

## Critical Review

REVIEW OF EMERGING CONTAMINANTS IN AQUATIC BIOTA FROM  
LATIN AMERICA: 2002–2016MARTA LLORCA,\*† MARINELLA FARRÉ,† ETHEL ELJARRAT,† SÍLVIA DÍAZ-CRUZ,† SARA RODRÍGUEZ-MOZAZ,‡  
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**Abstract:** Although it is known that emerging contaminants are widespread all over the globe, there is a gap of information about their distribution in some geographical areas, such as Latin America. The present bibliographic work reviews the available literature about the presence of organic emerging contaminants in Latin American freshwater and marine biota between 2002 and 2016 and includes 23 works from Argentina, Brazil, Chile, Colombia, Mexico, and Nicaragua. In particular, the present review provides an overview of the occurrence of continuously present contaminants such as pharmaceuticals, personal care products, and pyrethroid insecticides, as well as the new groups of persistent organic pollutants, the halogenated flame retardants and the perfluoroalkyl substances. A wide overview is provided, considering not only occurrence data but also effects and potential transfer through the food chain. *Environ Toxicol Chem* 2017;36:1716–1727. © 2016 SETAC

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## INTRODUCTION

Flame retardants, nonpolar pesticides (e.g., pyrethroids), perfluoroalkyl substances (PFASs), pharmaceuticals, and personal care products are considered to be emerging organic contaminants. In the case of flame retardants and PFASs, because of their persistence, potency of bioaccumulation and biomagnification, and wide environmental distribution as well as the toxicity of some congeners, these compounds are currently included as the new groups of persistent organic pollutants [1,2]. Both groups have been used for decades. Flame retardants have been employed to prevent fires, and they are applied to a wide range of materials, such as textiles, furniture, and electronic materials [3]. Halogenated flame retardants became one of the most used families of flame retardants, with a constantly increasing annual production [4]. In addition, because of their high usage and low elimination rates, this family of compounds has been found in environmental and biological matrices [5–9]. The PFASs are human-made compounds that are extremely stable to physical, chemical, and biological degradation [10]. They are used as repelling coatings, fire-fighting foams, textiles, prints, and adhesives, among many other uses [10]. Their environmental distribution has been worldwide [11,12] together with their bioaccumulation and biomagnification in wildlife and in humans [13–15]. In 2006, the US Environmental Protection Agency and the 8 major producer companies launched the Stewardship Program [16] to stop the emissions of perfluorooctanoic acid (PFOA) by 2015; in 2009, perfluorooctane sulfonate (PFOS) was listed in Annex B of the Stockholm Convention [16].

Pyrethroid insecticides and most of the used pharmaceuticals and personal care products are considered “continuously present pollutants,” indicating that the time period over which exposure occurs is less than the degradation time, according to Mackay et al. [17]. In fact, these groups are partly eliminated and/or transformed once they enter the environment; but because of their continuous usage and emission, in particular through wastewaters, background concentrations are detected in the environment. Finally, they can cause different damage at the toxicological level, they can create resistances (as in the case of antibiotics and certain biocides), and they can also be accumulated in biota. Pharmaceuticals have been related to different toxicological effects in aquatic life, including the feminization of male fish in effluent-dominated rivers with estrogens [18] or the alteration of animal behaviors because of the presence of antidepressants [19]. Although pharmaceuticals have not yet been regulated in the environment, the European Union has included diclofenac, 17 $\beta$ -estradiol, and 17 $\alpha$ -ethynylestradiol in a “watch list” of emerging aquatic pollutants [20]. This could lead to their inclusion in the “priority list” of compounds from the Water Framework Directive [21].

Personal care products or toiletries are consumer products used in personal hygiene and for beautification. Substances such as phthalates, parabens, sunscreens, and biocides may be related to allergy, obesity, neurotoxicity, cancer, endometriosis, decrease in semen quality, and birth defects [22–31]. Because of these effects, the sunscreen agent ethylhexyl methoxycinnamate (EHMC) has been included in the same “watch list” as pharmaceuticals [20]. In addition, once in the environment, the most lipophilic compounds tend to bioaccumulate in living aquatic organisms [32] and humans [33]. Finally, pyrethroids are synthetic insecticides derived from the natural pyrethrins and are used as the alternative to other biocides because of their low persistence and toxicity. However, despite the low environmental persistence of pharmaceuticals and pyrethroid

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pesticides, the presence of their metabolites in biota should also be assessed: pesticides and pharmaceuticals are designed to be bioactive, and some of their metabolites and transformation products can have equal or higher potency than the parent chemicals [34–39]. In fact, some recent studies have reported the presence of metabolites of these compounds in aquatic biota, mammals [40,41], and even human samples [42–44].

In this context, the widespread distribution of emerging contaminants constitutes a potential threat to the environment and to human health through drinking water and food. The expanding economies, such as those in Latin America, are the most susceptible geographical areas to increased levels of these contaminants, particularly in aquatic biota. In the present study, we review the current information about the occurrence, fate, and effects of selected emerging contaminants in biota from freshwater and marine environments in Latin America. The information from this area is put into a global context by comparison with data reported from other regions.

## EMERGING CONTAMINANTS IN BIOTA

### Persistent organic pollutants

*Persistent organic pollutants in freshwater environments.* The presence of halogenated flame retardants in biota from continental waters has been reported elsewhere [45–50]. The distribution of the most ubiquitous compounds in Latin America is shown in Figure 1, and a summary of data reported in freshwater is presented in Table 1.

Polybrominated diphenyl ethers (PBDEs) have been detected at an average of 1.46 ng/g wet weight in tissues of farmed salmon in southern Chile [45], between 0.27 ng/g wet weight and 1.05 ng/g wet weight in Chinook salmon from the Chilean Patagonia region [47], and from 0.10 ng/g wet weight (rainbow trout) to 0.18 ng/g wet weight (coho salmon) in species from fish farms, rivers, and lakes in the Aysen area (Chilean Patagonia) [46]. Higher concentrations of PBDEs were detected in salmonids from aquaculture than in wild species [46], which is in accordance with the pattern observed in Europe and North

