal distribution of this
87 pollutant both at the peri-urban agricultural and plot scales at 0-20 cm depth and the vertical
88 characterisation on 4 specific plots until 80 cm depth. The physicochemical parameters, including OCP
89 analysis (Hexachlorocyclopentadiene, Hexachlorobenzene, Simazine, Atrazine, Lindane, Alachlor,
90 Heptachlor, Heptachlor-epoxide, *cis*-Chlordane, *trans*-Chlordane, *cis*-Nonachlor, *trans*-Nonachlor,
91 Metoxychlor, Endrin, Aldrin and Dieldrin), were determined on the collected soil samples and data analysis
92 with statistic tools permitted to evaluate the influence of these parameters on Dieldrin distribution. To our
93 knowledge, this is the first study providing an evaluation of Dieldrin distribution in agricultural soils at a
94 peri-urban scale.

95 2. Material and Methods

96 2.1. Study area description

97 The study area is located in Bordeaux agglomeration (France), in a peri-urban perimeter which supports
98 and protects agricultural areas. The climate is warm temperate with heavy showers fall all year. The
99 average annual temperature on the study area is 13.8°C with a mean annual precipitation of approximately
100 803 mm.

101 The surface of this historical agricultural valley is about 4.9 km² and extends roughly 5 km from east to west
102 (Fig.1). Vegetables (potatoes, squashes, carrots, leeks ...) have been cultivated here for more than
103 100 years. As in many agricultural area, OCPs have been massively used from the 50's to the end of 70's,
104 but in the case of the present study, the exact products and quantities of OCPs have never been recorded
105 and are unknown.

106 In 2016, aerial photography showed the following surface covering: 15% afforestation, 37% market
107 gardening, 17% meadow and 31% by others (house, wasteland, etc.). The surfaces of agricultural plots
108 range from 0.02 to 5.5 ha with an average of 1 ha. The shape of the 170 agricultural plots is mainly square
109 or rectangular with an average dimension close to 100×100 m² (see Fig. 1).

110 2.2. General sampling strategy

111 In order to characterise horizontal and vertical OCPs distribution, a total of 99 soil samples were collected
112 in 18 cadastral plots. Samples for horizontal characterisation were collected in June 2019 (51) and those for
113 vertical characterisation in January 2020 (48). This was carried out over 2 periods (i) to observe if there
114 were differences in the availability of OCPs between these 2 seasons and (ii) to used first results to select
115 agricultural plots for vertical characterisation. For each of these 99 soil samples, approximately 400 g of soil
116 was collected using a manual auger and stored in 250 mL glass vials protected from light at 4°C until
117 analysis.

118 To fit with the intermediate scale approach of this study, the sampling strategy was adapted from Atteia et
119 al. (1994) and Oliver and Webster (1986) with semi-random nested sampling. This strategy enabled to
120 include the whole study area as a single entity and to be more precise on specific plots. According to
121 previous partial results on soil contamination in the study area (Hervieu and Garcia, 2016), 5 of the most
122 contaminated plots were selected as reference plots. These reference plots were selected because of their
123 identified high contamination and their well distributed location in the agricultural valley. A sixth plot was
124 added as reference plot to fill a spatial gap between the 5 others and thus to globally cover the whole
125 surface of the study area (Fig. 1). Except for the sixth plot which was a wasteland for 20 years, all reference
126 plots are still cultivated today. These 6 reference plots are randomly named hereafter from A to F, but plot
127 letters are not provided in Fig. 1 for confidentiality reasons

128 The characterisation of OCPs horizontal distribution was conducted on samples collected in the 0-20 cm
129 depth surface layer. The first sample of each plot was collected at its centre. From this centre, 4 circles
130 were drawn with a geometrical progression of 4.5 factor: 10, 45, 202 and 911 m. This geometrical step
131 progression of 4.5 was chosen to allow (i) the largest circle to criss-cross other circles and cover the whole
132 study area, and (ii) the two smallest circles to stay in the limit of the reference plot. At each step, the angles
133 were randomly determined among 16 possibilities (step of 22.5°). In order to obtain a third observation on
134 each reference plot, a complementary soil sample was collected in a corner of the plot. Furthermore, in
135 order to refine the horizontal distribution pattern of OCPs, two intermediate distances of 25 and 70 m from
136 the centre were added on plot B, C, D and F during the second soil sample collection (January 2020). These
137 4 specific plots were chosen because of their different SOM content and OCPs concentrations, determined
138 from the first soil samples collected in June 2019. An additional 10 kg of soil was collected at the centre of
139 the six reference plots (A to F) in order to characterise the distribution of OCPs on three different grain
140 sizes.

141 The OCPs vertical distribution was studied on reference plots B, C, D and F. In these reference plots, 4
142 vertical profiles were conducted at the location of sampling points of the four first distances (0, 10, 25 and
143 45 m). At these locations, 3 additional soil samples were collected between 35-45, 55-65 and 75-85 cm
144 depth.

145 2.3. Physicochemical properties of soil

146 In order to set the parameters influencing OCPs concentration in soils, the following physicochemical
147 properties of soils were investigated: grain size distribution, pH in water, CEC, humidity, SOM and OCPs
148 concentration. The following paragraphs describe the different analytical methods.

149 The grain size distribution of the agricultural soils was identified by NF X31-107 of September 2003 method,
150 which discriminates the following size fractions: clay (< 2 µm), fine silt (< 20 µm), coarse silt (< 50 µm), fine
151 sand (< 200 µm) and coarse sand (< 2000 µm). This analysis was conducted for each plot where soil samples
152 were collected. In parallel, the samples of 10 kg from the six reference plots (A to F) were mechanically
153 sieved (AS 200-digit cA, Retsch, Germany) (i) to separate the following soil fractions: coarse sand (2000-
154 200 µm), fine sand (200-50 µm), silts and clay (< 50 µm) and (ii) to determine the distribution of OCPs over
155 these 3 grain sizes. Silts and clay were gathered due to the small amount of these fractions in the sampled
156 soils.

