Fate of pyrethroids in freshwater and marine environments

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Contents

Abstract As a consequence of their increasing use, pyrethroid insecticides are recognized as a threat for nontarget species and ecosystem health. The present chapter gives a state-of-art overview of individual pyrethroid occurrence in waters and sediments worldwide, together with recent reports of their quantification in the atmospheric gas and aerosol phases. Degradation rates, transport processes, and partitioning of pyrethroids between environmental phases are reviewed. River flow efficiently transports pyrethroids to river mouths and estuaries, while pyrethroid

L. Méjanelle (✉)
Sorbonne Université/CNRS, UMR 8222 Laboratory of Ecogeochemistry of Benthic Environments, Observatoire Océanologique de Banyuls, Banyuls-sur-Mer, France
e-mail: laurence.mejanelle@upmc.fr

B. Jara
Programa de Postgrado en Oceanografía, Departamento de Oceanografía, Universidad de Concepción, Concepción, Chile

Facultad de Ciencias, Universidad de Magallanes, Punta Arenas, Chile

J. Dachs
Department of Environmental Chemistry, Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Barcelona, Catalonia, Spain

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impact on the marine environment remains difficult to appraise due to lack of comprehensive studies. Nevertheless, aquaculture arises as an important but poorly understood environmental burden. Owing to their large organic carbon pool, sediments may act as a sink for pyrethroids and impair nontarget aquatic species. Partitioning potential of pyrethroids is compared to that of other well-known legacy pollutants in the light of their position in the phase space defined by key physicochemical properties (K_{OW} and H'). The transport and partition of pyrethroids away from their source are strongly dependent on their half-life, but their quasi constant emissions in urban and agricultural area may compensate for their degradation, therefore sustaining the occurrence and behavior of some individual pyrethroids as "quasi persistent organic pollutants."

Keywords Air, Freshwater, Marine, Partition, Pyrethroids, Sediment, Transport, Water

1 Introduction

A major change in the use of pesticides over the last 20 years has been the gradual replacement of organophosphate and organochlorine pesticides by synthetic pyrethroids. The regulation and the ban of formerly used active agents have been followed by an increased use of a wide variety of current-use pesticides such as pyrethroids in agriculture and aquaculture [1]. Pyrethroids are also extensively used in urban and industrial areas and livestock farms to control pests such as mosquitoes, lice, and wood-destroying dwellers. In addition, synthetic pyrethroids have the advantage of low cost, low mammalian toxicity, and shorter persistence in the environment than other classes of pesticides [2].

The exposure mechanism leading to acute neuronal toxicity to insects and crustaceans is through dissolved water in the water column and through pore water in the sediments [3]. Other impacts have been reported and are related to trophic transfer in food webs. Even though pyrethroids are degraded faster than other pesticides, they have been shown to occur in water bodies, allowing their transfer to the aquatic food webs [4]. Pyrethroids have hydrophobicities in the same range as legacy organochlorine pesticides (log K_{OW} from 4.8 to 7.0) and thus tend to sorb on organic particles and sediments. Insecticides sorbed in particles may be consumed by filter feeders and be transferred to higher trophic levels, or alternatively, particles may consist in a reservoir for these pollutants, probably reducing their biodegradability in natural waters. As a result of biomagnification at high trophic levels, negative impact of pyrethroids has been suggested causing immunity and estrogenic disruption to mammalians [4].

The impact of pyrethroids is the result of both the exposure to dissolved pyrethroids and to particle-associated ones. A comprehensive understanding of pyrethroid impact to nontarget species starts with the understanding of pyrethroid occurrence in the various environmental phases: dissolved water phase, particles, and sediments. This chapter reviews the current knowledge on the occurrence of

pyrethroids in water, particles and sediments of freshwater and marine environments, and the underlying partition and transport processes between those phases. Pyrethroids are often applied to water bodies, and after introduction to the dissolved phase, they partition between the different environmental compartments, being subjected to a number of sinks, particularly degradation. The elucidation of the occurrence, partition, and sinks of pyrethroids will allow to identify research lines that would help to better constraint the environmental risk associated to pyrethroids and to orientate protection measures.

2 Pyrethroid Sources and Emissions in Surface and Marine Water Bodies

Because of their wide spectrum of targets, pyrethroids are used in a variety of applications; agriculture and urban householding pest control compose two of the major market shares. Accurate estimates of their use are made difficult because nonprofessional uses are often not reported and by off the counter sales. The use of pyrethroids by aquaculture activities leads to important amounts of pyrethroids directly released to the marine environment, which can be important in specific marine areas [5, 6]. Overall, pyrethroids represent more than one third of the insecticide market, with a worldwide annual use of active ingredients around 7,000 tons per year between 1990 and 2013 (with peaks above 12,000 tons in 1997 and 2012) [7].

Structural and householding usages constitute an important part of the pyrethroid market. Several studies report that these compounds are not completely eliminated in conventional wastewater treatment plants (WWTPs) [8, 9], and thus they can be introduced into the environment through WWTPs effluents. Pyrethroids from urban sources were identified as the cause of toxicity in 80% of river sediments in the vicinity of the city of Salinas in Southern California [10].

3 Occurrence and Composition of Various Pyrethroids in Water Ecosystems

In order to estimate the potential impact of pyrethroids on aquatic environments, research projects and monitoring programs have surveyed pyrethroid occurrence mostly in the vicinity of agricultural and urban areas concerned by pyrethroid primary use. California is the world location from which more data are available as a result of numerous monitoring programs setup at the municipal to state level [11]. As a result of their affinity for organic matter, pyrethroids have been detected both in the water phase and in the sediments. Table 1 reviews water concentrations of pyrethroid in the current literature, and Table 2 reports their levels in sediments.

