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# Spatio-temporal variability of water pollution by chlordecone at the watershed scale: what insights for the management of polluted territories?

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- 18 Abstract

19 Chlordecone, applied on soils until 1993 to control banana weevil, has polluted waters resources in the 20 French West Indies for more than 40 years. At the watershed scale, chlordecone applications were not 21 homogenous, generating a spatial heterogeneity of the pollution. The roles of climate, hydrology, soil, 22 agronomy and geology on watershed functioning generate a temporal heterogeneity of the pollution. 23 This study question the interactions between practices and the environment that induce such variability. 24 We analyzed hydrological and water pollution datasets from a two years monitoring program on the 25 Galion watershed in Martinique (French West Indies). We conjointly analyzed: i) weekly CLD concentration monitored on 3 river sampling sites, ii) aquifer piezometric dynamics and pollutions, and 26 27 iii) agricultural practices on polluted soils. Our results showed that chlordecone pollution in surface 28 waters are characterized by annual trends and infra-annual variations. Aquifers showed CLD 29 concentration 10 times higher than surface water, with CLD concentration peaks during recharge events. 30 We showed strong interactions between rainfall events and practices on CLD pollution requiring a 31 systemic management approach, in particular during post cyclonic periods. Small sub-watershed with 32 high CLD pollution, appeared to be substantial contributor to CLD mass transfers to the marine 33 environment via rivers, and should therefore receive priority management. We suggest increasing stable organic matter return to soil as well as external input of organic matter to reduce CLD transfers to water. 34 35 We identified hydrological conditions – notably drying periods – and tillage as the most influential factors on CLD leaching. In particular, tillage acts on 3 processes that increases CLD leaching: organic 36

- 37 matter degradation, modification of water paths in soil and allophane clay degradation.
- 38

#### 39 Keywords

40 Chlordecone, pollution, observatory, hydrology, environment, management, practices

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# 46 **1 Introduction**

47 The protection of surface and groundwater resources from pesticide pollutions is a remaining challenge. 48 Such question is a live issue in tropical volcanic island and especially in the French West Indies (FWI) where organochlorine pesticide, namely chlordecone (CLD; C10Cl10O; CAS number 143-50-0; 491 49 50 g.mol<sup>-1</sup>) was used in agriculture in Guadeloupe and Martinique islands. CLD was applied from 1972 to 1993 to control the black banana weevils (*Cosmopolites sordidus*). Since a few decades, it pollutes soils, 51 52 surface waters and groundwaters in a chronic manner. CLD is a very stable pesticide that shows a very 53 slow degradation rate that is not evenly quantifiable (Cabidoche et al. 2009; Clostre et al. 2015; Devault et al. 2016). Because of the very high affinity of chlordecone with soil organic matter -Koc ranging from 54 55 1200 to 17500 L.kg<sup>-1</sup> (Cabidoche et al. 2009; Fernandez-Bayo et al. 2013a)-, only small fractions of the soil CLD amounts are drained by infiltrated water. However, despite its low mobility, the drained 56 57 fraction of CLD was enough to highly contaminate other environmental compartments, such as aquifers and rivers (Cabidoche et al. 2009; Cattan et al. 2019; Charlier et al. 2015; Crabit et al. 2016; Della Rossa 58 59 et al. 2017; Gourcy et al. 2009; Mottes et al. 2015). Several crops grown on polluted soils might as well be contaminated depending on their nature (Clostre et al. 2017). Such pollution of food and water 60 61 exposed population to sanitary issues (Multigner et al. 2016). In order to face the problem, strategies 62 were developed to limit the exposure of the population: drinking water is treated using active carbon 63 (Ranguin et al. 2017) and decision rules were developed for cropping crops depending on their sensitivity to CLD pollution from soil (Clostre et al. 2017). The development of such management 64 65 strategies were helpful to reduce the exposure of the population to the pesticide.

66 Chlordecone was found into aquatic coastal fauna (Dromard et al. 2018) and until pelagic cetacean (Méndez-Fernandez et al. 2018). Such results suggest subsequent amount of CLD transferred into the 67 sea and raises the question of the sources, questioning the past or the present provenance of such 68 69 contamination. It is known that soils are still the main CLD storage (Lesueur-Jannoyer et al. 2012; Levillain et al. 2012) and that CLD transfers from soils to the other environmental compartments is 70 71 governed by water flows (Mottes et al. 2016). To that point, CLD behavior in soils has been investigated 72 (Cabidoche et al. 2009; Clostre et al. 2015; Fernandez-Bayo et al. 2013a; Fernandez-Bayo et al. 2013b), 73 especially, the effect of the allophanic clay of andosols favoring CLD retention in soil (Woignier et al. 74 2012a), or the effect of added organic matter on CLD transfers (Woignier et al. 2012b).

75 All of these characteristics draw a complex system whose evolution is difficult to assess. On that topic, Cattan et al. (2019) analyzed the spatio-temporal variability of CLD and its main metabolite (CLD-5b-76 77 hydro) in FWI. Authors showed significant decreasing trends of CLD concentrations in waters on some 78 large watersheds. This is consistent with general literature on pesticides: because CLD is not applied 79 anymore, one may expect slowly decreasing concentration in the terrestrial environment. However, 80 because of the very low degradability of CLD, authors highlighted that the pluri-annual CLD decrease in leaching water was likely mostly generated by CLD transfer to another compartment rather than its 81 82 degradation. This forces us analyzing jointly CLD concentration in the environmental compartments 83 that are related to each other in order to understand the CLD exportation from the watershed system. 84 According to the literature, several factors modify pesticides transfers at the watershed scale: climate, 85 hydrogeological context, cropping practice, soil properties as well as the interaction between these factors (Lewis et al. 2016; Mottes et al. 2014; Mottes et al. 2017). Evolution of CLD concentrations in 86 87 rivers may also show different variabilities depending on the time and space scales considered. Previous 88 studies showed that CLD seasonnal dynamics varied with the strong contributions of unpolluted water 89 from a forested upstream sub-watershed (Crabit et al. 2016). Gourcy et al. (2009) showed that 90 groundwater residence times in aquifers last from years to decades in FWI. We expect that such long 91 residence times may result in long-term evolution of CLD in rivers.

