



# Persistent organic pollutants (POPs) in coastal wetlands: A review of their occurrences, toxic effects, and biogeochemical cycling

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## ABSTRACT

Coastal wetlands, such as mangroves, seagrass beds, and salt marshes, are highly threatened by increasing anthropic pressures, including chemical pollution. Persistent organic pollutants (POPs) have attracted attention in these particularly vulnerable ecosystems, due to their bioaccumulative, pervasive, and ecotoxic behavior. This article reviews and summarizes available information regarding current levels, biogeochemical cycling, and effects of POPs on coastal wetlands. Sediment POP levels were compared with international quality guidelines, revealing many areas where compounds could cause damage to biota. Despite this, toxicological studies on some coastal wetland plants and microorganisms showed a high tolerance to those levels. These taxonomic groups are likely to play a key role in the cycling of the POPs, with an active role in their accumulation, immobilization, and degradation. Toxicity and biogeochemical processes varied markedly along three main axes; namely species, environmental conditions, and type of pollutant. While more focused research on newly and unintentionally produced POPs is needed, mainly in salt marshes and seagrass beds, with the information available so far, the environmental behavior, spatial distribution, and toxicity level of the studied POPs showed similar patterns across the three studied ecosystems.

## 1. Introduction

Coastal marine wetlands are ecosystems located in the interface between marine and terrestrial environments. They include salt marshes, mangroves, and seagrass beds, all characterized by the presence of vascular plants, but with their particularities. While salt marshes and seagrass beds are vegetated by herbaceous plants, mangroves are dominated by trees and shrubs. Moreover, salt marshes and mangroves are located exclusively in the intertidal area, meaning that vegetation is adapted to the fluctuating salinity and flooding whereas seagrass beds are mostly developed in the subtidal zone, with more constant conditions, although intertidal seagrass beds can also be found (Hemminga and Duarte, 2000; Grobicki et al., 2016; Hopkinson et al., 2019). Regarding geographical distribution mangroves develop in tropical and subtropical areas whereas salt marshes in temperate and polar regions,

following a latitudinal pattern (Himes-Cornell et al., 2018; Hopkinson et al., 2019). However, some infringing salt marshes are found in tropical zones and climate change is expanding the mangrove distribution in some locations (Saintilan et al., 2014). Seagrass beds are widely distributed ecosystems around the world, excepting the Arctic and Antarctic, where the ice cover limits their expansion (Himes-Cornell et al., 2018; Larkum et al., 2006). Hence, vegetated coastal wetlands are found all over the world (Fig. 1).

Despite some differences, salt marshes, mangroves, and seagrass beds play common important ecosystem services. For instance, vascular plants promote sedimentation, participating in erosion control and regulation of storm-induced disturbances (Barbier et al., 2011; Himes-Cornell et al., 2018). Moreover, coastal wetlands are usually highly productive ecosystems, meaning that they are important in nutrient cycling and carbon sequestration (Chmura et al., 2003; Himes-Cornell

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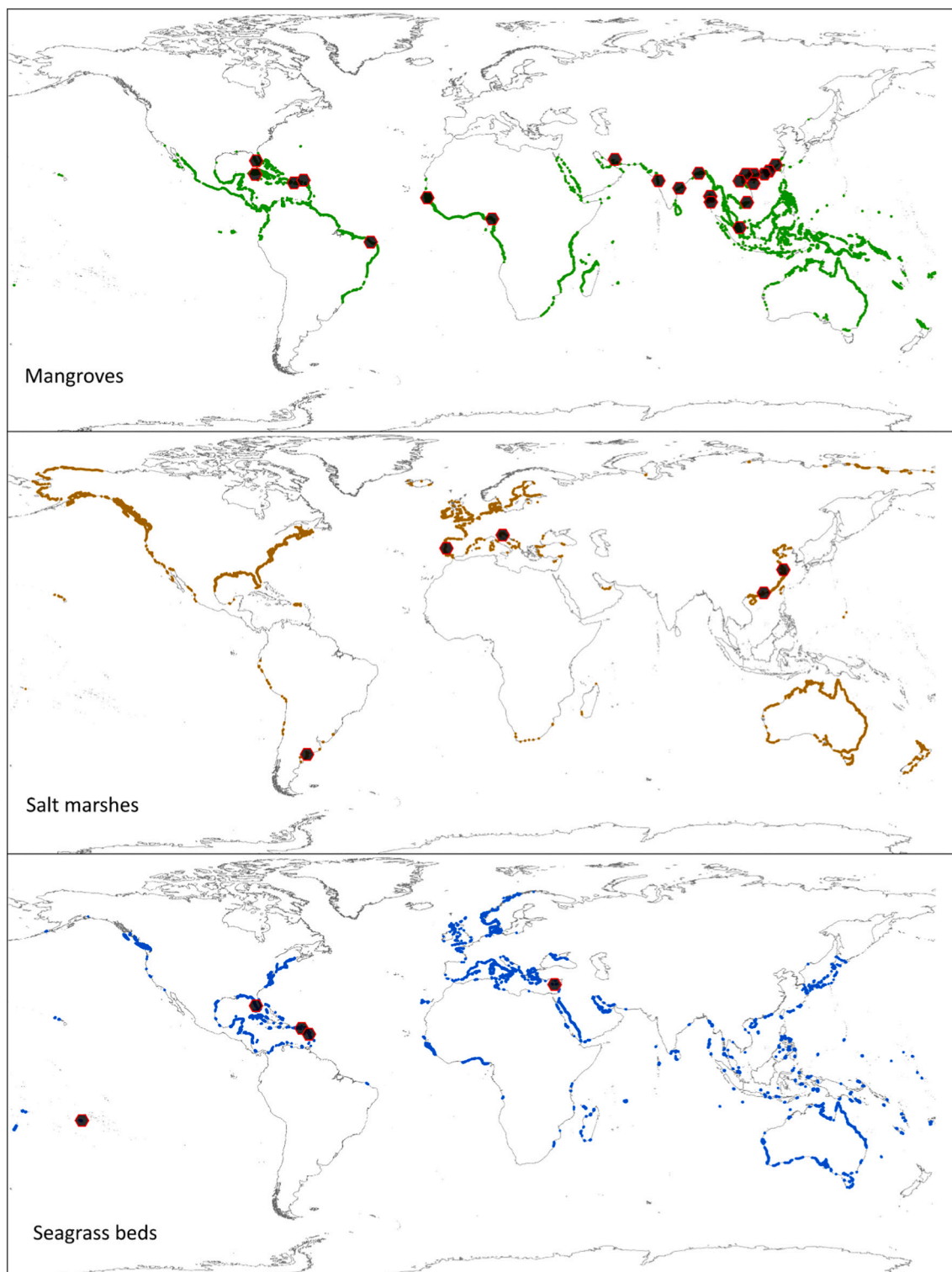
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et al., 2018). Besides, wetland plants have a well-developed root system that produces strong changes in the rhizosphere regarding sediment conditions and soil microorganisms which have a direct impact on the biogeochemical cycling of pollutants (Farzana et al., 2019c; Hu et al., 2020; Li et al., 2020; Negrin et al., 2019; Tam et al., 2016). Hence, they also play a key role in the reduction of pollutants through the uptake, accumulation, or degradation either in sediments or in plant tissues

(Lewis and Russell, 2015; Negrin et al., 2020; Pan et al., 2018). This is especially interesting given that pollution is one of the main threats of coastal wetlands, together with land reclamation for urbanization, accelerated sea-level rise, harvesting plants for human use, among others (Hopkinson et al., 2019).

Among pollutants, persistent organic pollutants (POPs) are commonly found in these environments. POPs are chemicals with high



**Fig. 1.** Global distribution of mangroves, salt marshes, and seagrass beds (Data source: <https://data.unep-wcmc.org/>). The evaluated ecosystems are marked with hexagons.

bioaccumulation or bioconcentration factors, resistance to degradation, ability to be transported long distances by air or water, and toxicity to biota including humans (CEC, 2006; UNEP, 2017). This review focuses on the POPs listed in the Stockholm Convention of the United Nations Environment Program (UNEP, 2017), which pursues the global reduction or elimination of the use and production of POPs. Initially, 12 chemicals, considered the “dirty dozen”, were listed: aldrin, chlordane, dichlorodiphenyltrichloroethane (DDT), dieldrin, endrin, heptachlor, mirex, toxaphene, hexachlorobenzene (HCB), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs). In subsequent years, other chemicals were included in the list (UNEP, 2017). Alpha-, beta-, gamma-hexachlorocyclohexane (HCH), chlordecone, pentachlorobenzene (PCBz), hexabromodiphenyl, polybrominated diphenyl ethers (PBDEs; BDE-47, -99, -153, -154, -175, and -183), and perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF) were included in 2009. Endosulfan and hexabromocyclododecane (HBCDs) were included in 2011 and 2013, respectively, while hexachlorobutadiene (HCBD), polychlorinated naphthalenes (PCNs), and pentachlorophenol and its salts and esters (PCP) were included in 2015. Moreover, decabromodiphenyl ether (BDE-209) and short-chain chlorinated paraffins (SCCPs) were included in 2017. The most recently added compounds to the list were dicofol and perfluorooctanoic acid (PFOA), its salts, and PFOA-related compounds in 2019. Besides, other chemicals are being evaluated for listing under the Convention; for example, Dechlorane Plus, methoxychlor, UV-328, and perfluorohexane sulfonic acid (PFHxS) (<http://www.pops.int/>).

The reported literature describing the levels, biogeochemical cycling, and toxic effects of POPs in coastal wetlands is sparse and scattered (Bayen, 2012; Haynes and Johnson, 2000; Lewis and Devereux, 2009; Lewis et al., 2011). This review provides an overview of the available information of current levels of the studied POPs reported in coastal wetlands around the world. Moreover, the toxicity of main POP groups to the microbial community and vascular plants and the influence of these biotic groups on the biogeochemical cycling of POPs, including their bioaccumulation, bioavailability, and degradation, are also discussed. Finally, this article identifies the gaps in the knowledge and proposes future perspectives and challenges.

## 2. Methodology

This work represents a comprehensive review of the international literature on POPs in mangroves, salt marshes, and seagrass beds. For this, the combination of broad keywords (e.g., “DDT+mangrove”; “Dioxin+salt marsh”; “PCB+seagrass”) in several databases (Google Scholar, Scopus, and PubMed) was used. Four hundred papers were reviewed, out of which about half are presented in this review. The information on the levels of POPs in sediments (Section 3) was screened from studies published between 2010 and 2021. Studies that did not strictly represent mangrove, marsh, or seagrass bed sediments were discarded. The information on the toxicity of POPs on microorganisms and plants of coastal wetlands (Section 4), and the role of these biological groups in the biogeochemical cycling of these pollutants (Section 5) included all the published works, regardless of the year of publication. Moreover, for those sections both experimental and field studies were considered.