Table 1 Non-exhaustive selection of concentrations ranges, in ng L^{-1}, of individual pyrethroids in water from different locations worldwide

	Year	Sample type	Individual pyrethroids								References
			Bifenthrin	Fenpropathrin	λ-cyhalothrin	Permethrin	Cyfluthrin	Cypermethrin	Fenvalerate	Deltamethrin	
Freshwater											
Northern California											
American River, flood events	2009–2010	WS	nd–106	nd	nd	nd–111	nd–26.6	nd–9.4	nd	nd	[12]
San Francisco Bay, drains sampled after storm	2014	WS	nd–9.9								[13]
Central California											
Creeks and drains in the San Joaquin watershed	2007	Diss	nd–15.8	nd–2.6	nd–19.8	nd–1.1	nd–2.9	nd–5.7	nd–5.1		[14]
Creeks and drains in the San Joaquin watershed	2007	P	nd–9.6	nd	nd–11.1	nd–1.1	nd	nd	nd–5.1		[14]
Puerto Creek channel into San Joaquim Rivers	2007	WS				nq–93					[15]
Wadworth channel into Sacramento River	2003	WS				nd–94					[15]
Sacramento River	2008–2009	Diss	nd–24	nd–8.5	nd	nd	nd	nd	nd	nd	[16]
Del Puerto and Oreshimba creek	2007–2008	WS?	nd–5	nd	nd–16	nd	nd–21	nd	nd	nd–6.28	[17]
Salinas River and Monterey Bay, storm events	2008–2009	P	0–21.6		0–7.6	0–36.0		0–23.4	0–35.6	0–1.8	[18]
Creeks and drain on the Salinas and Santa Maria River watershed	2014–2015	WS?	nd–11.4		nd–447	nd–17.1	nd	nd	nd–39.7		[19]
Southern California											
Los Angeles and San Gabriel Rivers low flow conditions	2011	WS	nd–9	nd	nd	nd–18	nd	nd	nd	nd	[20]
San Diego River during storm events	2017	Diss	1–20.4	nd–24.9	nd–30.3	nd–55.9	nd–50.2	nd–55.4	nd–102	nd–62.2	[21]
San Diego River during storm events	2017	P	1–347	nd–63.2	nd–96.9	x–367	nd–205	nd–492	nd–56.9	nd–253	[21]

Asia											
Leyte island, Philippine rice agriculture	2010	Diss									[22]
Rivers passsing through large Vietnamese cities	2011–2012	WS				x–4,390					[23]
Beijing GuanTin Reservoir, China	2003–2004	Diss						nd–1.89		nd–6.28	[24]
Urban stream, Guangzhou, China		Diss	0.28 ± 0.25[a]		0.52 ± 0.59[a]	3.7 ± 3.1[a]		5.0 ± 3.3[a]			[25]
Urban stream, Guangzhou, China		P	0.84 ± 0.48[a]		4.3 ± 4.4[a]	9.0 ± 7.2[a]		20.0 ± 14.5[a]			[25]
Chenab River, Pakistan		Diss	nd–92			nd–103		nd–97		nd–108	[26]
Europe											
Rivers in the Humber catchment, UK	1996–1997	P				nd–3,500					[27]
Ebro River delta, Spain	2008–2009	Diss	nd	nd	nd	nd	nd	0.73–57.2	nd	2–58.8	[28]
Ebro River delta, Spain	2008	Diss						5–30			[29]
Valencia paddy field, surface water and groundwater, Spain		Diss									[30]
Streams, Central Germany	2009	Diss			nd–55			nd–86	nd		[31]
Streams, Central Germany	2009	P			nd–88			nd–180	nd		[31]
Seawater											
Estuarine catchment sites, NE Australia	2016–2017	WS?	nd–20.6 mg L^{-1}			nd		nd			[32]
NW Portugal Coast	2016–2017	Diss	nd		nd	nd	nd	nd–31	nd	nd	[33]
South African estuary	2002–2003	P						0.33–2.78	0.03–0.79		[34]
Pearl River estuary, urban creek at Guanzhou, China	–	Diss	0.3 ± 0.3		0.5 ± 0.6	4 ± 3		5 ± 3			[25]
Pearl River estuary, urban creek at Guanzhou, China	–	P	0.8 ± 0.6		4 ± 4	9 ± 7		20 ± 14			[25]

(continued)

Table 1 (continued)

	Year	Sample type	Individual pyrethroids								References
			Bifenthrin	Fenpropathrin	λ-cyhalothrin	Permethrin	Cyfluthrin	Cypermethrin	Fenvalerate	Deltamethrin	
In seawater concerned by salmon aquaculture											
Close to salmon cages, Southern Chile	–	Diss						4.4 ± 0.7			[35]
Close to the shore, Southern Chile	–	Diss						2.1 ± 0.8			[35]
1–2 weeks after treatment, Norway	2014	Diss						nd		nd	[36]
Near aquaculture centers, New Brunswick, Canada	2010	Diss								nd–40	[5]
Near aquaculture centers, New Brunswick, Canada	2010	P								nd–400	[5]

The first part of the table reviews concentration from freshwater bodies, and the second part reviews data from marine environments. Sample type is referred to as follows: *WS* refers to Whole Samples (dissolved phase + particles), *Diss* stands for dissolved phase analyzed after prefiltration, *P* stands for for particles suspended in the water and collected on a filter. When the method description does not describe in detail if the water is prefiltred before extraction, its is assumed that the data concerns whole sample, and the sample type is indicated as WP?
nd not detected, *nq* below quantification limits, *x* minimum value not reported
[a]When the concentration range is not available in the reference, the average and standard deviation is reported instead

Table 2 Non-exhaustive selection of individual pyrethroid levels, in ng g^{-1}, in sediments from different locations worldwide

	Year	Sample type	Individual pyrethroids														References
			Allethrin	Resmethrin	Bifenthrin	Fenpropathrin	Tetramethryn	Ametryn	Promethryn	λ-cyhalothrin	Permethrin	Cyfluthrin	Cypermethrin	Denvalerate	Fenvalerate	Deltamethrin	
Freshwater sediments																	
Northern California																	
Del Puerto Creek	2005–2006	SED			0–286					43.3	23.1	0–21			[a]1.5–2.2		[37]
Central California																	
Orcutt Creek, Santa Maria River watershed	2002–2003	SED								nd–59.4	nd–107				nd–32.6		[38]
Lower Santa Maria River	2003	SED									1.54				0.56		[39]
Creeks and drains in the San Joaquin watershed,	2007	SED		nd–nq	nd–15.8	nd–2.6				nd–19.8	nd–14.5	nd–6.9	nd–5.7		nd–2.9		[14]
Southern California																	
Orange county		SED			21–487					nd–79.7	nd–165.2	nd–66.7	nd–34.4		nd–4.7	nd–23.1	[40]
Alamo River and New River, Salton Sea	2010	SED			nd–1.90	nd				nd	nd–17.56	nd	nd		nd	nd	[41]
Salton Lake sediments Southern California	–												nd–183				[42]
San Diego River during storm events	2017																[21]
Other sites from the USA																	
Metropolitan streams, nationwise survey in the USA	–			nd–38.3	nd–11.2					nd–3.0	nd–9.3		nd–8.9				[43]
Minnesota stormwater ponds	2009			nd	nd–37.2		nd			nd	nd–41.9	nd	nd		nd	nd	[44]
Argentina																	
Carnaval creek, Buenos Aires, Argentina	2015–2016				nd					1.8–649	nd		4.2–14.8			nd	[45]
Australia																	
Queensland rivers and drains	1998				0–29			0–130	0–45								[46]
Asia																	
Vietnamise Rivers	2011										nd–7,850					nd–59,700	[47]
Rice cultivation in Leyte island, Philippines	2010							59		nd–29			nd–1,400			nd–43	[48]

