Aquatic Botany 169 (2021) 103346

Contents lists available at ScienceDirect

Aquatic Botany

journal homepage: www.elsevier.com/locate/aquabot

Short communication

Biosorption capacity of genus *Dictyota* facing organochlorine pesticide pollutions in coastal areas of the Lesser Antilles

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ARTICLE INFO

Keywords:
Macroalgae
Coral reefs
Chlordecone
Guadeloupe
Martinique
Bioaccumulation

ABSTRACT

Measurements of chlordecone, an organochlorine insecticide with high persistence in natural environments, have been carried out on several species and genus of macroalgae in Guadeloupe and Martinique. These data were statistically compared to determine the ability of the genus *Dictyota* to accumulate chlordecone, compared to other collected macroalgae. The comparisons were conducted between phylogenetic groups (Rhodophyta, Phaeophyta and Chlorophyta), and between sites (Guadeloupe *vs* Martinique). Concentrations of chlordecone measured in *Dictyota* spp. samples were significantly higher than the other groups regardless to the site. Phaeophytes are generally characterized by a higher capacity for biosorption of contaminants. In this study, however, only the *Dictyota* spp. samples followed this pattern. Therefore, this genus is of interest in cases of phycoremediation of the chlordecone.

1. Introduction

Natural environments in the French West Indies, both terrestrial and aquatic, have been exposed to a contamination by chlordecone since the 1970s. Chlordecone is an organochlorine insecticide used in Guadeloupe and Martinique between 1972 and 1993 to control the banana weevil, under commercial names « Kepone » and « Curlone ». While this product had been banned in the United States as early as 1976, its authorization for sale was not withdrawn until 1990 in France and 1993 in Guadeloupe. Chlordecone was mainly used in the southern part of the Basse-Terre region in Guadeloupe and the north region of Martinique, where banana plantations are found. Runoff and infiltration phenomena, associated with tropical climatic conditions, have led to a transfer of chlordecone molecules from agricultural soils to coastal and pelagic marine environments. According to the nature of Guadeloupean soils, the pollution is bound to last for several decades for nitisol, centuries for ferralsol, and half a millennium for andosol (Cabidoche et al., 2009). Recent studies conducted on the contamination of marine ecosystems (mangroves, seagrass meadows and coral reefs) have shown that all the organisms of marine food chains are affected by this pollution, from primary producers to predators (Dromard et al., 2016, 2018a; Méndez-Fernandez et al., 2018). Such as the majority of Persistent Organic Pollutants (POPs), chlordecone can be absorbed and stored in organic tissues and/or adsorbed on the surface of biological tissues. Chlordecone molecules can then be transferred throughout the food chain *via* the trophic pathway (*i.e.* biomagnification process). Another mechanism of transfer has been identified and concerns "bathing" contamination, whereby marine organisms accumulate chlordecone *via* contact between teguments and gills with polluted water (*i.e.* bioconcentration process) (Van der Oost et al., 2003; Dromard et al., 2018a). It has also been shown that this contamination decreases with the distance from the coast, that is the source of pollution (Dromard et al., 2018b).

Contamination of marine fauna leads to major health risks, *via* the commercialization and consumption of seafood products, which has encouraged the establishment of several no-fishing zones in Guadeloupe and Martinique. Faced with these environmental concerns, there is a strong demand in the Lesser Antilles and a need to identify organisms that are bioindicators of pollution but also bioaccumulators, with a perspective of remediation.

Biosorption is a natural and passive physicochemical process, operating in certain species of bacteria, fungi, plants or animals, enabling them to passively bioconcentrate metals, radionuclides, minerals or toxic organic molecules. These biochemical properties make it possible to develop innovative methods to treat water contaminated by toxic metals or POPs, and offer the possibility of treating different types of

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https://doi.org/10.1016/j.aquabot.2020.103346
Received 25 May 2020; Received in revised form 10 December 2020; Accepted 19 December 2020

Table 1
List of species and genus, number (n) of samples collected and concentrations in chlordecone (mean ± SD, min and max) in μg kg^{-1}.