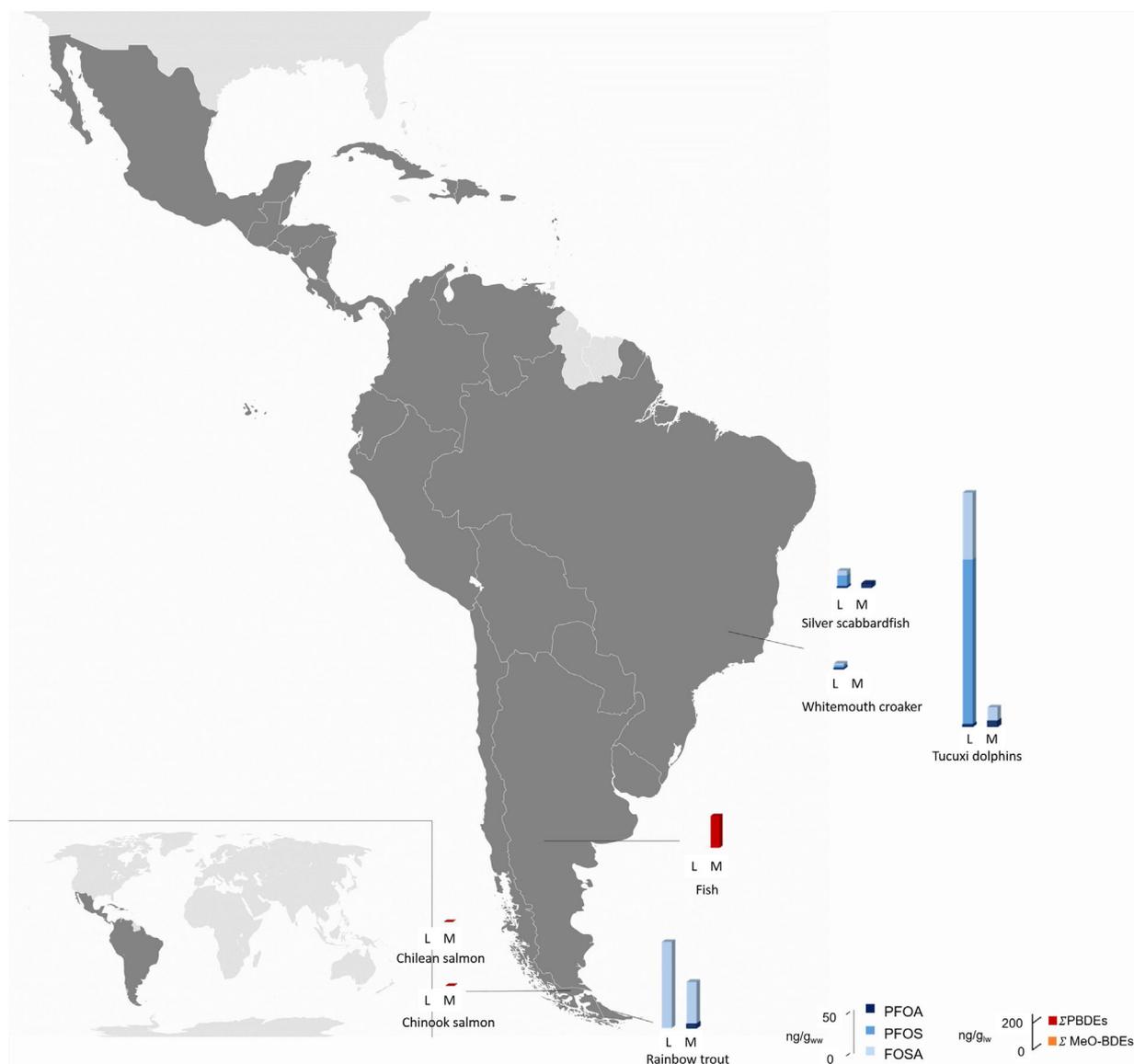


Figure 1. Accumulated concentration of the sum of polybrominated diphenyl ethers ( $\Sigma$ PBDEs; red) and the sum of methyl-brominated diphenyl ethers ( $\Sigma$ MeO-BDEs; orange), as well as accumulated concentration of perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), and perfluorooctane sulfonamide (FOSA) (blue colors) in liver (L) and muscle (M) from freshwater biota of Latin America. The information summarized in this figure can be seen elsewhere [10,46,47,49,54].

Table 1. Concentrations of halogenated flame retardants in biota from Latin America

Country	Species	Matrix	Detected compounds	Min. (ng/g lipid wt)	Max. (ng/g lipid wt)	Mean (ng/g lipid wt)	Ref.
<b>Freshwaters</b>							
Northern Patagonia, Chile	Chinook salmon ( <i>Oncorhynchus tshawytscha</i> ) (n = 12)	Muscle	PBDEs	0.27	1.05		[47]
Aysen Patagonia, Chile	Chilean salmon (n = 1) and rainbow trout (n = 18)	Muscle	PBDEs		0.18		[46]
Argentina	Fish	Muscle	PBDEs	120	240	0.18	[49]
Andean Patagonia, Argentina	Brown trout ( <i>Salmo trutta</i> ) (n = 9)	Muscle Liver Gonads Gills Stomach	PBDEs and PCBs			80.7 81.3 91.4 79.2 47.6	[48]
Brazil	Silver scabbardfish ( <i>Lepidopus caudatus</i> ) (n = 10)	Liver Muscle	PBDEs and PCBs			10.2 3.9	[50]
	Whitemouth croaker ( <i>Micropogonias furnieri</i> ) (n = 9)	Liver Muscle				3.45 2.1	
<b>Marine environments</b>							
Chile	Primary consumers: <i>Venus antiqua</i> (n = 10) and <i>Aulacomya atra</i> (n = 10) Secondary consumers: <i>Odontesthes regia</i> (n = 4) and <i>Merluccius gayi</i> (n = 4)		PBDEs	2.6	26		[57]
Chile	Primary consumers (n = 29), 5 filtering species: Giant barnacle ( <i>Austromegabalanus psittacus</i> ), keyhole limpet ( <i>Fissurella</i> sp.), sea squirt ( <i>Pyura chilensis</i> ), clam ( <i>Venus antiqua</i> ), and razor shell clam ( <i>Tagelus dombeii</i> ) Secondary consumers (n = 11): Crustaceans, crab ( <i>Homalaspis plana</i> ) and "panchote" ( <i>Taliepus dentatus</i> ), Peruvian morwong ( <i>Cheilodactylus variegatus</i> ), and damselfish ( <i>Chromis crasma</i> ) Tertiary consumers (n = 17): Sand perches ( <i>Pinguipes chilensis</i> ) and Chilean abalone ( <i>Concholepas concholepas</i> )		PBDEs ΣMeO-BDEs Halogenated norbornenes	30 nd nd	47 12 9.8		[56]
Brazil	Franciscana dolphins ( <i>Pontoporia blainvillei</i> )	Liver	PBDEs DBDPE ΣMeO-BDEs	6 nq 74.0	1797 352 13 884		[62]
Brazil	Franciscana dolphins ( <i>P. blainvillei</i> )	Liver	Dechlorane DBDPE Mirex	6.3 nd 7.63	119 14.9 275	36.4 7.29 57.0	[62]
Brazil	Dolphins: <i>Sotalia guianensis</i> (n = 8) and <i>Steno bredanensis</i> (n = 5)	Muscle Liver	PCBs and PBDEs	30 65	710 1290		[60]
Brazil	Franciscana dolphin ( <i>P. blainvillei</i> ) (n = 73 and 41)	Blubber	PBDEs	7.9	764		[64]
Brazil	Cetaceans (n = 51)	Liver	PBDEs ΣMeO-BDEs	3 26	5940 249 000		[58]
Brazil	Atlantic spotted dolphins ( <i>Stenella frontalis</i> ) (n = 9)	Blubber	PCBs and PBDEs	23	1326	629	[61]
Brazil	<i>Sotalia guianensis</i> (n = 9) <i>Pontoporia blainvillei</i> (n = 8) <i>S. frontalis</i> (n = 2) <i>S. bredanensis</i> (n = 1)	Blubber	PBDEs			65.6 60.3 770 475 64.2	[59]
Brazil	<i>Tursiops truncatus</i> Silver scabbardfish ( <i>Trichiurus lepturus</i> ) (n = 21), whitemouth croaker ( <i>Micropogonias furnieri</i> ) (n = 25), and mullet ( <i>Mugil liza</i> ) (n = 15)		PCBs	1.68	5.13		[55]
Brazil	Tucuxi dolphins ( <i>S. guianensis</i> )	Livers (n = 10), kidneys (n = 2), and muscle (n = 2)	PBDEs		(liver) 53.0 ng/g wet wt		[50]
Argentina	Common dolphins ( <i>Delphinus delphis</i> ) Fraser's dolphins ( <i>Lagenodelphis hosei</i> )	Subcutaneous adipose tissue (n = 12) Subcutaneous adipose tissue (n = 3)	ΣPCBs	3.87 1.98	7.54 6.22	5.92 3.68	[102]