92 In this study, we aimed to characterized factors that determine CLD transfer outside the watershed 93 system. Given that CLD is mainly exported through rivers, we focused on the conjoint analysis of 94 agricultural practices and the evolution of CLD into surface and groundwater. We considered the case 95 of the Galion watershed in Martinique (FWI). This watershed is monitored to survey CLD pollutions in

96 surface and underground water compartments. First, we identified trends and variabilities of CLD

- 97 concentration in the different environmental compartments monitored. Second, we discussed factors that
- 98 may have influenced the modification of CLD concentrations in both, rivers and aquifers. Third, we 99 assess the contribution of different sub-watersheds to CLD transfers into the sea (Galion bay). Finally,
- 100 we propose strategies to prioritize actions and to help reduce CLD transfers into the environment.

# 101 2 Materials and Methods

### 102 **2.1 Study site**

103 The Galion river watershed (61°4.4004′W/14°36.5352′ N) is located on the East coast of the Martinique, 104 a volcanic island in the French West Indies. This watershed is part of the OPALE observatory 105 (Observatoire des Pollutions Agricoles aux Antilles - Observatory for agricultural Pollutions in 106 Antilles). It was selected for its representativeness of the various agropedoclimatic conditions of 107 Martinique.

- 108 The watershed covers 44.5 km<sup>2</sup> ranging from altitudes 0 to 694 m above sea level. The climate is humid
- 109 tropical with oceanic influence. Rainfall range from 1500 mm.y<sup>-1</sup> downstream up to 4000 mm.y<sup>-1</sup>
- 110 upstream. The hydrosystem is composed of 4 major permanent watercourses and a very dense network
- 111 of intermittent gullies (Figure 1).
- 112 Steep slopes (>80%) with tropical forest and agricultural land for livestock and traditional food
- 113 production characterize the watershed upstream. The soils are volcanic ash soils (andosol) characterized
- by high infiltration rates (Cattan et al. 2006) and high organic matter concentration (Dorel et al. 2000).
- 115 Soft slopes (~35%) cropped with banana and mixed farming on intergrade soils between andosol and 116 compact ferralsol characterize the intermediate zone. A flood plain characterize the downstream zone
- where industrial crop productions, including banana and sugar cane, take place on ferralsols (Figure 1).
- where industrial crop productions, including banana and sugar cane, take place on terraisois (Figure 1).
- 118 The bedrock is composed of volcanic formations of andesitic type (Germa et al. 2011). Geological 119 formations are thus composed by ash flows, lava flows, and reworked formations as well as atmospheric
- 120 fallout on a larger scale. Such geology generates a high spatial variability of lithology strata and
- 121 contrasting weathering levels between geological units. Consequently, volcanic aquifer's units have
- 122 small dimensions of a few square kilometres at most, generating complex groundwater flows according
- 123 to more or less permeable materials (Charlier et al. 2011; Vittecoq et al. 2015).



125

124

Figure 1: Map of the Galion watershed, positions of the 3 sub-watersheds, wells, rain gauges, risk of CLD pollution risk. Pollution risks following the method described in Desprats et al. (2004) and applied by Della Rossa et al.

128 (2017).

We monitored the two sub-watersheds BDL (Base de Loisirs - 8.5 km<sup>2</sup>) and LD (La Digue – 1.9 km<sup>2</sup>) in addition to the whole GG (Grand Galion) sub-watershed that covers 35.9 km<sup>2</sup> (Figure 1). The monitoring of the GG sub-watershed aims at representing the functioning of the whole Galion watershed with widely integrated flow from upstream to downstream. The BDL sub-watershed corresponds to the upstream watershed and its monitoring aims at representing the functioning of the upstream zone. The LD watershed is a small sub-watershed located on extremely polluted soils and its confluence with the Galion River is located downstream the GG outlet. The monitoring of LD aims at representing the

136 functioning of small tributaries. LD has no direct hydrological connection with BDL or GG.

#### 137 2.2 Spatial variability of pollution

- The 3 monitored sub-watershed (GG, BDL and LD) have different characteristics in terms of risk of pollution (section 2.4.2). Two sub-watersheds have a majority of surface with low risk of pollution, with BDL being the less polluted: 86% with no risk, followed by GG (75%). LD with 29% of low risks area
- has a majority of its area polluted (**Erreur ! Source du renvoi introuvable.**). Figure 1 shows that on
- 142 GG, the polluted areas are mainly located in the intermediate area of the sub-watershed. They are located
- downstream on BDL and all over the watershed on the small LD sub-watershed because of its very large
- 144 rate of polluted area.

5

	Very high risk 1970+1980+1992	High risk (1970or1980)+1992	Medium 1992	Medium 1970	No historical banana
BDL	0.5%	11.3%	0.9%	1.1%	86.2%
GG	2.2%	14.6%	4.9%	3.4%	74.9%
LD	29.7%	27.6%	3.5%	10.5%	28.7%

145 Table 1 : Percentage of risk of contamination for each watershed (percentage of total area)

#### 146 2.3 Hydrological monitoring and water sampling

#### 147 **2.3.1 Rainfall, hydrological and hydrogeological monitoring**

148 Daily rainfall for station « Bois Lézard » (BL) and « Trinité Réservoir » (TR) were acquired from Météo

149 France. « Bois Lézard » is located upstream and « Trinité Réservoir » midstream (see Figure 1 for

150 locations). This combination of stations provided an overview of the rainfall gradient from up to 151 downstream.

152 Discharges at the watershed outlets of BDL and LD were measured at a 3 minutes time step using a

153 MS5 sensor (HYDROLAB<sup>®</sup>) and recorded on DuoSens stations (OTT<sup>®</sup>). We gauged BDL and LD using

154 current meter and Salinomadd (MADD®). We used the Manning-Strickler relationship based on

155 measurement of sections of the stream to estimate discharge for high water levels.

156 The direction of the environment, management and housing (DEAL) from Martinique performed the

157 GG watershed gauging and hydrological monitoring. Data are accessible through the HYDRO 158 EauFrance website (http://www.hydro.eaufrance.fr/).

EauFrance website (<u>http://www.nydro.eaufrance.fr/</u>).

159 Groundwater level was recorded in 5 wells (see Figure 1 for location), equipped with automatic

160 piezometric level recorders (OTT<sup>®</sup>): Malgré Tout (FMT) – depth = 45 m, Mont-Vert (FMV) – 15 m,

161 Bassignac (FBASS) -50 m, Grand Galion (FGG) -50 m and Petit Galion (FPG) -43 m.

#### 162 2.3.2 Water sampling in rivers and wells

163 We sampled water in rivers using two different methods. A first campaign was performed in 2013 by

sampling all river confluences within 5 days with punctual (one off) sampling. For more detail, the

165 protocol is described in Della Rossa et al. (2017).