157 In order to determine soil pH, 20 g of soil was mixed with 100 mL (1/5 (w/v)) of demineralised water,
158 agitated for 10 min and left to settle for 2 min prior to pH measurement (Rodier, 1978).

159 Cation exchange capacity (CEC) was determined by the NF X31-130 of December 1999 method. Because of
160 the weak relationship of this parameter with OCPs content identified in literature, these analyses were only
161 conducted on 30 soil samples collected at 20 cm depth.

162 Humidity rate and SOM content were determined using the Loss On Ignition (LOI) method (Rodier, 1978).
163 Approximately 10 g of soil was heated in an oven at 105°C for 6 h and then heated at 525°C for 4 h, and
164 both parameters were determined by mass differences.

165 In order to determine OCPs concentrations, an aliquot of soil samples was dried at 30°C and then crushed
166 with a planetary mill (PM 100, Retsch, Germany) during 10 min at 400 rpm to obtain fine powder. Liquid-
167 solid extractions were conducted with 25 g of this powder mixed with 10 mL of n-heptane (n-Heptane,
168 99+%, residues analysis, ACROS Organic, UK) in 50 mL glass flask, and then agitated during 72 h at 250 rpm.
169 Supernatant was recovered after 8 min of centrifugation at 4000 rpm and placed in three vials of 2 mL.
170 Before analysis, each vial received 50 ng of Phenanthrene d-10 (Restek, France) used as internal standard.

171 The OCPs were analysed using Gas Chromatography (GC) (7820A, Agilent, USA) coupled with a Mass
172 Spectrometer (MS) (5977A, Agilent, USA) system. Ultra-high purity He (99,999%, Air Liquide, France) was
173 used as carrier gas. The GC was equipped with a 30 m × 250 µm × 0.25 µm HP-5ms capillary column
174 (Agilent, USA), and the oven temperature was programmed starting at 45°C and held 0.5 min, followed by
175 an increase of 30°C.min⁻¹ up to 90°C, held 0.5 min, then 10°C.min⁻¹ up to 310°C for 3 min. The injector
176 temperature was 280°C and 1 µL of sample was injected with pulsed splitless mode. The MS was used in
177 Single Ion Monitoring (SIM) mode, with source and quad temperatures set at 300 and 200°C, respectively.
178 OCPs quantification was conducted using a standard solution (EPA 505, Restek, France) containing 16 OCPs
179 (list in Supplementary Material). The validation results of this analytical method are presented in
180 Supplementary Material.

181 2.4.Data analysis and statistics

182 Because the sampling campaigns were conducted at two different periods (summer and winter), the OCPs
183 availability was checked. Results confirmed that this did not influence Dieldrin availability estimation
184 (Fig.S1). The sampling period was then not considered hereafter.

185 All linear modelling approaches (ANOVA, linear regressions, ANCOVA), described in the following
186 paragraphs, were performed using R software (R Core Team, 2016). The “nlme” package was used for
187 mixed modelling. In case of significant effect of a factor with more than 2 levels, posthoc multiple Tukey
188 comparisons were performed to detect the groups significantly different from the others. Whenever
189 necessary, data were transformed to fit linear modelling assumptions (normality and homoscedasticity of
190 model residuals). Different transformations were tested (square root, cube root, log₁₀) and the
191 transformation providing the best results regarding modelling assumptions were kept.

192 2.4.1.Horizontal distribution

193 During both campaigns, a total of 51 soil samples were collected at 0-20 cm depth. Because of the semi-
194 random sampling strategy inducing low point pairs for some distance ranges, the experimental variograms
195 present an erratic shape (Fig.S2). In order to interpret Dieldrin variations on the study area, the average

196 Dieldrin concentration variance at each fixed distance (0, 10, 25, 45, 70, 202 and 911 m) was calculated for
197 the 6 reference plots with the following equation (1):

198
$$\text{Dieldrin spatial variance} = \frac{1}{6} \sum_{p=1}^6 [C_{i,p} - \overline{C_p}]^2 \quad (1)$$

199 where $C_{i,p}$ is the soil Dieldrin concentration at the fixed distance i from the centre of reference plot p , and
200 $\overline{C_p}$ the mean of Dieldrin concentration in reference plot p . Additionally, to estimate Dieldrin variability
201 between reference plots, an ANOVA was performed.

202 [2.4.1. Vertical distribution](#)

203 Based on 48 samples collected in January 2020, Dieldrin concentrations and SOM contents were analysed
204 according to depth (considered as a factor here) and agricultural plot belonging, performing a two-ways
205 ANOVA. As the Dieldrin concentration in many samples was below LOQ, a random value between 0 and the
206 LOQ was assigned to be able to perform the analysis. The objective here was to perform a quantitative
207 analysis of variance to verify if depth and plot belonging could influence Dieldrin concentration. It implies
208 comparing Dieldrin concentrations over several orders of magnitude, with some measurements below LOQ.
209 In these conditions, the uncertainty due to the random assignment for very low values does not influence
210 the statistical results.

211 [2.4.2. Relationships between soil properties and OCPs concentration](#)

212 A correlation matrix was conducted with all measured parameters (depth, pH, humidity, CEC, and SOM) to
213 identify those which are the most linked to Dieldrin concentration in soil. Concerning relationship between
214 Dieldrin and SOM at different grain sizes, an ANCOVA was performed. A linear mixed modelling was
215 performed with the original soil sample as random effect to take into account the dependency of the three
216 measurements made on this soil sample.