(continued)

Table 2 (continued)

	Year	Sample type	Individual pyrethroids														References
			Allethrin	Resmethrin	Bifenthrin	Fenpropathrin	Tetramethryn	Ametryn	Promethryn	λ-cyhalothrin	Permethrin	Cyfluthrin	Cypermethrin	Denvalerate	Fenvalerate	Deltamethrin	
Pearl River sediments, South China	–				0.38–6.54	0.37–1.49				0.35–1.87	0.88–35.4	nd	0.22–20.4		nd	nd–1.29	[49]
Wetland, Beijing, China	2004–2006												nd–0.008		nd–0.047	nd–0.448	[50]
Beijing GuanTin Reservoir, China	2003–2004	Diss											nd–8.87	nd–26.3	nd–54.2		[24]
Beijing GuanTin Reservoir, China	2003–2004	SED											nd–0.00877	0.0454–0.158	0.0786–0.301		[24]
Urban creek in Guangzhou, South China	–	SED			6 ± 1					11 ± 8	40 ± 56		68 ± 67				[25]
Liaohe River, northeastern China	2014	SED	0.6–29		nd–0.33	nd–23	nd–1.7			nd–4.4			1.6–33		nd–4.6	nd–4.7	[51]
Chenab river, Pakistan	2015–2016	SED			nd–325						nd–291		nd–343			114–411	[26]
Europe																	
River United Kingdom, river sediments	1996–1997	SED									50–300						[27]
Ebro River delta sediments	Jun 2009	SED		nd	nd	nd	nd			nd	nd	nd	8.27–71.9		nd	nd	[28]
Ebro River delta sediments	Oct 2009	SED											0.13–2.92				[29]
Marine sediments																	
Southern California																	
Creeks and estuary, Ballona creek,	2007–2008	SED			3–80[b]					nd–15[b]	5–150[b]	nd–25[b]	1–190[b]		nd–2[b]		[52]
Southern California Bight	2008	SED			nd–64.8						nd–132						[53]
Ports and bays, Monterey Bay	2008–2009	SED			2.80 ± 3.31[a]												[18]
Europe																	
North Western Portugal Coast	2016–2017	SED			nd		nd		nd	nd	nd	nd	nd		nd	nd	[33]
China																	
Heibei creek, Guangzhou, Southern China	–	SED			nd–18.8	nd–54.5				nd–32	nd–128	nd–2.5	nd–179		nd–5.4		[54]
Pearl River estuary, China	2012	SED			5 ng g												[55]

The first part of the table documents freshwater sediments and the second part reviews results obtained from marine sediments

Sample type is referred to as follows: *SED* refers to the solid phase of the sediment; *Diss* stands for pore water dissolved phase

nd not detected, *nq* non quantified, compound identified in concentrations below the limits of the calibration curve

[a]When the concentration range is not available in the reference, the average and standard deviation is reported instead

[b]For [53], numbers were graphically read on Fig. 4 in [35]

Many studies reported pyrethroid concentrations in total water samples: the water collected is directly adsorbed on a SPE cartridge or is directly solvent-extracted, without previous filtration [12, 17, 22, 30]. Therefore, in these reports, both dissolved and particle-bound pyrethroids are jointly extracted and reported. A filtration step before pre-concentration was the preferred approach in some studies [26, 28, 29, 31, 33, 48], and the concentrations reported herein are that of dissolved pyrethroids, which includes the truly dissolved form and the colloidal-associated pyrethroids as part of the dissolved organic carbon pool. Pollutants associated to dissolved organic carbon are also retained in the adsorbents designed for sampling truly dissolved pollutants, together with pollutants associated to colloids, as known to occur for other hydrophobic chemicals [56]. Distinguishing concentrations of dissolved active compounds from those of particulate ones is important because both modes of occurrence are affected by distinct processes of transport and degradation rates (see later), in turn shaping differently the ultimate fate of pesticides. A strong recommendation for futures studies is to analyze separately the dissolved and particulate phases [21], and in any case, to state clearly which phase is characterized. The first part of Table 1 reviews dissolved and particle-bound pyrethroid concentration ranges. Whereas dissolved pesticides are bioavailable, it is not clear if the sorbed pyrethroids are toxic through feeding intake or as a transient repository, being desorbed later on and supporting the dissolved phase levels [31].

Pyrethroids dissolved in fresh and marine waters have been measured in a number of studies worldwide with the objective to check whether their concentrations were below thresholds of water quality guidelines. The dissolved form of pesticides is the form that is bioavailable and represents a threat for arthropods and fish. Dissolved pyrethroids were detected in agricultural drains, creeks, streams, and also in their collecting large rivers downstream agricultural land (Table 1). For example, in seven counties of California, 65–153 metric tons of pyrethroids were sold for licensed use between 1999 and 2008 [52], and 422 tons for the whole California state in 2010 [18].

The occurrence of individual pyrethroids varies geographically and seasonally as a response to agricultural use [19], and the consequent emission to the water, but probably also to different seasonal and site degradation potential. In Hospital Creek, a tributary of the San Joaquin River (Central California), bifenthrin was responsible for the greatest part of the toxicity of particles, whereas cyhalothrin was the prominent toxicant of particles in Ingram Creek, another tributary located less than 50 km away from the former [14]. Esfenvalerate and permethrin occurred in some water samples of tributaries of the Sacramento River after storm events in 2003 [15]. In tributaries of the San Joaquin River, cyfluthrin and cyhalothrin were the most frequent pyrethroids detected after winter storms, whereas bifenthrin and cyhalothrin were only identified in samples collected in March [17]. In central California, several surveys also reported bifenthrin as the main pyrethroid detected, its occurrence being related to storm events [13, 14, 16], while cyhalothrin and esfenvalerate dominated in the San Joaquin watershed [16]. Another study in Southern California sampled San Diego River during storm events and showed that six pyrethroids were present for 80% of the particle samples: bifenthrin, λ-cyhalothrin, permethrin, deltamethrin,

cypermethrin, and cyfluthrin [21]. Even though the same compounds were also detected in the dissolved phase, their relative abundance differed from that of the particles. Comparison of the suspended/dissolved concentration ratio to the soil-water partition constant showed that bifenthrin was not at equilibrium and in excess in the particles [21]. In contrast, dissolved+particulate samples collected in two others rivers of Southern California during low flow period showed much lower concentrations, and only bifenthrin and permethrin were detected [20].