## 3. POP levels in coastal wetland sediments

Monitoring studies on POPs in coastal wetlands from recent reports (2010–2021) were mainly concentrated in mangroves, especially in China and India (Fig. 1 and Table 1), mostly regarding PBDEs pollution. On the other hand, in America, Europe, and Africa the most studied POPs were organochlorine pesticides and PCBs. Besides, some POPs, such as PFOs, PFOA, HBCDs, HCBD, chlordecone, and PCDD/Fs have been poorly studied worldwide, and other POPs, such as polychlorinated

naphthalenes (PCNs), short-chain chlorinated paraffins (SCCPs), pentachlorobenzene (PCBz), and toxaphene, were never studied in coastal wetlands.

POPs levels from recent studies were summarized and compared with international guideline levels associated with ecotoxicological risks (Table 1). Average and maximum levels were compared to the Norwegian Environmental Quality Classification System (NEQCs) (Bakke et al., 2010), which proposes sediment guideline values for most of the POPs: lindane (gamma-HCH), DDTs, endosulfan, HCB, PCBs, SCCPs, HBCDs, PBDEs, PCBz, PCP, and PCDD/Fs.

PBDEs, which have been widely used as halogenated flame-retardants (HFRs), were thoroughly addressed in the mangroves of China but poorly studied in other coastal wetlands over the world. According to NEQCs, the reported levels would cause damage to the biota following chronic exposure (yellow in the table) in many of the evaluated sites, especially near densely populated areas such as the mangroves in the Pearl River estuary, China (Table 1; e.g., Chai et al., 2019a; Wu et al., 2015, 2017). Meanwhile, HBCD, another commonly used HFR, was studied only in the mangroves of Singapore and China, and in the Pearl River estuary it was observed at levels expected to cause damage to biota according to NEQCs (Li et al., 2019). The information reported here evidences that, despite their global regulation, HFR levels are increasing and could become a threat to coastal wetlands (Hu et al., 2019; Zhang et al., 2015a; Zhu et al., 2014c).

Organochlorine pesticides (OCPs), such as DDT, lindane, HCB, and endosulfan, and PCBs were the most studied POPs in non-Asian coastal wetlands. In-between OCPs, HCHs and DDTs were the most evaluated and have been widely detected in sediments (Table 1). In general, OCP concentrations were lower than reference levels (e.g., Alonso-Hernandez et al., 2014; Commendatore et al., 2018; Fey et al., 2019; Habibullah-Al-Mamun et al., 2016; Kalyani, 2016; Loi et al., 2011; Murugan et al., 2013; Pait et al., 2014; Shete et al., 2009; Zhang et al., 2015b). Nevertheless, some of them, such as endosulfan -a pesticide recently banned by the Stockholm Convention- exceeded the safety thresholds in some sites (Table 1; e.g., Bhupander and Debapriya, 2012; Bodin et al., 2011; Chen et al., 2020a; Oliveira et al., 2016; Zhang et al., 2019), suggesting toxic effects to the associated biota. Meanwhile, the reported PCB levels were generally not associated with damage to biota (green in the table; e.g., Bouchon et al., 2016; Fraser et al., 2020; Kalyani, 2016; Mugnai et al., 2011; Ren et al., 2019; Zanardi-Lamardo et al., 2019), excepting for some coastal wetlands such as the mangroves of Puerto Rico, southern China, and Singapore (Table 1; Alegria et al., 2016; Bayen et al., 2019; Zhao et al., 2012).

Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOs) are man-made chemicals that have been widely used in industrial and commercial applications (e.g., commercial household products, food packaged, coatings, and surfactants). Despite this, only three studies after 2010 evaluated their presence in coastal wetlands sediments (Table 1). At the studied sites, PFO levels would not be associated with adverse effects on the biota according to NEQCs. NEQCs have not yet determined guideline levels for PFOAs in sediment; hence, their possible danger to the associated biota in coastal wetlands is unknown. However, Corsolini et al. (2012) found that the levels of PFOA in the Sundarban mangrove were similar or higher than those reported in other marine environments.

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are extremely toxic pollutants originated as by-products in different processes, with combustion as the main contributor (Chovancová et al., 2005). Unfortunately, the presence of these compounds in coastal marine wetlands has been scarcely studied in recent years, partly due to the high cost and complexity of the analysis. Only two studies published after 2010 investigated the presence of PCDDs and PCDFs in coastal wetland sediments (Table 1; Kishida et al., 2010; Nunes et al., 2014). In these studies, toxic equivalents concentrations (TEQs; ng/g) indicated that PCDD/Fs would not cause harmful effects on biota according to NEQCs (Table 1).

**Table 1**

Mean concentrations (first rows) and ranges (second rows) of POPs in coastal wetland sediments from the last decade (2010–2021), and classification according to the Norwegian Environmental Quality Classification System (NEQCs): no toxic effects (green); toxic effects following chronic exposure (yellow); toxic effects following short-term exposure (red). Column “CW” defines the coastal wetland type: mangrove (M), salt marsh (SM), or seagrass bed (SB). The number of analyzed compounds from the same POP group is shown in parenthesis. All concentrations are expressed in ng/g dry weight of sediment. Levels below the detection limits are shown as ND. N/A represents non-available data.

Location	CW	γ-HCH	DDTs	Endosulfan	HCB	PCBs	PBDEs	References
<b>Asia</b>								
Hangzhou Bay, Zhejiang, China	SM					1.13 (9) N/A		Fraser et al., 2020
Zhangzhou, Fujian, China	M						11.1 (8) 6.1–15.5	Chai et al., 2019a
Zhang River Estuary, Fujian, China	M	0.03 N/A	0.66 (3) ND–4.74	1.63 (3) 0.26–12.74				Chen et al., 2020a
Jiulong River Estuary, Fujian, China	M		52 (8) 21–84			1.4 (22) 0.52–2.5		Zhang et al., 2019
Zhuhai, Shantou, and Shenzhen, Guangdong, China	M					20.24 (19) 3.03–41.33		Zhao et al., 2012
Shantou, Guangdong, China	M					N/A (41) 0.04–0.63	N/A (14) 6.1–180	Ren et al., 2019
Shantou, Guangdong, China	M						39.1 (10) 19–68.5	Liu et al., 2017
Shenzhen, PRD, Guangdong, China	M						N/A (16) 46.4–119	Hu et al., 2020
Hong Kong, PRD	M						N/A (8) 0.5–112	Zhu et al., 2014c
Guangzhou, PRD, Guangdong, China	M						61.2 (16) 17.5–216.1	Hu et al., 2019
Zhuhai, PRD, Guangdong, China	M						20.3 (16) 6.97–53.1	Hu et al., 2019
Shenzhen, PRD, Guangdong, China	M						72.2 (16) 46.4–119.4	Hu et al., 2019
Shenzhen, PRD, Guangdong, China	M						N/A (8) 28.1–361.7	Zhou et al., 2019
Guangzhou, PRD, Guangdong, China	M						14.1 (16) 1.25–36.3	Zhang et al., 2015a
Zhuhai, PRD, Guangdong, China	M						24.1 (16) 7.37–70.2	Zhang et al., 2015a
Shenzhen, PRD, Guangdong, China	M						143 (16) 82.3–206	Zhang et al., 2015a
Nansha, PRD, Guangdong, China	M	N/A 0.06 – 0.17	N/A (6) 5.61–7.50	N/A (3) ND–0.31			135.6 (18) N/A	Wu et al., 2015, 2017
Shenzhen, PRD, Guangdong, China	M						73.4 (8) 43.8–112.1	Chai et al., 2019a
Shenzhen, PRD, Guangdong, China	M						1404.5 (8) N/A	Chai et al., 2019b
Qi'ao Island, PRD, Guangdong, China	M						36.5 (18) N/A	Wu et al., 2016
Shenzhen, PRD, Guangdong, China	M						47.0 (8) N/A	Chai et al., 2019b
Shenzhen, PRD, Guangdong, China	M						4.8 (7) N/A	Chai et al., 2019b
Shenzhen, PRD, Guangdong, China	M						81.4 (8) N/A	Chai et al., 2019b
Zhanjiang, Guangdong, China	M						5.6 (8) 4.1–7.9	Chai et al., 2019a

In summary, according to the reviewed literature and NEQCs, the concentrations of many POPs could damage the biota in some coastal wetlands. Sites where possible effects on biota could be observed coincide with point sources located near coastal wetlands (e.g., wastewater discharge, electroplating plants, electronic waste recycling plants, and illegal dumping), highlighting some mangroves of the Pearl River Delta Area in China, which is the largest urban area in the world, and Jobos Bay in Puerto Rico, which is near a power generation complex, and places where DDT were used recently, such as Cameroon and Iran (Fusi et al., 2016; Nozar et al., 2013). However, NEQCs do not propose reference values for all POPs and those guidelines are based almost exclusively on toxic effects on fauna, barely considering the effects on vegetation and microbial communities (Lewis et al., 2011), characteristic features of coastal wetlands. Consequently, in the next section, the

available studies since 1970 addressing POP effects on the microbial community and vascular plants in coastal wetlands will be discussed.

#### 4. POP toxicity in coastal wetlands

##### 4.1. Effects on microbial communities

The impact of POPs on the composition and activity of the sediment microbial community is complex and not clear (Chen et al., 2016; Yang et al., 2016). Table 2 summarizes toxicological studies in coastal wetland sediments. As Table 2 shows, the effect of POPs on the microbial community has been poorly studied, with some compounds only tested at very high concentrations and others not even tested. Some POPs (e.g., BDE-153, -209, PCP, chlordecone, DDT, among others) could modify,

