Environmental fate of chlordecone in coastal habitats: recent studies conducted in Guadeloupe and Martinique (Lesser Antilles)

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18

19 **Abstract**

20 The organochlorine pollution by chlordecone, an insecticide spread in the past in banana plantations, is now
21 recognized as a major ecological, economic and social crisis in Guadeloupe and Martinique Islands. Due to its
22 physical and chemical properties, this molecule is particularly persistent in the natural environment. Volcanic
23 soil of Guadeloupe and Martinique contain allophanes (amorphous clays), which favor chlordecone trapping due
24 to their structure and physical properties. Thus, with this trapping ability, allophanes could constitute a vector
25 allowing chlordecone to contaminate runoff waters, and finally the sea. In the present publication, several studies
26 recently conducted in the Lesser Antilles have been compiled in order to evaluate the desorption of chlordecone
27 from allophanes when arriving in the estuarine environment and to determine the transfer of chlordecone along
28 marine trophic food webs. The experiments showed that 20% of the initial quantity of chlordecone was released
29 from allophones in estuarine conditions and 10% in marine environment. These results could explain the high
30 level of contamination found in the suspended organic matter and zooplankton in the coastal areas located
31 downstream the contaminated watersheds. The contamination of the marine food webs of mangroves seagrass
32 beds and coral reefs, is dominated by a contamination 'by bath" in littoral waters containing chlordecone and by
33 bioamplification seawards.

34 **Keywords**: *organochlorine pollution, desorption, allophane, zooplankton, trophic food webs, bioamplification*

35

Introduction

The organochlorine pollution by chlordecone, an insecticide spread in the past in banana plantations, is now recognized as a major ecological, economic and social crisis in the French West Indies. Used between 1972 and 1993 in fields of Guadeloupe and Martinique, chlordecone (commercialized as Kepone® then Curlone®) has been globally banned by the Stockholm Convention on Persistent Pollutant since 2009. This molecule is responsible for toxicological consequences such as an increased risk of prostate cancer, motor skills delays, an increased risk of preterm birth, endocrine disruptions and reproduction impairments (Epstein 1978; Multigner *et al.* 2010; Boucher *et al.* 2013; Kadhel *et al.* 2014; Multigner *et al.* 2016).

Due to its physical and chemical properties, this hydrophobic molecule has an affinity with soil organic matter (partition coefficient $Koc = 2500$ l.kg^{-1}, Howard *et al.* 1981). Chlordecone has a low volatility (vapour pressure = 2.5×10^{-5} mm Hg), presents high thermodynamic stability and resistance to chemical or biological degradation, involving a high persistence in the environment (Cabidoche *et al.* 2009). Consequently, it remains in the soil before degradation into at least 5b-hydrochlordecone (Devault *et al.* 2016). The time to reach the depollution level (at the threshold of quantification of 10 µg.kg^{-1}) depends on the nature of the soils: a few decades for nitisol, two to three centuries for ferralsol, five to six for andosol (Cabidoche *et al.* 2009).

Andosols contain amorphous clays, called allophanes, issued from the transformation of volcanic materials with very specific properties. Allophanes present drastically different structures and physical properties compared to usual clays, that is a very high poral volume and an important pores surface. Hygroscopic water contributed to allophanes spherical form, leading them to stack in a three-dimensional fractal labyrinth in which chlordecone could be trapped (Woignier *et al.* 2007). Due to its trapping ability, allophanes allow chlordecone to reaches runoff and ground waters, and finally end up in the sea. Nitisols are tropical and subtropical deep (iron oxides dominate), red, well-drained soils with clay content of more than 30%. Clays are more aged than andosols, *i.e.* water content is less important and clays present flatten structure compared to andosols. Nitisols are well-drained type of ferralsol, which are commonly low-draining and muddy due to the high clay content, and more aged than andosols. Andosols and nitisols are particularly abundant in the south of Basse Terre (Guadeloupe) and in the north of Martinique, in the areas where banana plantations occur (Sierra and Desfontaines 2018).

Indeed, in Guadeloupe, approximately 11,400 ha present a high risk of contamination that is 90% of probability to find chlordecone in these areas. This area represents 25% of the land surface used for agriculture. In Martinique, this value reaches 40% of agricultural lands (Direction de l'Alimentation, de l'Agriculture et de la Forêt, data 2018).

Since 2003, several studies conducted in the Lesser Antilles have highlighted the presence of a contamination by chlordecone in soil (Cabidoche *et al.* 2009), vegetables (Clostre *et al.* 2015), aquatic and marine organisms (Coat *et al.* 2006; Bertrand *et al.* 2013; Coat *et al.* 2011; Bouchon *et al.* 2016; Dromard *et al.* 2016; Monti *et al.* 2016, Méndez-Fernandez *et al.* 2018). However, few studies have been conducted on the fate of chlordecone between agricultural fields and marine ecosystems, especially when it arrives in estuarine environments. The studies on Kepone cycling in aquatic environments has been principally conducted in Virginia, because the original production of Kepone began in Hopewell. In 1975, it was discovered that the Kepone factory had not only exposed workers, but also severely contaminated the James River estuary (Nichols 1990; Luellen *et al.* 2006).