DBDPE = decabromodiphenylethane; MeO-BDE = methoxybrominated diphenyl ether; nd = not determined; PBDE = polybrominated diphenyl ether; PCB = polychlorinated biphenyl.

America [51]. Other studies in Argentina reported concentrations up to 138 ng/g lipid weight in rainbow trout (P. Ondarza, Universidad Nacional de Mar del Plata, Mar del Plata, Argentina, unpublished data) and similar concentrations in brown trout from the Andean Patagonia (Argentina) [48]. Both results are comparable to those found in fish from China [52] and Europe [51] but lower than those found in fish from North America (340 ng/g lipid wt [53]). However, the concentrations reported in Argentina were in general higher than those found in aquaculture salmon (*Salmo salar*) and Chinook salmon from Chile [45,47]. In contrast, up to 220 ng/g wet weight was detected in fish from the coastal area of the Buenos Aires metropolitan area (Argentina) [49]. Quinete et al. [50] reported mean concentrations of PBDEs in liver of scabbardfish (10.2 ng/g wet wt) and in liver of croaker (3.45 ng/g wet wt) from the Paraíba do Sul River (Brazil). Even though the Paraíba do Sul River is the largest river in southeastern Brazil (1145 km long) that flows through the most important urban and industrial centers (Rio de Janeiro and São Paulo), these concentrations were similar to those reported in the above-mentioned data for fishes from Chile [45–47], China [52], and some locations in the United States [53] and Europe [51].

The distribution of the most ubiquitous PFASs in Latin America is presented in Figure 1. In addition, the concentrations for biota samples reported in the literature are summarized in Table 2. Only 2 studies [10,54] have been carried out, hindering comparison with other geographical areas.

The presence of 10 PFASs including PFOA and PFOS in silver scabbardfish, whitemouth croaker, and tucuxi dolphins from Paraíba do Sul River (Brazil) was investigated [54]. The species studied are superior consumers, and it is noteworthy that silver scabbardfish and whitemouth croaker are not only an important stage of the freshwater food web but also edible fish for human consumption. The concentrations detected in liver from these 2 species ranged from <0.45 ng/g wet weight (PFOA) to 9.99 ng/g wet weight (PFOS) [54]. Nonetheless, these values are much lower compared with those from areas of the Northern Hemisphere, such as Europe (e.g., Spain [13]). In the case of tucuxi dolphin livers ( $n = 10$ ), concentrations of PFASs were between <0.49 ng/g wet weight (perfluorononanoic acid [PFNA]) and 149 ng/g wet weight (PFOS) [54]. In the region of Argentine Patagonia, higher concentrations of perfluorobutane sulfonate, perfluorooctane sulfonamide (FOSA), perfluorobutanoic acid (PFBA), perfluorohexanoic acid (PFHxA), and perfluorodecanoic acid (PFDA) were found in rainbow trout livers (from 0.15 ng/g dry wt [PFDA] to 232 ng/g dry wt [PFHxA]) [10].

*Persistent organic pollutants in marine environments.* The occurrence of halogenated flame retardants in marine biota has been studied with particular interest in the accumulation in mammals and fish (Table 1 and Figure 2). Three fish species from the Ilha Grande Bay (southern state of Rio de Janeiro, Brazil) had concentrations of PBDEs below the limit of quantification (1.68–5.13 ng/g dry wt) [55]. During the same period, however, Barón et al. [56] investigated the presence of PBDEs, emerging brominated flame retardants, halogenated norbornenes, and naturally occurring methoxy-PBDEs (MeO-PBDEs) in fish species from primary, secondary, and tertiary marine food concentrations from the coast of Concepcion (Chile). In this case, the compounds were detected at concentrations ranging from 5.8 ng/g lipid weight (halogenated norbornenes) to 170 ng/g lipid weight (PBDEs) [56]. The calculation of biomagnification factors, expressed as the ratio of the concentration in predator versus the concentration in

prey [54,56], showed values higher than 1 for some PBDE congeners in all trophic levels and for MeO-PBDEs in tertiary consumers [56]. These results highlight the capacity to accumulate PBDEs of primary and secondary consumers as well as to accumulate PBDEs and MeO-PBDEs of tertiary consumers [56]. These findings agree with results observed during the investigation of primary and secondary fish consumers from Concepción Bay (Gulf of California, Mexico) after the 2010 tsunami [57]; concentrations of PBDEs in primary consumers were 1 order of magnitude lower than those for secondary consumers, indicating different accumulation patterns depending on marine food level [57].