217 3. Results

218 3.1. Soil physicochemical properties and Dieldrin concentration in the peri-urban 219 agricultural area

220 The physicochemical properties of soils collected in the study area are presented in Table 1. The soil pH
221 ranged from 4.1 to 8.1, with a mean of 6.6 ± 0.1 and a median of 6.8. Humidity rate ranged from 3.5 to
222 52.2%, with a mean of $14.8 \pm 0.7\%$ and a median of 13.5%. SOM content ranged from 0.1 to 52.1%, with a
223 mean of $3.2 \pm 0.6\%$ and a median of 1.9%. CEC ranged from 1.9 to $92.0 \text{ cmol.kg}^{-1}$, with a mean of
224 $10.8 \pm 2.9 \text{ cmol.kg}^{-1}$ and a median of 6.3 cmol.kg^{-1} . Note that the maximal CEC level corresponds to one soil
225 sample collected from forest area. Among 15 analysed OCPs, Dieldrin was clearly the most abundant in the
226 study area (Table 1). It was detected in 90 and quantified in 60 soil samples (over 99), with concentrations
227 up to $203.9 \text{ } \mu\text{g.kg}^{-1}$, (mean = $38.2 \pm 5.9 \text{ } \mu\text{g.kg}^{-1}$; median = $14.7 \text{ } \mu\text{g.kg}^{-1}$). Information about others OCPs are
228 presented in supplementary material (Table S2).

229 3.2. Horizontal distribution of Dieldrin at the peri-urban agricultural area

230 Figure 2 presents the results of equation (1) for all distances studied. This figure shows Dieldrin spatial
231 variance below $1500 \text{ } \mu\text{g}^2.\text{kg}^{-2}$ until 70 m and over $3000 \text{ } \mu\text{g}^2.\text{kg}^{-2}$ at 202 and 911 m. The last distances
232 correspond to the samples which are not located in the reference plot. This indicates an important inter-
233 plot variation with a random Dieldrin distribution at the agricultural valley scale and a more homogeneous
234 Dieldrin contamination in each particular plot.

235 Besides, the ANOVA shows that plot factor has a strong effect on Dieldrin contamination ($P < 0.001$,
236 $R^2 = 0.732$). This demonstrates that 73.2% of variations of the Dieldrin concentrations in soil are explained
237 by sample affiliation to a specific plot. The Dieldrin contamination is thus homogenous in each plot, but
238 heterogeneous at the scale of the peri-urban agricultural area. This is also highlighted by Fig.3 which shows
239 that (i) plots C and D were the least contaminated, with similar Dieldrin concentrations below $20 \text{ } \mu\text{g.kg}^{-1}$,
240 (ii) plots A, B and E presented Dieldrin concentrations between 10 and $100 \text{ } \mu\text{g.kg}^{-1}$, and (iii) the soil of the
241 plot F was the most contaminated with Dieldrin concentrations between 80 and $200 \text{ } \mu\text{g.kg}^{-1}$. Indeed, the
242 posthoc Tukey multiple comparisons test conducted on these data shows that plot C had a concentration
243 significantly lower than the other plots except plot D. On the other hand, plot F showed a concentration
244 significantly higher than the other plots, except plot A. Finally, plots A, B and E had similar Dieldrin
245 concentrations.

246 3.2.1. Correlations between Dieldrin concentration and soil physicochemical parameters

247 The results of correlation matrix (Fig.S3) indicates that SOM content and depth were the parameters that
248 correlated the most with Dieldrin concentrations. Additionally, no significant correlation was found
249 between Dieldrin concentration and the other physicochemical parameters measured (pH, CEC, and

250 humidity). Furthermore, the table 2 shows that pH values are not significantly different between grain sizes
251 ($P = 0.45$) and no correlation with Dieldrin concentrations are shown ($P = 0.13$)

252 3.2.2. Dieldrin distribution on grain size fractions

253 Coarse sand was the most representative fraction in the soil samples with a mean of $80.6 \pm 1.1\%$, while fine
254 sand and clay represent $6.3 \pm 0.5\%$ and $8.2 \pm 0.5\%$ of the total soil dry weight, respectively (Table 2). The
255 coarse and fine silts were the two least represented grain sizes in the soil samples, with proportions of
256 $1.6 \pm 0.5\%$ and $3.2 \pm 0.3\%$, respectively. The Dieldrin concentration was higher on finest grain size fractions,
257 with concentrations of 122.1 ± 43.1 for fine sand and $154.8 \pm 48 \mu\text{g.kg}^{-1}$ for silts and clay, while coarse sand
258 shows Dieldrin concentration of $21.9 \pm 8.5 \mu\text{g.kg}^{-1}$.

259 The Figure 4 presents the Dieldrin concentration against SOM content, taking into consideration of 3 grain
260 size fractions for 6 reference plots. Dieldrin concentration depended on both grain size ($P = 0.04$) and SOM
261 content in each fraction ($P < 0.001$). Indeed, the strong relationship between Dieldrin and SOM showed a
262 significantly higher intercept for coarse sand (0.88) in comparison to the ones of fine sand (0.03) and silts
263 and clay (0.06), which are not significantly different. The slopes are equivalent (1.52 ± 0.26) for all grain size
264 fractions and are not significantly different from 1 (95% confidence interval: 0.92 to 2.11), showing a linear
265 relation between SOM and Dieldrin concentration once grain size fractions are discriminated. Additionally,
266 the higher intercept in the log-log relationship indicates that at equivalent SOM content, coarse sand shows
267 a 33 times greater Dieldrin concentration in comparison to fine sand or to silts and clay fractions.