	Martinique		Guadeloupe	
	n	Mean ± SD (Min-Max)	n	Mean ± SD (Min-Max)
Chlorophyta	**3**	**9.3 ± 2.1 (7.0–11.0)**	**15**	**12.5 ± 11.1 (1.1–31)**
Caulerpa racemosa	3	9.3 ± 2.1 (7.0–11.0)		
Caulerpa sertularoides			9	19.2 ± 9.3 (9.1–31.0)
Halimeda incrassata			6	2.4 ± 1.1 (1.0–3.8)
Phaeophyta	**22**	**164.9 ± 194.7 (3.8–1458.0)**	**18**	**246.9 ± 395.6 (1.5–588.0)**
Dictyota spp.	10	514.7 ± 467.3 (151.0–1458.0)	12	245.8 ± 192.9 (85.0–588.0)
Lobophora variegata	3	23.6 ± 26.4 (7.5–54.0)		
Padina sp.	6	31.4 ± 30.7 (6.4–90.0)	6	3.1 ± 1.5 (1.5–4.8)
Sargassum sp.	3	8.6 ± 6.5 (3.8–16.0)		
Rhodophyta	**3**	**105.3 ± 9.1 (95.0–112.0)**	**9**	**1.8 ± 0.7 (1.0–2.7)**
Acanthophora spicifera			3	1.8 ± 0.8 (1.0–2.5)
Galaxaura rugosa			6	1.7 ± 0.7 (1.0–2.7)
Laurencia sp.	3	105.3 ± 9.1 (95.0–112.0)		
Total	**28**	**206.3 (3.8–1458.0)**	**42**	**75.5 (1.0–588.0)**

waste (industrial pollutants, pesticides, *etc.*). The living organisms used, called "biosorbents", allow to apply alternative methods, environmentally friendly and cost-effective remediation technologies compared to other technologies (Fourest and Volesky, 1995; Cardoso et al., 2017).

In the aquatic environment, phycoremediation focuses on the ability of algae to clean up waters. A large number of studies have been conducted on the use of microalgae to depollute freshwater, including domestic and industrial wastewater (Rao et al., 2011; Rawat et al., 2016). In marine environments, phycoremediation studies have focused on the ability of microalgae, and to a lesser extent macroalgae, to store metallic pollutants (Ben Chekroun et al., 2013; Sooksawat et al., 2013; Chakraborty et al., 2014). Recent studies have shown that Phaeophytes exhibit high uptake capacities for a number of heavy metals and chemicals (Davis et al., 2003; Xiong et al., 2013). This observation is explained by the biochemical composition of algal exudates that can associate with diverse hydrophobic pollutants such as Polychlorinated biphenyls (PCBs) (Lara et al., 1989; Ben Chekroun et al., 2014) or by a number of metal-binding processes taking place with components of the cell wall. The adsorption capacity of brown algae could be directly related to the abundance of carboxylic groups (most abundant acidic functional group in brown algae) on the alginate polymer (Baghour, 2017).

Information on the ability of marine macroalgae to accumulate and store organochlorine molecules remain scarce. Most studies on the subject focus on the accumulation of inorganic contaminants and only 3% are concerned with organic contaminants (García-Seoane et al., 2018). In the few studies available, the main organic pollutants studied are PCBs, PAHs and DDT or their metabolites (Cheney et al., 2014; Anacleto et al., 2017; García-Seoane et al., 2018). To date, no studies have been conducted on the contamination of macroalgae by chlordecone.