166 The second campaign started in February 2016. We sampled water at the 3 sub-watershed outlets (BDL,

167 LD and GG) with a time dependent sampling protocol. To that purpose, each pollution measurement

station was equipped with an automatic sampler: ISCO 6712 (ISCO Incorporation<sup>®</sup>) sampler on BDL;
 Sigma SD900 (Sigma<sup>®</sup>) sampler on GG and LD. Throughout each week, that lasted from Monday to the

next Monday unless exception, the sampling frequency of each sampler was set to sample twice 100 mL

every 1h15. One sample was stored in a plastic container while the other in a glass container. Both

172 containers were collected once a week meaning that each week the composite sample in each bottle

173 integrated on average 135 samples. At the end of each week, we collected the two containers containing

174 the composite samples and filled the bottles provided by the laboratory (3 glass bottles:  $2 \times 1 L + 100$ 

175 mL and 2 plastic bottles : 2 x 150 mL totaling 2.4 L) with the composite samples stored in the plastic

and glass containers. Samples were collected every weeks from 01/02/2016 to 01/02/2018 and sent in

177 ice coolers.

From October 2016 to March 2017, GG station was destroyed by a large storm (Matthew). During thatperiod, we performed punctual sampling each week.

180 During our sampling Campaign, French Water Office ODE also sampled water monthly at the GG

181 outlet. Punctual sampling was performed once a month and analyzed by LDA26 for pesticide 182 concentration.

- 183 For groundwater, sampling was based on standard NF EN ISO 5667-3, and the FD T 90-523-3 and FD
- 184 X31-615 guidelines. Before sampling in wells, at least three purge volumes were pumped with a

- 185 submersible pump until stabilization of the chemical groundwater parameters. Samples were stored at
- 186  $5^{\circ}$ C and shipped in ice coolers before expedition for analysis.

#### 187 2.3.3 Chlordecone analysis

- 188 We send the aliquots to laboratory for pesticide analysis. The selected LDA26 laboratory has been
- 189 accredited by Cofrac, the French Accreditation Committee for pesticide analyzes providing guarantees
- 190 for their technical skills and reliability as well as good management practices. LDA26 complies with
- 191 ISO 17025 standards for testing and calibration.
- Laboratory performed liquid/liquid extractions on samples. One liter of water sample was submitted to
   3 extractions by using 50 mL of a mix of dichloromethane (80%) and ethyl acetate (20%). One cycle
- 194 was performed at pH 7 and two cycles at pH 2. Extract was concentrated to 1mL in ethyl acetate. The
- extract was then split into twice 500  $\mu$ L. 500  $\mu$ L were use for GC MS and 500  $\mu$ L for HPLC MS MS.
- 196 The HPLCC MS-MS was done on two transitions: 506.7/424.5 and 506.7/426.5 with a Sciex API 4000
- 197 QTRAP. Internal standards used as tracers were hexabromobenzene, tributylphosphate (added at
- 198 extraction step), 2.4D3, Atrazine D5 (added at injection step) in multiple residual analysis.
- 199 The validation was done according to NFT 90210 standards. The limit of quantification was determined
- 200 using six times two repetitions, the reproducibility using at least eight additions of CLD at LOQ at
- different dates. The trueness, recovery were estimated by using six times two additions of CLD at 3
   concentrations. Uncertainty was estimated using six times two additions of CLD.
- A GC quality control is performed every 20 samples at LOQ. Laboratory performed an internal calibration on 5 points before each analysis sequence. CLD addition on matrix and participation to inter
- 205 laboratory comparison were also performed to control the quality of results.
- 206 CLD concentrations are given by the laboratory with a  $\pm 35\%$  error interval, a limit of quantification
- 207 (LOQ) of 0.01  $\mu$ g.L<sup>-1</sup>, a limit of detection (LOD) of 0.0033  $\mu$ g.L<sup>-1</sup>. The extraction efficiency is 89%.

# 208 2.4 Agricultural practices and risks of soil pollution

# 209 2.4.1 Actual agricultural practices

- 210 Surveys on farms located on the watersheds were performed between November 2016 and January 2016.
- 211 During surveys, decision rules for practices application and plantation dates were inquired. We analyzed
- the evolution of fallow and crop plantations at the watershed scale using the field geographical register
- 213 (RPG) from 2016 and 2017 (Direction of Agriculture And Forest of Martinique DAAF 972). These
- 214 georeferenced data describe agricultural land uses in 2016 and 2017 as declared by farmers.

# 215 **2.4.2** Mapping the risk of soil pollution

- The risk of soil pollution by CLD was estimated following the method described in Desprats et al. (2004) and applied by Della Rossa et al. (2017) on the Galion watershed. The method rely on a retrospective
- analysis of banana land use during the period of CLD application in Martinique (1972–1993). Soil
- 219 pollution risk was classified according following rule: i) Very high risk for banana plantations present
- 220 in 1970, 1980 and 1992, ii) High risk for banana plantations present for two out of the three years, iii)
- 221 Medium + for banana plantations present in 1992 only, iv) Medium for banana plantations present in
- 222 1970 only, and v) No historical banana.

# 223 2.5 Data analysis

- 224 We compared distributions of CLD concentrations between the two years using the non-parametric
- 225 Wilcoxon Mann-Whitney test. In order to visualize CLD concentration trends, we applied a Hodrick-
- 226 Prescott filter on the data. This filter was designed to separate long-term trends to short-term variations,
- suiting our need for pollutants dynamic analysis as previously applied by Sun et al. (2013). The best
- 228 captures of trend were obtained with lambda parameter:  $1600 \times 3^4$ . The baseflow component of the
- discharge time series was calculated using the one-parameter recursive digital filter proposed by Lyne

and Hollick (1979) implemented in the HydRun package (Tang and Carey 2017). The best capture of
 baseflow component of the discharge time series were acquired with parameter value of 0.8.

#### 232 2.6 Transfers estimation

Chlordecone mass transferred at the outlet of each instrumented watersheds was computed for each dayusing the formula.