The presence of PBDEs has been reported in different studies in dolphins from the Brazilian coast. Dorneles et al. [58] were the first authors to report PBDE concentrations in liver from 10 dolphin species that were stranded in a highly industrialized and urbanized region in the southeast of Brazil (3–5960 ng/g lipid wt). Although these results are similar to those detected in dolphins from different regions of the Northern Hemisphere [8], it is noteworthy that the concentrations reported for MeO-PBDEs (up to 250  $\mu\text{g/g}$  lipid wt) in continental shelf dolphins from Brazil were among the highest reported in cetaceans [58]. These results have prompted the study of halogenated flame retardant in Brazilian dolphins. For example, Yogui et al. [59] detected PBDEs in the blubber of small cetaceans from the coast of São Paulo (Brazil, southwestern Atlantic) and found the following gradation for the different species: *Stenella frontalis* (770 ng/g lipid wt) > *Steno bredanensis* (475 ng/g lipid wt) > *Sotalia guianensis* (65.6 ng/g lipid wt) > *Tursiops truncatus* (64.2 ng/g lipid wt) > *Pontoporia blainvillei* (60.3 ng/g lipid wt). These results followed the same pattern reported by Dorneles et al. [58], where *Stenella frontalis* presented concentrations between 96 ng/g lipid weight and 2440 ng/g lipid weight, followed by *S. bredanensis* (360–1600 ng/g lipid wt), *S. guianensis* (13–1620 ng/g lipid wt), and *T. truncatus* (270–1350 ng/g lipid wt). Other works reported similar values for PBDEs in liver tissue of *S. guianensis* [50,60] and *S. frontalis* [61]. However, the concentrations of PBDEs reported by Lavandier et al. [60] in a recent work on *S. guianensis* were 1 order of magnitude lower than those found by Dorneles et al. [58]; the study carried out by Lavandier et al. [60] was from the Ilha Grande Bay, whereas Dorneles et al. [58] studied Guanabara Bay, the most contaminated marine area in Brazil.

Polybrominated biphenyls, PBDEs, pentabromoethylbenzene, hexabromobenzene, decabromodiphenylethane, halogenated norbornenes, and naturally generated MeO-PBDEs were studied in Franciscana dolphins (*P. blainvillei*) from Brazil. The concentrations were between 6 ng/g lipid weight (PBDEs) and 14  $\mu\text{g/g}$  lipid weight (MeO-PBDEs) [62]. Polybrominated biphenyls were detected in samples collected in all of the locations, whereas decabromodiphenylethane was found only in the most industrialized areas of Brazil [62]. Halogenated norbornenes were determined for the first time in marine biota, as were 6 of 8 detected MeO-PBDE congeners [62]. Concentrations of PBDEs were similar to those observed in cetaceans from the Northern Hemisphere and China [63]. A time-trend study between 1994 and 2005 in blubber samples of *P. blainvillei* from Rio Grande do Sul and São Paulo state [64] showed an exponential increase of PBDE concentrations. This finding is similar to the results observed between 1989 and 1998 in the blubber from seals from San Francisco harbor [65]; however, some studies indicated a considerable decrease of PBDEs during the first decade of the 21st century in the fur seal

Table 2. Concentrations of perfluoroalkyl substances in biota from freshwaters and marine environments from Latin America

Country	Species	Matrix	Compounds detected	Min. (ng/g wet wt)	Max. (ng/g wet wt)	Mean (ng/g wet wt)	Median (ng/g wet wt)	Ref.	
Freshwaters									
Argentina Patagonia (Tierra del Fuego)	Rainbow trout ( <i>Oncorhynchus mykiss</i> ; ng/g dry wt)	Fish skin (n = 4), individual sample	PFPeA	0.28	0.47	0.385	0.395	[10]	
			PFHxA	10.9	12.3	11.6	11.6		
			PFHpA	2.09	3.19	2.64	2.64		
			PFOA	0.26	4.7	2.27	2.07		
			PFOS	3.07	4.36	3.72	3.72		
			FOSA	0.74	65.5	25.5	17.9		
			PFNA	0.36	5.68	2.82	2.61		
			PFDA	0.19	0.81	0.5	0.5		
			PFDS	0.04	0.08	0.062	0.062		
			PFBA	7.16	8.4	7.89	8.13		
			PFBS	0.51	0.68	0.62	0.66		
			PFHxA	207	232	220	222		
		Liver (n = 3), individual sample	FOSA	47.7	77.8	63.3	64.4		
			PFDA	0.15	0.29	0.22	0.22		
			PFBS	1.28	1.29	1.29	1.29		
			PFHxA	42.2	71.7	58.6	61.8		
		Muscle (n = 4), individual sample	PFOA	2.89	3.69	3.29	3.29		
			FOSA	2.27	38	17.7	15.3		
			PFNA	0.09	0.98	0.37	0.21		
			PFHxA	1.44	2.31	1.88	1.88		
Roe (n = 2), individual sample	PFOA	0.72	1.09	0.91	0.91				
	PFOS	25.7	27.3	26.5	26.5				
	FOSA	0.57	0.58	0.58	0.58				
	PFNA	0.99	2.35	1.67	1.67				
Paraiba do Sul River, near Campos dos Goytacases (Brazil)	Silver scabbardfish ( <i>Lepidopus caudatus</i> )	Liver (n = 10)	PFOS	3.36	9.9	5.54	[54]		
			PFDS	<0.54	2.72	1.31			
			FOSA	0.6	4.15	2.1			
		Muscle (n = 5)	PFHpA	<1.54	3	2.34			
			PFOA	0.86	3.56	1.63			
			PFOS	<0.62	2.35	1.2			
	Whitemouth croaker ( <i>Micropogonias furnieri</i> )	Liver (n = 10)	PFDS	<0.54	6.1	2.05			
			FOSA	<0.45	1.71	0.79			
			PFOA	<0.46	0.71	0.47			
		Coast of Rio, Paraiba do Sul River (Brazil)	Tucuxi dolphins ( <i>Sotalia guianensis</i> )	Liver (n = 10)	PFHxS	0.55		0.91	0.69
					PFOS	25.9		149	90.5
					PFDS	<0.54		7.65	2.87
Muscle (n = 2)	FOSA			3.38	60.5	25.9			
	PFOA			0.7	1.86	1.12			
	PFNA			<0.49	1.7	1.02			
Kidney (n = 2)	PFDA	<0.58	2.55	1.23					
	PFOS			95.8					
	FOSA	2.81	12.35	7.58					
	PFOA	2.95	5.03	3.99					
	PFHxS	1.35	3.19	2.27					
Marine environments: Vegetation	Argentina Patagonia (Tierra del Fuego)	<i>Macrocystis pyrifera</i> (ng/g dry wt)	(n = 9), composite sample	PFHxS	18.00	44.20	31.10		
				PFOS	1.57	4.71	3.14		
				FOSA	10.17	21.83	16.00		
				PFOA	0.99	2.37	1.68		
				PFBA	0.1	1.52	0.685	0.61	
Marine environments: Primary consumers	Guanabara Bay (Brazil), point BV	Brown mussel ( <i>Perna perna</i> )	(n = 3)	PFPeA	1.18	3.22	2.23	[54]	
				PFHxA	3.42	240	126		146
				PFHpA	1.48	2.98	2.44		2.61
				PFOA	0.12	2.4	0.88		0.43
				PFNA	0.1	1.3	0.495		0.17
	Guanabara Bay (Brazil), point VC1	(n = 4)	PFDS	1.48	1.84	1.7	1.78		
			PFOS	<0.95	3.95	3.46			
			PFHpA	<1.17	3.65	2.52			
			PFOA	2.04	5.53	3.93			
			PFOS	<0.95	4.7	4.04			
Guanabara Bay (Brazil), point VC2	(n = 3)	PFHpA	<1.17	2.9	2.64				
		PFOA	0.84	14.9	6.02				
		PFUnA	<5.09	121.6	109.3				
		PFDA	<1.17	6	5.65				
		PFNA	<1.06	24.6	14.1				