Dongzhaigang, Hainan, China	M						4.3 (8)	Chai et al., 2019a
Dongfang, Hainan, China	M						3.2–6.6	Chai et al., 2019a
Hainan Island, China	M	0.01	2.84 (6)	0.01 (1)	0.11	0.17 (29)	2.1 (8)	Qiu et al., 2019a,b
Fangchenggang, Guangxi, China	M	N/A	1.14–6.82	N/A	0.01–0.71	0.08–0.23	1.7–2.4	Chai et al., 2019a
Mumbai, India	M		0.53 (3)	0.18 (2)			0.71 (10)	Shete et al., 2009
Sundarban, Bay of Bengal, India	M	ND	1.93 (6)	ND (2)		1.7 (182)	0.08–2.92	Zanardi-Lamardo et al., 2019
Sundarban, Bay of Bengal, India	M	4.82	5.15 (3)				6.3 (8)	Bhupander and Debapriya, 2012
Chouldari, Andaman Islands, India	M	0.12–25.25	N/A	ND			3.1–9.7	Murugan et al., 2013
Kishorinagar, Andaman Islands, India	M	ND	0.76 (3)	ND				Murugan et al., 2013
Rangat, Andaman Islands, India	M	N/A	N/A	N/A				Murugan et al., 2013
Krishna River, India	M		N/A (1)			N/A		Kalyani et al., 2016
Singapore	M	0.011	0.769 (3)	0.089 (2)	0.023	0.683 (25)	0.031 (5)	Zhang et al., 2015b
Singapore	M	N/A	N/A	N/A	N/A	N/A		Bayen et al., 2019
Hormozgan province, Iran	M		8.34 (3)	ND (1)	ND	2.22 (28)		Nozar et al., 2013
			ND-122	N/A	N/A	ND-19.1		
			17.08 (3)			N/A (7)		
			13.32–36.75			5.67–15.55		
<b>Africa</b>								
Sine-Saloum, Senegal	M	1.25	1.15 (3)		0.1			Bodin et al., 2011
Wouri River Estuary, Cameroon	M	N/A	N/A		N/A			Fusi et al., 2016
			ND-40					
<b>Europe</b>								
Tejo estuary, Portugal	SM					N/A (12)		Nunes et al., 2014
Venice Lagoon, Italy	SM					0.005–0.01		Mugnai et al., 2011
						N/A (7)		
						0.23–0.43		
<b>America</b>								
Tampa Bay, USA	M, SB		ND (6)			N/A (209)		Lewis and Russell, 2015
Jobos Bay, Puerto Rico	M		N/A			ND-1.73		Alegria et al., 2016
Jaguaribe River Estuary, Brazil	M	1.58	7.53 (4)	67.77 (2)	1.94	217.65 (50)		Oliveira et al., 2016
Gulf of Batabanó, Cuba	M	N/A	5.76–8.98	45.67–87.2	N/A	0.42–1232.13		Alonso-Hernandez et al., 2014
St. Thomas, U.S. Virgin Islands	SB, M	ND-0.050	ND-1.27			N/A (25)		Pait et al., 2014
Guadeloupe Island	SB		N/A (5)			ND		Bouchon et al., 2016
San Blas Bay, Argentina	SM		ND-3.61			N/A (38)		Commendatore et al., 2018
		ND	ND (3)	0.12 (3)		ND-65.9		
		N/A	N/A	0.04–0.34		ND (38)	ND (8)	
						N/A	N/A	
		0.40 (22)	0.15 (6)			0.02–0.88	ND-0.65	
<b>Oceania</b>								
Moorea island	SB	0.08	0.76 (3)	0.43 (2)		12.03 (15)		Fey et al., 2019
		N/A	N/A	N/A		N/A		
<b>PFOs PFOA HBCDs HCBd TEQ PCDD/Fs</b>								
Sundarban, Bay of Bengal, India	M	ND	11.61					Corsonini et al., 2012
		N/A	9.17–14.09					
Hong Kong, PRD	SM	0.168	0.065					Loi et al. 2011
Sundarban, Bay of Bengal, India	M	N/A	N/A					Habibullah-Al-Mamun
		0.61	0.5					

depending on the concentration, the composition and abundance of the microbial communities in coastal wetland sediments and consequently affect their activity and functionality, inhibiting methanogenesis, sulfate reduction, CO<sub>2</sub> production, and nitrification, among other processes (Table 2). However, if the current levels reported in coastal wetland sediments (see Table 1) are compared with the concentrations where effects were observed in the microbial community and related processes (Table 2), it might be suggested that such levels would rarely generate harmful effects on microorganisms. However, more studies on the topic are needed, especially in seagrass beds and for untested pollutants, and

also considering possible interactions between pollutants and, especially, sediment characteristics, which are key factors in the bioavailability of POPs.

#### 4.2. Effects on plants

Plants can be adversely affected by POPs at several levels. They can affect cell ultrastructure and biosynthesis of proteins and pigments, which might affect vital processes such as photosynthesis, and they can alter membrane stability through lipid peroxidation (Zhang et al.,



		0.3–0.85	0.09–0.71		et al. 2016
Shenzhen, PRD, Guangdong, China	M	9.97 (2)			Li et al. 2019
Guangzhou, PRD, Guangdong, China	M	0.44–127.5			
		7.55			Hu et al. 2019
Zhuhai, PRD, Guangdong, China	M	0.94–22.2			
		1.26			Hu et al. 2019
Shenzhen, PRD, Guangdong, China	M	0.44–3.22			
		21.1			Hu et al. 2019
Singapore	M	4.68–127.5			
		0.525 (3)			Zhang et al 2015b
Vasiliko Bay, Cyprus	SB	N/A			
		N/A			Demetris 2019
Tejo estuary, Portugal	SM	10–460		0.0051 (29)	
				–	Nunes et al. 2014
Can Gio, Vietnam	M			0.0027 (29)	
				–	Kishida et al. 2010

2017). Most toxicity effects of these pollutants were studied on crops or other terrestrial plants (Zhang et al., 2017) but lipid peroxidation was already registered in mangrove plants (Farzana and Tam, 2018; Pan et al., 2017; Wang et al., 2014a). However, plants, especially those in coastal wetlands which are exposed to several environmental stressors, can minimize oxidative cell damage through their antioxidant defense system using several antioxidant enzymes (Liu et al., 2017; Wang et al., 2014a; Wang and Tam, 2018). Further, non-enzymatic compounds such as total polyphenol and carotenoids have also been reported to help cope with POP-induced cell damage (Parida et al., 2004; Wang et al., 2014a). Also, plants can produce substances that would act as physical “barriers” against pollutants, including POPs; for example, Fe plaque formation (a natural process) on the root surface of mangrove, salt marsh, and seagrass species would immobilize pollutants and reduce their uptake by roots (Gao et al., 2021; Pi et al., 2017).

However, depending on the species and the type and the concentration of the pollutant, the above-mentioned mechanisms are not always efficient and toxic effects can be appreciated in coastal wetland plants. The results of available studies reporting the physiological effect of some POPs on wetland plant species are summarized in Table 3. This table shows great variability in responses among species, POP type and concentration. However, as observed for the microbial community, when comparing the levels at which the plants showed negative effects (Table 3) with the current levels found in the studied coastal wetlands (Table 1), it seems that the plants would tolerate current levels of contamination. Still, more toxicological and monitoring studies are needed, especially in poorly studied environments, such as seagrass beds and salt marshes. Moreover, unintentionally produced and new POPs need further research and special attention should be given to associations between different pollutants.

In addition to the type and concentration of the pollutant and the species, sediment characteristics could influence the POP toxicity on coastal wetlands plants. For example, Farzana et al. (2019b) and Farzana and Tam (2018) found that nutrient-rich aquaculture effluents reduced the damaging effect and oxidative stress of BDE-99 and BDE-209, respectively, in *K. obovata* and *A. marina*. This might be achieved by increasing the activity of antioxidant enzymes and the content of antioxidant pigments, especially carotenoids, partly because nutrients are essential elements to produce these molecules (Farzana et al., 2019b; Farzana and Tam, 2018). Anyway, there is still a lack of knowledge about the contribution of environmental conditions on the POP effects on plants, especially in salt marshes and seagrasses.

## 5. Biogeochemical cycle of POPs in coastal wetlands

### 5.1. Influence of microorganisms on the biogeochemical cycling of some POPs in coastal wetlands

Microorganisms affect the biogeochemical cycling of POPs, including their fate and degradation, in coastal wetland sediments in several ways (Table 4). So far, PBDEs and PCP were the only POPs studied in those ecosystems. To evaluate the importance of microorganism-mediated degradation of PBDEs and PCP in the sediments of these environments, mainly in mangroves, some studies compared degradation rates under sterile and non-sterile conditions (Chen et al., 2017; Cheng et al., 2019; Pan et al., 2017, 2018, 2020; Yang et al., 2016; Zhu et al., 2014a, 2014b, 2018). In all the evaluated cases, PBDE and PCP degradation in the sterile medium was insignificant or very low and always lower than in non-sterile sediments. For example, Yang et al. (2016) observed that BDE-209 could be biotransformed almost completely, up to di-BDE (BDE-15) in mangrove sediment. Although the comparison between abiotic and microbial-mediated degradation in coastal wetlands was made only for PBDEs and PCP, the reduction of other POPs such as DDT, HCB, chlordane, lindane, and PCBs was studied in agricultural soils and river sediments and was also higher if microbially mediated compared with abiotic conditions (Hirano et al., 2007; Horváthová et al., 2018; Ortíz et al., 2013; Pesce and Wunderlin, 2004). Consequently, it is suggested that the main degradation pathway for these compounds in coastal wetlands would be degradation mediated by microorganisms; however, more studies are needed to confirm this.

The mechanisms of POP biodegradation in coastal wetland sediments are varied and, generally, complementary (Fig. 2). Firstly, microorganisms, as well as some plants (see next section), can secrete enzymes to the soil, such as dehydrogenase (Cardona and Suarez, 2010; Hechmi et al., 2014; Margesin et al., 2000), which can directly participate in the biochemical degradation of some POPs, catalyzing compounds already partially degraded (Xie et al., 2012; Zhu and Zhang, 2008). For example, Hechmi et al. (2014) found a significant positive correlation between the dehydrogenase concentration and the PCP removal in wetland soils, both in unplanted and, especially, in planted soils with *P. australis*. Secondly, POP degradation mediated by aerobic microorganisms, i.e., that could occur in surface sediments or rhizospheric sediments, would be another important POP removal pathway. Under these conditions, the transformation of less halogenated POPs and partially dehalogenated compounds would prevail, through oxidative dehalogenation and hydrolytic dehalogenation, among others (Hundt

**Table 2**

Summary of adverse effects of POPs on the microbial communities of coastal wetlands. Column “CW” defines the coastal wetland type: mangrove (M), salt marsh (SM), and seagrass bed (SB). Sediment concentrations are expressed in µg/g dry weight (dw) or wet weight (ww); concentrations in water are expressed in µg/L.

