Chapter 3

Pesticides in Worldwide Aquatic Systems: Part I

Catarina Cruzeiro, Eduardo Rocha and
Maria João Rocha

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.71644

Abstract

The occurrence of pesticides in aquatic environments is registered worldwide, but few or no approaches have been used to summarize and integrate the data. In this work, 30 countries and 95 aquatic systems were taken into consideration, using the data collected in the past 17 years. Data were evaluated by continent, with a special focus on Europe, as the continent with the most information available. However, in terms of analyzed pesticides, the insecticides were the most common category of pesticides being applied in excess in several Asian countries. Moreover, priority pesticides settled for elimination were/are still present in almost all the continents, demonstrating that those compounds continue to be used. This leads to the existence of environmental mixtures containing both legal and illegal pesticides, which are able to affect different trophic levels, including humans. Thus, action plans like international discussions and pacts should exist to regulate the adequate usage of pesticides, and a continuous environmental monitoring should be enforced to understand potential toxicological risks promoted by these compounds. Further considerations, based on the Stockholm Convention list and European Directive 2013/39/EU as references, were used to evaluate the degree of contamination in the studied aquatic systems.

Keywords: insecticides, herbicides, fungicides, water, estuaries, 2013/39/EU, Stockholm Convention

1. Preamble

The current overuse and abusive application of pesticides may impact diverse aquatic ecosystems in both the short and long term. Due to their physicochemical properties, pesticides can circulate through various mechanisms, converting into an additional source of contamination to aquatic environments, mainly the estuaries. Although many scientific and governmental works have been published to alert to these facts, poor approaches have been used to connect all available data. With this in mind, the main goal of this work is to review a significant amount of published representative data from a variety of aquatic systems, including rivers, estuaries, and coastal areas, and discuss the published results, around the world, taking into consideration factors such as geographic variability (continental and regional), matrices, pesticide category, and the European legislation.

Due to the volume of available information, the review is restricted to a period of 17 years (from 2000 to 2017) of publications. All the available data—average minimum (av-min), average maximum (av-max), and average of averages (av-av) concentrations—were collected and expressed as ng/L. Data were grouped by pesticide category. Europe is used as the main pillar of this study because it is the continent with the largest amount of data available. Online databases, as Web of Science (Thomson Reuters) and PubMed (NCBI), were used to access the indexed articles used in this work.

2. Water matrix

Eighty-eight articles were reviewed and compiled in **Table 1**. Matrices such as surface waters and dissolved aqueous phase represent a total of 79 and 6% of the collected data, respectively. Among these, 62% of the analyzed data refers to Europe, and the rest is divided between Africa and Asia (each with 13 and 18%, respectively), followed by South America and Oceania. No data were found for North America and Antarctica with the above presented criteria (**Table 1**); thus, when citing herein "worldwide", these continents are not included. Fifty aquatic systems were studied in Europe, from which Spain stands out with 13 (published in 19 journals).

Overall, the data collected between 1993 and 2017 show average concentrations of pesticides ranging from ~17 to ~9936 ng/L (**Table 1**). Among the selected articles, 141 compounds were detected and quantified in Europe, 57 in Asia, 42 in Africa, 21 in Oceania, and 33 in South America. The highest average concentrations and standard deviations (SD) were measured in Asia (875 ng/L; SD 3468), followed by Europe (638 ng/L; SD 10761), South America (487 ng/L; SD 2448), Africa, and finally, Oceania (230 ng/L; SD 1500).

On a worldwide scale, the insecticides prevail (60%) in terms of available and quantified data when compared with both herbicides (33%) and fungicides (7%). Per continent, the percentage of insecticides are more than 90% in Africa and Asia, summing approximately 45% in Europe, 71% in South America, and 19% in Oceania. No cases were reported in North America and Antarctica (**Figure 1**). While the high percentage of insecticides in Asia may be due to the high cereals production (more than 13×10^8 tonnes), in Africa, it can be linked to cereals production, plague control, and vector-borne diseases control [86–88]. In South America, studies alert to abusive usage of insecticides for pest control due to resistant species and the introduction of nonnative ones [89, 90]. In **Figure 1**, a peculiar different pattern is observed for the percentages of types of pesticides in Europe versus Oceania, which for the first case may be due to the high number of compounds quantified (141) or, more likely, to a response to diverse agriculture practices and industrial needs [91].