(continued)

Table 2. (Continued)

Country	Species	Matrix	Compounds detected	Min. (ng/g wet wt)	Max. (ng/g wet wt)	Mean (ng/g wet wt)	Median (ng/g wet wt)	Ref.
Guanabara Bay (Brazil), point JJ		(n = 4)	PFOS	<0.95	4.65	4.46		
			PFHpA	<1.17	3.97	2.58		
			PFOA	<0.84	5.55	2.76		
Guanabara Bay (Brazil), point MG		(n = 3)	PFOA	<0.84	4.04	2.13		
Marine environments: Higher consumers								
Cartagena Bay (Colombia)	Mullet ( <i>Mugil incilis</i> )	Bile (n = 24)	PFOA	<50	1116	370		[103]
Totumo marsh (Colombia)		Bile (n = 23)	PFHxS	<0.7	1.9	0.489		
			PFOA	<50	230	47.4		
Caimanera marsh (Coveñas, Colombia)	Mullet ( <i>Mugil spp.</i> )	Bile (n = 4)	PFHxS	<0.7	16	1.27		
			PFHxS	<0.7	0.8	0.463		
Guanabara Bay (Brazil)	Mullet ( <i>Mugil liza</i> )	Liver (n = 15)	PFOS	2.17	9.44	4.3		[54]
			PFDS	<0.54	2.18	1.21		
			PFHpA	<0.66	1.16	0.88		
		Muscle (n = 8)	PFOA	0.6	1.42	0.87		
			PFOS	1.95	5.44	3.49		
			PFOA	1.98	4.65	3.39		
		Kidney (n = 17)	PFOS	1.64	5.46	3.86		
			PFHpA	<0.9	2.03	1.32		
			PFOA	<0.6	1.76	1.22		
		Silver scabbardfish ( <i>Lepidopus caudatus</i> )	Liver (n = 12)	PFUnA	<4.47	21.8	13.4	
				PFHxS	0.55	0.91	0.69	
				PFOS	3.36	28.9	9.83	
				FOSA	1.47	6.19	3.72	
				PFOA	0.62	1.07	0.83	
				PFDA	<0.58	1.15	0.88	
Whitemouth croaker ( <i>Micropogonias furnieri</i> )	Muscle (n = 4)	PFOA	<0.82	1.27	1.04			
		PFOS	1.57	5.13	3.07			
		PFDS	<0.54	5.65	2.28			
	Liver (n = 7)	FOSA	0.51	1.67	0.83			
		PFOA	<0.46	0.6	0.52			
		PFOS	3.6	42	24	[69]		
Southern Brazil	Franciscana dolphin ( <i>Pontoporia blainvillei</i> )	Liver (n = 13)	PFDS	<0.1	0.4	0.2		
			FOSA	0.4	2.6	1.1		
			PFUnA	<0.2	0.46	0.24		
	Subantarctic fur seal ( <i>Arctocephalus tropicalis</i> )	Liver (n = 22)	PFOS	<0.1	21.6	4.2		
			PFDS	<0.1	1.36	0.33		
			PFUnA	<0.2	0.74	0.25		
Cartagena Bay (Colombia)	Brown pelican ( <i>Pelecanus occidentalis</i> )	Brain (n = 5)	PFOS	1.3	11.4	3.5		[103]
			FOSA	1	1.8	1.3		
		Heart (n = 5)	PFOS	1.7	6.9	2.1		
			PFOS	2.9	11.3	7.5		
		Lung (n = 5)	FOSA	<1	1.5	1.1		
			PFOS	4.02	55.73	36.5		
		Liver (n = 5)	PFOS	0.7	2.7	0.8		
			FOSA	<1	2.2	1.1		
		Muscle (n = 5)	PFOS	6.2	131.5	59.8		
			FOSA	<1	1	<1		
Kidney (n = 5)	PFOS	1.2	17.3	4.3				
	FOSA	<1	2.7	1.6				
Argentine Patagonia (Tierra del Fuego)	Guano (n = 6), composite samples	PFPeA	17.1	62.2	31.48	25.6	[10]	
		PFHxA	1190	2480	1626	1210		
		PFOA	5.73	14.5	9.82	9.65		
		PFNA	3.3	16.2	8.84	8.23		
		PFDA	2.51	3.45	3.01	3.07		
		PFDS	2.11	2.62	2.3	2.18		
		PFUnA	5.52	5.7	5.61	5.61		
		PFTeA	0.99	1.44	1.215	1.215		

OSA = perfluorooctane sulfonamide; PFBA = perfluorobutanoic acid; PFBS = perfluorobutane sulfonate; PFDA = perfluorodecanoic acid; PFDS = perfluorodecane sulfonate; PFHpA = perfluoroheptanoic acid; PFHxA = perfluorohexanoic acid; PFNA = perfluorononanoic acid; PFOA = perfluorooctanoic acid; PFOS = perfluorooctane sulfonate; PFPeA = perfluoropentanoic acid; PFTeA = perfluorotetradecanoic acid; PFUnA = perfluoroundecanoic acid.

from the Pacific coast of Japan [66]. These decreases are likely the result of changes in practices and regulations in Europe and Japan that have gradually controlled the use of PBDEs [67].

Perfluoroalkyl substances have been found in a great variety of organisms, from algae to different fish species, with 8-carbon chain compounds being prevalent, despite their ban, as well as PFHxA because it is the degradation compound of the new

PFASs used in the replacement of PFOS and PFOA. For example, 7 different compounds including the shorter-chain compounds (PFBA, perfluoropentanoic acid [PFPeA], PFHxA, perfluoroheptanoic acid, PFOA, PFNA, and perfluorodecane sulfonate [PFDS]) were quantified in the alga *Macrocystis pyrifera* from Tierra del Fuego (Argentina) [10]. The highest values corresponded to PFHxA with concentrations ranging