Compound	Concentration	CW	Observed effect	References
BDE-209	10 µg/g dw	M	• It reduced microbial diversity	Yang et al., 2016
BDE-209	20 µg/g dw	M	• It inhibited the nitrification potential activity • It decreased the abundance and diversity of ammonia-oxidizing archaea and bacteria	Chen et al., 2018
BDE-153	1.38 µg/g ww	M	• It modified the microbial composition	Pan et al., 2018
PBDEs	1.21–18.77 µg/L (different compounds)	M	• BDE-154 was identified as the most influential PBDE on the microbial community structure	Wang et al., 2014b
PCP	20 µg/g dw	M	• It inhibited sulfate reduction • It modified the microbial composition. • It promoted the reduction of Fe <sub>3</sub> <sup>+</sup> and methanogenesis.	Xu et al., 2017
PCP	800 µg/g dw	SM	• It inhibited CO <sub>2</sub> production by 50% under methanogenic conditions	D'Angelo and Reddy, 2000
PCP and Chlordecone	>850 µg/g dw 100,000 µg/L	SB	• It inhibited CH <sub>4</sub> production by 50% under methanogenic conditions • It reduced nitrogenase activity of bacteria associated with the roots and rhizomes of the seagrass <i>Zostera marina</i>	Brackup and Capone, 1985
Toxaphene	100,000 µg/L	SB	• It had no significant effect in the N <sub>2</sub> fixation of bacteria associated with the roots and rhizomes of the seagrass <i>Zostera marina</i>	Brackup and Capone, 1985
Chlordecone	20–2000 µg/L	SM	• It reduced the number of colony-forming units • It did not affect the number of anaerobic microorganisms	Mahaffey et al., 1982
Toxaphene	10 µg/g dw	SM	• It did not affect significantly the CO <sub>2</sub> and CH <sub>4</sub> production or sulfate reduction	Kiene and Capone, 1984
	100 µg/g dw	SM	• It inhibited methanogenesis • It did not affect the CO <sub>2</sub> evolution or sulfate reduction	Kiene and Capone, 1984
	1000 µg/g dw	SM	• It inhibited methanogenesis and sulfate reduction • It did not affect the CO <sub>2</sub> evolution	Kiene and Capone, 1984
PCP	10 µg/g dw	SM	• It did not affect significantly the CO <sub>2</sub> and CH <sub>4</sub> production or sulfate reduction	Kiene and Capone, 1984
	100 µg/g dw	SM	• It inhibited methanogenesis and affected the carbon dioxide evolution • It did not affect the sulfate reduction	Kiene and Capone, 1984
	1000 µg/g dw	SM	• It inhibited methanogenesis • It did not affect the CO <sub>2</sub> evolution or sulfate reduction	Kiene and Capone, 1984
Endrin	1000 µg/g dw	SM	• It did not affect significantly the CO <sub>2</sub> and CH <sub>4</sub> production or sulfate reduction	Kiene and Capone, 1984
Lindane	1000 µg/g dw	SM	• It did not affect significantly the CO <sub>2</sub> and CH <sub>4</sub> production or sulfate reduction	Kiene and Capone, 1984
	1000 µg/g dw	SM	• It inhibited methanogenesis and sulfate reduction	Kiene and Capone, 1984
Chlordane	10 µg/g dw	SM	• It did not affect significantly the CO <sub>2</sub> and CH <sub>4</sub> production or sulfate reduction	Kiene and Capone, 1984
	100 µg/g dw	SM	• It did not affect significantly the CO <sub>2</sub> and CH <sub>4</sub> production or sulfate reduction	Kiene and Capone, 1984
	1000 µg/g dw	SM	• It inhibited methanogenesis and sulfate reduction • It did not affect the CO <sub>2</sub> evolution	Kiene and Capone, 1984
Chlordecone	10 µg/g dw	SM	• It did not affect significantly the CO <sub>2</sub> and CH <sub>4</sub> production or sulfate reduction	Kiene and Capone, 1984
	1000 µg/g dw	SM	• It inhibited methanogenesis • It did not affect the CO <sub>2</sub> evolution or sulfate reduction	Kiene and Capone, 1984
Heptachlor	10 µg/g dw	SM	• It did not affect significantly the CO <sub>2</sub> and CH <sub>4</sub> production or sulfate reduction	Kiene and Capone, 1984
	100 µg/g dw	SM	• It inhibited sulfate reduction • It did not affect the methanogenesis or CO <sub>2</sub> evolution	Kiene and Capone, 1984
	1000 µg/g dw	SM	• It inhibited methanogenesis • It did not affect the sulfate reduction or CO <sub>2</sub> evolution	Kiene and Capone, 1984
PCBs (Aroclor 1221)	1000 µg/g dw	SM	• It did not affect significantly the CO <sub>2</sub> and CH <sub>4</sub> production or sulfate reduction	Kiene and Capone, 1984
PCBs (Aroclor 1254)	1000 µg/g dw	SM	• It promoted methanogenesis • It did not affect sulfate reduction or CO <sub>2</sub> evolution	Kiene and Capone, 1984
DDT	10 µg/g dw	SM	• It did not affect significantly the CO <sub>2</sub> and CH <sub>4</sub> production or sulfate reduction	Kiene and Capone, 1984
	100 µg/g dw	SM	• It did not affect significantly the CO <sub>2</sub> and CH <sub>4</sub> production or sulfate reduction	Kiene and Capone, 1984
	1000 µg/g dw	SM	• It inhibited methanogenesis • It did not significantly affect the CO <sub>2</sub> evolution or sulfate reduction	Kiene and Capone, 1984
PCBs (Aroclor 1242)	14–16 µg/L	SM	• It did not affect the decomposition of <i>S. alterniflora</i> detritus	Marinucci and Bartha, 1982

et al., 1999; Marinucci and Bartha, 1982; Schmidt et al., 1992; Zacharia, 2019). In contrast, highly halogenated POPs, including PCBs, PBDEs, and PCDDs, could not be biotransformed aerobically (Arbeli, 2009; Marinucci and Bartha, 1982; Zhu et al., 2014a). For example, Zhu et al. (2014a) found that in mangrove sediments, the three tested PBDE congeners (tetra-, hexa- and deca-BDE) remained intact after 30 days of

aerobic incubation. In opposition, D'Angelo and Reddy (2000) observed similar PCP reductive dechlorination rates under aerobic and anaerobic conditions in salt marsh sediments. Those opposite results highlight that more research is needed to fully understand the aerobic POP biodegradation in coastal wetlands sediments.

POP biodegradation under anaerobic conditions has been more

**Table 3**

Summary of effects attributable to POPs on coastal wetland plants. Column “CW” defines the coastal wetland type: mangrove (M), salt marsh (SM) and, seagrass bed (SB). Column “Time” defines the exposure time in months, unless another time period is specified. Sediment concentrations are expressed in µg/g dry weight (dw) or wet weight (ww); concentrations in water are expressed in µg/L.

Compound	Concentration	Time	CW	Species	Effects on growth and physiology	References
Endosulfan	50 µg/L	6hs	SB	<i>H. uninervis</i> and <i>H. ovalis</i>	• It did not affect photosynthesis nor respiration	Ramachandran et al., 1984
Lindane	50 µg/L	6hs	SB	<i>H. uninervis</i>	• It reduced photosynthesis • It did not affect respiration	Ramachandran et al., 1984
Lindane	50 µg/L	6 hs	SB	<i>H. ovalis</i>	• It did not affect photosynthesis nor respiration	Ramachandran et al., 1984
p,p-DDT	50 µg/L	6 hs	SB	<i>H. uninervis</i> and <i>H. ovalis</i>	• It did not affect photosynthesis nor respiration	Ramachandran et al., 1984
Dieldrin	0.038 to 6 µg/g <sup>a</sup>	2	M	<i>R. mangle</i>	• It did not show effects	Walsh et al., 1974
Methoxy-chlor	0.038 to 6 µg/g <sup>a</sup>	2	M	<i>R. mangle</i>	• It did not show effects	Walsh et al., 1974
Mirex	0.038 to 6 µg/g <sup>a</sup>	2	M	<i>R. mangle</i>	• It did not show effects	Walsh et al., 1974
PCBs	0.038 to 6 µg/g <sup>a</sup>	2	M	<i>R. mangle</i>	• It did not show effects	Walsh et al., 1974
PCBs	0.0022 µg/g ww in mud	1.5	SM	<i>S. alterniflora</i>	• It did not affect total biomass • It increased mortality • It changed the aboveground/belowground biomass ratio • It reduced the number of stems	Mrozek et al., 1983
PCBs	0.0022 µg/g ww in sand	1.5	SM	<i>S. alterniflora</i>	• It did not affect total biomass • It decreased the height of stems • It reduced the number of living leaves • It increased the number of stems	Mrozek et al., 1983
PCP	50 and 250 µg/g dw	2.3	SM	<i>P. australis</i>	• It reduced 20% and 40% the total biomass in plants exposed to 50 and 250 µg/g, respectively	Hechmi et al., 2014
PCP	1000 µg/L	40 hs	SB	<i>T. testudinum</i>	• It reduced respiration and photosynthesis after 40 h of exposure, but there was a total recovery 48 h later	Walsh et al., 1982
PFOA and PFOs	50 µg/L. hydroponic system	1	SM	<i>P. australis</i>	• It did not show effects	Wang et al., 2020
BDE-209	52.6 µg/g dw	3	M	<i>K. obovata</i>	• It increased root and leaves biomass and pigment content	Farzana et al., 2017
BDE-209	6670 µg/L <sup>b</sup>	24	M	<i>A. corniculatum</i>	• It did not affect root and stem biomass • It reduced leaf biomass and pigment content	Farzana et al., 2019c
BDE-209	6670 µg/L <sup>b</sup>	24	M	<i>A. marina</i>	• It did not affect root, stem, and leaf biomass nor pigment content	Farzana et al., 2019c
BDE-209	6670 µg/L <sup>b</sup>	24	M	<i>K. obovata</i>	• It reduced root, stem, and leaf biomass and pigment content	Farzana et al., 2019c
BDE-209	0.2 and 5 µg/g dw	7	M	<i>A. marina</i> and <i>K. obovata</i>	• It did not show effects	Zhu et al., 2014b
BDE-209 <sup>a</sup>	53.13 µg/g dw	6	M	<i>A. marina</i>	• It did not affect stem biomass nor pigment content • It reduced root and leaf biomass	Farzana and Tam, 2018
BDE-209 <sup>a</sup>	53.13 µg/g dw	6	M	<i>K. obovata</i>	• It did not affect root biomass nor pigment content • It reduced stem and leaf biomass.	Farzana and Tam, 2018
BDE-47	2.14 µg/g dw	12	M	<i>A. corniculatum</i> and <i>A. marina</i>	• It did not result in visible effects • It did not affect leaf biomass nor pigment content	Chen et al., 2017
BDE-47	100 and 1000 µg/L	2	M	<i>K. obovata</i>	• It did not affect root and leaf biomass.	Wang and Tam, 2018
BDE-47	5000 and 10,000 µg/L	2	M	<i>K. obovata</i>	• It reduced root and leaf biomass	Wang and Tam, 2018
BDE-47	100 and 1000 µg/L	2	M	<i>K. obovata</i>	• It did not affect the number of leaves, root and leaf biomass, nor pigment content	Wang et al., 2014a
BDE-47	5000 and 10,000 µg/L	2	M	<i>K. obovata</i>	• It resulted in fewer leaves • It reduced root and leaf biomass • It reduced chlorophyll-a content • It increased chlorophyll-b content	Wang et al., 2014a
BDE-47	100 and 1000 µg/L	2	M	<i>A. marina</i>	• It did not affect the number of leaves, root and leaf biomass, nor pigment content	Wang et al., 2014a
BDE-47	5000 and 10,000 µg/L	2	M	<i>A. marina</i>	• It did not affect the number of leaves, root and leaf biomass, nor pigment content	Wang et al., 2014a
BDE-47	0.2 µg/g y 5 µg/g dw	7	M	<i>A. marina</i> and <i>K. obovata</i>	• It did not result in visible effects • It did not affect total biomass	Zhu et al., 2014b
BDE-99	0.578 µg/g dw	3	M	<i>K. obovata</i>	• It delayed germination and early growth • It reduced root biomass • It increased leaf biomass and pigment content	Farzana et al., 2017
BDE-99	0.602 µg/g dw <sup>c</sup>	6	M	<i>A. marina</i>	• It did not affect stem biomass	Farzana et al., 2019b
BDE-99	0.602 µg/g dw <sup>c</sup>	6	M	<i>K. obovata</i>	• It did not affect root, stem, and leaf biomass nor pigment content • It did not affect root, stem, and leaf biomass • It increased pigment content	Farzana et al., 2019b

<sup>a</sup> Weight basis not expressed in the original article basis.