Continent/country	Number of aquatic systems	Quantified pesticides	Sampling year	av-min	av-max	av-av	Reference
				ng/L			
Africa							
Benin	1	6	2010	138.7	358.0	224.9	[1]
Egypt	2	12–13	1993	0.1	0.2	0.1	[2]
Ghana	2	4–11	2004	0.3	0.9–120.5	0.1–97.3	[3, 4]
Kenya	1	2	na	na	na	9375	[5]
Mozambique	1	16	na	24	43.4	30.6	[6]
Nigeria	5	1–14	2014	405.5–1930	431.0–3267	190.0–2163	[7–9]
South Africa	5	4–15	1999–2002	na–25	na–135	35.2–77.9	[10, 11]
Asia							
China	11	5–30	1999–2014	0.3–794.3	4.6–31,261	1.5–7384	[12–22]
India	3	3–13	2009–2015	0–2133	2.2–194,700	0.2–13,166	[23–25]
Macau	1	18	2001	0.8	3.5	1.6	[26]
Russia	2	7	2003–2005	na	na	0.1	[27]
Vietnam	1	13	2012	na	2246	398.5	[28]
Europe							
Central and Eastern Europe	1	9	2007	na	24.1	6.3	[29]
Belgium	2	6–7	2002–2004	na	na	48.4–312.1	[30–31]
Bulgaria	1	8	na	6.6	10.4	5.3	[32]
France	6	3–19	2003–2010	81.7–317.4	94.3–3452	26.9–566.7	[33–37]
Germany	6	1–19	2001–2003	4	250–5600	9.1–580	[38–39]
Greece	7	3–23	1996–2007	11.6–47.3	29.2–803.3	19.6–99.3	[40–43]
Hungary	1	2	2010	na	na	417.1	[44]
Italy	1	9	2008	1.2	4.4	1.9	[45]
Norway	1	12	2014	0.1	0.6	0.3	[46]
Poland	2	8–12	2002–2003	1.3–525.4	55.6–1323	8.5–42	[47–48]
Portugal	7	8–48	2004–2012	5.9–6487	125–290,345	31.2–17,667	[49–57]
Romania	3	7	2004–2013	8.3	9.8–39.7	1.6–37.1	[58–59]
Spain	13	1–45	1996–2013	6.1–58.4	35.8–947	4–940	[60–74]
The Netherlands	na	13	2008	34.6	79.2	43.8	[75]
Oceania							
Australia	5	4–10	2006–2010	1.5–138.3	8.5–3399	2.8–759.1	[76–80]

Continent/country	Number of aquatic systems	Quantified pesticides	Sampling year	av-min	av-max	av-av	Reference
				ng/L			
South America							
Argentina	2	3–8	2012	20–28.3	139.6–3783	53.5–323.3	[81–82]
Brazil	2	10–11	1999–2005	4.9–18.1	40.1–50.6	12.9–23.6	[83–84]
Chile	1	8	2013–2014	na	na	2.6	[85]

Table 1. Pesticide concentrations [average minimum (av-min), average maximum (av-max) and average of averages (av-av) values; ng/L] in water samples, displayed by continent, country, and aquatic system; the number of quantified pesticides and sampling year were also added (na: not applicable).

Looking at the nature of the matrices, while most studies have been using surface water as target (78%), the rest have been tackling groundwater (9%), dissolved aqueous phase (6%), and even others (**Figure 1**).

In spite of these facts, we should be aware that these results are dependent on the authors' selection, which may not correspond entirely to what is present in the aquatic systems.

Amid continents, the number of quantified compounds was similar (~12) with the exception of Europe, which presented a higher number of measured pesticides (~23) and a higher number of aquatic systems monitored.

The quantified pesticides data were also compared to the average and maximum levels set by Directive 2013/39/EU. Considering this aspect, the pesticides with levels above those established by the Directive are referred herein as positive cases (**Table 2**). A higher number of positive cases were registered for average concentrations (with percentages ranging from 31 to 75%) than for maximum concentrations (with percentages ranging from 12 to 39%). Considering both average and maximal concentrations, higher percentages of pesticides considered dangerous and banned by the Directive 2013/39/EU were registered in Asia (mainly China) and in South America. However, in South America (mainly Brazil), several pesticides that are legally forbidden in Europe (at least in European Union) still are legal in South America. The last observation leads to an over usage of these compounds in the respective region. In Asia (China), dicofol (structural similarity to DDT) will become forbidden in 2018 by the governmental agencies.