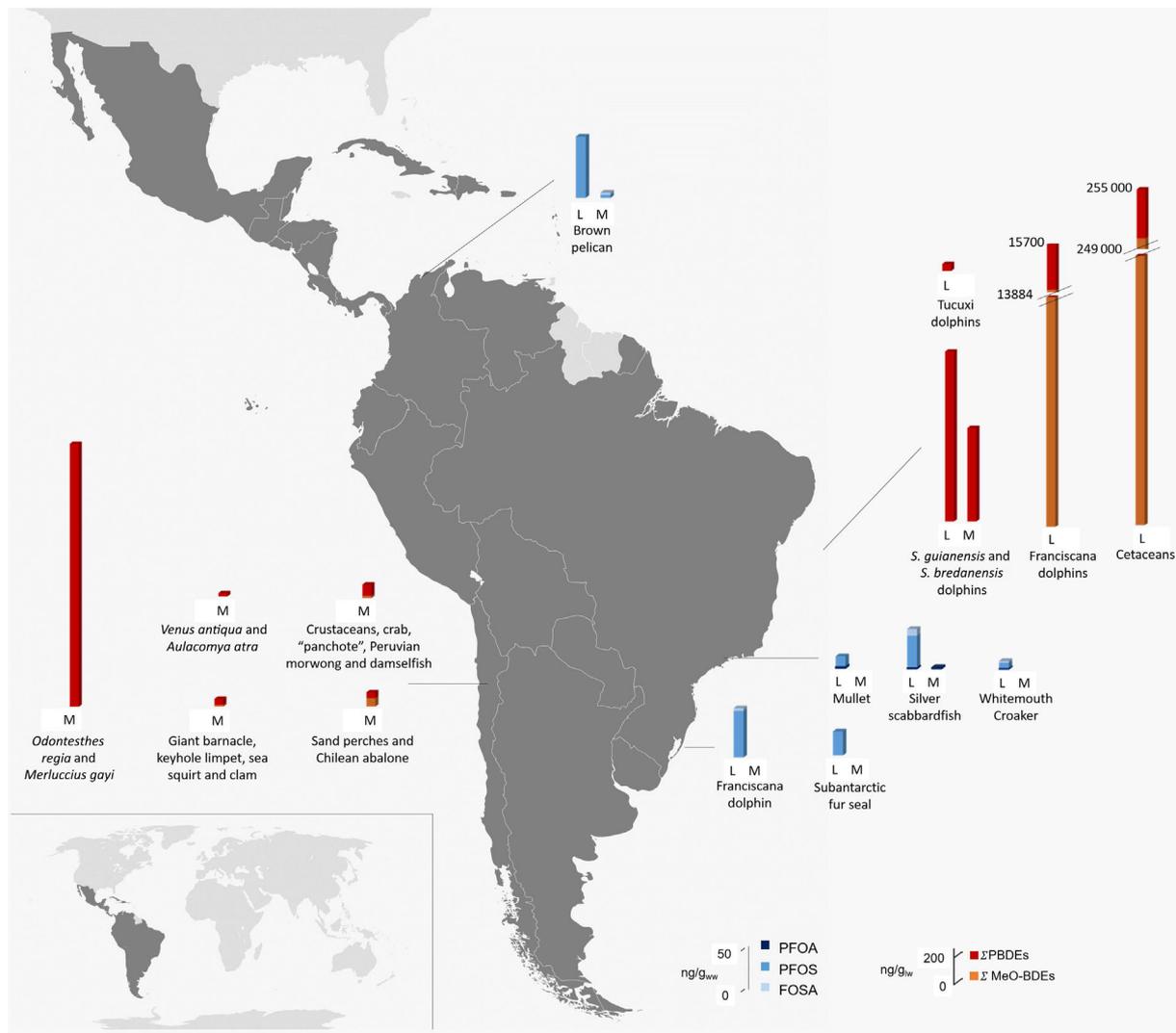


Figure 2. Accumulated concentration of the sum of polybrominated diphenyl ethers ( $\Sigma$ PBDEs; red) and the sum of methyl-brominated diphenyl ethers ( $\Sigma$ MeO-BDEs; orange), as well as accumulated concentration of perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), and perfluorooctane sulfonamide (FOSA) (blue colors) in liver (L) and muscle (M) from marine biota from Latin America. The information summarized in this figure can be seen elsewhere [50,54–58,60,62,69]. *S. bredanensis* = *Steno bredanensis*; *S. guianensis* = *Sotalia guianensis*.

from 3.42 ng/g dry weight to 240 ng/g dry weight, while the other compounds were detected between 0.1 ng/g dry weight and 3.22 ng/g dry weight [10] (Table 2). In another study, brown mussel (*Perna perna*) from 5 locations in Guanabara Bay (Brazil) were analyzed [54]. Both PFOS and PFOA were detected in 4 of the 5 locations at concentrations ranging from <0.84 ng/g wet weight to 14.9 ng/g wet weight [54] (Table 2). The ability of the organisms to accumulate chemical compounds can be assessed by the bioconcentration factor, which is expressed as the ratio of the concentration in biota versus the concentration in water [54,56]. Quinete et al. [54] estimated bioconcentration factors for PFOS (138–297) and for PFOA (63.5–266) using this approach. These estimations were similar to the values observed for phytoplankton in a subtropical marine food web near Hong Kong [15].

In another study, different fish species at higher trophic levels, such as edible mullet from the coast of Colombia, were investigated [68]. The compounds found at quantifiable concentrations were PFOA (<50–1116 ng/L) and perfluorohexane sulfonate (<0.7–16 ng/mL) in bile samples. Later, Quinete et al. [54] investigated PFAS accumulation in liver, muscle, and kidneys from mullet (*Mugil liza*), silver

scabbardfish (*Lepidopus caudatus*), and whitemouth croaker (*Micropogonias furnieri*) from Guanabara Bay (Brazil). The results indicated that the distribution of PFOS in fish was liver > muscle > kidney, whereas for PFOA the order was muscle > kidney > liver, denoting different patterns depending on the functional group of PFASs [54] (Figure 2 and Table 2). The bioconcentration factors estimated by the authors for the 3 species ranged from 20 to 190 for PFOS and from 0.9 to 14 for PFOA, which were lower than those calculated for mussels during the same study [54]. Concentrations of PFASs in higher marine food web predators such as dolphins, fur seals, and seabirds have been reported elsewhere [68,69]. In the case of marine mammals, livers from dolphins and fur seals showed the presence of PFOS at highest concentrations; PFOS and perfluoroundecanoic acid (PFUnA) also were detected in both species, whereas FOSA was found only in dolphin [69]. In the case of pelicans from Cartagena Bay (Colombia) [68], PFOS was widely distributed, present in spleen (131.5 ng/g wet wt) and liver (55.73 ng/g wet wt) at higher concentrations but also in brain, heart, lung, muscle, and kidney. In addition, FOSA was detected in brain, lung, muscle, spleen, and kidney but at much lower concentrations (Table 2). A study of guano samples from

Tierra del Fuego (Argentina) denoted the presence of PFPeA, PFHxA, PFOA, PFNA, PFDA, PFUnA, perfluorotetradecanoic acid, and PFOS [10]. The highest concentrations were for PFHxA (up to 2480 ng/g dry wt), followed by PFPeA (average of 31.48 ng/g dry wt). The authors hypothesized that these compounds were previously ingested during fish feeding and eliminated through excretion without being metabolized [10].