74 Chlordecone desorption in the James River estuary has been studied by Nichols (1990) who showed that

75 chlordecone stayed sorbed to organic particles when arriving in estuarine environment in the range of pH (7-8)

76 and salinity (0.006 to 19.5). To our knowledge, chlordecone desorption has never been studied in the Lesser

77 Antilles that present a particular context due to their tropical pedoclimatic conditions. Our first hypothesis is that

78 chlordecone could be trapped by allophanes, due to their physical structure, and stayed sorbed during its transfer

79 to the marine environment.

80 Along the James River and at the mouth of this river, contamination of aquatic fauna by chlordecone has been

81 highlighted, starting with plankton, the first link in the trophic food web. Zooplankton is broadly highly impacted

82 by this organochlorine pollution (Bahner *et al.* 1977; Luellen *et al*. 2006). Our second hypothesis is that

83 zooplankton could represent a major way of transfer between chlordecone from the water column (adsorbed on

84 terrestrial particles or dissolved) and others organisms from the trophic food-web.

85 Finally, some studies demonstrated that chlordecone passes through the different levels of the food chain and

86 shows accumulation phenomena, like many other organochlorine pollutants (Bahner *et al.* 1977). In Guadeloupe

87 and Martinique, the degree of contamination of marine organisms depends mostly on their location around the

88 two islands (Dromard *et al.* 2016). Fish and crustacean are generally more contaminated when they are located

89 downstream the contaminated watersheds and when they are close to the coast (Dromard *et al*. 2017). At the

90 same time, detrivorous and carnivorous organisms generally display higher levels of chlordecone contamination

91 than other trophic groups (Luellen *et al*. 2006; Dromard *et al*. 2017). Our third hypothesis is that chlordecone

92 concentrates in marine organisms, depending on their location (close or far from the source of pollution) and on

93 their feeding ecology.

94 The principal objective of the present study is to compile the results of recent studies on the environmental fate

95 of chlordecone from estuaries to the marine ecosystems in the Lesser Antilles, with two main objectives: 1) to

96 study chlordecone desorption as its arrival in the marine environment, 2) to evaluate the transfer of chlordecone

97 in marine trophic food web, from plants to top predators. To do so, three studies recently conducted in

98 Guadeloupe and Martinique are presented in the present work.

99

100 **Material and Methods**

101 **Experimental protocol to measure chlordecone desorption on allophanes**

102 A selected allophanic soil (6.1% w.w.) historically contaminated was sampled in Martinique and sieved on 2

103 mm-mesh stainless steel sieve. Samples of 1.5 g of soil has been incubated at dark and moderately stirred in

104 glass vial during 24h in artificial sea salted water at 0, 10, 20 and 35 psu. Artificial seawater results from a

105 mixture of Vittel® mineral water and coral reef "Instant ocean" sea salt from Aquarium Systems®. Each

106 experiment was performed in triplicates.

107 In order to estimate chlordecone adsorption on the glass of the vials, three positive controls were implemented

108 with Vittel water mixed with chlordecone up to a concentration of 0.1 $\mu g.l^{-1}$.

109 After incubation, suspended soils were filtered on Solid Phase Micro-Extraction (SPME) glass fiber filter

110 (PDMS 100 μm Merlin): soil was lyophilized, then extracted in a microwave extractor (4 ml of dichloromethane,

111 30 watts, 10 minutes) and filtered again on a glass fiber filter in order to collect the organic extract.

112   The latter was partially evaporated under 70 % agitation and 51 % vacuum (900 mb), using a Rapidvap provided

113   by Labocongo®, then reconditioned and fully evaporated under nitrogen stream. Extracts were reconstituted in 1

114   ml of acetonitrile and kept frozen until analysis.

115   Internal ^{13}C chlordecone was added to filtered water (about 150 ml) then liquid-liquid extracted with 3 x 10 ml

116   of dichloromethane. Extracts, dried on Na_2SO_4, were partially evaporated under 70 % agitation and 51 %

117   vacuum (900 mb) then reconditioned and fully evaporated under nitrogen stream. Extracts were reconstituted in

118   1 ml of acetonitrile and kept frozen until analysis. Extraction recovery was respectively of 106 ± 6 % and 111 %.

119   For this experiment, solvents (dichloromethane, acetonitrile) were at least of analytical grade and provided by

120   ICS (Belin-Beliet®, France). Certified solid standards for chlordecone were obtained from Cluzeau Info Labo.

121   Concentrations of chlordecone in water and soil were measured by liquid chromatography (Agilent series 1200)

122   using in tandem a mass spectrometer detector (Agilent® 6410a) that was provided by Agilent (Santa Clara,

123   California, USA).

124

125   **Samplings protocol to evaluate zooplankton contamination**

126   Samples of zooplankton and seawater were collected at the mouth of two rivers in Guadeloupe (Rivière Grande

127   Anse and Rivière du Grand Carbet) and two rivers in Martinique (Rivière Monsieur and Rivière Rouge) in

128   December 2010. A second sampling campaign was done in Guadeloupe in May 2011. These four rivers have

129   been chosen due to their high level of contamination by chlordecone. Samplings were conducted along three

130   transects oriented from the coast to the open sea, using a 500 μm-meshed net for the plankton and glass bottles

131   for seawater. On each site, nine stations were chosen to sample zooplankton and seawater (n = 3 replicates at

132   each station for each compartment). Samples were freeze-dried before analysis.