Insecticides are the only common pesticide category among continents, demonstrating its value in agriculture and urban gardening. The previous scenario, ruled by Asia and South America, is now changed, where Europe presents almost the double (n = 74) of positive cases (for average concentrations), when compared to Africa (n = 39) and Asia (n = 41). Few cases were observed in other continents. This denotes the importance of the European legislation and how far we are to accomplish its goals.

In Europe, pesticide levels averaged between ~4 and ~399 ng/L. Herein, the top three countries with published articles (from a total of 42 publications) are Spain (30%), Portugal (26%), and Greece (9%). These three countries reported the presence of more than 79 (Spain), 94 (Portugal),

http://dx.doi.org/10.5772/intechopen.71644

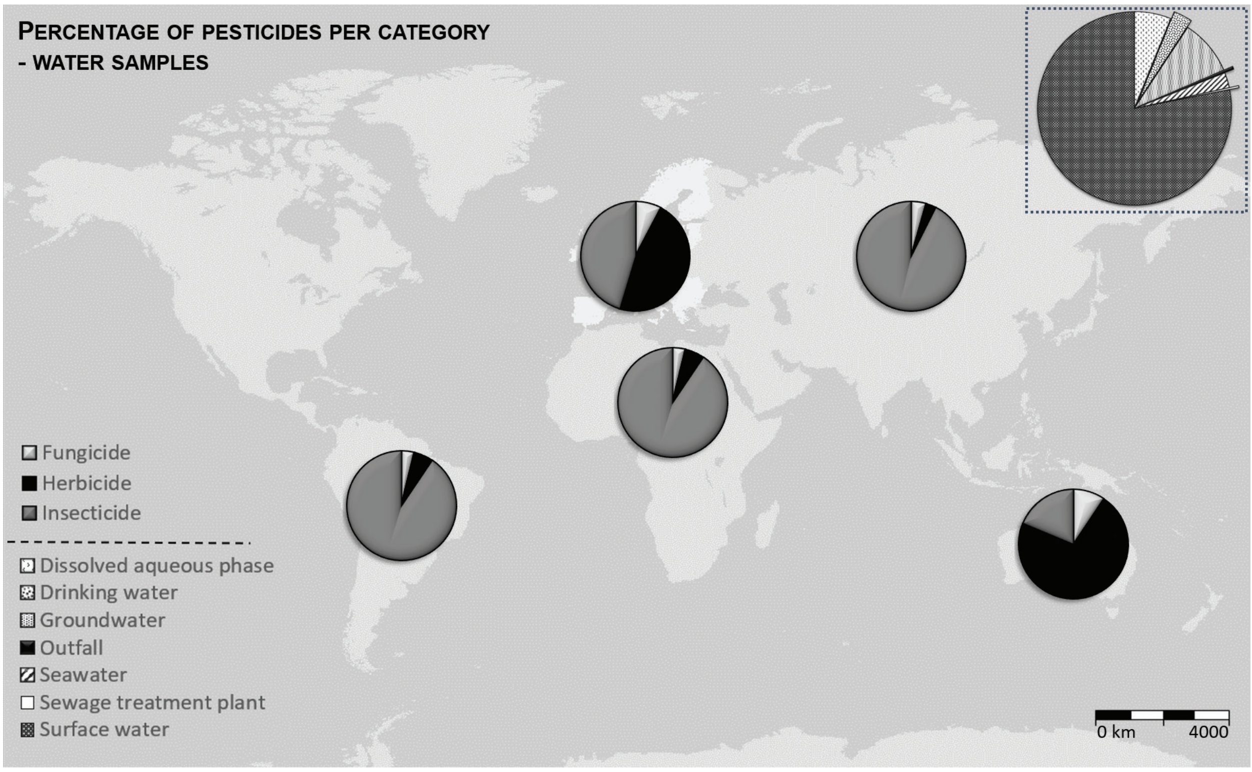

Figure 1. Representation of the quantified pesticides in water samples (%), per category, on each continent; the right upper corner figure represents the type of matrices found worldwide.

and 26 (Greece) pesticides in different aquatic systems. Looking at the number of positive cases, for average and maximum Directive established limits, Portugal (n = 74) stands out when compared to Spain (n = 10) and Greece (n = 28) [49, 51–57, 92]. These results demonstrate that the Portuguese aquatic systems are loaded with extreme high concentrations of pesticides, which can be due ineffective water treatment and/or abusive usage of pesticides along the water courses. It should be noted that the main rivers such as Minho, Douro, and Tagus have their origin in Spain, which can also contribute to the high levels observed in Portugal.