268 3.3. Vertical distribution of Dieldrin and SOM

269 The vertical distribution of Dieldrin and SOM in soil for reference plots B, C, D and F are presented in Figure
270 5. The Dieldrin concentrations significantly ($P < 0.001$) decreased with depth, with values lower than LOQ
271 below 40 cm for plots B and C. Concerning plot D, Dieldrin concentrations were both about $20 \mu\text{g.kg}^{-1}$ at 20
272 and 40 cm depth, and close to LOQ at 60 and 80 cm depth. For plot F, Dieldrin concentration decreased
273 from $128 \mu\text{g.kg}^{-1}$ at 0-20 cm to $5 \mu\text{g.kg}^{-1}$ at 80 cm depth. As mentioned for horizontal distribution, the
274 affiliation of each plot had significant effect ($P < 0.01$) on Dieldrin vertical distribution. However, the
275 decrease in Dieldrin concentration with depth is similar in all plots ($P = 0.51$), and contamination was
276 mainly (85%) located between 0 and 40 cm depth.

277 SOM contents significantly decreased with depth on all plots ($P < 0.001$). For plot B, the SOM content
278 decreased from 1.7% at 20 cm depth to 1.4% at 80 cm depth, with a slight increase to 2.0% at 40 cm depth.
279 For plot C, the SOM content decreased from 1.4% at 20 cm depth to 0.3% at 80 cm depth. For plot D, it
280 decreases from 3.4% at 20 cm depth to 1.3% at 60 cm depth with an increase to 2.8% at 80 cm depth,
281 probably due to wood residues located at this level. For plot F, SOM content decreased from 9.7% at 20 cm
282 depth to 1.1% at 80 cm depth. The affiliation on each plot had also significant effect ($P < 0.01$) on SOM
283 vertical distribution. Moreover, the interaction between SOM and depth was also significant ($P < 0.001$).
284 Thus, it could be concluded that SOM content decreased with depth and noticeably on each plot.

285 4. Discussion

286 4.1. Dieldrin distribution on peri-urban agricultural areas

287 4.1.1. Horizontal distribution

288 The results of the present study show that the horizontal distribution of Dieldrin is heterogeneous at the
289 study area scale and more homogeneous in each reference plot. This could be explained by the historical
290 use of Dieldrin, indeed each plot received specific amounts of pesticides depending on the farmers'
291 practices inducing concentration variability between plots, as mentioned in former studies (Hashimoto,
292 2005; Mattina et al., 1999; Qu et al., 2016; Wang et al., 2016). A consideration must also be made for
293 natural diffusion of OCPs by atmospheric transport and deposition presented in literature (Jiang et al.,
294 2009; Miglioranza et al., 2003; Shegunova et al., 2007; A. Zhang et al., 2011). For example, Jiang et al.
295 (2009) showed Dieldrin contamination in Chinese agricultural soils ranging up to $1.4 \mu\text{g}\cdot\text{kg}^{-1}$, while Aldrin
296 and Dieldrin have never been used in China. Contamination by this atmospheric pathway does however
297 seem to induce lower contamination levels compared to the legacy of the local initial application. This kind
298 of secondary distribution pattern was not confirmed by the present study and is unlikely to be the main
299 source of contamination in agricultural areas (Gong et al., 2004; Qu et al., 2016; Wang et al., 2018).
300 However, even if a global homogeneous distribution of Dieldrin was observed in each plot, intra-plot
301 variability suggested a slight heterogeneity in contamination within each plot (Fig.3) (Hilber et al., 2008).
302 The division of the former agricultural plots before 90's could justify this intra-plot variability since these
303 former plots have likely received different amounts of pesticides and different ploughing techniques, as
304 reported elsewhere (Hashimoto, 2005; Mattina et al., 1999). Since the 90's, the number of farmers has
305 dropped by 30% in the region (Department of Gironde, 2015) and the farmers unified several small plots
306 into bigger ones.

307 4.1.2. Vertical distribution

308 The vertical distribution pattern of Dieldrin shows the majority (85%) of Dieldrin located between 0 and
309 40 cm depth. This result is in accordance with literature showing that Dieldrin concentration sharply
310 declining under 30-40 cm depth (Hashimoto, 2005), which is also the case for other OCPs (Wang et al.,
311 2006; H. Zhang et al., 2009). Quantifiable Dieldrin contamination has been found at 60 and 80 cm depth,
312 mostly on the plot F. Leaching of Dieldrin through the soil by surface water is unlikely since it is nearly
313 insoluble (Jorgenson, 2001). However, soil structure affect the vertical flow of OCPs (Novak et al., 2001),
314 but soils must contain a large amount (> 80%) of silts and clay to develop preferential flows, which is not
315 the case in this study as the soils are mainly sandy (see Table 2). The vertical flows should therefore be the
316 same on the 4 studied plots. Thus, concentration of Dieldrin between 60 and 80 cm depth on plot F might
317 be linked to a higher quantity applied on the surface or related to deep soil ploughing, especially during
318 land consolidation, which are the main parameters influencing Dieldrin vertical distribution (Hashimoto,
319 2005). Further investigations on other agricultural plots should be conducted to validate or not these
320 assumptions.

4.1.3. Dieldrin mass balance and risk implications

In order to evaluate the Dieldrin residual quantity in soil, a mass balance was conducted on plots B, C, D and F. Assuming that recommendations of $1 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ of active substance (Gatignol and Étienne, 2010) were followed between 1950 and 1975, and no dissipation occurred, the amount of Dieldrin that might be expected to find nowadays would be about $2500\pm 500 \text{ mg}\cdot\text{m}^{-2}$. The apparent density of sandy soil was about $1.49\pm 0.12 \text{ g}\cdot\text{cm}^{-3}$ (Bruand et al., 2004), thus the estimated Dieldrin mass is approximately: 21 ± 2 , 4 ± 0 , 22 ± 2 and $54\pm 4 \text{ mg}\cdot\text{m}^{-2}$ for the plots B, C, D and F, respectively (calculations in supplementary materials). These calculations showed 2 or 3 orders of magnitude differing between the expected versus the remaining amount of Dieldrin. This suggests that a significant part of the amended Dieldrin was missing, this was in accordance with the Predicted Environmental Concentration in soil calculated by Tsiantas et al. (2021). Either Dieldrin was less used than previously thought, or some processes such as slight runoff, volatilisation, wind erosion, deep ploughing or biodegradation and bioextraction caused the decreased concentrations (Barriuso et al., 1996; Incorvia Mattina et al., 2000; Li et al., 2018; L. Zhang et al., 2009). Also to be considered the fact that a certain amount of Dieldrin could also be highly bound in soil structure and therefore not available with the extraction method used in the present study (Biswas et al., 2018; Jones and De Voogt, 1999). It is thus necessary to clarify these phenomena in order to predict the evolution of future contamination with time.