235 
$$Q_{cld} = WeeklyAVGCLD * dailyDischarge * \frac{3600 \times 24}{1000}$$
 (1)

With  $Q_{cld}$  the daily mass of CLD transferred at outlet (g), *WeeklyAVGCLD*, the weekly average CLD concentration in water samples (µg.L<sup>-1</sup>) and *dailyDischarge* the average daily discharge at sampling point (m<sup>3</sup>.s<sup>-1</sup>). The other term is a unit conversion factor.

- We calculated the daily mass of CLD transferred at outlet per unit of polluted area (classified in low, medium-, medium+, high or very high risks) by dividing  $Q_{cld}$  by the polluted surface of each subwatershed estimated with the methodology described in 2.4.2.
- watershed estimated with the methodology described in 2.4.2

#### 242 **3 Results**

#### 243 **3.1 Evolutions of CLD concentration in rivers**

#### 244 3.1.1 Infra-annual evolution

- Rainfall, discharge and CLD concentrations recorded on the 3 monitoring stations are presented in Figure 2. The proximity of rainfall and flood peaks for the 3 stations on a daily basis, illustrated that the
- 247 watershed quickly reacted to rainfall events at the sub-watershed as well as the watershed scales.
- 248 Reaction time of each watershed or sub-watershed was less than one day.



Figure 2 : Hydrology and chlordecone dynamics on the 3 sampling sites of the watershed. Red dots: ODE data.

Grey lines on CLD concentration graphics: Hodrick-Prescot filter and ±35% error interval. Grey dashed lines on
 discharge graphics: baseflow. Orange vertical line: Matthew storm.

253 Figure 2d and 2f shows that the trend of the CLD concentrations were correctly assessed by the Hodrick-254 Prescott filter at BDL and LD stations because most measurements fell within the ±35% interval around 255 the filtered values which correspond to the laboratory analytical uncertainty on CLD concentration measurements. Deviations from the trend may also results from shorter wavelength processes, such as 256 257 flooding, sampling uncertainty, organic matter or sediments in samples. The dynamics highlighted by 258 the filter showed patterns with period of increasing and decreasing concentrations. The up and down 259 trends highlighted by the filter were within the same periods on BDL and LD stations. According to this 260 result, it is likely that the dynamics we observed had a common causality. We observed that short-term increase of baseflow is associated with CLD concentration decrease on all stations, while short-term 261 262 baseflow decrease are associated with CLD increase (see between 02/2016 and 09/2016 - Figure 2). During that period, CLD concentrations decrease on all station between 02/2016 and 04/2016, then it 263 264 increased between 04/2016 and 05/2016, and decreased again between 05/2016 and 07/2016. This behavior corresponds to the hydrological functioning of the watershed and subwatersheds subjected to 265 266 small hydrological variations where the baseflow in not subjected to changes in regimes that last more 267 than few months. A finer analysis on the trends showed that an uptrend started few time after the 268 "Matthew" storm (29/09/2016) when baseflow decreased and ended in March 2017. The trends were 269 more difficult to assess on the GG station (Figure 2b) due to the lack of integrated data between 10/2016 and 03/2017 after debris transported in water few time after the Matthew storm destroyed our station. 270 271 In fact, punctual sampling at that time showed high values: from 12/2016 to 04/2017 in particular, 12 272 punctual samples out of 15 had CLD concentrations higher than 1.1 µg.L<sup>-1</sup> while the average concentration from 02/2016 to 02/2018 was 0.75 µg.L<sup>-1</sup>. The ODE follow up also suggested high CLD 273 274 concentrations during that period. Starting from June, ODE data followed a bell shaped dynamic while 275 our integrated sampling did not. In fact, concentrations measured by ODE decreased while the values 276 of our integrated measurements increased (see 10/2017 in Figure 2b). Punctual sampling results diverged 277 from the ones we obtained with integrated sampling indicating that CLD trends should not be easily 278 deduced from punctual sampling at the infra-annual temporal scale.

To summarize, we identified general trends in the dynamics of CLD according to our integrated sampling. It showed a good consistency between stations LD and BDL that have no direct hydrological connection. However, we also identified that punctual weekly samples led to record high variations of concentrations. It prevents from assessing trends of CLD concentration on punctual sampling and justify assessing CLD concentrations on a weekly basis.

#### 284 **3.1.2 Inter-annual evolution**

The inter-annual dynamics on LD (Figure 2f), highlighted an increase of CLD concentration in early 285 2017. Then, until late 2017, these concentrations remained higher than in 2016 (Table 2). Comparing 286 average concentration between 2016 and 2017, we observed i) a slight increase of CLD average 287 288 concentration on GG watershed (+15%), ii) average concentrations on BDL that remained stable over 289 the two years, and iii) that CLD average concentration almost doubled (+82%) between 2016 and 2017 290 on the LD watershed. However, average concentrations did not reflect distribution of pollution between 291 the two years The distributions of concentrations recorded in 2016 and 2017 were significantly different 292 for all sub-watersheds, being highly significant for GG and LD sub-watersheds (p-value<0.001), but in 293 a lower extent for BDL sub-watershed (p-value<0.05). This result shows that, on BDL, similar average 294 concentration (0.46 µg.L<sup>-1</sup>) resulted from different river behavior in 2016 and in 2017 (significantly 295 different distributions). Indeed, the trend analysis of BDL station showed that 2016 was characterized 296 by a stable CLD concentration surrounding 0.46 µg.L<sup>-1</sup>, while concentrations recorded during 2017 were 297 more variable with a CLD peak (>2  $\mu$ g.L<sup>-1</sup> - 03/2017) followed by an overall decrease of the 298 concentration ( $<0.46 \ \mu g.L^{-1}$ ) before returning to the initial value in 10/2017 (0.46 \ \mu g.L^{-1}) (Figure 2d).

- 299 Since we noticed in section 3.1.1 that LD and BDL have CLD trends showing similarities, the high
- increase in mean CLD concentration in 2017 for LD stemmed, on the one hand, from two CLD peaks
- instead of one for BDL and, on the other hand, from higher CLD contents after the first peak relative to
- 302 Matthew storm. This may be explained by the fact that the stabilized increase of CLD concentration in
- LD in 2017 is related to a higher baseflow level than in 2016 (Figure 2e and f). The fact that this small watershed is mainly drained by subsurface flows make it more responsive to modifications of land uses
- for instance. Such relationship with baseflow was not observed on BDL or GG. However, it might be
- that the increase of CLD concentration we observed on GG between 10/2017 and 01/2018 has the same
- 307 origin but delayed in time because it is 19 times larger than LD.