*Sources, presence, and effects of persistent organic pollutants in the food web.* Industrial emissions are 1 of the main contamination sources of persistent organic pollutants in the environment. This partially explains why the concentrations of persistent organic pollutants in the Southern Hemisphere are much lower than those reported in the Northern Hemisphere [12,70–72]. Once in the environment, some of these persistent organic pollutants have the potential of long-range environmental transport by a combination of gas-phase atmospheric transport and oceanic transport [72,73]. Because of different intrinsic physical–chemical properties, the global fate of persistent organic pollutants is associated with different biogeochemical cycles and geophysical drivers [73]. Another important factor is the tendency of persistent organic pollutants to be bioconcentrated in living organisms, and a few have a high potential for biomagnification through food webs. The capacity of these contaminants for bioconcentration and biomagnification in biota from Latin America has been evaluated by different authors (Barón et al. [56] and Pozo et al. [57] for halogenated flame retardants and Quinete et al. [54] for PFASs).

#### *Continuously present pollutants*

*Continuously present pollutants in freshwaters.* To the authors' knowledge, there is only 1 work dealing with the presence of continuously present pollutants (pharmaceuticals) in biota from freshwaters in Latin America. Valdés et al. [74] investigated the presence of 20 pharmaceuticals belonging to different therapeutic groups (6  $\beta$ -blockers: atenolol, carazolol, metoprolol, nadolol, propranolol, and sotalol; 8 psychiatric drugs: citalopram, diazepam, lorazepam, sertraline, venlafaxine, and carbamazepine and its metabolites epoxy carbamazepine and 2 hydroxy-carbamazepine; the 2 analgesics/anti-inflammatories codeine and diclofenac; the antiplatelet agent clopidogrel; the diuretic hydrochlorothiazide; the antihelminthic levamisole; and salbutamol) in 2 fish species (*Gambusia affinis* and *Jenynsia multidentata*) from the Suquia River (Argentina). The 2 species were captured during April (the wet season) and July (the dry season) in 2012 in the Suquia River, which is under the pressure of urban contamination, mainly caused by discharges from the wastewater-treatment plant of Córdoba city (Argentina) with 1.4 million inhabitants. All selected compounds were detected at least once in wild fish samples, whereas 7 of them—atenolol, nadolol, diazepam, lorazepam, clopidogrel, salbutamol, and hydrochlorothiazide—were found in all samples, ranging from 1 ng/g dry weight to 67 ng/g dry weight (Supplemental Data, Table S1). The analgesic codeine was found at the highest concentration of 163 ng/g dry weight. These results are similar to or even higher than those found in studies performed in fish from highly contaminated sites from other geographical areas [75]. These studies have revealed residues of psychiatric drugs and other groups of pharmaceuticals in fish and invertebrates captured downstream from wastewater-treatment plants, indicating that these compounds tend to be accumulated in biota. For example, Huerta et al. [76] reported similar values for clopidogrel, carazolol, sotalol, salbutamol, and diclofenac but lower values for propranolol, venlafaxine, and citalopram in homogenates of

fish collected at 4 Mediterranean rivers [76]. Recently, in another study performed at the Mar Menor Lagoon (Spain), up to 17 out of 20 pharmaceuticals were detected in golden gray mullet (*Liza aurata*) and black goby (*Gobius niger*) at concentrations similar to or lower than those reported in the fish from the Suquia River [77]. Also, carbamazepine concentrations in fish from the Suquia River (up to 33 ng/g dry wt) were similar to those reported in common carp (*Cyprinus carpio*) of the Taihu Lake in China [78]. Except for hydroxyl carbamazepine during the wet season, accumulation of carbamazepine and its metabolites occurred in *G. affinis* but not in *J. multidentata* [79–82]. This suggests different uptake–bioaccumulation pathways, as reported before [83,84]. A trend to higher pharmaceutical accumulation was observed in *G. affinis* during the dry season when river flow was low; however, the same pattern was not observed for *J. multidentata*, which showed greater variability during both wet and dry seasons [85,86]. Differences in the accumulation patterns of both studied fish species were observed: *G. affinis* accumulated a wider variety of compounds, affording a higher total load of pharmaceuticals, than *J. multidentata* during the dry season.

Although the presence of pharmaceuticals in natural water has been widely reported, including the above-mentioned report in Latin America [68], the presence of metabolically bioactive compounds is still a challenge, requiring the use of nontarget analysis to detect the presence of compounds derived from pharmaceuticals [87], which are usually neglected during monitoring surveys [88]. Furthermore, a more responsible prescription should be considered in the near future to avoid the unnecessary load of pharmaceuticals and their metabolites into the environment from humans [89,90].

*Continuously present pollutants in marine environments.* To the best of our knowledge, no field studies have reported the presence of pharmaceuticals in marine biota of Latin America. A study on the presence of antibiotics used in salmon aquaculture in Chile showed the presence of antibiotic resistance genes in bacteria that were growing close to aquaculture farms in Puerto Montt (southern Chile), but there were only traces of flumequine and an absence of other antibiotics (i.e., oxytetracycline, oxolinic acid, and florfenicol) in marine sediments [91]. However, a report on veterinary drug residues in seafood inspected by the European Union, the United States, Canada, and Japan revealed that exports from Latin America did not show a significant number of positive cases between 2000 and 2009 [92].

There are only 3 studies reporting concentrations of personal care product compounds in marine environments (Table 3). In the first study, the accumulation of musk fragrances was reported in marine mollusks from Colombia and Nicaragua [93]. The authors investigated the presence of the polycyclic musks galaxolide and tonalide in oysters (*Coptodisca rhizophorae*), clams (*Polymesoda solida*), and cockles (*Anadara tuberculosa* and *Anadara grandis*). Both compounds were ubiquitous and abundant in all samples (pool of 20 individuals per sample), with concentrations in the range of 42 ng/g dry weight to 81 ng/g dry weight except in oysters from Taganga (Santa Marta, Colombia) [93]. The other 2 studies analyzed personal care products in dolphins. Gago-Ferrero et al. [94] reported for first time evidence that organic ultraviolet (UV) filters from the environment reach Franciscana dolphins. The authors found that octocrylene was ubiquitously accumulated in liver (~40% of the samples) and at high concentrations (89–782 ng/g lipid wt) [94]. The highest concentration was observed in dolphins from Rio Grande do Sul (southern

Table 3. Concentrations of personal care products and pyrethroid insecticides in marine biota from Latin America