Presently, the identified risk for humans from Dieldrin concentrations in soil in this area is dependent on the cucurbits consumption, as no other vegetables were above regulatory thresholds. These regulatory thresholds were calculated to limit the risk of cancer below a 10^{-5} probability, including precaution factors. However, further studies investigating more deeply the risk assessment of this contamination are needed. Indeed, these Dieldrin concentrations also induce socio-economic issues, and they might represent an environmental and/or human health risks. For the latter, as Dieldrin is considered as a non-volatile compound, this risk should be evaluated through two pathways: mainly by dust ingestion and/or vegetable consumption. It is therefore necessary to establish realistic scenarios for risk assessment, taking into account (i) dust emission factors, (ii) Dieldrin transfer from soil into the different edible parts of the vegetables species and or varieties cultivated in this area, and (iii) appropriate exposures parameters concerning the different target populations (farmer, resident, adult, child...) (Niu et al., 2014; Phillips and Moya, 2013; Tsiantas et al., 2021).

4.2. Dieldrin and SOM relationship

Because of its high $\text{Log}(K_{ow})$, Dieldrin has a stronger affinity for hydrophobic moieties present in the SOM. In the present study, relationship between Dieldrin concentration and SOM was only clearly distinguished considering different grain size fractions, but no linkage with bulk soil analysis (Fig.4 and Fig.S4). This relationship was close to a Freundlich isotherm (Cornelissen et al., 2005; Huang et al., 2003; Sparks, 2003): $[\text{Dieldrin}] = a \times \text{SOM}^b$, where a and b are the partition coefficient and the correction factor, respectively. The ANCOVA results show that b is not significantly different from 1. However, additional data on other soils

357 are needed to complete this observation. Besides, at similar SOM content, the concentration of extractible
358 Dieldrin was 33 times higher for coarse sand than for other grain size fractions. As the amount of coarse
359 sand was 6 to 12 times higher than the other grain size fractions (Table 2), it probably received more active
360 substance. Moreover, as the amount of coarse sand varied significantly for each soil sample, it explains why
361 the correlation with SOM in bulk soils is more difficult to observe. It would be interesting to investigate in
362 future not only the quantity, but also the quality, location and composition of SOM on different grain sizes
363 for natural contaminated soil to highlight the potential relationships between OCPs concentration or
364 extractability, and the various forms of SOM as black carbon (Cornelissen et al., 2005; Huang et al., 2003;
365 Nam et al., 2008; Ren et al., 2018; Schmidt and Noack, 2000). It is important to study the dynamics of OCPs
366 in soil for a complete understanding of residual OCPs contamination in agricultural soils.

367 4.3. Dieldrin and its relationship with other soil properties

368 No relationship between humidity rate or CEC with Dieldrin concentration has been established in the
369 present study. Indeed, humidity cannot be a significant factor as Dieldrin is barely soluble in water:
370 0.186 mg.L^{-1} (INRS, 2007; Jorgenson, 2001). Few studies investigated the influence of CEC on Dieldrin
371 concentration, but the results of the present study are in accordance with Yu et al. (2013) work, in which no
372 correlation between CEC and OCPs was found.

373 Concerning soil pH, the results of the present study do not show any relationship between Dieldrin
374 contamination and pH, which is in accordance with Tan et al. (2020), in which no significant correlation was
375 found between OCPs and pH, except for Atrazine. Moreover, Gong et al. (2004) reported that pH can have
376 an indirect influence on pesticide retention in soils because of its effect on humic acids structures, one of
377 the main component of SOM (Huang et al., 2003). Their work discriminated two groups of soils, with pH
378 above and below 8. As the soil pH measured in the present study were below 8, except for 2 samples (8.1),
379 it was impossible to observe this influence here.

380 4.4. Linkage between sampling strategy and OCPs characterisation in peri-urban 381 agricultural area

382 Since the intermediate dimensions of a peri-urban agricultural area have been barely studied in literature,
383 there was high demand to develop and adapt a sampling strategy suitable to the spatial characteristics of
384 the study area. The method described here permitted to characterise the Dieldrin distribution pattern at
385 this peri-urban scale with an average sampling density of 10 samples per km^2 . This method was more
386 appropriate than the ones used at a regional scale ($10^{-2} \cdot \text{km}^{-2}$), and cheaper than the sample density used
387 for small surface studies ($10^4 \cdot \text{km}^{-2}$) (Hashimoto, 2005; Mattina et al., 1999; Meijer et al., 2001). Indeed, it
388 would have been impossible to characterise both homogeneity at plot scale and heterogeneity at peri-
389 urban scale with the previous methods, where the first one being inappropriate for the present scale
390 because indicating soil contamination heterogeneity on $100 \times 100 \text{ m}^2$ distant from several kilometres (Jiang
391 et al., 2009; Qu et al., 2016; Tao et al., 2008; Yu et al., 2013), while the second one would have led to the
392 collection and analyses of tens of thousands of soil samples. It can thus be concluded that this kind of semi-

393 random nested sampling strategy is efficient for characterisation of soil contamination in agricultural areas
394 of several square kilometres. Within these areas, to further characterise OCPs contamination and pilot
395 management options, the role of historical amendments and ploughing practices have to be considered in
396 relation with the high persistence of OCPs in the environment. In the same line of thoughts, the present
397 study confirms that in such areas with problematic levels of contamination, primary pesticide applications
398 appear to be more significant than secondary dispersion.