Generally, the past and on-going water survey programs setup in California have yielded an important and valuable amount of data on the occurrence of pyrethroids. These studies demonstrated that one or two pyrethroids were frequently present in whole water samples, and that the dominant active compound differed in space and time (both years and seasons), reflecting the distinct agricultural targets, shifts in usages, and emissions from urban pest control [11, 19]. A metadata analysis gave the integrated view that cyhalothrin and bifenthrin were the compounds most frequently exceeding Regulatory Threshold Levels in surface freshwater of the USA and reached higher maxima in concentration [2].

In developing countries, the impact of current-use pesticides on freshwater quality is a growing concern, and an increasing literature documents pyrethroids in Asian water bodies, whereas reports on Africa are still too scarce [34]. Together with hundreds of other micro-pollutants, two pyrethroids were monitored in rivers and canals flowing through Vietnamese large cities and showed occasionally very high permethrin concentrations [23]. Cypermethrin and permethrin also dominated in the dissolved phase and in suspended particles of an urban creek, close to Guangzhou (Southern China, [25]). In GuanTin reservoir close to Beijing, deltamethrin was the more frequently detected pyrethroid insecticide in spring [24]. In streams and rivers of a rice cultivation area in the Philippines, cyhalothrin, cypermethrin, and deltamethrin were frequently detected, at concentrations exceeding water quality thresholds in half of the samples [48]. In Pakistan, deltamethrin and permethrin were close to water quality threshold in winter samples [26].

In European Rivers, permethrin was detected in the UK [27], cyhalothrin and cypermethrin in dissolved water and suspended particles of seven streams of Central Germany, especially after rain events [31]. Cypermethrin was the most frequently detected pyrethroid in the dissolved phase of the Ebro Delta (Spain), where rice is cultivated [28, 29]. Cypermethrin and deltamethrin concentrations varied in space and time, with peaks in concentration at the end of May followed by an apparent removal within 3 weeks [28, 29]. This finding demonstrated, by in situ observations, the fast degradation of pyrethroids in freshwater. In another Spanish rice paddy area, cypermethrin, bifenthrin, esfenvalerate, and cyhalothrin were present in most surface and groundwater total water samples analyzed [30], with the number of pyrethroids detected and their concentrations exceeding those measured in the Ebro Delta. In addition to broadcast on paddy fields, urban emissions through waste water treatment plant emissaries were likely responsible for this contamination. Despite a more restricted literature on European waters than for American ones, pyrethroid residues occur in agricultural freshwater environments and their concentrations may exceed

threshold values especially in suspended particles after rain events (in 80% of the samples in Germany [31]).

Because pyrethroid pesticides have been quite often detected in streams, creeks, and receiving rivers, they should also reach marine coastal waters. However, research addressing the occurrence of pyrethroids in estuarine and marine environments is limited. Due to the dilution of river water into the sea, pesticides often fall below detection limits. For instance, in seawater off Portugal, only two of the nine targeted pyrethroids could be detected, and only one could be quantified, whereas five were present in oysters [33]. Analytical difficulties may be a reason for the scarcity of published data in seawater (Table 1).

A specific risk for the marine environment is associated with aquaculture treatment of salmon against ectoparasites [5, 57]. Formulations used in aquaculture contain deltamethrin or cypermethrin together with emulsifiers for bath treatment of caged fish. Once the treatment is over, the bath water is released into the seawater, where pyrethroids are diluted by currents. In a case study in Canada, the deltamethrin plume could be detected up to 5.5 h after emission and the plume extended a few km away from the cages [5]. In this study, deltamethrin was emitted as a dissolved pesticide, and it was monitored both in the dissolved phase and in the suspended particles. Interestingly, deltamethrin concentration in the particle phase was approximately three to four times greater than in the aqueous phase, which demonstrates the quick partition of pyrethroids to organic carbon in seawater and, thus, their affinity for particles [5]. Variable responses of natural marine microbial communities to the input of anti-lice pesticides have been evidenced in Southern Chile [58]. At some locations and season, deltamethrin inputs resulted in an increase of carbon fixation by photosynthesis, likely resulting from a decrease in arthropod grazing pressure; however increase in carbon fixation was also observed at other sites and seasons. The diverse responses observed evidenced complex relationships between environmental factors (nutrient levels, zooplankton abundance, etc.) and pesticide impacts. These responses of marine organisms, distinct from toxicity alone, need further research to understand the overall impact of aquaculture and, more generally, of pyrethroid emissions, on marine ecosystems. More detailed information on the effect of salmon industry in the marine environment is presented elsewhere [6].

However difficult it is to detect pyrethroids in the marine environment, this task should not be overlooked because marine crustaceans and fish have been reported to be more susceptible to pyrethroids than freshwater ones [29, 34, 48].

4 Occurrence and Composition of Pyrethroids in Sediments

Table 2 documents pyrethroid occurrence in sediments. The solid phase of sediments acts as a sorbent for pesticides and likely integrates over time water pyrethroid concentrations in the overflowing water and also the accumulation of sinking particles in sea and river beds. Because of their quick association to river sediment, pyrethroid contamination of riverbed sediment has emerged as an important environmental threat to benthic organisms, and the literature reporting sediment toxicity

of pyrethroids has developed in the recent decade. Sediment toxicities toward the benthic amphipod *Hyalella azteca*, toward the cladoceran *Ceriodaphnia dubia*, and toward the midge of the Diptera *Chironus dilutus* are common tools to survey environmental quality of freshwater sediments. When pesticides are also measured, it allows to identify which toxicant causes the observed impairment [11, 38, 49, 59].

Recent monitoring studies document the occurrence of several pyrethroids in riverbed sediments (Table 2) and have been reviewed at the global scale by Stehle and Schulz [60]. Their residual occurrence in sediments is presently recognized as a threat to diversity of sediment-dwelling invertebrates and also as the cause of a decrease of diversity in aquatic environments at a global scale. Table 2 reports sediment pyrethroid concentrations at sites covering several continents. In some studies, sediment pore water concentrations are also given together with solid phase sediment concentrations. The occurrence of pyrethroids in sediments evidences clearly the propensity of pyrethroids to sorb onto and into particles. Owing to the large organic carbon pool comprised in sediments, sediments have the potential to act as a sink for pyrethroids. Organic carbon content, silt, and clay fractions are sediment bulk characteristics that usually correlate with pesticide levels [11, 24].