133   Quantification of chlordecone in zooplankton and seawater was conducted by the Center for Analytical Research

134   and Technology at Liege University (CART, Belgium). Lipids and chlordecone were extracted with an

135   accelerated solvent extractor using n-hexane-dichloromethane (90:10; v:v). The extracts were then dried under

136   nitrogen flow until a constant weight is obtained. 3 ml n-hexane and a surrogate marker (PCB congener 112), at

137   a concentration of 50 pg.μl^{-1}, were added. Then, the extracts underwent an acid clean-up carried out with 2 ml of

138   sulphuric acid (98-100 %) in order to eliminate organic compounds (lipids, lipoproteins,...). Finally, the eluates

139   were evaporated under an almost dry nitrogen stream. 100 μl n-hexane and 100 μl PCB 209 congener, used as an

140   internal standard at a concentration of 50 pg.μl^{-1}, were added to the samples before injection. The analyses were

141   performed by GCMS-MS (ThermoQuest ITQ 1100 ion trap). With this method, the lower limit of quantification

142   (LOQ) was 0.010 μg.kg^{-1} w.w. for zooplankton and 0.010 μg.l^{-1} for seawater (Monti *et al.* 2017).

143

144   **Samplings protocol to evaluate trophic-food web contamination**

145 To study the contamination of marine food webs by chlordecone, samplings were conducted at Petit-Bourg in
146 Guadeloupe, in three habitats: mangrove, seagrass beds (located at 500 m from the coast) and coral reefs (4 km
147 from the coast), between January 2014 and February 2015. On each habitat, sediment, Superficial Sediment
148 Layer (SSL), Suspended Organic Matter (SOM), vegetal matter (macroalgae and seagrass) and consumers from
149 different trophic levels (primary consumers, secondary consumers, top predators) were collected. The
150 classification of species into trophic group was done according to the literature (Randall 1967, Froese and Pauly
151 2017). The full list of collected species is given in S1 Table. Macroalgae, fishes and crustaceans were collected
152 by hand, spearfishing or using nets in seagrass beds and mangroves. Whenever possible, three replicates were
153 made for each species. Each individual was rinsed, measured (total length (TL) in centimeters) and weighed
154 (w.w. in grams). For each organism, a piece of flesh was collected and frozen (-18°C) until analyses.
155 To sample the suspended organic matter (SOM), seawater was collected in the three habitats in acid-cleaned
156 plastic drums. Water was then filtered on Whatman® GF/F 47 mm filters. Sediments were recovered using a
157 corer to a depth of about 20 cm. Superficial sediment layer (SSL) was sampled on the first 2 cm of sediment.
158 Concentrations in chlordecone were quantified by LABOCEA (Plouzané, France) with liquid chromatography
159 coupled to mass spectrometry in tandem (UPLC-MS/MS). The lower LOQ with this method was 1 μg.kg^{-1}
160 (w.w.) for organic material and 10 μg.kg^{-1} (w.w.) for sediment.

161

162 **Results**

163 **Chlordecone desorption on allophanes**

164 No adsorption on the glass of the vials has been observed on controls.

165 Initial concentration of chlordecone measured in soil was 957 ± 13.2 μg.kg^{-1} that is about 1.145 μg of
166 chordecone in each sample of 1.5 g of soil. After 24h of incubation, the maximal desorption of chlordecone was
167 observed in the minimal salinity conditions (0 psu) while the minimal desorption was observed in the maximal
168 salinity condition (35 psu) (Table 1).

169

170 **Table 1** Concentrations of chlordecone ([CDC]) measured in soil after 24h of incubation. Initial concentration of
171 chlordecone in soil was 957 ± 13.2 μg.kg^{-1}. SD: Standard Deviation; RSD: Relative Standard Deviation.

172

Salinity (psu)	Replicates	[CDC] μg.kg^{-1}	Mean [CDC] $\pm$ SD μg.kg^{-1}	RSD %
	1	729		
0	2	983	788 ± 173.1	22.0
	3	653		
	1	905		
10	2	733	799 ± 92.6	11.6
	3	759		
	1	821		
20	2	902	837 ± 57.8	6.9
	3	790		
	1	674		
35	2	1 002	814 ± 169.2	20.8
	3	766		

173

174

175   After 24h of incubation, 78 % of the initial quantity of chlordecone was still adsorbed on soil in the freshwater

176   condition (0 psu) and 90 % for the marine condition (35 psu) (Fig. 1). About 20 % of the initial quantity of

177   chlordecone was desorbed from soil in estuarine conditions (10 and 20 psu).