Due to the different number of compounds analyzed per published articles, the most frequent pesticides (more than 10 observations, i.e., quantification of pesticides in different aquatic systems or countries) were re-analyzed to compare the average concentrations between the different continents. The majority of the quantified pesticides (**Table 3**) belong to the priority list of persistent organic pollutants [94, 95]. Among these substances, which were settled in the Stockholm Convention list to be eliminated, the hexachlorocyclobenzene (HCB), DDT, aldrin, dieldrin, endrin, and hexachlorocyclohexane (HCH) were quantified in almost all the continents even after 2001, showing a continuous usage of these illegal substances. The same was registered for DDT, heptachlor, and hexachlorocyclobenzene after 2009. In fact, while HCB, aldrin, and dieldrin were measured in higher average concentrations in Europe, DDT and HCH were more prominent in Asia and endrin, endosulfan, and heptachlor were quantified in higher amount in Africa. In South America, the levels of the banned compounds were not particularly high; nonetheless, further studies should be undertaken to confirm the published data.

Continent/country	Average amounts (ng/L)	Number of cases	Samples above 2013/39/EU		References
			av	max	
Africa					
Fungicide	32.5	6	4	0	[2, 10]
Insecticide	312.9	51	39	7	[1–4, 6–8, 10, 11]
Asia					
Fungicide	4.1	3	1	0	[12, 27]
Insecticide	2270	72	41	29	[12–27]
Europe					
Fungicide					
Greece	72.5	2	2	1	[41]
Portugal	45.0	8	6	1	[50, 53, 55–57, 92]
Herbicide					
Belgium	243.3	8	1	0	[30, 31]
France	294.6	10	4	3	[34, 36, 37]
Germany	73.5	19	2	3	[38, 39]
Greece	49.8	8	1	1	[40, 42, 43]
Portugal	370.6	32	7	4	[49–54, 56, 57, 92]
Spain	125.0	59	2	2	[61, 63, 65–72, 74]
Insecticide					
Belgium	56.0	1	1	0	[30]
Bulgaria	17.2	3	2	1	[32]
France	140.1	5	5	2	[34–36]
Greece	48.5	16	14	9	[40, 41]
Italy	2.8	2	1	1	[45]
Poland	47.2	6	4	2	[47, 48, 93]
Portugal	398.5	54	42	14	[49–51, 53–57]
Romania	4.1	5	2	2	[58, 59]
Spain	9.0	20	3	3	[62–64, 66–69, 74]
Oceania					
Herbicide	503.1	11	3	3	[76–80]
Insecticide	2.0	2	1	1	[76, 77]
South America					
Insecticide	112.1	11	8	6	[82–85]

Table 2. Pesticides average (av) and maximum (max) concentrations (ng/L) in water samples, displayed by continent and pesticide category; the number of quantified pesticides, as well as the number of samples above 2013/39/EU Directive levels, were also included; Europe is presented with more detailed information; references are only defined for the samples above the 2013/39/EU Directive, per category.

Higher average concentrations of the same order of magnitude in Africa and Europe (global average ~38 ng/L) and lower amounts in Asia (~4 ng/L) were registered for the fungicide HCB. Herbicides such as atrazine and simazine were measured in Europe, Oceania, and South America, where the highest average concentrations were observed for the first two continents. Among herbicides, diuron stands out with concentrations 6-fold higher in Oceania (~1200 ng/L), when compared to the other continents (~200 ng/L). Among insecticides, ∑DDT, ∑cyclodiene, chlorpyriphos, ∑endosulfan, ∑heptachlor + heptachlor epoxide, ∑HCH, and malathion were most frequent in Africa, Asia, Europe, and South America. Comparing the total average sum of these insecticides (∑), Asia had the highest concentrations (~10,000 ng/L), followed by Africa (~3000 ng/L), Europe (~1800 ng/L), and finally, South America (~300 ng/L). The extremely high values in Asia are due to punctual observations in the Deomoni River (India) and in the Yellow River (China), which do not reflect the average concentration in Asia [21, 24]. However, when considering all pesticides from **Table 3**, we recorded similar concentrations (from ∑ ~7460 ng/L to ∑ ~10,540 ng/L) among Africa, Asia, and Europe, confirming that high punctual concentrations occur in different continents. The high concentrations reported for chlorpyriphos (in Asia and South America) and for diazinon (in Africa) are above the LC_{50} and/or EC_{50} observed in short-time exposures (48–96 h), for fish (as the rainbow trout) and invertebrates (as the crustaceans daphnia and mysid shrimps). Individually, these compounds can already cause mortality to 50% of the exposed population; however, a worst-case scenario may occur if these compounds are present in an environmental mixture (further considerations are done in chapter *Pesticides in Worldwide Aquatic Systems: Part II*).