The concern about pyrethroid sorption to sediments in Californian streams exposed to agricultural and urban emissions led to the development of monitoring programs addressing the benthic environment in addition to water-based surveys. The considerable amount of data generated by those programs points to bifenthrin being the most commonly found residues in the sediments (Table 2). In Del Puerto Creek, a northern California stream flowing through agricultural land, it was the main contributor to sediment toxicity, with a smaller contribution of cyhalothrin, esfenvalerate, and cyfluthrin [37]. In sediments from the Santa Maria River (central California), the pesticide chlorpyrifos was the main contributor to the toxicity to the benthic amphipod *Hyalella azteca*, while cyhalothrin and permethrin also contributed to sediment toxicity in some locations in June 2002, but not in May 2003 [38]. In sediments collected in California from 2008 to 2012, the most frequent pyrethroid detected was bifenthrin; the other active compounds cyfluthrin, cyhalothrin, cypermethrin, deltamethrin, esfenvalerate/fenvalerate, fenpropathrin, or permethrin, occurred in one fifth to one third of the samples [11]. Bifenthrin was also the main pyrethroid in sediments of rivers alimenting Salton Sea in southern California [41]. In an urban estuary of southern California (Ballona Creek, Los Angeles), permethrin dominated over bifenthrin, while cypermethrin and cyfluthrin were next in abundances [52]. In Minnesota, permethrin and bifenthrin were at the top of pyrethroid sales, permethrin for animal care, structural applications, home and garden holding, while bifenthrin was mostly used as crop chemical [44]. In this state, 33% of sediments of stormwater ponds contained permethrin and 20% bifenthrin; this pattern was in line with results from other urban locations statewide as reviewed by Crane [44]. Another nationwide study addressed metropolitan streams in the USA and found bifenthrin detected in 47% of the bed sediments followed by cyhalothrin, while permethrin, resmethrin, and cypermethrin occurred with much lower frequency [43]. Recent observations in 99 streams across Midwest USA also found

bifenthrin responsible for most of the toxicity in half of sediments and also attributed urbanization rather than agriculture as responsible for its emission [59].

In Southern America (Argentina), cyhalothrin was the dominant pyrethroid in sediments of rivers flowing through large monocultural horticultural fields [45]. The percentage of detected herbicides and pesticides varied seasonally according to their application, while pyrethroid residues were consistently detected in sediments, attesting for an environmental risk for the benthic biota.

An increasing body of literature evidences pyrethroid occurrence in Asian riverbed sediments and shows the prevalence of cypermethrin at many sites (Table 2). In large cities of Vietnam, permethrin was the dominant pyrethroid, and its geographical repartition brings evidences that it is sourced by structural and householding uses and disease vector controls rather than agricultural spraying [47]. Deltamethrin was only detected once in this study but at very high levels from an undetermined source. In Southern China, cypermethrin, cyhalothrin, permethrin, and deltamethrin dominate over other pyrethroids in sediments of the Pearl River; their concentrations may reach notably high values in small creek sediments collected upstream in the river [49]. Cypermethrin and permethrin also dominate in sediments from an urban creek, close to Guangzhou (Southern China, [25, 61]). In Beijing GuanTin reservoir, fenvalerate and deltamethrin were the dominant pyrethroids [24]. In Pakistan deltamethrin and permethrin were the dominant pyrethroids, with deltamethrin present in all samples and reaching concentrations above environmental quality thresholds (namely, NOEC of *Hyalella azteca* [26]).

Australia's state Queensland has a low population and sugarcane and cotton cultivation dominate its agricultural activities. Ametryn and prometryn were the most frequent pyrethroids detected in sediments from irrigation drains and channels, reaching high concentration levels, while bifenthrin occurred in only one cotton production area [46].

In Europe, cyhalothrin and cypermethrin are ubiquitous at large river mouths, whereas riverbed sediment also showed frequent amounts of bifenthrin and tefluthrin, together with cypermethrin and cyfluthrin in some rivers of Italy and France [62]. In sediments of the Ebro Delta (Spain), cypermethrin was detected in some sediments, whereas deltamethrin, detected in the water, was below detection limits in the sediments [28]. In contrast, cypermethrin, cyfluthrin, and esfenvalerate were abundant in the paddy fields of Albufera de Valencia [30]. These paddy fields are filled with water coming from a lake receiving agricultural and urban effluents, and both surface water and groundwater contained high levels of dissolved phase pyrethroids.

Similarly to the reports of seawater concentrations, pyrethroid abundances in marine sediments are evaluated by a limited number of comprehensive studies. In an intensely urbanized estuary in Southern California, bifenthrin and cyfluthrin were the most frequently detected pyrethroids with their highest concentrations at 132 and 65 ng/g, respectively, at sites located near sources of runoff emissions from urban watersheds. They accounted for a part of the toxicity of the sediments to a standard amphipod *Eohaustorius estuarius*; however they were not the major toxicant at all the studied stations [52]. Samples with the highest concentrations of pyrethroids

were located in close proximity to river mouths and cities, whereas samples located more offshore showed lower concentrations, or pyrethroids were below detection limits. This distribution supports urban pyrethroid emissions. In another area of Southern California, sediments from the Monterey continental shelf were analyzed together with suspended solids in the three rivers flowing into this marine region. Whereas pyrethroids were found in almost all rivers particles (sampled after rain events), with bifenthrin and permethrin as the dominant pyrethroids, they could not be detected in the estuary nor in the deeper sediments of the Monterey canyons (from 100 to 300 m depth). A similar situation was observed in marine coastal waters off Portugal, whereas no pyrethroid could be detected in sediments, while cypermethrin was detected in the dissolved phase and tetramethrin, bifenthrin, cyhalothrin, fenvalerate, and permethrin occurred at low concentrations in some samples of oysters collected in the same area [33]. In marine sediments, contaminated river particles are diluted by the autochthonous marine particles and by older riverine particles in which pyrethroids have had the time to be degraded. As a consequence of dilution, pyrethroids are often below detection limits in marine sediments (Table 2).

A recent review documented the occurrence of pyrethroids in sediments worldwide and showed significant correlations between pyrethroid occurrence and sediment toxicity [7]. The good correlations obtained proved that pyrethroids were the main cause of toxicity and strongly suggested potential ecological risk to nontarget aquatic species. Nevertheless, at some locations, such as in sediments from the Pearl River Delta (China), other pollutants than pyrethroids likely contributed to the overall toxicity of sediments. The authors concluded that the frequent occurrence at high concentrations of pyrethroids in sediments from agricultural and residential areas constitute a threat to freshwater ecosystems [7].