Sampling	CLD	CLD	
site	Mean	Mean	
	(2016)	(2017)	
	(µg.L <sup>-1</sup> )	(µg.L <sup>-1</sup> )	
GG	0.70	0.81	
BDL	0.46	0.46	
LD	5.54	10.08	

Table 2 : Average chlordecone concentration on the 3 sampling points for the 3 sampling campaigns (2013, 2016 and 2017).

310 Monitoring CLD concentrations on the 3 stations showed that CLD is a relatively stable and chronic

311 pollution in rivers. We showed that the CLD dynamics observed in river has two components: a trend

312 of inter-annual evolution that may be driven by baseflow as well as infra-annual variations surrounding

that trended evolution whose intensities vary according to stations and may be driven by specific event

314 like storms in the present case.

#### 315 3.1.3 Mass transfers

The average daily CLD mass transferred at the outlet of each sub-watershed, as well as the average daily

CLD mass transferred per unit of area polluted by CLD are presented in Table 3. According to Erreur !
 Source du renvoi introuvable., we deduced potentially polluted area on the 3 sub-watersheds: 116 ha

for BDL, 901 ha for GG and 136 ha for LD, meaning that the area between GG and BDL holds 785

320 potentially polluted hectares. The highest values of daily average CLD transferred at outlet were

321 recorded on GG, while lowest values were recorded on BDL (Table 3).

	2016			2017			
	Daily average (g.day <sup>-1</sup> )	Daily average per unit of polluted area	Specific discharge (m <sup>3</sup> .s <sup>-1</sup> .km <sup>-2</sup> )	Daily average (g.day <sup>-1</sup> )	Daily average per unit of polluted area	Specific discharge (m <sup>3</sup> .s <sup>-1</sup> .km <sup>-2</sup> )	
GG	91±171	(g.day <sup>1</sup> .na <sup>1</sup> ) 0.10	0.047	137±303	(g.day <sup>1</sup> .na <sup>1</sup> ) 0.15	0.065	
LD	52±169	0.38	0.052	68±124	0.5	0.042	
BDL	49±24	0.42	0.147	51±53	0.44	0.144	
GG-BDL	49±159	0.06	0.018	 97±266	0.12	0.027	

322 Table 3 : Chlordecone mass transferred by each watershed monitored

323 Table 3 shows that sub-watersheds with larger polluted area (GG and GG-BDL) are not necessarily the 324 one that transfers the most CLD toward our monitored outlet. BDL and LD having transfers rates by polluted area 4 times higher that GG or GG-BDL (Table 3). It means that in terms of mass, the area 325 between BDL and GG, in spite of large potentially polluted area had a lower transfer's rate to outlet. 326 327 The upstream zone (represented by BDL) is humid with large rainfall and characterized by a larger 328 specific discharge than the other sub-watersheds (Table 3). Large water volumes at relatively low CLD concentrations generated stabilized transfers at outlet as shown by the lower standard deviation than on 329 330 GG or LD (Table 3). This also means that GG and LD are more subject to large variations of daily CLD mass transferred. The small specific discharge of GG-BDL also indicate that the area between GG and 331 332 BDL has a small contribution to the discharge. Our results also shows that LD, in spite of its small size

- (191 ha) and low discharge compared to GG or BDL, transfers unneglectable mass of CLD because ofvery high water CLD concentrations.
- 335 Daily mass transferred by GG gave annual values from 33 kg.y<sup>-1</sup> to 50 kg.y<sup>-1</sup> of CLD transferred to the Galion Bay. For LD watershed, annual value transferred to the Galion bay ranged from 19 kg.y<sup>-1</sup> to 25 336 kg.y<sup>-1</sup>. This means that the total yearly contribution of that two outlets to the Galion bay may be 337 estimated from 50 kgCLD.y<sup>-1</sup> to 75 kgCLD.y<sup>-1</sup>. Using a simple assumption of constant transfer rate, and 338 339 without considering years of applications, we estimated total transfers to the bay from 1993 to 2018 to 340 be between 2500 kg and 3750 kg. This might be even more because we did not took into account 341 transfers from 1970 to 1993. These amounts represent between 2.4 and 3.6 kgCLD per ha of polluted area. This is low compared to the amount of CLD applied  $\approx 3 \text{ kg.ha}^{-1}$  at each application (Cabidoche et 342 al. 2009; Levillain et al. 2012) during more than 20 years. Calculations of CLD stocks in soils according 343 to Levillain et al. (2012) gave values of few kg of CLD stocked in soils in the 0-60 cm depth. This 344 345 suggests that, it is very likely that large amounts of CLD already transferred to other environmental 346 compartments, meaning that substantial amount of CLD could be in the marine environment and in 347 aquifers. Because CLD was applied around banana stems and banana fields were mainly cropped on 348 bare soils with stemflow at that period (Charlier et al. 2009) that conjointly favors surfaces transfers. It 349 is likely that the larger fraction of CLD that lacks in our CLD balance went mainly to the marine 350 environment during storms towards fast surface transfer processes such as runoff or subsurface flows,
- both concentrated in surface drains that were a very common on banana field at that time.

We showed that small watershed can nowadays have significant chlordecone transfers contributions to the ocean. In spite of the potentially large amounts of CLD that transferred in the past, we suggest that such areas with fast hydrological response should be managed with care and prioritized for pesticides reduction strategies as well as decontamination. We expect that the results of mitigation measures could be observable in the river in a couple of years for these areas.