Macroalgae are interesting organisms for monitoring organochlorine pollution: most of them are sessile, widely distributed and available all year round, they tolerate wide ranges of salinity, turbidity and high levels of pollutants. In addition, they are easy to collect, treat and can be easily maintained under experimental conditions (García-Seoane et al., 2018). During previous studies on the contamination of marine fauna by chlordecone in Guadeloupe and Martinique, several species and genus of macroalgae were collected and analyzed. Samples belonging to the genus *Dictyota* (Phaeophyta), very common in the Caribbean coastal waters, appeared to be highly contaminated compared to other macroalgae species. These preliminary observations suggested a strong bioaccumulative capacity of the samples of *Dictyota* spp. facing chlordecone pollution. Thus, the main objective of the present study is to highlight bioaccumulative capacities of chlordecone by *Dictyota* spp. macroalgae. To do so, concentrations of chlordecone were measured in different macroalgal species and genus and compared to (1) attest that *Dictyota* spp. present higher levels of contamination compared to other macroalgae, (2) evidence that capacities of bioaccumulation of *Dictyota* spp. are function to the study sites.

2. Materiel and method

2.1. Study sites

Macroalgae were hand-collected along two sites in Guadeloupe (Petit-Bourg and Goyave) and one site in Martinique (Baie du Galion), during two sampling campaigns (2015 in Guadeloupe and 2019 in Martinique). Study sites were constituted by shallow reefs and seagrass beds, located in the coastal area, on west coast of each islands. These sites were chosen due to their location downstream contaminated terrestrial areas and are known to receive chlordecone by runoff waters and rivers. For each species or genus of macroalgae, between three and five replicates were sampled in each site, totalizing 70 samples in total (Table 1). Macroalgae were sorted into different phylogenetic groups (Chlorophyta, Rhodophyta and Phaeophyta), and samples belong to the genus *Dictyota* have been classified separately due to their propensity to accumulate chlordecone. After being identified and classified, macroalgae were cleaned and frozen in aluminum contents until analyses.

2.2. Chlordecone extraction and analysis

Chlordecone was extracted from homogenized sampled tissues with a solution of organic solvents (hexane-acetone) and turned into chlordecone hydrate (hydrosoluble) in the presence of sodium hydroxide. The aqueous phase was rinsed with hexane to eliminate fats. Chlordecone was then reassembled in acid conditions, extracted with a solution of hexane and acetone. Concentration of chlordecone was quantified with liquid chromatography coupled to mass spectrometry in tandem (UPLC-MS/MS). Chlordecone concentrations were expressed in μg kg^{-1} (ww). The lower limit of detection (LOD) was 0.5 μg kg^{-1} (dw) and the lower limit of quantification (LOQ) with this method was 1 μg kg^{-1} (dw) with measurement precision of 0.1 μg kg^{-1} when data were superior to the LOQ.

2.3. Statistical analyses

Data normality was tested using Shapiro-Wilks tests. As data did not follow a normal distribution, comparisons of chlordecone concentrations between phylogenetic groups or genus, and between sites were conducted using Kruskal-Wallis non-parametric tests, followed by Wilcox pairwise comparisons.

3. Results and discussion

Concentrations in chlordecone measured in macroalgae varied between 1 and 588 μg kg^{-1} in Guadeloupe and between 3.8 and 1458 μg kg^{-1} in Martinique (Table 1), with large variations among species.

Concentrations in chlordecone were first compared between the two study sites in Guadeloupe (Petit-Bourg and Goyave), respectively to each macroalgae category (Rhodohyta, Phaeophyta, *Dictyota* spp. and Chlorophyta). Concentrations were not significantly different between the two Guadeloupean sites (Kruskal-Wallis, all $p > 0.05$). This result