399 5. Conclusion

400 Because of the characteristics of the agricultural area, composed by several plots of about 1 ha, a semi-
401 random nested sampling strategy was adapted from literature. This sampling strategy allowed to
402 characterise OCPs contamination at both plot and peri-urban agricultural area scales. Therefore, future
403 research conducted on these particular dimensions could use the sampling method developed here to
404 optimise spatial characterisation and analyses costs.

405 Among 15 OCPs studied here, Dieldrin was the predominant contaminant in vegetable growing soils with
406 concentrations ranging up to 203.9 $\mu\text{g}\cdot\text{kg}^{-1}$. This Dieldrin contamination was homogenous in each plot but
407 heterogeneous at the scale of the peri-urban agricultural area. Although the exact amounts were unknown,
408 the main factor influencing the Dieldrin horizontal distribution at the study area was the anthropogenic
409 historical amendments of Dieldrin conducted on each plot in the second part of the XXth century. The
410 characterisation of vertical distribution of Dieldrin showed that contamination concentrations decreased
411 with depth and more than 85% of the contamination was located in shallow subsurface (0-40 cm depth).

412 In this study, no correlation was observed between soil Dieldrin concentration and the investigated soil
413 parameters (humidity, grain size fractions, pH and CEC) except SOM for which Dieldrin contamination was
414 clearly relevant at different grain size but not at bulk soil scale. This grain size discrimination allowed to
415 observe a linear relation between Dieldrin concentration and SOM content, with a partition coefficient 33
416 times higher for coarse sand than fine sand, and silts and clay fractions. Because of the predominance of
417 coarse sand fraction in the investigated soils, this highlights the major contribution of coarse grain size
418 fraction in the extractability of Dieldrin concentrations from the soil. Because of this different
419 contamination contribution and the variations of coarse sand repartition in soils, it prevents identification
420 of relationships between SOM and Dieldrin contamination in bulk soil at the studied agricultural peri-urban
421 area scale. Future research is necessary to investigate the SOM composition in different grain size fractions
422 that could explain the difference of Dieldrin concentration/extractability observed in the present study.

423

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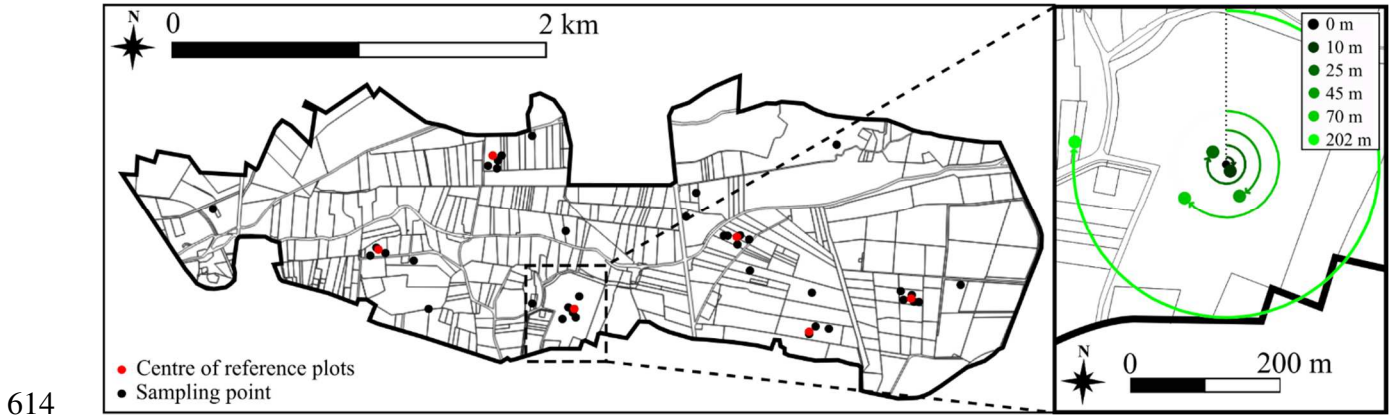
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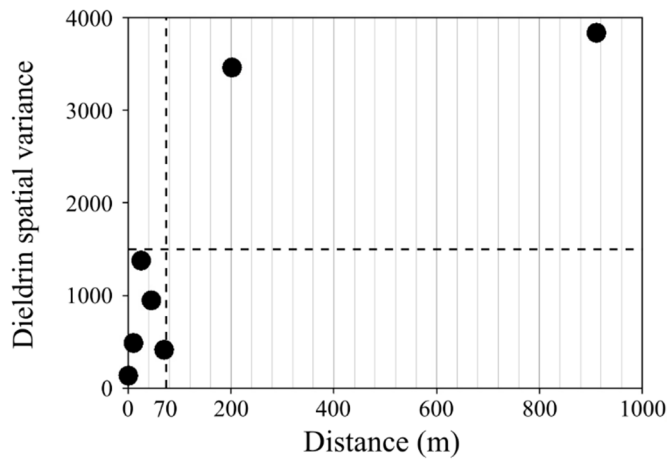
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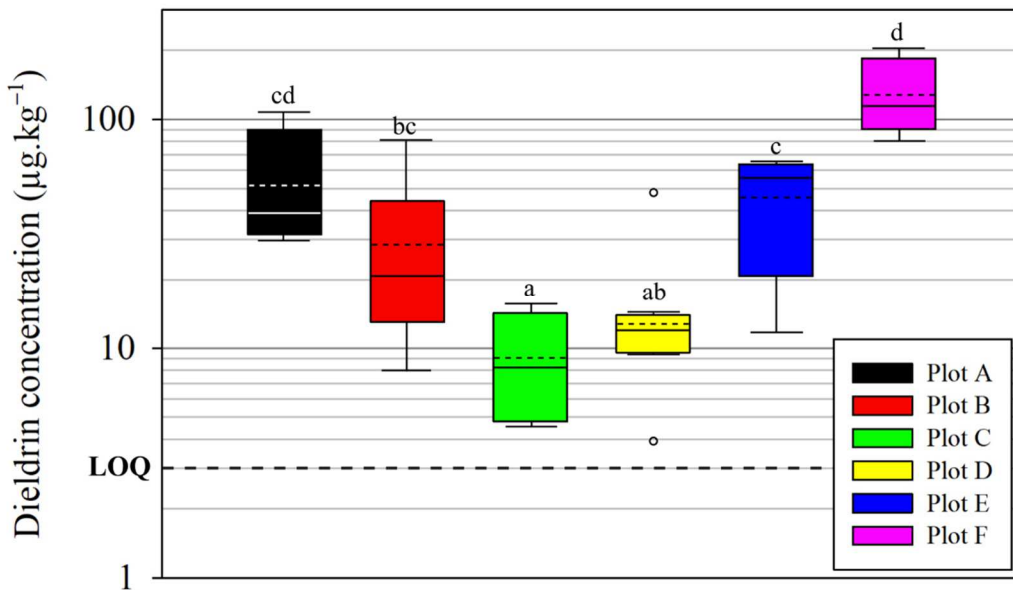
613 6. Artworks