<sup>b</sup> Equivalent to 65.64 ± 6.51 and 8.92 ± 1.17 µg/g dw in surface and underground sediment.

<sup>c</sup> No extra nutrients.

studied in coastal wetland sediments since anoxic or suboxic sediments are predominant below the first millimeters of the surface. Besides, the main way of initially degrading some highly halogenated compounds such as PCBs, PCDD/Fs, and PBDEs is the anaerobic microbial reductive dehalogenation (Arbeli, 2009; Zanaroli et al., 2015). Consequently,

anaerobic biodegradation in coastal wetlands has been studied to enhance bioremediation and phytoremediation technologies.

Naturally, microbial reductive dehalogenation is a slow process where functional microorganisms, mainly obligate or facultative organohalide-respiring bacteria (OHRB), transform highly halogenated



**Table 4**

Summary of the main results of experimental studies on PBDE and PCP microorganism-mediated degradation in mangroves and salt marshes. Column “CW” defines the coastal wetland type: mangrove (M) and salt marsh (SM). Column “Time” defines the exposure time in months.

Compound	Experimental conditions	Time	CW	Results	Reference
BDE-47, BDE-209	Planted soils with N addition	3	M	BDE-47 removal efficiency in the rhizosphere was significantly higher than in unplanted soil. In planted soils, removal activity was enhanced by N addition.	Chen et al., 2015
BDE-47	Multispecies planted soil	12	M	Plant species can synergically interact accelerating PBDEs removal by enhancing microbial activity and altering bacterial community composition	Chen et al., 2017
BDE-47	Planted soils with mushroom biochar addition	5	M	Biochar improved the microbial activity and stimulated the reductive debromination processes of BDE-47.	Chen et al., 2018
BDE-47	Planted soils with straw biochar addition	4	M	Reductive PBDE debromination was favored by highly diversified Organohalide-Respiring Bacteria (OHRB) while their activity was modulated by pyrolysis temperature and straw type	Chen et al., 2020b
PCP	Planted soils with nitrate and molybdate addition	3	M	Nitrate and molybdate treatments enhanced PCP dechlorination by promoting different microbial consortiums.	Cheng et al., 2019
PCP	Planted soils with electron-donor/acceptor addition	1	SM	PCP reductive dechlorination was enhanced by electron donor/acceptor supply and increased microbial biomass, while it was inhibited under denitrifying and $\text{SO}_4^{2-}$ reducing conditions.	D'Angelo and Reddy, 2000
BDE-47	Planted soils, variable depths	5	M	Upper sediments with higher bacterial abundance showed higher removal rates while deeper sediments (mostly anaerobic) showed lower removal potential	Pan et al., 2017
BDE-153	Mangrove, mudflat, marine, and freshwater sediments	5	M	The removal percentages of BDE-153 in the mangrove, mudflat, marine, and freshwater sediments were 77.1, 76.2, 66.2, and 62.3%, respectively, mainly associated with <i>Proteobacteria</i> (Phylum).	Pan et al., 2018
BDE-47	Soil amended with different carbon sources	5	M	Carbon addition significantly enhanced degradation percentages with higher yields for methanol, acetate, and succinate. Degradation activity correlated with the abundance of bacteria	Pan et al., 2020
BDE-47, -100, -99, -154, -153 and -209	Planting with <i>K. obovata</i> and different tidal regimes	8	M	Frequently flooded sediments showed higher biodegradative power probably driven by reductive debromination and upper sediments accumulated higher PBDE residuals	Tam et al., 2016
PBDEs and PAHs	Co-planting with <i>E. agallocha</i> or <i>K. obovata</i> under two tidal regimes	8	M	Flooding frequency prevailed over plant species influencing the biodegradative power. Daily tidal flooding favored biodegradation through anaerobic microorganisms.	Wang et al., 2014b
PCP	Soil amended with electron donors (acetate)	3	M	PCP dechlorination was driven by phylum <i>Bacteroidetes</i> at first, followed by <i>Proteobacteria</i> and <i>Firmicutes</i> groups while reductive dechlorination was driven by <i>Clostridium</i> , <i>Geobacter</i> , and <i>Dehalococcoides</i> -like organisms	Xu et al., 2017
BDE-209	Sediments collected in different seasons; addition of zerovalent iron.	2.5	M	Debromination rates were enhanced by zerovalent iron while different bacterial assemblages exhibited different abilities for BDE-209 anaerobic debromination.	Yang et al., 2016
BDE-47, BDE-209	Planting with <i>K. obovata</i> and <i>A. marina</i>	7	M	High debromination yields were obtained for BDE-47 mainly driven by microbial activity	Zhu et al., 2014a
BDE-47, -153, and -209	Different soils with aerobic and anaerobic treatments	3	M	The higher debromination of BDE-47 and BDE-153 occurred in anaerobic freshwater and mangrove sediments, respectively. BDE-209 concentrations did not show any significant change during the 90 days in any type of sediment. Under aerobic conditions (1 month), the percentages of residual BDE-47, -153, and -209 in the surface sediment slurry did not show any significant changes.	Zhu et al., 2014b

pollutants to less halogenated end-products in anaerobic conditions (Maphosa et al., 2010; Tokarz et al., 2008; Zanaroli et al., 2015; Fig. 2). However, the rate at which this process occurs can vary substantially according to the presence of functional microorganisms, the sediment characteristics, and the type and concentration of the contaminant (Zanaroli et al., 2015). The reviewed studies agreed that the type and quantity of electron donors and acceptors present in the sediment would be one of the most influential variables in this process (Chen et al., 2015; Ding and He, 2012; Zanaroli et al., 2015). This is explained because in reductive dehalogenation highly halogenated POPs compete with other electron acceptor compounds such as  $\text{NO}_3^-$  and  $\text{CH}_4$  and, especially,  $\text{Fe}_3^+$  and  $\text{SO}_4^{2-}$ , which are usually quite abundant in mangroves and salt marshes (Cheng et al., 2019; Li et al., 2009; Pan et al., 2017; Xu et al., 2017). For example, D'Angelo and Reddy (2003) observed that  $\text{NO}_3^-$ ,  $\text{Fe}_3^+$ , and  $\text{SO}_4^{2-}$  inhibited PCP transformation in anaerobic salt marsh sediments. Moreover, Zanaroli et al. (2015) noted that high  $\text{SO}_4^{2-}$  concentrations could delay or slow PCB dechlorination and suggest that the growth and activity of many dechlorinating bacteria could be hampered in marine environments and restricted to environments with low  $\text{SO}_4^{2-}$  content. However, they also pointed out that some sulfate reducers could promote the growth of PCB dehalorespirators (Zanaroli et al.,

2015). In line with this, Xue et al. (2017) observed that the iron dissimilation and/or sulfate reduction processes have a positive effect on the PCP reduction process in anaerobic mangrove sediments, especially when sufficient electron donors were provided. Xu et al. (2015) also observed higher dehalogenation rates by increasing the electron donor levels in mangrove sediments: PCP dechlorination of 96% and 21% in soil with and without extra acetate, respectively. Besides, they observed that extra electron donors increased the diversity and abundance of functional microorganisms. Consistent with this, Pan et al. (2017) observed that the highest removal rates of BDE-47 occurred in the upper layers of the sediment, where total and OHRBs (except *Dehalobacter*), as well as organic substrates and electron acceptors, were more abundant.

Other factors that affect the promotion or inhibition of reductive dehalogenation are salinity and redox potential (Hemkemeyer et al., 2015; Pan et al., 2017). Salinity would affect soil microbial communities (Rietz and Haynes, 2003) by reducing their enzymatic synthesis and metabolic rates (Cortes-Lorenzo et al., 2012); however, Yang et al. (2016) observed that the highest debromination rate of BDE-209 occurred in mangrove sediments collected in autumn when salinity was the highest. Furthermore, a lower redox potential would trigger a higher efficiency in the reductive dehalogenation of the highly

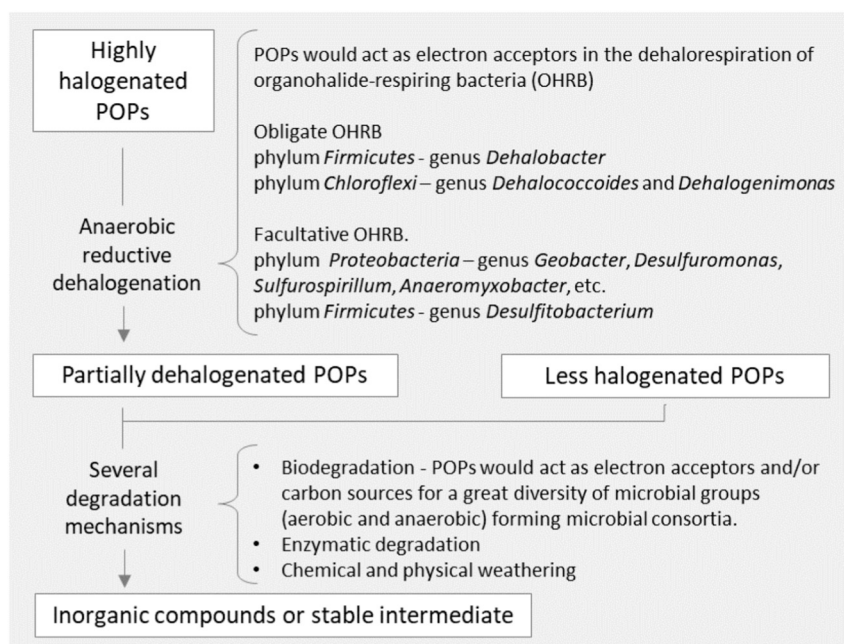


Fig. 2. Summary of the most important processes and actors during the POP biodegradation in coastal wetland sediments.

halogenated POPs (Gerecke et al., 2005; Pi et al., 2017). In this sense, the tidal regime is essential because it could affect the duration and frequency of waterlogging and, consequently, the oxygen level and redox potential in the sediment. For example, Tam et al. (2016) observed that the highest PBDE reduction rate occurred in mangrove sediments exposed to a daily tidal regime, instead of biweekly or without flooding. However, the tidal regime creates oscillation between aerobic and anaerobic conditions, which promote a greater microbial diversity (Wang et al., 2014b); thus, degradation pathways can follow different routes (Scrimshaw et al., 1996). Moreover, Mirsatari et al. (1987) suggested that a very efficient method to reduce the toxaphene, and probably other POPs, would be to establish a series of cycles of flooding and evaporation to dryness, as occurs in some sectors of coastal wetlands.