178

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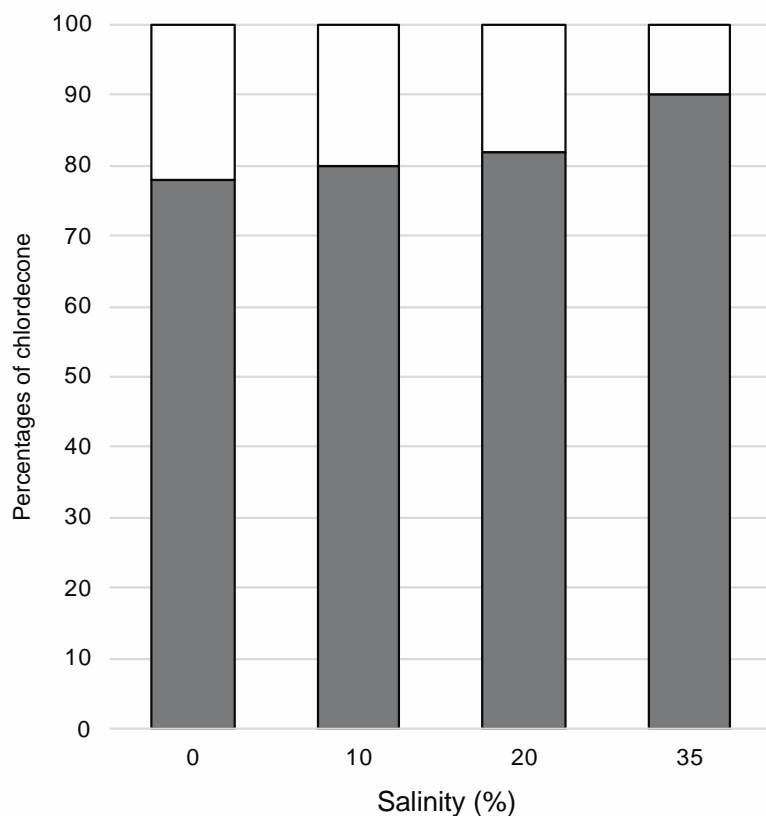
180   **Fig. 1** Percentages of chlordecone in water (white) and in soil (grey) related to salinity after 24h of incubation.

181

182

183   **Contamination of the planktonic compartment**

184   In Martinique, the minimal concentration of chlordecone found in zooplankton was 22 µg.kg^{-1} (Rivière Rouge)

185   while the maximal concentration was measured at the mouth of Rivière Monsieur (272 µg.kg^{-1}). In Guadeloupe,

186   concentrations in chlordecone varied between 40 and 306 µg.kg^{-1} (Fig. 2). Concentrations of chlordecone in

187   seawater were under the LOQ in 53% of the studied stations. In the other stations, concentrations varied from

188   0.01 to 0.053 µg.L^{-1}. No correlation was found between the concentration of chlordecone measured in seawater

189   and zooplankton.

190   Temporal variations in the level of contamination of zooplankton were tested in Guadeloupe. No statistical

191   significant difference was found on the level of contamination in zooplankton between samples collected at the

192   end of the dry season (May) and those collected at the end of the wet season (December), according to the two

193   sites in Guadeloupe.

194   Spatial variations in the level of contamination of zooplankton were tested between the four sites (two in

195   Martinique and two in Guadeloupe) sampled in December 2010. Mean concentrations of chlordecone in

196   zooplankton show significant spatial differences (Kruskal-Wallis, X^2 = 13.9, p = 0.002). These spatial

197 differences were globally due to the lower concentrations of chlordecone measured in zooplankton at the mouth

198 of Rivière Rouge compared to the other sites.

199 The bioconcentration factor (BCFw), calculated as the ratio between concentrations of chlordecone measured in

200 zooplankton and those measured in seawater, varied from 440 and 27200 (Table 2).

201

202 **Table 2** Mean concentrations of chlordecone (min - max) measured in zooplankton (in µg.kg^{-1} w.w.), seawater

203 (in µg.l^{-1}) and mean bioconcentration factors (BCFw) at the mouth of four rivers. WS: end of the wet season

204 (December), DS: end of the dry season (may), n: number of samples, "-" indicates absence of measures.

205

| Islands	Rivers	Seasons	n	Zooplankton	Seawater	BCFw
Martinique	Rivière Rouge	WS	9	62.3 (22 - 99)	0.028 (0.01 - 0.05)	4320 (440 - 9900)
Martinique	Rivière Monsieur	WS	9	164.3 (79 - 272)	0.01	27 200
Guadeloupe	Grande Anse	WS	9	104 (40 - 294)	0.023 (0.02 – 0.027)	5338 (2095 - 10889)
Guadeloupe	Grande Anse	DS	9	167.8 (79.5 - 271.8)	-	-
Guadeloupe	Grand Carbet	WS	9	133.0 (50.9 - 231.7)	-	-
Guadeloupe	Grand Carbet	DS	9	164.7 (100 - 306)	0.027 (0.017 – 0.053)	7 422 (2509 - 14647)

206

207

208

209

210 Mean BCFw was maximal at the mouth of Rivière Monsieur in Martinique. The three other sites reached similar

211 order of magnitude: 4320 at Rivière Rouge, 7422 at Grand Carbet and 5338 at Grande Anse (Fig. 2).