#### **357 3.2** Evolutions of CLD in groundwaters

Piezometric levels on the 5 wells located on the watershed and CLD concentrations recorded in 4 of 358 359 these aquifers are presented in Figure 3: FPG (Fig.3b), FMT (Fig.3c), FBASS (Fig3d), FMV (Fig3e). 360 FBASS an FMT are deep aquifers while FGG, FPG, and FMW have piezometric levels around few 361 meters. CLD concentrations in groundwaters located in contaminated areas were 10 to 50-fold higher than concentrations measured in rivers (Figure 2 and 3). No chlordecone was found in FPG waters that 362 363 is consistent with its location upstream the polluted areas (Figure 1). Based on the punctual data set, we 364 can say that the CLD concentrations in aquifers varied along the year, but we could not define a clear 365 relationship between CLD concentrations and piezometric levels due to the scarcity of sampling. All aquifers sampled on the 03-11-2016, at the beginning of the high water level period, had particularly 366 high CLD concentrations. Then, CLD concentrations decreased in the following samples (Figure 367 3b,d,e), but remained always in a high range of values. Besides, each aquifer had its own piezometric 368 dynamic as shown in Figure 3. For instance, FMT had more inertial dynamic than FBASS or FMV, and 369 370 even more than FGG or FPG. According to Charlier et al. (2015), the dynamic between recharge and discharge to rivers can be very long for deep aquifers with residence times from 4 years (FMV), 6 to 8 371

372 years (FMT) to more than 20 years (FBASS).





Figure 3 : Piezometric levels and CLD concentrations in aquifers of the Galion watershed. Black dots: chlordecone
 concentrations. Grey lines: analytical uncertainty on chlordecone concentrations.

#### 376 **3.3 Evolutions of agricultural practices**

377 CLD polluted soil of the watershed are still mainly cropped with banana tree. This is because CLD is not quantified in banana fruit even when cropped on highly polluted soils (Clostre et al. 2017). CLD 378 being stored into soil, several grower practices might affect CLD transfers. According to our banana 379 380 grower survey, we could draw a general cropping system practiced by banana growers. Banana cropping system usually last around 7 years. During those 7 years, 5 or 6 years are indeed cropped with banana 381 and the remaining 1 or 2 years consist in a fallow period. The fallow period allows for the soil to rest 382 383 and eliminates diseases that developed in soil (nematodes and weevils) during the repeated banana cropping cycles. The fallow is established using herbicide injected into banana trees to kill them. Then, 384 385 soil is tilled (Figure 4b). A fallow cover crop may either be planted, for instance with C. spectabilis or B. decumbens, or results from spontaneous species (such as C. ruditosperma). Depending on farms, at 386 the end of the fallow period, either soil is tilled again before plantation, or banana tree are planted in a 387 388 mulch of plants killed with herbicide. On the farms of the Galion watershed, tillage is usually carried on 389 before or during the fallow period.

- Figure 4a shows the field of one farmer of the LD watershed right after the Matthew storm. This farmer cut all developed banana tree in its farm (25 ha out of the 79 ha of cropped area by all farmers on the
- 202 cut all developed balana tier in its farm (25 ha out of the 79 ha of cropped area by an farme.
- 392 watershed) because most developed trees were laid down by the storm.



393

- Figure 4 : a) Cycloned field just after the Matthew storm on the La Digue (LD) sub-watershed (C. Mottes
  Oct-2016). b) Fallow (grass with dead banana tree on the left) been tilled with excavator (bare soil) on
  the La Digue (LD) sub-watershed (C. Mottes Apr-2017).
- Figure 5 shows fallows surface evolution between 2016 and 2017. We can see that 2017 was characterized by large increase of fallow area on the watershed that almost doubled: in 2016 fallow covered 79 ha whereas it covered 139 ha in 2017. This means that larger area than usual were tilled on the watershed between 2016 and 2017. This practice of large fallow integration after a cyclone or a violent tropical storm is a common practice among banana growers in the FWI resulting in large-scale
- 402 modification of agricultural practices.



404 Figure 5: Evolution of fallow and banana between 2016 and 2017 (data from RPG 2016 and 2017 DAAF).

# 405 **4 Discussion**

403

#### 406 **4.1 CLD evolutions in rivers and aquifers**

407 Our results showed that river and aquifer pollutions by CLD was roughly stable and chronic. Several 408 authors have reported this (Crabit et al. 2016; Mottes et al. 2015; Mottes et al. 2017). However, CLD 409 concentrations in rivers vary according to sites. On the small LD subwatershed, we showed that CLD 410 interannual variability observed in river may be driven by baseflow. In the case of watersheds draining

- the highest reliefs of volcanic islands, Crabit et al. (2016) found correlation between CLD concentration
- 412 and discharge because the main process of CLD evolution was the dilution of water drained from lateral
- 413 cultivated areas by high amounts of unpolluted waters from the forested areas upstream. In the case of 414 watersheds draining mostly cultivated zones, Mottes et al. (2016) did not find such relationship on the
- watersheds draining mostly cultivated zones, Mottes et al. (2016) did not find such relationship on the
   Ravine watershed, highlighting complex conditions of CLD transfers. At the watershed scale, Della
- 415 Ravine watershed, inginighting complex conditions of CLD transfers. At the watershed scale, Dena 416 Rossa et al. (2017) showed that the spatial variability of CLD concentration in water during low flow
- 417 periods was explained by the potential pollution of the fields located on the watershed of the sampled
- 418 points. At the regional scale, comparing numerous watersheds in Martinique Island, Cattan et al. (2019)
- 419 showed that the spatial variability of CLD concentration may be explained by a combination of the
- 420 location of banana cropping areas, soil and geological factors; these conditions defining a high diversity
- 421 of situations in terms of the mid- to long-term duration of pollution.
- 422 Unlike previous studies, our results highlights that, at a weekly time step, CLD concentrations in rivers 423 showed annual evolution trends (Figure 2). Aquifers located in polluted area (Figure 1) showed higher 424 CLD concentrations during recharge (Figure 3) then followed by CLD uptrends in rivers (Figure 2). 425 Figure 2 and Figure 3 analyzed conjointly showed that the uptrends we observed in rivers followed the 426 generalized CLD peak in aquifer observed in 11/2016. Here, we are in the opinion that CLD 427 concentration increased in aquifers and rivers as the consequence of, either translatory flow (Lischeid et 428 al. 2002), or recent leaching of water highly concentrated with CLD. This suggests that surrounding that 429 time, factors generated an increase of CLD leaching to aquifers and subsurface flows.
- 430

# 431 **4.2 Factors explaining increased CLD leaching**

Increased CLD leaching from soils, that is still a large reservoir of CLD (Lesueur-Jannoyer et al. 2012),
to aquifers and subsurface flows is likely to have generated the increases of CLD concentrations in
aquifers and rivers we observed. Several factors that increase the availability of CLD into soil to water
flows can explain an increase of CLD leaching.