Another fundamental factor in the microbial reductive dehalogenation of POPs is the nutrient and organic matter content. For example, D'Angelo and Reddy (2000) observed that total carbon, nitrogen, phosphorus, and microbial biomass were positively correlated with PCP degradation under methanogenic conditions; however, a high organic matter content could favor the retention of POPs in the sediment and reduce their bioavailability for microorganisms (Zhu et al., 2014a). Bioavailability, mediated by sorption-desorption kinetics, is essential in regulating the transformation rates of compounds (Schlebaum et al., 1998) and becomes more important when environmental concentrations are low and compounds are aged (D'Angelo and Reddy, 2000; Taylor et al., 2019). Palekar et al. (2003) observed that fresh 2,6-dibromobiphenyl (26-BB) and 2,3,4,5,6-pentachlorobiphenyl (23456-CB) enriched in salt marsh sediments were significantly dehalogenated, but native PCBs (Aroclor 1268) were not, probably due to the low bioavailability of weathered pollutants. The complexity of the POPs bioavailability related to aging and nutrient and carbon content requires more studies addressing the topic. For instance, the reviewed studies have been carried out in sediments enriched with fresh compounds and biodegradation has not yet been studied under real-world conditions, where POPs are commonly aged and poorly bioavailable. Therefore, more research is required to understand the interactions between pollutants, environmental factors, and the microbial community in situ. Furthermore, future research should use high-throughput sequencing techniques and qPCR simultaneously to obtain a more complete picture of functional microbial groups and even of the entire microbial

community composition involved in the dehalogenation of POPs and other organohalides.

## 5.2. Influence of plants on the biogeochemical cycling of POPs in coastal wetlands

### 5.2.1. Influence of plants on sediment processes

Vascular plants -typical of coastal wetlands- can stimulate the removal of POPs. This is explained by the interrelation of several processes involving vegetation (Fig. 3). Plants can remove POPs from the sediment by uptaking them through the roots; POPs can be then accumulated there or translocated to aboveground tissues (see next section). Besides, plants can facilitate the immobilization of some POPs on the Fe plaque formed on root surfaces of coastal wetland plants, as already mentioned (Gao et al., 2021; Pi et al., 2009, 2010, 2017). For example, Pi et al. (2017) observed that up to 25% of PBDEs added to a mangrove microcosm were immobilized in the Fe plaque of *E. agallocha* and *K. obovata*. Moreover, partially dehalogenated and less halogenated POPs can be chemically transformed in sediments by enzymes secreted by plant roots, e.g. peroxidases and dehydrogenases (Chu et al., 2006; Hechmi et al., 2014). In this sense, Huesemann et al. (2009) suggested that eelgrass roots could excrete enzymes that would carry out the initial steps of PCB biodegradation, such as dechlorination or aromatic ring cleavage, with indigenous microorganisms that complete the PCB mineralization process. Finally, it has been well documented that the most important pathway for the POP dissipation involving coastal wetland plants would be the stimulation of the growth and development of both anaerobic and aerobic POP degrading microorganisms (e.g., Chen et al., 2015, 2017; Farzana et al., 2019a; Huesemann et al., 2009; Li et al., 2020; Toyama et al., 2011; Yang et al., 2016).

According to the reviewed studies, radial oxygen loss from roots, typical of wetland plants (Colmer, 2003), would promote the aerobic biodegradation of the less halogenated POPs in marine coastal wetlands sediments (Carvalho et al., 2011; Huesemann et al., 2009; Pi et al., 2016). Added to this, Huesemann et al. (2009) observed that *Zostera marina* not only improved the degradation of less chlorinated PCBs in sediments, but also that of highly chlorinated PCBs. Therefore, other mechanisms apart from aerobic ones would be occurring, since highly halogenated POPs require anaerobic conditions for dehalogenation (see

the previous section). The secretion of exudates such as organic acids and inorganic minerals by plant roots can contribute to the increase of nutrients and energy sources in the sediment (Arslan et al., 2017) which in turn improve the microbial activity, including the biodegradation of POPs such as PBDEs and HBCDs (Hu et al., 2019; Chen et al., 2016, 2017). The extra nutrients would stimulate the anaerobic reductive dehalogenation by adjusting the C:N ratio to an optimal level and providing more renewable sources of electron donors, such as hydrogen, increasing the abundance of OHRB (Chen et al., 2017; Yu et al., 2014). Moreover, root exudates could act as biosurfactants promoting desorption and mobility of organic pollutants and increasing their bioavailability and, as they are soluble in water, they could diffuse throughout the sediment and promote the removal of POPs further than the vicinity of the roots (Farzana et al., 2019c; Huesemann et al., 2009; Qiu et al., 2019a).

The aforementioned about the role of plants in the biogeochemical cycle of POPs was inferred mostly from mesocosm studies since field studies are scarce and usually not conclusive and are sometimes contradictory. For instance, on the one side, Nunes et al. (2014), which studied salt marsh sediments in the field, found somewhat lower concentrations of PCDDs, PCDFs, and dioxin like-PCBs in planted sediments than in non-planted ones; hence, they suggested that plants would contribute to the degradation of these POPs. On the other side, other studies found that concentrations of POPs, including toxaphene, PBDEs, DDT and PCBs, and alternative halogenated flame retardants (AHFR) in vegetated areas were higher than in adjacent mudflats (e.g., Carvalho et al., 2011; Gallagher et al., 1979; Liu et al., 2017; Masters and Inman, 2000; Scrimshaw et al., 1994, 1996; Wu et al., 2016). Wu et al. (2016) attributed this to the higher organic matter content, Eh, and shade in the planted areas, which would increase adsorption of HFR and DDE to sediment particles (Carvalho et al., 2011; Zhang et al., 2015a), reduce the microbial degradation of PBDEs (Gerecke et al., 2005; Lee and He, 2010), and reduce the photolytic degradation of PBDEs and HFRs (Söderström et al., 2004; Wang et al., 2012), respectively. Furthermore, Gallagher et al. (1979) noted that the presence of macroorganic matter, such as dead roots, can contribute to higher levels of toxaphene in the sediment since dead roots develop numerous tiny cracks and fissures on the cell surface which increase the number of sites for adsorption and absorption of toxaphene. Otherwise, Sanger et al. (1999) observed a large spatial variability of PCB and DDT concentrations between vegetated and unvegetated areas within a salt marsh and did not find a significant correlation with organic matter content. Those findings imply that more studies in coastal wetlands are needed to better understand the distribution of POPs in those dynamic ecosystems, especially in seagrasses where information is lacking.

### 5.2.2. Bioaccumulation of POPs in plant tissues

All evaluated POPs, e.g., DDTs, PCP, PBDEs, PCBs, PFOs, PFOA, and PCDD/Fs, can be bioaccumulated in tissues of coastal wetland plants, i. e., plants can remove these pollutants from the environment (e.g., Carvalho et al., 2011; Chai et al., 2019b; Chen et al., 2015; Hechmi et al., 2014; Li et al., 2019; Pi et al., 2017; Zhou et al., 2019). However, this process could be severely limited. In all the reviewed experimental studies the load of pollutants in plant tissues was less than 1% of the total incorporated into the system. For instance, after a few months of POP enrichment, seagrass accumulated <0.3% of PCBs (Huesemann et al., 2009), mangrove plants accumulated 0.05% to 1% of PBDEs (Chen et al., 2015; Chen et al., 2017; Farzana et al., 2019c; Li et al., 2020), and salt marshes plants accumulated <0.3% of PCP (Hechmi et al., 2014). This could be explained both by the hydrophobic nature of POPs, which contribute to the strong adsorption on sediment particles and low bioavailability (Huesemann et al., 2009; Zhang et al., 2017), as well as by the low lipid content of plants (Gaeckle, 2016). Anyway, due to their trophic position, plants could act as a secondary source of POPs, as will be discussed later (see Section 5.2.2.2). Hence, despite the general low accumulation, the concentration of POPs in tissues of coastal wetland

plants should not be overlooked.

**5.2.2.1. Bioaccumulation in belowground tissues.** According to the reviewed studies, POPs uptake from the sediment by roots is the main route of entry for POPs into belowground tissues. The efficiency in such uptake is generally studied using the ratio of root/sediment concentration: RCF (sediment-root concentration factor). RCF values in coastal wetland plants are highly variable regarding the pollutant and the species (Table 5). Several authors have found significant negative correlations between RCF and lipophilicity (expressed as the octanol-water partition coefficient;  $K_{OW}$ ) of POPs in different plant species. This correlation was found for HCHs and DDTs in *Scirpus* spp. (Liu et al., 2006) and in nine mangrove species (Qiu et al., 2019b); for PCDD/Fs in *Halimione portulacoides* and *Sarcocornia perennis* (Nunes et al., 2014); for PBDEs in *A. marina* and *K. obovata* (Zhu et al., 2014b) and *P. australis* (Zhou et al., 2019); and for PCBs in *Spartina alterniflora* (Mrozek and Leidy, 1981) and nine mangrove species (Qiu et al., 2019b). Despite this, other authors did not find significant correlations between RCF and  $K_{OW}$ , concluding that other factors would be affecting the uptake from the roots. For example, Li et al. (2019) and Nunes et al. (2014) did not observe significant correlations between RCF and  $K_{OW}$  of HCBd diastereoisomers and PCBs, respectively. Consequently, Nunes et al. (2014) suggested that, in addition to the  $K_{OW}$ , the position of chlorine atoms would affect the DL-PCB uptake by the salt marsh plants. Besides, Liu et al. (2006) observed that RCF decreased when the HCH and DDT levels in sediments increased, and they suggested that the bioaccumulation was kinetically limited at higher levels of exposure. Meanwhile, Wang et al. (2020) highlighted that, in addition to molecular size and  $K_{OW}$ , the type of anionic functional group is a key property in the uptake of PFOs, being the PFOs with the sulfonic acid functional group the most accumulated by the roots of plants in a hydroponic culture experiment. Consequently, the physicochemical properties of the pollutants seem to be the most important factors determining the