212
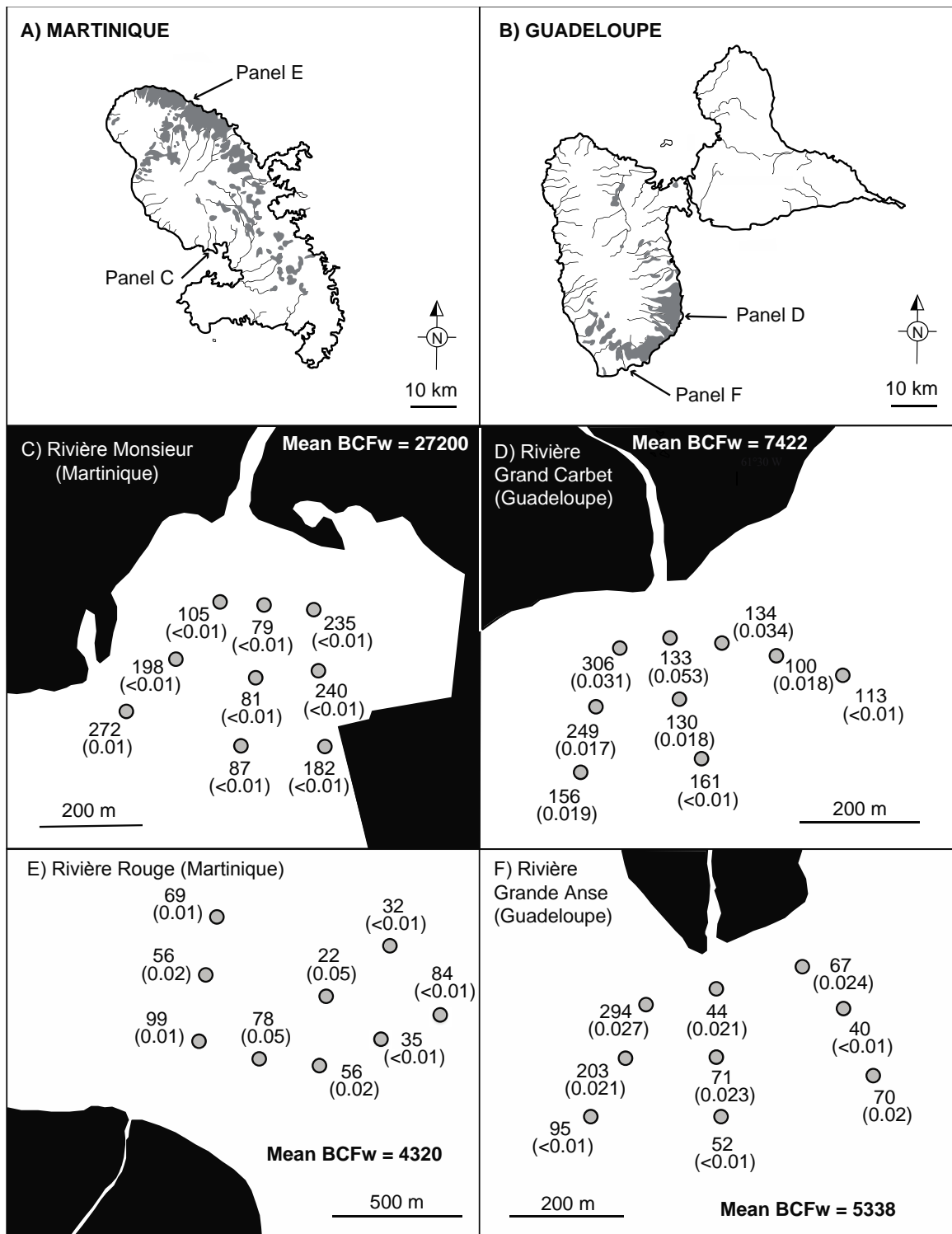
Fig. 2 Mean concentration of chlordecone measured in zooplankton (in $\mu g.kg^{-1}$ w.w.) and seawater (into brackets, in $\mu g.l^{-1}$ w.w.) in Martinique (A) and in Guadeloupe (B) at the mouth of four rivers (C to F). BCFw: Bioconcentration factor (data from Monti *et al.* 2012); grey surfaces in A and B panels indicate soils contaminated by chlordecone.