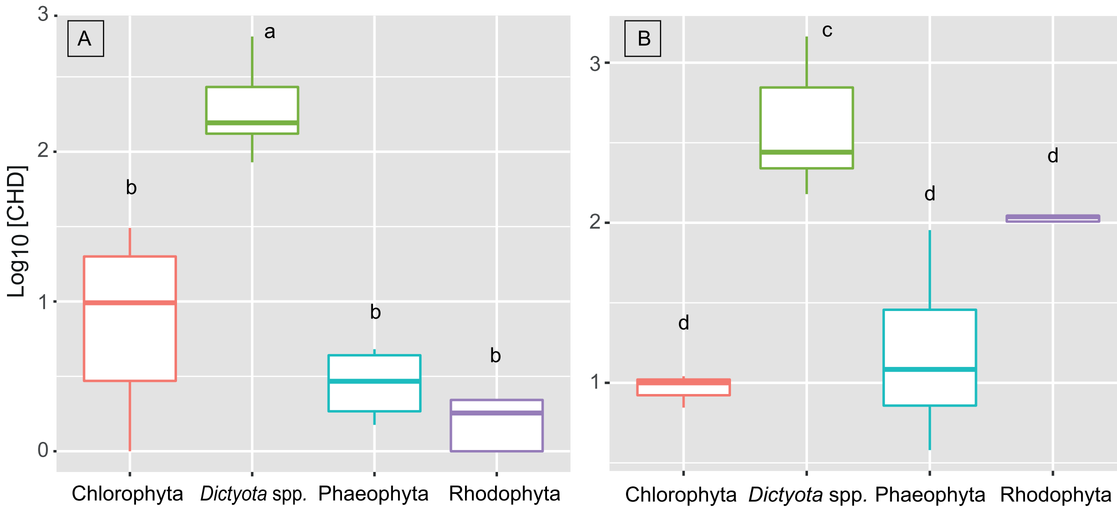

Fig. 1. Log-transformed concentrations in chlordécone (log_{10}[CHD]) measured in different macroalgal groups, in Guadeloupe (A) and Martinique (B). Statistical tests were made with Kuskal-Wallis tests followed with Wilcox pairwise comparisons.

can be explained by the geographical proximity and topographic similarities of both sites. By consequence, samples from Petit-Bourg and Goyave were pooled together to compare macroalgae between groups.

Concentrations in chlordecone were statistically different between macroalgal species or genus in Guadeloupe (Kruskal-Wallis, $X^2 = 35.5$, df = 5, $p < 0.001$) and in Martinique (Kruskal-Wallis, $X^2 = 22.6$, df = 5, $p < 0.001$). Pairwise comparisons indicated that samples from the genus *Dictyota* were characterized by higher concentrations in chlordecone than others species or genus. Comparisons were also performed between macroalgal groups (Rhodophyta, Chlorophyta, *Dictyota* spp. and Phaeophyta). Concentrations in chlordecone were significantly different according to the phylogenetic group in Guadeloupe (Kruskal-Wallis, $X^2 = 30.9$, df = 3, $p < 0.001$) and in Martinique (Kruskal-Wallis, $p < 0.001$) (Fig. 1). Pairwise comparisons indicated that Chlorophyta, Rhodophyte and Phaeophyta (except *Dictyota* spp.) presented similar level of contamination, which were relatively low (medians values were 9.8, 1.8 and 3.2 μg kg^{-1} respectively), while the median value for *Dictyota* spp. was 156.5 μg kg^{-1}). In comparison with previous data on marine organisms, *Dictyota* spp. from Guadeloupe were more concentrated in chlordecone that spiny lobsters, *Panulirus argus*, which are known to accumulate organochlorine pollutants and exhibited median value equal to 93 μg kg^{-1} (Dromard et al., 2018b). In Martinique, median values were also low for Chlorophyta and Phaeophyta (except *Dictyota* spp.) (10.0 and 12.6 μg kg^{-1} respectively). Rhodophyta, represented by the genus *Laurencia* sp., showed a median equal to 109.0 while *Dictyota's* median was 276.0 μg kg^{-1}. In the same site, median values for *Panulirus argus* was 405.1 μg kg^{-1} (C. Dromard, non-published data). These results showed that *Dictyota* spp. can be 2.5–87 times more concentrated in chlordecone that others groups of macroalgae and can present higher levels of contamination than some animals from similar study sites.