The parent compound/residues ratios were calculated for DDT, endosulfan, and heptachlor. Results demonstrate an active use of DDT in Asia (1.4), while for endosulfan and heptachlor, the active use is spread among diverse continents (Africa, Asia, Europe, and South America).

The most frequent pesticides (equal or more than 10 quantifications in different aquatic systems or countries) were selected and grouped by category for the European countries (**Table 4**), reaching 23 compounds. The concentrations of eleven of these pesticides are above the Maximum Residue Limits (MRLs) set by 2013/39/EU Directive. The range of concentrations (min-max) was assessed, displaying the most substantial differences between countries. Seven pesticides (alachlor, aldrin, dieldrin, chlortoluron, dimethoate, diuron, and terbuthylazine) stand out with the highest ranges (numbers in bold, **Table 4**). Alachlor is present in the Iberian Peninsula at levels above the 2013/39/EU Directive limits set for average concentrations in surface waters, which may relate to a regional application of this herbicide [49–51, 53–57, 60, 63, 66, 67, 71, 72]; the same was observed for diuron, in Spain, France, and Belgium [30, 34, 37, 60, 63, 67, 70, 72]. The cyclodiene pesticides (∑aldrin and dieldrin) were above the annual average concentrations (∑ ~5 ng/L) set by the same directive for all registered cases, presenting extremely high amounts in Portugal (∑cyclodienes ~2174 ng/L), demonstrating an abusive and illegal use of these compounds in these regions [50, 51, 53, 55, 57]. Remarkably, none of these pesticides were above the LC_{50} and/or EC_{50} documented for the most typical organisms representative of the various trophic models.

Average amounts (ng/L)	Africa	Asia	Europe	Oceania	South America	References
Fungicide						
HCB	32.5	4.1	43.0			[2, 10, 12, 27, 32, 41, 50, 53, 55, 56]
Herbicide						
Alachlor		1.7	529.9		11.0	[34, 36, 38, 40, 49–57, 60, 63, 66, 67, 71, 72, 83]
Atrazine	107.9		138.9	482.9	17.0	[34, 36, 38, 40, 49–57, 60, 63, 66, 67, 71, 72, 83]
Atrazine-desethyl	6.0		173.2	65.2		[6, 29, 33, 38, 40, 43, 50, 53–57, 61, 63, 66, 67, 69, 71, 72, 78, 80, 96]
Chlortoluron			68.0			[34, 36, 38, 49, 63, 67, 72, 75]
Diuron	200.0		239.7	1200		[6, 29, 30, 37, 38, 46, 49, 63, 67, 70–72, 74, 78–80, 97]
Isoproturon			34.7			[29, 30, 36, 38, 46, 63, 67, 72, 74, 75, 97]
Metolachlor		22.7	57.4		5.0	[12, 30, 33, 34, 36, 38, 46, 49, 50, 52–54, 56, 63, 65–67, 71, 72, 74, 83]
Simazine	9.0		88.8	120.3	9.0	[6, 29–31, 38, 40, 43, 49, 50, 53, 55, 56, 61, 63, 65–68, 70–72, 74, 76, 77, 79, 80, 83]
Terbuthylazine	27.5		280.2			[6, 29, 31, 38, 46, 49, 50, 53–57, 61–63, 65–67, 69–72]
Terbutryn			98.9	5.0		[37, 39, 53, 55–57, 66, 69, 76]
Trifluralin		4.5	133.6		7.0	[12, 34, 36, 40, 42, 53, 55, 56, 71, 83]
Insecticide						
ΣDDT	744.7	1765	122.9		105.0	
2,4′-DDD	138.8	25.1	31.0			[1, 7, 10, 23, 25, 26, 64]
2,4′-DDT	212.7	369.0	4.0		6.0	[7, 10, 12, 15, 17, 20–23, 25, 26, 64, 84]
4,4′-DDD	103.3	132.7	15.2		41.0	[1, 2, 4, 7, 10, 12, 14, 15, 17, 19–21, 23, 26, 35, 50, 53, 55, 56, 59, 62, 64, 68, 84, 93]