Contamination of the trophic food web

Concentrations in chlordecone were measured in different sources of matter and marine organisms in three marine habitats: mangrove, seagrass beds and coral reefs (Fig. 3).
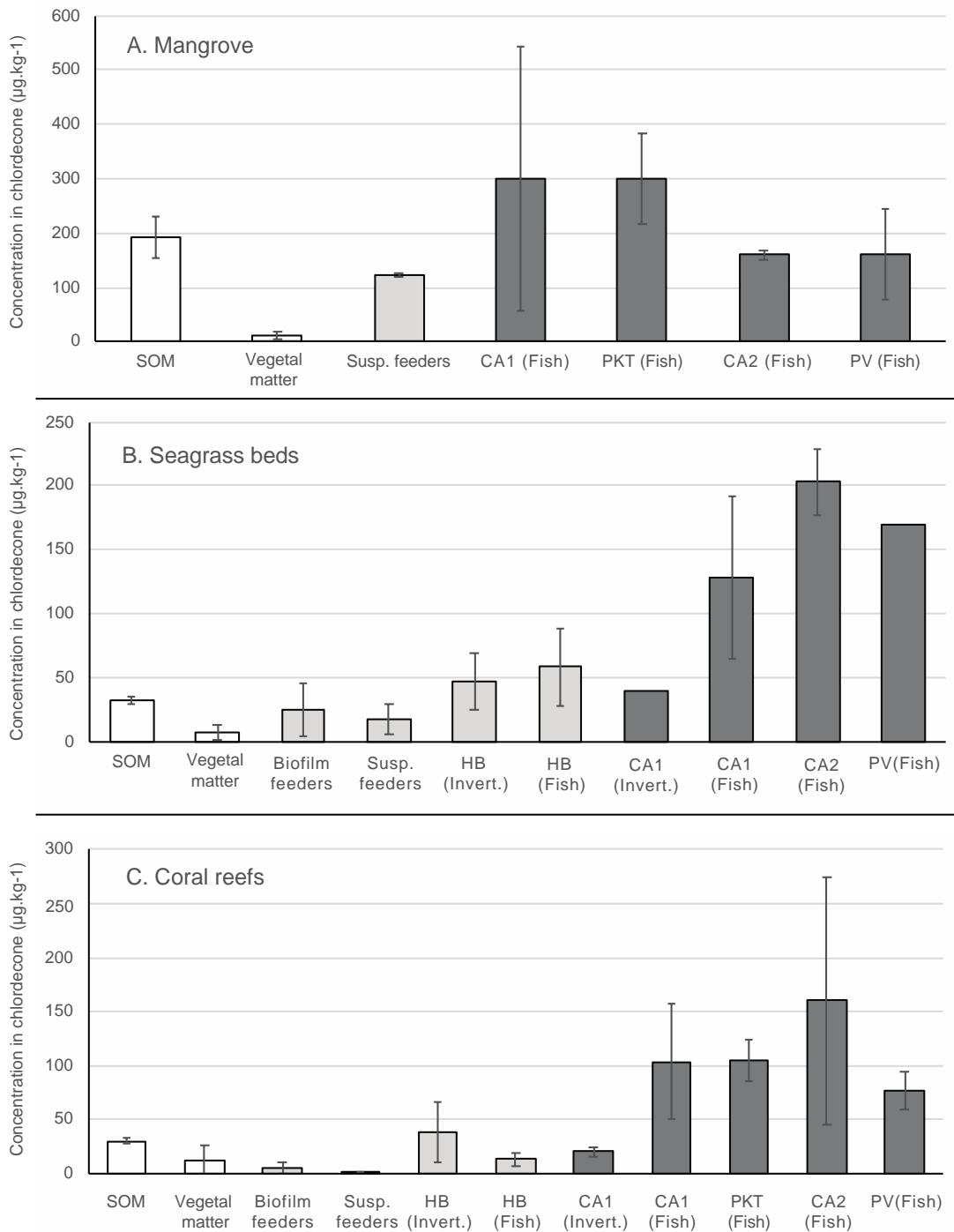
Fig. 3 Mean concentration of chlordecone $\pm$ SD (in $\mu g.kg^{-1}$) measured in sources of carbon (in white, SOM: Suspended Organic Matter; Vegetal matter: algal turf, macroalgae, seagrass), primary consumers (in light grey, Susp. Feeders: suspension feeders, HB: herbivores) and secondary consumers (in dark grey, CA1: invertebrate feeders, PKT: planktivores, CA2: fish and invertebrate feeders, PV: piscivores), in mangrove (A), seagrass beds (B) and coral reefs (C).

230

231

232   Mean concentrations per trophic category were calculated in pooling all individuals from similar trophic group.

233   Concentrations in chlordecone in sediment and superficial sediment layer (SL) were found under the limit of

234   quantification (10 µg.kg^{-1}). However, chlordecone was found in SOM and vegetal matter in the different habitat.

235   SOM exhibited the highest values among the different sources of carbon. Primary consumers, including biofilm

236   feeders, suspension feeders and herbivorous organisms, presented intermediate mean concentrations of

237   chlordecone from 122.3 ± 3.8 µg.Kg^{-1} in mangrove to 17.0 ± 22.0 µg.Kg^{-1} in coral reefs. Secondary consumers,

238   that are carnivorous organisms (invertebrates feeders, invertebrates and fish feeders and piscivorous), showed the

239   highest mean concentrations of chlordecone among the studied trophic categories from 232.6 ± 172.3 µg.Kg^{-1} in

240   mangrove to 91.9 ± 57.6 µg.Kg^{-1} in coral reefs. In each habitat, significant differences in the mean

241   concentrations of chlordecone were found between the food sources (SOM, vegetal matter) and the trophic

242   categories (primary consumers and secondary consumers) (Table 3). In mangrove, multiple post-hoc

243   comparisons tests indicated that differences of chlordecone concentrations between trophic categories are due to

244   the low value in vegetal matter. In this habitat, SOM, primary and secondary consumers showed similar levels of

245   contamination but were statistically different from the level in vegetal matter. In seagrass beds and coral reefs,

246   the patterns of contamination were similar: SOM, vegetal matter and primary consumers were not statistically

247   different according to their level of contamination. However, these three trophic categories significantly

248   displayed lower concentrations of chlordecone than secondary consumers (Table 3).