In previous studies, Phaeophyta have been identified as natural biosorbent organisms, especially regarding metallic pollutions (Davis et al., 2003; Xiong et al., 2013). This observation was explained by the biochemical composition of their cell walls, in particular the presence of fucans and alginates (Lara et al., 1989; Ben Chekroun et al., 2014). In the present study, different species and genus of Phaeophyta were analyzed, but only the genus *Dictyota* has a proven ability to accumulate chlordecone. This observation is in line with the results of Chakraborty et al. (2014), who demonstrated a great ability of *Dictyota bartayresiana* to accumulate contaminants, such as metal in the Mediterranean Sea. In the present study, the results suggested that *Dictyota* spp. is also characterized by a high capacity to accumulate organochlorine molecules.

Samples of *Dictyota* spp. were the only one to display large variations in their concentrations of chlordecone (Table 1, Fig. 1). This observation can be explained by different hypotheses. Firstly, several species of *Dictyota* were sampled at the same time. The specific identification of *Dictyota* generally needs genomic analyses, which were not possible in the present study. Thus, the fact that several species of *Dictyota*, with potential divergent behaviors regarding chlordecone, could have laid to high differences in the level of contamination of the different samples, in both sites. Secondly, the sampling effort was higher for *Dictyota*. This set of data may have included individuals at different stages of development, which could result in different levels of accumulation between samples. To solve these investigations, further analyses could be done on the different species of *Dictyota* commonly found in the Caribbean, with the support of genomic analyses.

Following their work, *Dictyota* spp. could be proposed as a bioindicator species of pollution by chlordecone, as it has been suggested in Mediterranean region with *Dictyota bartayresiana* facing metallic pollutions (Chakraborty et al., 2014). The research of bioindicators species has been increasing since several year, in the perspective of long-term monitorings of pollutions (Hédouin et al., 2008; Schaible and Denton, 2013; García-Seoane et al., 2018) or solutions of phycoremediation (Ben Chekroun et al., 2014).

Concentrations of chlordecone measured in *Dictyota* spp. were higher in Martinique rather than in Guadeloupe (Kruskal-Wallis, $X^2 = 5.0$, df = 1, $p = 0.02$). The Baie du Galion, in Martinique, was also characterized by extreme concentrations (maximum values equal to 1458 μg kg^{-1}) compared to Guadeloupe (maximum value = 588 μg kg^{-1}). The difference of concentrations between the two islands are unlikely to be due to temporal variations in the inputs of chlordecone to the marine environment (between 2015 and 2019) because climatic conditions (rainfalls) are constant year after year and similar between the two islands. On the other hand, this difference can be explained by the geomorphology of the study sites. In Martinique, samples were collected in a semi-enclosed bay, with probably longer water turnover time. In Guadeloupe, the two sites are directly exposed to dominant swell and wind all year long, which could lead to faster turnover of water and dilution of pollution along the coast. Furthermore, the different rivers close to the study sites do not exhibit similar level of pollution. In Guadeloupe, a concentration equal to 0.16 μg l^{-1} was found in the River Moustique while the annual mean concentration of chlordecone in the River Galion in Martinique was 7.48 μg l^{-1} in 2017.

The maximal capacity of biosorption of chlordecone by *Dictyota* spp. needs to be investigated as well as the kinetic of accumulation to propose phycoremediation actions in the Lesser Antilles.

Fundings

A part of this work was supported by the Prefecture de Martinique (Projects "ChloHal", "ChloAnt" and "DIREC"), in the Plan National Chlordecone III (2014-2020).

CRediT authorship contribution statement

Paul-Emile Contarini: Investigation, Formal analysis, Methodology, Visualization, Writing - original draft. **Charlotte R. Dromard:** Conceptualization, Formal analysis, Funding acquisition, Investigation, Project administration, Resources, Supervision, Visualization, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Authors gratefully thank Claude and Yolande Bouchon, Sébastien Cordonnier and Salim Arkam for their help during fieldwork and Jonathan Pratt for proofreading this article.

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