5 Pyrethroid Degradation

A characteristic feature of pyrethroid contamination in water and benthic ecosystems is that a few compounds of the pyrethroid family may be present but not all the series, in concentrations generally under the 100 ng/L range for water samples or under the 100 ng/g range for sediments. Pyrethroid occurrence is highly variable in time and space, so that samples from a given area may show detectable amounts of one or several pyrethroids while others do not or comprise other active compounds. This feature is much different from other ubiquitous pesticides classes and is a consequence of their higher lability. The routes of degradation of pyrethroids may be abiotic (hydrolysis, photolysis, and oxidation) or mediated by bacteria and fungi. Pyrethroids degradation by microorganisms and fungi have been studied in soils [63, 64]. Various carboxylesterases may induce the degradation of pyrethroids; generally one gene exists in one pyrethroid-degrading microorganisms, with the exception of *Ochrobactrum anthropi*, that possesses two pyrethroids degrading genes [63]. Optimal conditions of pyrethroid biodegradation are between 30 and 35°C. Organic matter and clay content are also important parameters controlling

pyrethroid bioavailability to microorganisms. Half-lives of bifenthrin, cypermethrin, and permethrin in soils were 12–1,410, 14–106, and 5–55 days respectively, under temperature conditions between 25 and 30°C (Table 2 in [63]). The biodegradation rates in freshwater sediments have been seldom determined, and they are longer than in soils [18]. Depending on conditions, long persistence was observed for bifenthrin and permethrin. Under both aerobic and anaerobic conditions, and the half-life of bifenthrin in sediment of drainage channels ranged from 8 to 17 months at 20°C, while that of *cis* and *trans* permethrin varied between 2 to 13 months [65]. In liquid media, bacteria (*Bacillus*, *Brevibacillus*, *Ochrobactrum*, *Pseudomonas*, *Serratia*, and *Sphingobium*) and fungi (*Cladosporium*, *Candida*) degrade efficiently pyrethroids. At temperatures ranging from 27 to 38°C, most strains degraded pyrethroids within 5 days, with the fastest degradation observed for permethrin in 3 days [63]. However, the experimental conditions at which the experiments were carried out were not the same as natural field conditions, where lower temperatures and lower bacteria or fungi abundance can be expected to increase half-life of pyrethroids.

6 Pyrethroid Occurrence in the Atmosphere

Because of their relatively low vapor pressure, pyrethroids are assumed to have low tendency to volatilize during application, as well to revolatilize from soils or water bodies [7]. During application, 20–30% of the applied doses can be emitted as aerosols and drift away from their source by atmospheric transport [66]. Post-application emissions have also been reported to occur via volatilization [67]. For deltamethrin, having one of the lowest Henry's law constant values among pyrethroids, it was experimentally demonstrated that 70% of deltamethrin sprayed on the surface of the water was quickly emitted as aerosols [68]. Taken as a whole, these evidences point to likely atmospheric emissions of pyrethroids, at least during and shortly after application by spray broadcasting.

The widespread occurrence of pyrethroids in some areas also questions whether their volatilization to the gas phase is possible, ensuing a likely atmospheric transport to proximate or remote ecosystems (see Sect. 7). A few reports have recently evidenced that pyrethroids were present in the atmosphere, both as aerosols and as vapors in the gas phase. The particle-bound fraction is susceptible to be atmospherically deposited or to be washed out by rain or snow whereas gas-phase pyrethroids will be removed by photodegradation or air-soil, air-vegetation, or air-water diffusive exchange, probably resulting in longer atmospheric residence times [69]. Table 3 reviews the concentrations of pyrethroid insecticides bounds to aerosols or as vapors. The first report of pyrethroids in the gas phase of Brazilian alpine reserves showed that cypermethrin was the second pesticide in abundance, whereas gas phase concentrations of legacy pollutants, such as chlordane, chlorinated cyclodienes and hexachlorobenzene, were around background levels [70]. In aerosols and in the gas phase of Guangzhou (south China), eight pyrethroids were detected, and

cypermethrin was the dominant one [71]. Concentrations of aerosol-bound cypermethrin were comparable to those measured in a horticulture area in Malaysia [72]. Li et al. measured allethrin and tetramethrin in higher proportions in the gas phase whereas bifenthrin, cyhalothrin, permethrin, cyfluthrin, and cypermethrin were predominantly associated with the aerosols [71]. Bifenthrin was also detected in almost all samples of fine aerosols in Northern Brazil [73].

The recent recognition of pyrethroid occurrence in aerosols and in the gas phase opens a challenging view of their biogeochemical cycle and prompts further research to assess the relevance of atmospheric transport and occurrence of pyrethroid insecticides.

7 Key Physicochemical Properties of Pyrethroids, Transport Processes, and Modelling

Legacy pollutants like polychlorinated biphenyls (PCBs), chlorinated pesticides such as *p*,*p*′-dichlorodiphenyltrichloroethane (DDT), lindane, and organophosphate pesticides persist long enough in the environment to be transported by advective and diffusive processes and undergo long-range transport far away from their primary emission regions. Diffusive transport of pesticides results in an environmental partitioning of these pollutants among the different environmental matrices, such as water, particles, air, soils, biota, and sediments. For instance, water-particle partitioning is the result of a net quantity of pesticides transferred from the dissolved water phase to the organic part of the particles. Meanwhile the quantities of water, of particles, and of organic carbon do not change concurrently when pesticides partition among these phases. A change of any of these quantities would induce a re-partitioning of the chemical. Other relevant diffusive processes are air-water exchange, water-sediment partitioning, gas-aerosol partitioning, bioconcentration in organisms at different trophic levels, etc. Organic carbon occurrence in water stretches from truly dissolved organic carbon to particulate organic carbon, with a continuum in particle sizes. The division of dissolved and particle phase is operational, usually the dissolved phase refers to the pesticides passing through the filter cut-off size (e.g., 0.7 μm for a GF/F filter), but this dissolved phase can also include the colloidal phase. In Fig. 1 relevant diffusive (partitioning) processes for pyrethroids are represented by the wide gray arrows. Diffusive partitioning is always driven by a fugacity gradient among the two phases and is always a bidirectional process. In contrast to diffusive processes, an advective transport consists in the movement or flux of the phase itself, transporting the pesticides which it contains. Advective transport processes of pyrethroids in aquatic environments are represented by the thin black arrows in Fig. 1. For example, the transfer of atmospheric pesticides to soils or aquatic ecosystems can be by air-water exchange (partitioning) or by wet and dry deposition, which are advection transport processes. In dry deposition there is a settling of aerosol-bound pesticides, while in wet

Table 3 Selection of individual pyrethroid concentration in the atmospheric gas phase, in ng m^{-3}, and in aerosols in ng g^{-1} from different locations worldwide