249

250   **Table 3** Mean concentrations of chlordecone (± SD) in µg.kg^{-1} measured in food sources (SOM and vegetal

251   matter), primary consumers and secondary consumers. Differences in chlordecone concentrations between the

252   trophic categories were tested with a Kruskal-Wallis test. Letters indicate the results of multiple comparisons

253   conducted with post-hoc tests.

254

Trophic categories	Mangrove	Seagrass beds	Coral reefs
SOM	191.3 ± 38.5 [b]	31.7 ± 2.9 [a]	30.3 ± 2.1 [a]
Vegetal matter	12.3 ± 6.4 [a]	6.8 ± 5.6 [a]	12.3 ± 13.5 [a]
Primary consumers	122.3 ± 3.79 [b]	34.6 ± 25.9 [a]	17.0 ± 22.0 [a]
Secondary consumers	232.6 ± 172.3 [b]	147.5 ± 66.0 [b]	91.9 ± 57.6 [b]
X^2	15.1	44.1	35.6
p values	0.002	<0.0001	<0.0001

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256

257

Discussion

259   In the Lesser Antilles, all the environmental compartments that have been in contact with chlordecone present a

260   signal of contamination: agricultural soil, rivers, seawater, zooplankton and fauna from the marine food webs. In

261   the present work, the experiments conducted to study the behavior of chlordecone during its arrival in estuarine

262   and marine environments show that molecules stay strongly linked to the particles of terrestrial organic matter,

263   whatever the salinity (0 to 35 psu). About 20 % of the initial quantity of chlordecone was desorbed from soil in

264   estuarine conditions (10 and 20 psu) and 10 % was released in marine conditions (35 psu). Thus, even if furthers

265   investigations should be conducted to verify this affirmation, marine conditions seem to be the least conducive to

266   desorption. These results are in accordance with those of Nichols (1990), who demonstrated that once

267   chlordecone is sorbed it stays adsorbed in the range of pH (7-8) and salinity (0.006 to 19.5). Bakir *et al.* (2014)

268   demonstrated that salinity generally does not affect desorption rates of persistent organic pollutants (POP),

269   however their study was conducted on sorption of POP on microplastics. The capacity of POP sorption and

270   desorption on allophanes could be different. In the present study, salinity appears to limit chlordecone desorption

271   because of a process which needs furthers investigations. The present experiments could explain the high

272   concentrations of chlordecone measured in the suspended organic matter (SOM), collected after filtration of

273   seawater in the coastal areas (from 28 to 233 µg.kg^{-1}). Chlordecone was not encountered in superficial sediment

274   layers and marine sediments cores (all samples presented concentrations inferior to the limit of quantification: 10

275   µg.kg^{-1}). These results could be due to the fact that some samples of sediments collected in the present study

276   were poor in organic matter (for example, less of 2 % of OM in sediments collected in coral reefs). Indeed, the

277   level of contamination of sediments is generally associated with the nature of sediment: organic-rich sediment

278   has much greater capacity to sorb chlordecone than organic-poor sand or kaolinite (O'Connor and Connolly

279   1980). Bodiguel *et al.* (2011) and Robert (2012) also found a very low level of contamination for these two

280   compartments in a bay in Martinique (22 samples, all were < 0.5 µg.kg^{-1}). In 2005, Bocquené and Franco found

281   a disparity between the concentrations of chlordecone measured in sediment (<10 µg.kg^{-1}) and SOM (52 and 22

282   µg.kg^{-1}). Chlordecone can be transferred to estuaries and the marine environment in particulate form (Crabit *et*

283   *al.* 2016) *via* SOM to which it is firmly attached. This suspended matter does not seem to settle on the bottom

284   directly when it arrives at sea, since the sediment compartment is very little affected by the contamination.

285   Several hypothesis could explain these observations: 1) contaminated SOM is constituted by very fine and low

286   density particles which may settle far from estuarine and coastal areas (but this explanation cannot be plausible

287   in semi-enclosed bays), 2) contaminated SOM may be directly consumed in the water column by planktonic

288   compartment upon arrival in the marine environment, 3) contaminated SOM may settle in estuaries and coastal

289   areas but may be rapidly degraded by microorganisms in the sedimentary compartment, 4) samples were

290   collected during the wet season, which can induce intense rainfall and disturbances of estuarine and coastal

291   waters, preventing sedimentation of contaminated SOM (Eggleton and Thomas 2004; Noegrohati *et al.* 2008).