Country	Species	Matrix	Compounds detected	Min. (ng/g lipid wt)	Max. (ng/g lipid wt)	Ref.
<b>PCPs</b>						
Colombia	Oyster ( <i>Crassostrea rhizophorae</i> ) Clams ( <i>Polymesoda solida</i> ) Cockles ( <i>Anadara tuberculosa</i> and <i>Anadara grandis</i> )		Galaxolide and tonalide (ng/g)	42	81	[93]
Brazil	Franciscana dolphin ( <i>Pontoporia blainvillei</i> ) (n = 56)	Liver	Octocrylene	89	782	[94]
Brazil	Mother–fetus pairs of Franciscana dolphin ( <i>P. blainvillei</i> )	Blubber (n = 7) Fetal blubber (n = 5) Muscle (n = 4) Fetal muscle (n = 4) Placenta (n = 4) Milk (n = 3)	EHMC, 4-MBC, OD-PABA, Octocrylene	nd 6 43 70	219 205 920 11 530 1385 140	[41]
	Mother–fetus pairs of Guiana dolphin ( <i>Sotalia guianensis</i> )	Blubber (n = 3) Fetal blubber (n = 3) Muscle (n = 3) Fetal muscle (n = 3)		nd nd 1405 280	505 34 10 475 365	
<b>Pyrethroid insecticides</b>						
Brazil	Franciscana dolphins ( <i>P. blainvillei</i> ) (n = 23)	Liver	Pyrethroid insecticides	7.04	68.4	[104]
Brazil	Mother–fetus pairs of Franciscana ( <i>P. blainvillei</i> ) (n = 5) Mother–fetus pairs of Guiana dolphins ( <i>S. guianensis</i> ) (n = 3)	Blubber, fetal blubber, muscle, fetal muscle, placenta, and milk Blubber, fetal blubber, muscle, and fetal muscle	Pyrethroid insecticides	8.00	6340	[41]

EHMC = 2-ethyl-hexyl-4-trimethoxycinnamate; 4-MBC = 4-methylbenzylidene camphor; nd = not determined; OD-PABA = octyl dimethyl-*p*-aminobenzoic acid.

Brazil; 42% frequency of detection within that area), whereas specimens from São Paulo (southeastern Brazil) showed the highest frequency of detection at 70% [94]. The highest mean concentration (373 ng/g lipid wt) was observed in Santa Catarina (southern Brazil), an enclosed estuary receiving urban and industrial wastewater discharges. The concentrations were similar to those detected for anthropogenic persistent organic pollutants in similar marine species as reported in the section *Persistent organic pollutants*. The authors suggested that octocrylene biomagnifies through the marine food web [94]. That study also provided evidence that maternal transfer to the fetus might occur through the placenta and likely through breast milk [94]. This hypothesis was proven shortly afterward by the same authors, examining 38 samples including blubber, muscle, and milk from 12 mother–fetus dolphin pairs from the Franciscana and Guiana species [41]. Octocrylene and 3 other organic UV filters (EHMC, 4-methylbenzylidene camphor, and octyl dimethyl-*p*-aminobenzoic acid) were measured in 36 of the 38 samples and in all mother–fetus pairs; accumulation was predominant in muscle samples [41]. There are scarce data to compare regarding the presence of UV filters in marine fish. Fish liver tissue of *Gadus morhua* from Oslofjord (Norway) had concentrations of benzophenone-3 in the range of <20 ng/g wet weight to 1037 ng/g wet weight and of EHMC from <30 ng/g wet weight to 36.9 ng/g wet weight, whereas octocrylene reached values as high as 11 875 ng/g wet weight (median 115 ng/g wet wt) [95]. In general, these values are much higher than those reported for fish and mammal species from Latin America (Table 3). In contrast, reported concentrations of UV filters in bulk fish samples and liver samples from many different fish species from the Ariake Sea (Japan) were much lower, in the range of 74 ng/g lipid weight to 219 ng/g lipid weight [96]. The same family of UV filters was reported to be accumulated in fish samples from Manila Bay (Philippines), with total concentrations in the range 6.5 ng/g lipid weight to 316 ng/g lipid weight [97].

Finally, the presence of pyrethroids in marine environments from Latin America has been reported in 2 works on mammal species (Table 3). In the first work, Alonso et al. [40] demonstrated for the first time the capacity of pyrethroids to be bioaccumulated in marine mammal tissues. Twelve pyrethroids were determined in liver samples from 23 male Franciscana dolphins from Brazil. The median concentration values for total pyrethroids were 7.04 ng/g lipid weight and 68.4 ng/g lipid weight in adults and calves, respectively [40]. Pyrethroid concentrations had a peculiar pattern of distribution according to dolphin length. The major concentrations appeared in the smallest individuals (calves) and decreased until dolphins reached adolescence. Then, the concentrations started to increase again when approaching the age of sexual maturation. Finally, concentrations began to decline. In an attempt to assess potential maternal transfer, the authors published a second study in which pyrethroids, together with personal care products, were investigated in tissues of paired mother–fetus dolphins from the Brazilian coast [41]. Pyrethroids were detected in all of the samples, which included blubber and muscle of female and fetus, as well as placenta, milk, and umbilical cord. The higher pyrethroid concentrations were found in fetuses, and it was hypothesized that these compounds are efficiently transferred through the placental barrier [41]. Lastly, interest in this family of contaminants grows in marine areas of Latin America where salmon farming is one of the main activities. In those farms, pyrethroid baths are applied to combat sea lice in salmon. There are no studies of the potential impact on marine biota inhabiting areas near the salmon farms.

## CONCLUSIONS

The emerging contaminants reviewed in the present study have been detected on a widespread scale around the world. In the case of Latin America, the studies based on halogenated

flame retardants, PFASs, and pharmaceuticals in biota from freshwaters showed concentrations ranging from the low nanograms per gram dry weight for pharmaceuticals (fishes from Argentina [74]) to 77.8 ng/g dry weight for PFASs (rainbow trout liver from Argentinian Patagonia [10]). The most ubiquitous compounds were PBDEs, PFOA, and PFOS. In marine environments, halogenated flame retardants, PFASs, personal care products, and pyrethroid insecticides were found to be bioaccumulated in the lower trophic levels, including primary consumers such as algae, as well as in higher trophic levels (e.g., in marine mammals). The highest concentrations reported in the present review were for MeO-PBDEs in cetaceans from Brazil (up to 250 ng/g lipid wt) [58]. Perfluorohexanoic acid showed the highest concentrations in guano samples from Patagonia (2480 ng/g dry wt) [10]. Finally, personal care products reach top predators, being detected in muscle of fetal dolphins (up to 11 530 ng/g lipid wt) together with pyrethroids [41].

The present study is the first work that compiles all of the different studies regarding the presence of halogenated flame retardants, PFASs, pharmaceuticals, personal care products, and pyrethroid insecticides in aquatic biota from Latin America. The presence of these compounds in this geographical area, where most of the countries have expanding economies, is of high interest since they are likely to increase the contamination background for emerging contaminants. Some regions of Europe, Asia, and North America, with long histories of the synthesizing and use of these compounds, have banned their use and regulated their presence in the environment. Latin America must be a focus of study in the coming years to better assess the presence and effects of emerging contaminants in biota for future legislations and regulations. However, the importance of another class of contaminants in biota from Latin America cannot be neglected, such as biotoxins [98] and dioxin-like polychlorinated biphenyls [99,100], among others [101,102].

**Supplemental Data**—The Supplemental Data are available on the Wiley Online Library at DOI: 10.1002/etc.3626.

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