	Year	Sample type	Individual pyrethroids							
			Allethrin	Bifenthrin	Tetramethryn	λ-cyhalothrin	Permethrin	Cyfluthrin	Cypermethrin	References
Gas in pg m^{-3}										
Brazilian alpine mountains, nationa parks	2013–2015	G					nd–40		nd–881	[70]
Guangzhou, urban area, South China	2011–2012	G	nd–66	nd–48	nd–8	nd–nq	nd–37	nd–nq	nd–16	[71]
Floriculture region Malaysia	2004	G							142–2,740	[72]
Aerosols in pg m^{-3}										
Guangzhou, urban area, South China	2011–2012	A	nd–139	nd–54	nd–28	nd–51	nd–88	nq–17	17.1–1,380	[71]
Todos os Santos, Northern Brazil	2010	A		14–72			62–945			[73]

nd not detected, *nq* under quantification limits, *G* atmospheric gas phase, *A* atmospheric aerosols

deposition by rain or snow, there is a scavenging of gas and aerosol phase pesticides by the rain drops or snowflakes. In terms of primary sources, after pesticide application on agriculture fields (rice, cotton, wineyard, etc.) by spraying, pyrethroids may reach surface aquatic environments through edge of field runoff, which is an advective soil to water input of irrigation water or rain water, entraining dissolved pyrethroids and also pesticides bound to particles or that have re-partitioned to the run-off water. Storm events after pesticide treatment have been shown to release high amount of pyrethroids into freshwater streams in the vicinity of fields [37]. Despite degradation and dilution processes, pyrethroids sorbed to river suspensions are effectively transported to the lower stretches of rivers [18, 63]. Particle vertical settling and sediment resuspension are advective processes transporting pyrethroids between water and sediment, which transport chemicals in parallel to the water-sediment diffusive partitioning. Nevertheless, the latter may only be effective for sediment pore water and benthic waters, while settling of organic carbon-bound pyrethroids is an advective flux affecting all the water column. Soils may act as transient repositories for pyrethroids that may gradually be desorbed into irrigation or rain water by leaching. In addition, sorption to soils, particle, and sediment may lower their degradability and thus increase their persistence in the environment [65]. Similarly to diffusive sediment-water exchange, particle-water exchange (or partitioning) continuously occurs, with a distribution of the chemical between organic carbon and the dissolved phase depending on temperature and quality of the organic matter.

The key condition for pyrethroids to be transported away from their source is that they persist long enough in the environment before being degraded. Their potential for being transported is also dictated by their physicochemical properties. The octanol-water partitioning coefficient, K_{OW}, characterize the potential of compounds for being absorbed into organic matter, either in sediments or in suspended particles. Even though, conceptually, it does not take into account surface adsorption, it is a common practice to use K_{OW} as a surrogate for adsorption/absorption, as experimentally it is very difficult to discern organic pollutants adsorbed or absorbed to particulate organic carbon. Henry's law constant (H) or the dimensionless Henry's law constant ($H' = K_{AW}$=H/RT) of a given pollutant characterizes its air-water diffusive partitioning and thus its potential to accumulate in water or being volatilized to the atmosphere facilitating their long-range transport. Each pyrethroid has specific values for these physicochemical constants. Figure 2 shows the phase space for organic chemicals and compares the values of both constants for pyrethroids to the values of these partitioning constants for other pollutant classes which behavior in the environment is better studied and understood. The phase space shown in Fig. 2 provides a simplified view of environmental partitioning and transport potential. Compounds in the upper area of the plot space have a higher potential to partition to the gas phase relatively to water than compounds on the bottom area of the plot. Similarly, compounds plotted on the right area of the plot have a greater potential to partition to organic carbon relatively to water than those plotted on the left side. Permethrin is plotted very close to PCB 101, thus have the similar partition characteristics than PCB101 and bifenthrin have an even higher K_{AW}. Therefore, both

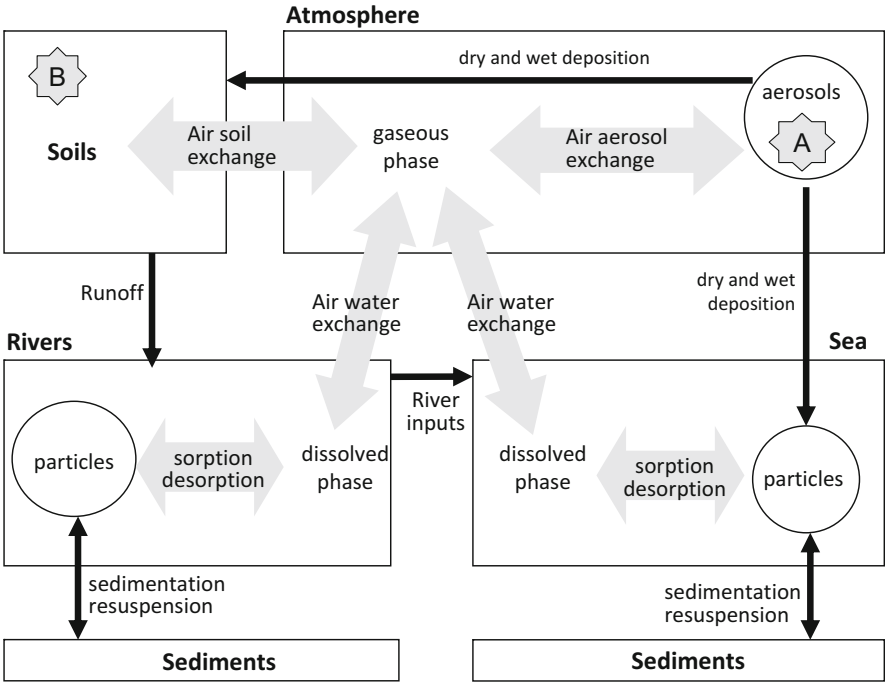

Fig. 1 Scheme of the geochemical cycle of pyrethroids in the environment. Boxes represent the environmental phases. The soil box represents both the solid phase of soils (plants and soil particles) and the soil porous water. Arrows represent the fluxes between phases, thin black arrows stands for fluxes of key transport (advective) processes and large gray arrow show key partition (diffusive) fluxes. Gray stars symbolize pyrethroid direct emissions to the environment; A is the emission that remains as aerosol during spray application, mostly to cropland; B is the emission that is deposited on soils and plant during spray application. See text in Sect. 7 for more explanation

compounds have a potential for long-range transport through grasshopping, that is, successive volatilization and deposition steps. In the case of pyrethroids, the potential for long range transport is limited by their potential degradation in the environment. It has to be underlined that in the case of cold environments with snow deposition events, even chemicals with high K_{AW} partition coefficients can be deposited due to the high sorption capacity of snow [74]. More importantly, the physicochemical characteristics of the other pyrethroids are similar to that of high molecular weight polycyclic aromatic hydrocarbons (PAHs), DDT and its degradation products (DDE and DDD), and hexachlorobenzene; therefore pyrethroids can be expected to have the same environmental behavior. In contrast, organophosphosphate pesticides have a greater solubility in water (lower K_{AW}) and will behave more as "swimmers," tending less to sorb on particles and with limited atmospheric transport [75].