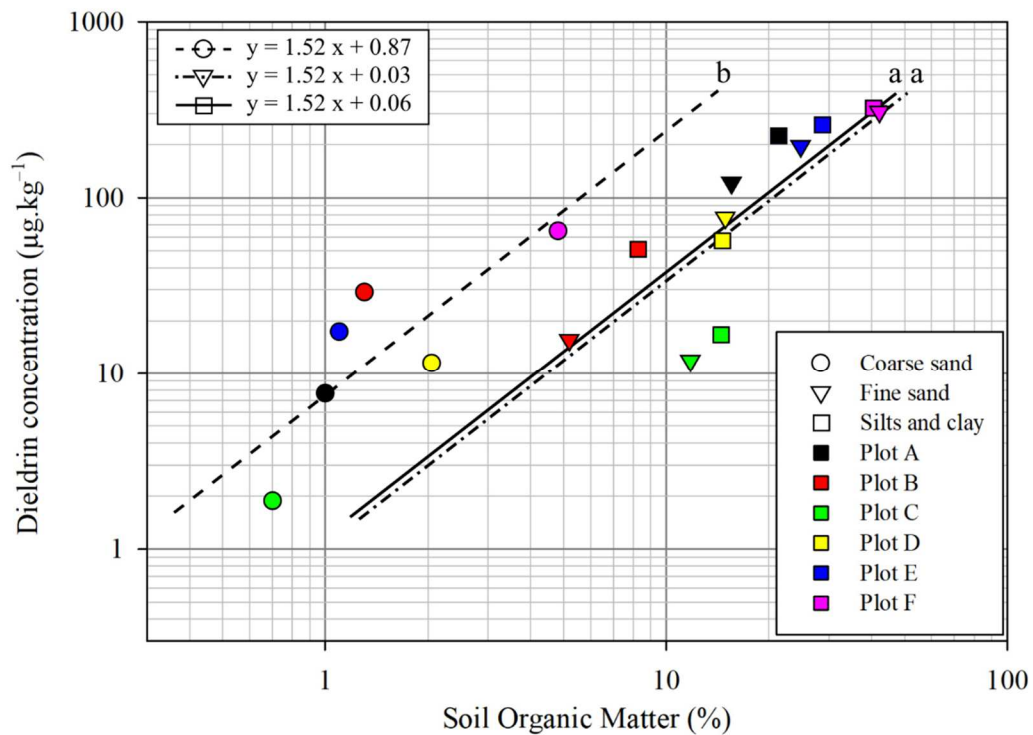
615 *Figure 1: Location of the soil samples collected in the study area (left) and example of the sampling strategy with the central point,*
 616 *the associated distances and the random angles (right).*