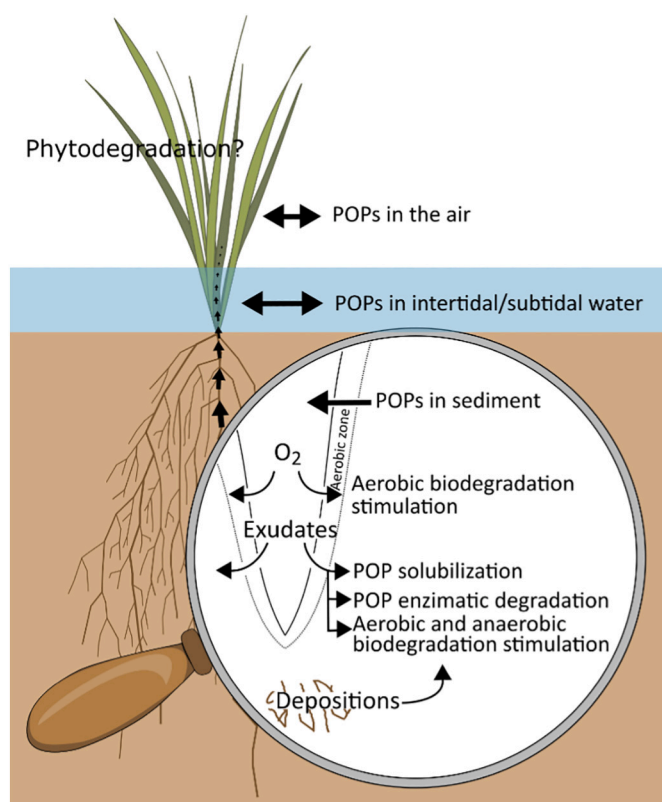


Fig. 3. Schematic representation of the main POP biogeochemical processes mediated by coastal wetland plants.



uptake by roots and include the molecular mass, the chemical structure, and the  $K_{OW}$  (Girones et al., 2021; Masters and Inman, 2000; Nunes et al., 2014; Wang et al., 2020).

As observed in Table 5, POP uptake by plants appears to be species-specific (Qiu et al., 2019b; Zhu et al., 2014b). For example, the RCFs of PBDEs and HCHs in *Sonneratia* spp. were more than double that of other mangroves species in southern China (Qiu et al., 2019a, 2019b). Moreover, the RCF of BDE-47 and its metabolites in *A. marina* were higher than those of *K. obovata* in a mesocosms study (Zhu et al., 2014b), and the accumulation of PFAs in eight wetland species showed significant differences in a hydroponic culture experiment (Wang et al., 2020). Several factors could explain these differences, the most important ones being the anatomical and physiological characteristics of the plants, the exudates, and the lipid content of the roots. Pi et al. (2017) observed that the thin and weak outer layers of *K. obovata* roots facilitated the PBDE uptake, while the thick outer layers of *E. agallocha* roots hindered it. Furthermore, Zhu et al. (2014b) suggested that the higher RCF of PBDEs in *A. marina* than in *K. obovata* was due not only to the thickness of the root outer layers but also to other anatomical and physiological characteristics related to adaptation to flooded environments, such as the absence of differentiated suberized walls between the epidermis and the hypodermis, more aerenchyma, and more radial oxygen loss in *A. marina*. Meanwhile, Nunes et al. (2014) highlighted that the root exudates of different plant species would have different solubilization capacities of hydrophobic compounds and, consequently, this would affect the RCF.

**5.2.2.2. Bioaccumulation in aboveground tissues.** Once inside the root, the compound can be accumulated there, metabolized, or translocated to aboveground tissues. POP translocation is generally evaluated with the concentration ratio of aboveground tissue/roots: TF (Translocation Factor). Translocation factors from field studies are reported in Table 5 whereas those calculated from laboratory results are shown in Table 6. Despite the variability observed in both tables, regarding the compound or the plant species, there is a clear difference between the results of the studies under experimental and field conditions. In the former, the TFs were usually  $<1$  (Huesemann et al., 2009; Zhu et al., 2014b; Table 6). In contrast, in field studies, TFs were generally higher than in experimental studies and usually close to or greater than 1 (Table 5). Just as an example, translocation of PCB by the seagrass *Zostera marina* differed greatly between field and experimental studies. After 14 months of mesocosms experiment, Huesemann et al. (2009) found detectable concentrations of PCB in belowground tissues of the plant but not in aboveground tissues (i.e., the translocation factor was close to 0), while Gaeckle (2016) detected higher concentrations of PCBs in aboveground tissues than in belowground tissues of the same seagrass species in a field study in Puget Sound, Washington State, USA, with an average TF of 1.77. The observed differences could be attributed to the fact that in the experimental studies the plants are usually exposed to POPs present only in sediment, while in the field studies they are also exposed to POPs from air and water.

In experimental studies analyzed, pollutant concentrations followed a generally decreasing order from root to leaf, as evidenced in the TFs (Table 6), and  $K_{OW}$  was identified as the main influencer in POP translocation (Hu et al., 2020; Li et al., 2019; Wang et al., 2020), suggesting that the main pathway would be through the transpiration stream. For example, Li et al. (2019) and Hu et al. (2020) observed a significant negative correlation between  $\log K_{OW}$  and TF stem/root of HBCD diastereoisomers and PBDE, respectively. However, other factors could affect translocation in plants, including the anatomical and physiological differences of the different species. For example, Zhu et al. (2014b) observed a similar total accumulation of PBDE in *A. marina* and *K. obovata* but with higher levels in roots of *A. marina*, since *K. obovata* translocate part of the pollutants to the large size propagules, which are absent in the other species. Therefore, these results evidence the

importance of species-specific differences in the translocation of POPs.

In field studies, the chemical concentration did not commonly follow the order root > stem > leaf (Qiu et al., 2019a, 2019b; Table 5), and TFs generally did not significantly correlate with  $K_{OW}$  (Li et al., 2019). Therefore, the translocation by the transpiration stream was probably not the main way to accumulate POPs in the aboveground tissues and other factors, such as absorption from air and water might be playing an important role (Fig. 3). As an example, in a study of PBDE in mangrove plants, in addition to the lack of correlation between  $K_{OW}$  and TFs, PBDE levels were as follows: stem bark > root > senescent leaf > mature leaf > young leaf (Zhou et al., 2019). The authors suggested that this pattern might be occurring since stem bark and leaves could absorb particles-bound and dissolved PBDEs from water during periodic tides and/or from the air; besides, PBDEs are also translocated from the roots and tend to accumulate over time, explaining the differences observed between young and mature leaves (Zhou et al., 2019; Fig. 3). Another field study found that DDT levels in stems of *Spartina foliosa* were significantly higher than in those of *Salicornia virginica*, but there were no significant differences between root concentrations. The authors suggested that this could be explained by the fact that the DDT can be bound to particles in water and that *S. foliosa* is exposed daily to water during high tides whereas *S. virginica* is rarely submerged (Masters and Inman, 2000). Moreover, Liu et al. (2006) observed that HCH concentrations in *Scirpus* spp. were higher in aboveground tissues than in roots and that  $\alpha$ -HCH, the isomer with the highest atmospheric transportability, was the dominant isomer in aboveground tissues, suggesting that uptake from the air was the main source of HCH for those tissues. From this analysis, it can be inferred that POP uptake from water and air might be important in coastal wetland plants and deserves further research. Moreover, the accumulation of POPs in aboveground tissues is particularly interesting since these tissues constitute the base of the detrital food web, which is an important way of energy flow in these environments (Serrano et al., 2019), and consequently these tissues might be acting as a secondary source of contamination. The importance of wetlands plants as a source of POP is magnified by the general high primary productivity of coastal wetlands (Barbier et al., 2011).

Another factor that can influence the POP levels in plants is their metabolization to simpler molecules within the plant tissue or by photolysis on the plant surface (photodegradation) (Li et al., 2019; Zhou et al., 2019). Deng et al. (2016) observed that the BDE-209 accumulated in the roots of seven species of aquatic plants was not translocated to aboveground tissues, but its metabolites were. Li et al. (2019) suggested that the enzymatic transformation of specific enantiomers of HBCD would be occurring within mangrove plants and Li et al. (2020) suggested that metabolic PBDE debromination was occurring in *K. obovata*, as they observed higher concentrations of BDE-100 and -154 in roots than in soil. Furthermore, Mrozek and Leidy (1981) observed a change in the pattern of PCBs towards less chlorinated congeners in aboveground tissues of *S. alterniflora*, and Zhu et al. (2014b) observed the accumulation of less brominated PBDEs in the aboveground tissues of *K. obovata* and *A. marina*. Therefore, they suggested that this could be due both to the direct absorption from the sediment and to the degradation of the parental compounds accumulated in the plant tissue. However, studies are still lacking to clarify the role of plants in the enzymatic transformation of POPs within their tissues.

## 6. Conclusions, future perspectives, and challenges

The available information in regards to POPs in coastal wetlands is scarce, especially in seagrasses and salt marshes, while for mangroves, studies are principally centered in China and India. The most studied family of POPs are PBDEs, followed by organochlorine pesticides and PCBs. Studies on unintentionally produced and new POPs, such as PCDD/Fs, DL-PCBs, PCNs, SCCPs, Dechlorane Plus, HBCDs, PFOs, and PFOAs, among others, remain as a gap in the knowledge.

According to the Norwegian Environmental Quality Classification

**Table 5**

Summary of sediment-root concentration factor (RCF) and translocation factor between stems and roots (TF s/r), leaves and stems (TF l/s), and aboveground tissues and roots (TF ab/r) of individual POPs or group of POPs in coastal wetland plants in field studies. Column “CW” defines the coastal wetland type: mangrove (M), salt marsh (SM) and, seagrass bed (SB).