In the case of legacy persistent organic pollutants (POPs), their important emissions combined to analytical progresses made it possible to quantify their

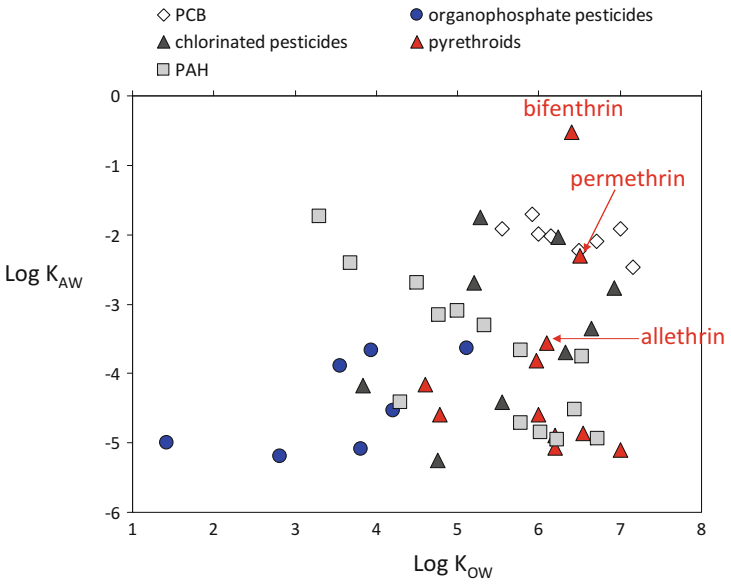

Fig. 2 Comparison of the partition behavior of current-use pyretroid insecticides and of other legacy pollutants. K_{AW} is the air-water partition coefficient, and K_{OW} is the octanol-water partition coefficient

abundances in water, suspended particles, sediments, atmospheric gas, and aerosols phases from regional to a global scales. Scientific efforts addressing pollutant detection in several environmental compartments brought quantitative appraisals and understanding of transport fluxes between air, seawater, soils, etc. This holds true for PCBs [76] and PAHs [77] but also for pesticides like lindane [78]. In contrast to legacy pollutants, pyrethroids are current-use pesticides, and they have been used and emitted to the environment for only the last few decades, and scientists have been able to quantify pyrethroids at environmental levels only for a decade [79]. As a consequence, the occurrence of pyrethroids in environmental phases relevant to the understanding of their biogeochemical cycle is still incompletely understood.

A comprehensive assessment of pyrethroid cycle in an urban area of Southern China used a fugacity-based model coupled to concentrations measured in different environment phases to calculate the diffusive and advective fluxes [25]. Sinking of suspended particles accounted for the higher fluxes, and resulted in water bed sediments fluxes 1 or 2 order of magnitude higher than air-water diffusive exchange. The higher fugacity of pyrethroid in water than in the gaseous atmosphere drove volatilization fluxes from the water to the air, permethrin, and cypermethrin having the higher fluxes. Despite this work, pyrethroids have received less attention in terms of their fate, transport, and biogeochemistry, and how these processes ought to be modelled. The comparison with other families of POPs with similar properties provide clues of their environmental fate and point to potential research efforts to be carried out in the future. Unless pyrethroids are efficiently degraded in the

atmosphere, some of them have the potential for long range transport as pentachorinated PCBs, 4–5 rings PAHs and DDD (Fig. 2). In comparison to those legacy pollutants and hydrocarbons, current-use pesticides such as pyrethroids are often reported in one environmental phase, chiefly dissolved freshwater phase or riverine sediments. Both dissolved phase and suspended particles [31] or suspended particles and sediments [14] or dissolved water phase and sediments [24, 27, 28, 33] are considered jointly in order to assess combined risks for the water ecosystem and for the benthic ecosystem. Future research efforts should address their multiphase partitioning, including the atmosphere, to elucidate their capacity to affect proximate or distant ecosystems from their primary sources. The advective transport of pyrethroids has been largely addressed only in relation to their dispersion by river flow notably during storm events. However, the partition between dissolved pyrethroids and particles is specifically addressed by one study, showing that for this particular site, a diffusive flux of bifenthrin existed from the particles toward the dissolved water [21].

8 Future Research Integration

Because of their rapid decay, pyrethroids are reported above detection levels in areas and at times closed to their point sources, and a global appraisal is still missing. It can be foreseen that pyrethroids might threaten biodiversity in some geographical areas where data is still lacking to date. Most croplands are indeed not studied for pyrethroids (Africa, Brasil, etc., see review [62]). In African market, esfenvalerate was the highest pesticide residue in fruits and vegetables, and allethrin was also detected, attesting for their use [80–83]. Ukraine, Pakistan, Turkey, Paraguay, and India registered the larger pyrethroid use while environmental informations on pyrethroid occurrence are mainly lacking for those countries [7, 26].

Pyrethroids are degraded in the environment so that they are not conspicuously detected, with the exception of some agricultural or urban areas. Their high degradation rates with respect to legacy pollutants support the belief that they are unlikely to persist in the environment. However, extension of cropland and of urbanized space will likely result into an increase in pyrethroid uses and emissions, because better alternatives to control pests are still lacking. In the case where the rate of inputs of pyrethroids would compensate for their degradation, pyrethroid occurrence may become more continuous and their behavior may then be assimilated to that of “quasi persistent organic pollutants”, with secondary transport evading them away from their application area. In California, past and current monitorings have demonstrated that there is a persistent threat to aquatic ecosystems because of current-use pesticides, with an increasing share by pyrethroids [19].

In conclusion, the shift to current-use pesticides demands a better understanding of the occurrence of pyrethroids in developing countries where the market shares are the highest. The partition, transport, and degradation fluxes of pyrethroids need to be

better appraised locally, regionally, and globally, taking into account the so far underestimated importance of atmospheric transport.

River flow efficiently transports pyrethroids to river mouths and estuaries. It is difficult to detect pyrethroids in the marine environment because of dilution. However aquaculture is a locally direct source that likely constitutes an important environmental burden for seawater, which it is very poorly surveyed and comprehensively understood.

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