617 *Figure 2: Dieldrin spatial variance against distance from the centre of each reference plot in the peri-urban agricultural area*
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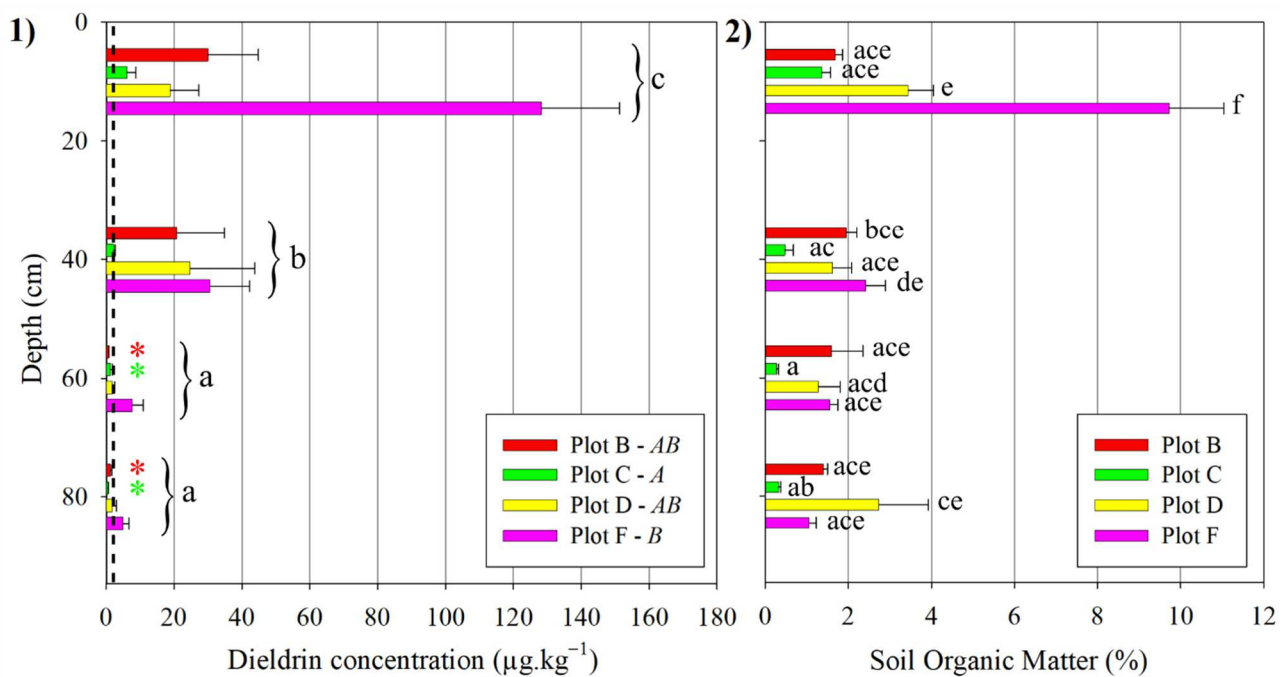
619 *Figure 3: Soil Dieldrin concentration on the 6 reference plots at 0-20 cm depth (solid line in box: median, dotted line in box: mean,*
 620 *LOQ: Limit of Quantification). The different letters indicate significant differences (posthoc Tukey multiple comparisons). Note that*
 621 *Dieldrin concentrations are shown and analysed on the log scale to fit linear modelling assumptions.*
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Figure 4: Relation between Dielddrin concentrations and SOM content according to the 3 different grain sizes of the 6 reference plots. Fitted lines by linear mixed modelling (random effect = plot belonging) for the relationship between Dielddrin and SOM for each grain size are shown. Different letter indicates significant difference of intercept between lines (posthoc Tukey multiple comparisons). The relationships were analysed on a log-log scale to fit linear modelling assumptions.



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Figure 5: Dielddrin and SOM vertical distribution patterns on plot B, C, D and F. 1) Dielddrin vertical distribution (dashed line indicates LOQ and * indicate Dielddrin concentrations below LOQ). Different letters indicate significant differences between Dielddrin values for each depth (posthoc multiple Tukey comparisons). The different plots also influenced Dielddrin concentrations as shown by capital italic letters next to plot names in the legend (posthoc multiple Tukey comparisons). The interaction between depth and plot is not significant. 2) SOM vertical distribution. Depth, plot affiliation and finally, the interaction between depth and plot being significant, different letters indicate significant difference between all combined situations (posthoc multiple Tukey comparisons)

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636 7. Tables
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Table 1: Soil physicochemical properties and Dieldrin contamination

Soil property	N samples	Mean (SE)	Median	Range	Detection frequency	Quantification frequency
pH	99	6.6±0.1	6.8	4.1 - 8.1	/	/
Humidity rate (%)	99	14.8±0.7	13.5	3.5 - 52.2	/	/
SOM (%)	99	3.2±0.6	1.9	0.1 - 52.1	/	/
CEC (cmol.kg ⁻¹)	30	10.8±2.9	6.3	1.9 - 92.0	/	/
OCP						
Dieldrin (µg.kg ⁻¹)	99	38.2±5.9	14.7	<LOD to 203.9	90	60

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Table 2: Percentage of grain sizes in soils and associated Dieldrin concentration and pH of the six reference plots (mean (SE))

Plot		Coarse sand	Fine sand	Coarse silt	Fine silt	Clay
		(2000 – 200 µm)	(200 – 50 µm)	(50 – 20 µm)	(20 – 2 µm)	(< 2 µm)
A	Fraction %	79.6 (0.4)	8.4 (0.2)	1.9 (0.1)	3.2 (0.1)	6.9 (0.2)
	[Dieldrin] (µg.kg ⁻¹)	7.7	120.1		224.2	
	pH	6.6	6.3		6.2	
B	Fraction %	80.1 (0.4)	8.0 (0.6)	1.1 (0.1)	2.5 (0.2)	8.3 (0.2)
	[Dieldrin] (µg.kg ⁻¹)	29.1	15.6		50.9	
	pH	7.7	6.8		6.7	
C	Fraction %	84.5 (1.2)	6.3 (0.5)	1.0 (0.5)	1.8 (0.2)	6.4 (0.1)
	[Dieldrin] (µg.kg ⁻¹)	1.9	11.8		16.8	
	pH	5.5	5.0		4.8	
D	Fraction %	73.7 (3.9)	6.1 (2.2)	4.4 (2.0)	4.9 (0.4)	11.0 (0.9)
	[Dieldrin] (µg.kg ⁻¹)	11.5	77.2		56.6	
	pH	7.0	6.7		6.5	
E	Fraction %	85.3 (0.6)	4.6 (0.2)	0.6 (0.0)	3.0 (0.2)	6.6 (0.6)
	[Dieldrin] (µg.kg ⁻¹)	17.4	196.5		259.6	
	pH	5.8	5.4		5.4	
F	Fraction %	80.6 (0.9)	4.6 (0.5)	0.7 (0.2)	3.9 (0.2)	10.3 (0.8)
	[Dieldrin] (µg.kg ⁻¹)	64.2	311.5		321.0	
	pH	7.2	6.8		6.8	
All plots	Fraction %	80.6 (1.1)	6.3 (0.5)	1.6 (0.5)	3.2 (0.3)	8.2 (0.5)
	[Dieldrin] (µg.kg ⁻¹)	21.9 (8.5)	122.1 (43.1)		154.8 (48.0)	
	pH	6.6 (0.3)	6.2 (0.3)		6.1 (0.3)	

Graphical abstract