# 436 4.2.1 Effect of hydroclimatic conditions

437 Our results showed higher CLD concentrations on all wells situated in polluted area on the watershed at 438 a specific date: 03-11-2016 but we could not conclude on a relationship with piezometric levels. This 439 pattern is coherent with previous works carried out in similar hydrogeological context in Martinique 440 Island by Arnaud et al. (2016). Based on a higher resolution of sampling (monthly), these authors 441 showed that the intensity of piezometric fluctuations was not correlated with the amplitude of variations 442 in CLD concentration, but that the CLD higher concentrations were often observed during periods of 443 rising groundwater levels. Our results suggest that period of soil drying may increase the availability of 444 CLD to water flow during the first leaching events. This is in accordance with the observations of 445 Arnaud et al. (2016), showing that the main CLD peak in groundwaters from the last decade occurred 446 during the first major recharge event after a several year period of deficient recharge that resulted in a very low water table. This was true for 8 wells located all over the contaminated zones of the Martinique 447 Island, meaning that such regional pattern is likely controlled by hydroclimatic conditions. Following 448 449 this explanation, we expect that the main CLD higher concentrations observed in rivers of the Galion watershed after the storm of October 2016 is related to the higher groundwater concentrations observed 450 451 at that time.

# 452 **4.2.2 Effects of cropping practices**

453 CLD applications were forbidden after 1993, so that theoretically no applications occurred from that 454 date. As a result, the only agricultural practices that could have increased CLD leaching are the one that 455 modified environmental characteristics that affect pesticide transfers (Mottes et al. 2014). Here, 456 modifications of the soil organic matter content, allophane clay content, or both potentially decreased 457 CLD retention by soil (Woignier et al. 2016; Woignier et al. 2012a; Woignier et al. 2012b; Woignier et 458 al. 2013). It has been shown that the peculiar hierarchical (fractal) microstructure of allophane clay traps 459 CLD (Woignier et al. 2012a; Woignier et al. 2013). It is known that tillage activate soil organic matter 460 decomposition (Haddaway et al. 2017) and expose soil to direct sunlight, hence, to strong drying at its surface resulting in destruction of allophane (Quantin 1972) and allophane microstructure. During 461 462 drying, the fractal microstructure progressively disappears (Woignier et al. 2008). As a result, tillage would act on both degradation of soil organic matter and allophanes trapping properties in andosols. On 463 464 top of that, tillage destroy the soil structure. The destruction of the soil structure imply a modification of the water paths into soil (Alletto et al. 2010). Indeed, structured soils present preferential infiltration 465 flow that may be washed from extractible CLD after several time. Destroying those paths induce water 466 467 to access more porosity in soil and thus extract more CLD from soil. This may explain the difference of one order of magnitude found in CLD soil organic carbon coefficients (Koc) between modelling field 468 studies (Cabidoche et al. 2009; Mottes et al. 2015) and laboratory data (Baran and Arnaud 2013; 469 470 Fernandez-Bayo et al. 2013a). In the last, soils are totally destroyed (Oecd 2000) while in the first one structured soils are considered. Finally, tillage induces modifications of soil organic matter and clay 471 472 characteristics are modified as well as the soil structure. All these evolutions favor the leaching of CLD.

473 The modification of water path in soil could results from tillage but mays also results from modifications 474 of soil covers. According to Lewis et al. (2016) and to Mottes et al. (2014) practices that modify ground cover may modify pesticide leaching. This is particularly true for vegetative ground cover such as 475 476 banana tree. According to several authors, we know that banana trees concentrate rainfall along their 477 stem by a process called stemflow (Cattan et al. 2007; Charlier et al. 2009; Sansoulet et al. 2008). This 478 means that, in a cropped banana field, water will preferentially infiltrate right under banana tree (Cattan 479 et al. 2007; Sansoulet et al. 2008) generating preferential flow paths under banana tree. As for structured soil, we can expect that such preferential water path are "washed" from CLD after several time of semi-480 481 perennial banana cropping. Stemflow was also shown to increase runoff (Charlier et al. 2009), meaning 482 that this process also acts on reducing the overall leaching on banana fields. Consequently, stemflow 483 increases erosion of particulate CLD transfers as well as other surface pollutant transfers. To conclude, 484 it means that any modification that reduce stemflow is likely to increase leaching on the field.

485 Our results showed that between 2016 and 2017 the surface of tilled polluted fields increased (Figure 5) 486 on all monitored sub-watershed. Figure 1 shows that most soils of the watersheds contain allophane 487 clay, meaning that either tillage, dry period or both could have resulted in CLD uptrend. This means that 488 it increased the access of CLD to leaching water in 2017. Such processes could have generated 489 increasing CLD concentration in subsurface flows thus generating uptrends in river CLD concentrations 490 we observed on LD and BDL.

#### 491 **4.3** Integration of processes at the watershed scale

492 Our results showed that the different aquifers have contrasted piezometric inertia (Figure 3). In the 493 Galion watershed, Charlier et al. (2015) showed variable mean residence times varying from 4 years 494 (FMV), 6 to 8 years (FMT) to more than 20 years (FBASS). They also reported smaller residence times 495 of one year for sources or during high water levels. Because, rivers in FWI are mainly governed by 496 underground flows (Charlier et al. 2008; Crabit et al. 2016; Mottes et al. 2015), this means that, at the 497 watershed scale the river is likely to be fed by different aquifer's units having different inertia. The 498 combination of residence times and the multiplicity of aquifers contribute to the stability of CLD 499 concentration at the weekly time step. According to our results along with the ones of Charlier et al. 500 2015, there is every likelihood that only underground major contributors changing conjointly may 501 modify the trend of CLD concentration in rivers. The increased CLD concentration at LD confirms this. 502 LD watershed is mainly governed by subsurface flow and the monitored aquifer (FMV) has a short mean 503 residence time of 4 years, allowing it to be sensitive, among others, to strong cyclonic events. Our results 504 showed that the mid-term CLD concentration increase in 2017 is related to the increase of the baseflow 505 on this river (Figure 2e). According to our results, we are in the opinion that increasing CLD 506 concentrations rely on the activation of new water paths on polluted areas on the sub-watershed.