292   Levels of contamination of zooplankton compartment were investigated to verify the second hypothesis on

293   chlordecone pathway (see above). Zooplankton is closely linked and in direct contact to SOM in estuarine and

294   coastal waters. Indeed, previous studies have highlighted the sensibility to this compartment towards

295   organochlorine pollutants, probably due to its lipid content (Jordan 1979; Day 1990; Nichols 1990). Nichols

296   (1990) measured a mean concentration equal to 4 800 µg.kg^{-1} in zooplankton from the James River estuary. Coat

297   *et al.* (2011) reported a mean concentration equal to 5 100 µg.kg^{-1} in the river mouth and 3 500 µg.kg^{-1} in the

298   coastal waters of Guadeloupe. In the present study, concentrations of chlordecone measured in zooplankton were

299   considerably lower and varied between 22 and 306 µg.kg^{-1}. Concentrations of chlordecone in zooplankton also

300   spatially varied. The lowest concentrations were observed in front of Rivière Rouge, probably due to the

301   exposure of the site to swell on this Atlantic coast. No temporal variations of chlordecone concentrations were

302   observed between zooplankton collected at the end of the wet season and those collected at the end of the dry

303   season. However, the number of samples was relatively low and samples were taken in the same day during each

304   campaign. Because the planktonic compartment displays very short turn-over, further sampling effort should

305 highlight temporal variations in the level of chlordecone contamination of zooplankton. Bioconcentration factors
306 (BCFw) were calculated as the ratio between concentrations of chlordecone in zooplankton and those in
307 seawater. The highest BCFw was found at the mouth of Rivière Monsieur, probably due to its high degree of
308 confinement (semi-enclosed bay). Zooplankton is a keystone component of both marine and rivers systems. It
309 represents a link between invertebrates and fish by providing food and by recycling essential nutrients through
310 feeding on living and detrital material. The accumulation of organochlorine pollutants in zooplankton is a severe
311 threat to ecosystems and a potential way of transfer of the molecule along marine and freshwater food webs.

312 Bioaccumulation phenomena of chlordecone have been demonstrated experimentally (Bahner 1977) and in the
313 field (Dromard *et al.* 2018). Two processes of bioaccumulation were demonstrated in the present study. In
314 mangrove, the ambient level of contamination is high (SOM: 191.3 µg.kg^{-1}) and this value from the basis of the
315 trophic food web is not statistically different from the other trophic categories (excepted with vegetal matter).
316 Indeed, in mangrove, the entire trophic food web exhibits high concentrations of chlordecone, reflecting the
317 contamination of the baseline. This first way of contamination indicates a prevalence of a contamination "by
318 bath", *i.e.* by contact between organisms (*via* teguments and gills) and contaminated surrounding waters. In
319 seagrass beds and coral reefs, food sources and primary consumers shared similar level of contamination that
320 were significantly different from those of the secondary consumers. In these two habitats, a phenomenon of
321 bioamplification, *i.e.* a contamination by trophic way, is highlighted. The introduction of carnivory in fish diet is
322 linked to a significant increase in the chlordecone concentrations of marine organisms, probably due to the
323 higher lipid content in the preys. In the Lesser Antilles, the degree of contamination of marine systems by
324 chlordecone was drastically lower than that measured in the James River estuary, due to the difference of
325 pollution discharge between the two sites. However, the majority of the studied species were impacted by
326 chlordecone and showed concentrations above the maximal residue limit (LMR) authorized by the French food
327 and safety authorities for the consumption and the commercialization of seafood products (LMR = 20 µg.kg^{-1}).

328 The variations among species from similar trophic category were sometimes very high, suggesting that other
329 processes could influence the level of contamination of marine fishes, such as their physiology, their size or their
330 movement among the different habitats. Indeed, Luellen *et al.* (2006) indicated that fish ecology could
331 considerably influence the level of contamination of marine fishes, especially for migratory species that spend a
332 period of the year in an estuarine environment.

333 To conclude, molecules of chlordecone can reach marine ecosystems with two principal processes. Firstly,
334 dissolved molecules of chlordecone can infiltrate ground waters during percolation process and join marine
335 environment with resurgences inside rivers or in the sea (Crabit *et al.* 2016). In the present study, this pollution
336 was highlighted by the concentrations of chlordecone measured in seawater samples. Secondly, due to its strong
337 affinity with soil particle (allophane or others terrestrial particles), molecules of chlordecone can reach runoff
338 waters, rivers and estuaries by leaching of the contaminated soil throughout the erosion process of the catchment
339 (Crabit *et al.* 2016). When chlordecone arrive in marine environment, it seems to stay sorbed on allophanes and
340 this fact could be similar with other organic compounds, as salinity generally does not affect desorption rates
341 (Bakir *et al.* 2014). Chlordecone, adsorbed or dissolved, is then integrated in SOM and zooplankton. These two
342 compartments are located at the base of trophic food-web and contribute to the contamination of the entire food
343 chain, *via* contact or trophic way.

344 In perspectives, several aspects of chlordecone transfer between terrestrial, rivers and marine ecosystems should
345 be developed in future studies. The low proportion of chlordecone desorbed from allophanes requires further
346 studies on the physical and chemical behavior of allophanes when arriving in marine environments. The
347 potential ways of chlordecone degradation in marine sediment could also be investigated in order to understand
348 the low concentrations of chlordecone found in marine sediment. Measurements of chlordecone metabolites in
349 the sediment could help with the understanding of a potential bacterial degradation in this compartment. Finally,
350 studies on the kinetic of contamination *versus* decontamination in marine fauna could be useful to explain the
351 high variations in the concentrations of chlordecone between species and individuals.

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