Location	Compounds	Species	CW	RCF	TF s/r	TF l/s	TF ab/r	References
Newport Bay, California, USA	DDE	<i>Spartina foliosa</i>	SM	0.07 <sup>b</sup>	2.11 <sup>b</sup>			Masters and Inman, 2000
Newport Bay, California, USA	DDE	<i>Salicornia virginica</i>	SM	0.34 <sup>b</sup>	0.22 <sup>b</sup>			Masters and Inman, 2000
Yangtze Estuary, China	DDTs	<i>Scirpus spp.</i>	SM	3.32 <sup>a</sup>			1.37 <sup>b</sup>	Liu et al., 2006
Futian, Shenzhen, China	HBCDs	<i>Kandelia obovata</i>	M	0.01 <sup>a</sup>	10.60 <sup>a</sup>	0.76 <sup>a</sup>		Li et al., 2019
Futian, Shenzhen, China	HBCDs	<i>Bruguiera sexangula</i>	M	0.03 <sup>a</sup>	8.33 <sup>a</sup>	0.13 <sup>a</sup>		Li et al., 2019
Futian, Shenzhen, China	HBCDs	<i>Avicennia marina</i>	M	0.10 <sup>a</sup>	4.11 <sup>a</sup>	11.70 <sup>a</sup>		Li et al., 2019
Yangtze Estuary, China	HCHs	<i>Scirpus spp.</i>	SM	4.54 <sup>a</sup>			1.91 <sup>b</sup>	Liu et al., 2006
Florida, USA	PBDEs	<i>Zostera marina</i>	M				1.67 <sup>b</sup>	Gaeckle, 2016
Futian, Shenzhen, China	PBDEs	<i>Bruguiera sexangula</i>	M	0.03 <sup>a</sup>	2.09 <sup>a</sup>	0.91 <sup>a</sup>		Hu et al., 2020
Futian, Shenzhen, China	PBDEs	<i>Kandelia obovata</i>	M	0.03 <sup>a</sup>	0.95 <sup>a</sup>	1.63 <sup>a</sup>		Hu et al., 2020
Futian, Shenzhen, China	PBDEs	<i>Avicennia marina</i>	M	0.03 <sup>a</sup>	0.92 <sup>a</sup>	1.45 <sup>a</sup>		Hu et al., 2020
Hainan Island	PBDEs	9 mangrove species	M	0.76 <sup>b</sup>	0.91 <sup>b</sup>	2.10 <sup>b</sup>	1.17 <sup>b</sup>	Qiu et al., 2019a
Shenzhen, China	PBDEs	<i>Kandelia obovata</i>	M	0.97 <sup>a</sup>	1.12 <sup>a,c</sup>			Zhou et al., 2019
Shenzhen, China	PBDEs	<i>Sonneratia caseolaris</i>	M	2.55 <sup>a</sup>	1.01 <sup>a,c</sup>			Zhou et al., 2019
Shenzhen, China	PBDEs	<i>Aegiceras corniculatum</i>	M	2.72 <sup>a</sup>	0.98 <sup>a,c</sup>			Zhou et al., 2019
Shenzhen, China	PBDEs	<i>Phragmites australis</i>	SM	1.66 <sup>a</sup>	0.85 <sup>a,c</sup>			Zhou et al., 2019
Shenzhen, China	PBDEs	<i>Sonneratia apetala</i>	M	2.53 <sup>a</sup>	0.83 <sup>a,c</sup>			Zhou et al., 2019
Shenzhen, China	PBDEs	<i>Juncellus serotinus</i>	M	2.77 <sup>a</sup>	0.69 <sup>a,c</sup>			Zhou et al., 2019
Tejo estuary, Portugal	DL-PCBs	<i>Sarcocornia perennis</i>	SM	0.15 <sup>b</sup>	0.16 <sup>b</sup>	0.19 <sup>b</sup>		Nunes et al., 2014
Tejo estuary, Portugal	DL-PCBs	<i>Halimione portulacoides</i>	SM	0.38 <sup>b</sup>	0.11 <sup>b</sup>	0.16 <sup>b</sup>		Nunes et al., 2014
Florida, USA	PCBs	<i>Zostera marina</i>	SB				1.77 <sup>b</sup>	Gaeckle, 2016
Tejo estuary, Portugal	PCDDs	<i>Halimione portulacoides</i>	SM	0.09 <sup>b</sup>	0.11 <sup>b</sup>	0.06 <sup>b</sup>	0.09 <sup>b</sup>	Nunes et al., 2014
Tejo estuary, Portugal	PCDDs	<i>Sarcocornia perennis</i>	SM	0.05 <sup>b</sup>	0.10 <sup>b</sup>	0.09 <sup>b</sup>	0.09 <sup>b</sup>	Nunes et al., 2014
Tejo estuary, Portugal	PCDFs	<i>Halimione portulacoides</i>	SM	0.15 <sup>b</sup>	0.14 <sup>b</sup>	0.09 <sup>b</sup>	0.11 <sup>b</sup>	Nunes et al., 2014
Tejo estuary, Portugal	PCDFs	<i>Sarcocornia perennis</i>	SM	0.08 <sup>b</sup>	0.14 <sup>b</sup>	0.12 <sup>b</sup>	0.13 <sup>b</sup>	Nunes et al., 2014
Dupree Creek, Georgia, USA	Toxaphene	<i>Spartina alterniflora</i>	SM	1.77 <sup>b,d</sup>			3.94 <sup>b,d</sup>	Gallagher et al., 1979

<sup>a</sup> Values copied from the publications.

<sup>b</sup> Values calculated from average available concentrations in the publications.

<sup>c</sup> Tree bark concentration was used.

<sup>d</sup> Living root and rhizomes concentration was used.

System, within the available data, most of the revised POPs could generate damage to the associated biota in some coastal wetlands; however, POPs levels at most coastal wetlands worldwide remain unknown. Nevertheless, these levels would rarely show adverse effects on vascular plants and/or the microbial community according to the reviewed toxicological studies. However, toxicological studies were usually carried out with higher POP concentrations than those commonly reported in the environment. Then, although biochemical,

physiological, or ecological effects were triggered by POPs this should be interpreted with care when relating to real-world effects. In addition, experimental results were highly variable depending on the compound, its concentration, the plant species, and the characteristics of the sediment.

Plants and microorganisms were proven to play a key role in the biogeochemical cycle of POPs in coastal wetlands. Microorganisms are the main actors in their removal: the heterogeneity and dynamics of the

**Table 6**

Summary of the translocation factor between stems and roots (TF s/r), leaves and stems (TF l/s), and aboveground tissues and roots (TF ab/r) of individual POPs or group of POPs in coastal wetland plants in experimental studies. “de-PBDE” abbreviates debrominated products of the parental BDE. Column “CW” defines the coastal wetland type: mangrove (M), salt marsh (SM) and, seagrass bed (SB). Column “Time” defines the exposure time in months.

Compound	Species	CW	Time	TF s/r	TF l/s	TF ab/r	References
BDE-47	<i>Aegiceras corniculatum</i>	M	3	0.08	0.16	0.05	Chen et al., 2015
BDE-209	<i>Aegiceras corniculatum</i>	M	3	0.02	0.49	0.01	Chen et al., 2015
De-PBDEs of BDE-47	<i>Avicennia marina</i>	M	12			0.09	Chen et al., 2017
De-PBDEs of BDE-47	<i>Aegiceras corniculatum</i>	M	12			0.11	Chen et al., 2017
De-PBDEs of BDE-99	<i>Kandelia obovata</i>	M	3	0.20	1.16	0.30	Farzana et al., 2017
De-PBDEs of BDE-209	<i>Kandelia obovata</i>	M	3	0.07	1.90	0.10	Farzana et al., 2017
BDE-99	<i>Kandelia obovata</i>	M	3	0.05	0.16	0.07	Farzana et al., 2017
BDE-209	<i>Kandelia obovata</i>	M	3	0.03	0.62	0.02	Farzana et al., 2017
BDE-99	<i>Kandelia obovata</i>	M	12	0.01		0.35	Farzana et al., 2019a
De-PBDEs of BDE-209	<i>Avicennia marina</i>	M	24	1.01	0.25	0.75	Farzana et al., 2019c
De-PBDEs of BDE-209	<i>Kandelia obovata</i>	M	24	0.89	0.32	2.03	Farzana et al., 2019c
De-PBDEs of BDE-209	<i>Aegiceras corniculatum</i>	M	24	0.68	0.38	1.10	Farzana et al., 2019c
BDE 209	<i>Avicennia marina</i>	M	24	0.57	0.33	0.38	Farzana et al., 2019c
BDE 209	<i>Kandelia obovata</i>	M	24	0.44	0.24	0.57	Farzana et al., 2019c
BDE 209	<i>Aegiceras corniculatum</i>	M	24	0.16	0.12	0.09	Farzana et al., 2019c
PCP	<i>Phragmites australis</i>	SM	2.3			0.24	Hechmi et al., 2014
PCBs	<i>Zostera marina</i>	SB	14			0	Huesemann et al., 2009
PCBs (Aroclor 1254)	<i>Spartina alterniflora</i>	SM				0.13	Mrozek and Leidy, 1981
BDE-47	<i>Avicennia marina</i>	M	7	0.15	0.17		Zhu et al., 2014b
BDE-47	<i>Kandelia obovata</i>	M	7	0.04	0.23		Zhu et al., 2014b
De-PBDEs of BDE-47	<i>Kandelia obovata</i>	M	7	0.02	0		Zhu et al., 2014b
De-PBDEs of BDE-47	<i>Avicennia marina</i>	M	7	0.07	0		Zhu et al., 2014b



wetlands conditions promote great microbial diversity which favors the formation of consortia able to metabolize a wide variety of compounds. Further, coastal wetland sediments are mainly anaerobic which favors the growth of bacteria that cause the reductive dehalogenation process. This favors the main degradation pathway of highly halogenated POPs such as PCBs, PBDEs, and PCDD/Fs. Despite this, biodegradation efficiency largely depends on the physicochemical properties of the analytes and sediment characteristics.

Vegetated sediments improve the degradation of POPs by generating an adequate environment for POP-degrading microorganisms or directly extracting and even degrading POPs, especially the less halogenated ones.

Wetland plants can extract, accumulate, and even degrade some POPs from their surrounding environment. In general, in the experimental studies, the total POP loads in plant tissues are generally <1% (dry weight basis) and are mainly concentrated in the roots, with rare translocation. Meanwhile, in field studies, it has been found that many POPs would enter not only from sediments, but also from water, and the air.

Finally, we identified the main scientific challenges in regards to POPs in wetlands:

- There is a need to monitor total and bioavailable POPs levels, especially those from unintentional production and new POPs, in different environmental compartments of coastal wetlands, especially near large cities and garbage (including electronics) recycling sites.
- The study of the toxicological effects of POPs on plants and microorganisms should be deepened.
- Is necessary to evaluate the capacity of wetlands plants to absorb POPs from sediments, water, and the air and further, study the behavior of POPs within plant tissues, including movements towards different parts of the plant and biochemical transformations.
- Research on POPs removal by plants either by enzymatic or microbial degradation is still needed in order to improve phytoremediation technologies.
- It is also necessary to assess the relative importance of the wetland environmental conditions for the biogeochemical cycling (oxygen levels, pH, particle size distribution, nutrients, salinity, electron donors and acceptors, etc.)
- Further research is needed in the microbiology field in order to accurately identify the microbial species responsible for the biodegradation of POPs.

#### CRedit authorship contribution statement

**Lautaro Girones:** Conceptualization, Formal analysis, Writing – original draft, Writing – review & editing, Visualization. **Ana L. Oliva:** Conceptualization, Writing – original draft, Writing – review & editing, Supervision. **Vanessa L. Negrin:** Methodology, Validation, Investigation, Writing – review & editing. **Jorge E. Marcovecchio:** Supervision. **Andrés H. Arias:** Conceptualization, Methodology, Writing – review & editing, Supervision.

#### 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.

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