507

508 Our results showed that in rivers, CLD concentration in punctual and integrated sampling diverged 509 (Figure 2b). This behavior was unexpected, because we would expect to see both monitoring programs 510 showing the same dynamics for a chronic pollution such as CLD. One explanations could be that CLD concentrations shows large variations with time at the event scale as it was shown for CLD (Mottes et 511 al. 2016) and for other pesticides (Liger et al. 2012). The variability of CLD concentrations we obtained 512 when we performed weekly punctual sampling instead of integrated sampling (between Oct 2016 and 513 514 April 2017) supports that hypothesis because CLD concentration variation are very high at that period. 515 This could mean that integrated sampling integrates the contributions of the different zones of the watersheds taking into account the delayed transfers' times according to positioning on the watershed. 516 517 The CLD concentration trend we measured corresponds to the evolution of average concentrations that 518 integrates such variability. A variable transfers time according to positioning on the watershed was 519 suggested by Mottes et al. (2015) who included a delay in modelling CLD transfers into river according 520 to the distance of contributing areas. On large watershed, this short-term effect might be buffered at the weekly time step or induce larger dynamics on CLD transfers. On that point, our results showed that the 521 spatial organization of polluted fields differed in the 3 sub-watersheds, with LD being polluted on almost 522 523 all its area, BDL downstream and GG mid-stream. It could be that the spatial organization of polluted 524 area affected the CLD dynamics observed at the watershed scale (Figure 2): BDL showed uptrend 525 followed by downtrend that could correspond to downstream contributions followed by upstream contributions. As a result, the variation of CLD concentration of punctual and integrated sampling might 526 527 results from the contributions of the different transfer times of surface and subsurface flow generating a 528 dynamics at the short to mid-time scale depending on the size of the watershed.

529 CLD short terms variation could also come from the fact that sediments interacts with CLD in the 530 dissolved phase, especially in the sampling containers of our sampling stations. With automatic 531 integrated samplers, erosion events are sampled along the week with water. As a result, sediments enters 532 into the sampling container. They could increase CLD concentration in the sample because of CLD 533 bound to sediments. According to ODE data, sediments analyzed at the GG station between 2008 and 534 2015 revealed CLD concentration varying between  $<10 \ \mu g.kg^{-1}$  and  $30 \ \mu g.kg^{-1}$ . These values are low compared to soil CLD concentrations  $(0.1 - 5 \text{ mg.kg}^{-1})$ , but could be sufficient to modify CLD 535 concentrations in sampling containers according to the concentration value measured (Table 2) (Katagi 536 537 2006). Finally, higher variability of punctual sampling may be related to the difficulty to follow the same protocol at each sampling date. Notably sampling site may differ according to the possibilities of 538 539 access to the river.

540 Our results suggest either that there are variability of CLD concentrations at the instant time scale or a 541 strong interaction between dissolved and particulate phases. This means that the average concentration 542 we obtain in weekly samples results from CLD trends, variations of CLD concentrations all over the 543 week and from sediment dynamics in the river.

#### 544 **4.4 How to manage CLD pollution ?**

545 Our results showed that causes and processes that modify CLD concentration in water, are interrelated, 546 making it difficult to isolate single effects. A complexity exists at the watershed scale where different 547 organization levels and processes interact. Agricultural practices triggered according to climatic 548 windows stand for an example of such interaction. Banana is still mainly cropped on polluted soils 549 because it is not sensitive to soil pollution by CLD. Banana farming practices follow decision rules 550 based on climate (cyclonic season, dry season), market.... Banana plantations increase in July to reach 551 good price marked at the first harvest. Fallow, are largely practiced post-cyclonic after banana trees are 552 laid down by high speed winds. Tillage is easier and recommended at medium humidity conditions 553 corresponding to conditions of the beginning or of the end of the dry season. This means that monitoring 554 of CLD in river will always show systemic response to event such as storm of cyclones. After them, 555 large recharge occurs, stemflow disappear, tillage and fallow are practiced during dryer periods, all these potential causes of CLD increase have a similar triggering event, which is the storm. In a counterpart, it 556 557 means that we can acts on several leeways at the watershed scale. In a mid-term objective, we 558 recommend to integrate knowledge on pesticides transfers at different scale into modelling tools such as WATPPASS (Mottes et al. 2015) and to adapt their formalism to help farmers along with extension workers and decision makers to test and assess the effect of different scenarios on CLD transfers. Test the collective response of farmers at the watershed scale to specific climatic events such as storm that actually induce practice response with deleterious effects on CLD concentrations.

563 Our analysis showed that processes at different scale interact. Because, we cannot act on the aquifers-564 river relationship, we recommend focusing on limiting transfers from polluted fields. To that point, we showed that hot spots, such as LD watershed are heavy polluted by CLD resulting in large CLD 565 566 concentrations in water. Such high concentration results in large amount transferred at outlet and reaching the marine environment. At the watershed scale, we recommend to focus management of 567 568 transfers, on that kind of area for 3 major reasons. First, in spite of their small surface, they are large contributor to pollution transfers. Second, according to our results, such small watershed react quicky 569 to practices and hydroclimatic conditions so that monitoring will be able to assess the positive impact 570 571 of practices change on water quality. Third, they are managed by less farmers, making it easier to 572 consistently manage all fields from the zone.

- 573 Decontamination of soils remains the final objective (Chaussonnerie et al. 2016; Mouvet et al. 2017). In
- the meanwhile, in terms of actions, we showed that tillage that active different processes favoring CLD
- transfers should be avoided as much as possible on polluted soils, or at least positioned on specific area
- 576 where required such as plantation lines. To avoid pollution peaks, we recommend to avoid long drying
- 577 of soils, in particular soils with allophanic clays. Maintaining a ground cover and a minimal controlled 578 irrigation to maintain minimal hydratation could help reduce CLD peak at the end of the dry season.
- 579 Sequestration method using organic matter could be applied (Clostre et al. 2014). Using farm available
- 580 organic matter, returning large amount of crop residues, the use of grass or covercrop to produce large
- amount of OM returned to soil, and bringing externals sources of OM from unpolluted fields could help
- 582 increase OM concentration that stabilize CLD into soils.

# 583 **5 Conclusion**

We showed that CLD s concentrations vary at different spatial and time scale. The large variability of biophysical and decisional processes as well as their interactions at that scale require a systemic approach for their understanding and management. Such systemic analysis requires a local characterization of the hydrogeological functioning and of the agricultural practices to better understand losses in rivers. In the French West Indies, these involves historical CLD application, soil characteristics and the modifications by agricultural practices, and the reload conditions of aquifers defined by climatic events and the permeability of underground geological formations modulating transfers times.

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