Average amounts (ng/L)	Africa	Asia	Europe	Oceania	South America	References
4,4′-DDE	139.9	679.0	18.8		36.0	[1–4, 7, 12–14, 16, 17, 19, 20, 22, 23, 26, 41, 54–56, 64, 68, 84, 93]
4,4′-DDT	150.0	559.2	54.0		22.0	[1–3, 7, 10, 12–17, 19–23, 25, 26, 32, 35, 41, 47, 50, 53, 55, 56, 59, 64, 68, 84, 93]
DDT/DDE + DDD	0.9	1.1	0.9		0.4	
ΣCyclodiene	334.8	48.4	1324		1.5	
Aldrin	251.3	16.6	392.1		1.5	[4, 7, 8, 10, 12–14, 16, 17, 19, 20, 25, 26, 32, 41, 48, 50, 51, 53, 55, 56, 68, 85]
Dieldrin	44.5	12.7	898.7	3.0		[4, 6, 8, 10, 12, 19, 20, 25–27, 30, 41, 48, 50, 51, 57, 68, 76, 81]
Endrin	39.0	19.1	32.8			[8, 10, 12, 13, 16, 17, 19, 20, 25, 26, 32, 48, 50, 53, 55, 56, 68]
Chlordane γ	24.9	4.0	3.9			[2, 4, 10, 12, 13, 53, 57, 59, 72, 73, 83]
Chlorpyrifos	2.6	3103	14.9		110.0	[6, 12, 25, 40, 45, 50, 53, 55–57, 66, 69, 71, 74, 82]
Diazinon	4040		39.4			[5, 6, 37, 40, 42, 43, 45, 47, 49, 50, 53, 55–58, 63, 67, 69, 72, 74]
Dimethoate		360.0	4304	2.0	35.0	[18, 40, 45, 46, 49, 50, 53–57, 67, 69, 72, 74, 76, 81]
ΣEndosulfan	103.3	50.3	112.2		33.3	
Endosulfan α	77.8	15.0	87.1		10.8	[6, 8, 11, 12, 16, 19, 25–27, 32, 41, 50, 53, 55–57, 59, 64, 83–85]
Endosulfan β	25.5	35.4	25.0		22.5	[4, 6, 8, 12, 13, 16, 19, 26, 41, 50, 53, 55–57, 64, 83, 84]
Endosulfan sulfate	22.6	41.4	40.8		7.0	[4, 6, 8, 11, 13, 16, 19, 25, 41, 53–57, 83, 84]
Endosulfan/Endosulfan sulfate	4.6	1.2	2.8		4.8	
Fenitrothion			77.5			[24, 40, 45, 47, 50, 53, 55–57, 63, 67]

Average amounts (ng/L)	Africa	Asia	Europe	Oceania	South America	References
ΣHCH	1135	4768	136.1		41.1	
HCH α	85.1	756.2	24.7		8.3	[2, 8, 10, 12–17, 19–23, 26, 27, 41, 48, 58, 71, 84, 85]
HCH β	91.5	1335	39.1		21.0	[2, 4, 10, 12–17, 19–21, 23, 26, 27, 41, 48, 58, 61, 85]
HCH δ	669.0	2299			4.5	[4, 14, 17, 19–21, 26, 85]
HCH γ	289.7	377.5	72.3		7.3	[2, 3, 7, 8, 13, 14, 16, 17, 19–23, 25–27, 30, 32, 34, 36, 38, 41, 47–50, 53–58, 63, 64, 66–68, 71, 84, 85, 93]
ΣHeptachlor, Heptachlor epoxide	580.6	31.1	34.5		1.6	
Heptachlor	150.6	24.1	17.7		0.9	[1, 2, 4, 8, 10, 12, 14, 16, 17, 19, 20, 23, 26, 41, 48, 53, 55–57, 59, 85]
Heptachlor epoxide	430.0	7.0	16.8		0.7	[8, 13, 14, 16, 17, 19, 20, 26, 41, 48, 50, 53, 57, 68, 85]
Heptachlor/ heptachlor epoxide	0.4	3.4	1.1		1.2	
Malathion	100.0	360.0	102.7		42.0	[6, 18, 40, 43, 45, 49, 50, 53, 56, 57, 63, 67, 72, 83, 92]
Methoxychlor	7.0	18.9	120.3			[4, 12–14, 16, 19, 35, 47, 50, 53, 56, 57]
Σ	7456	1054	8278	1875	419	

Data are displayed by category and continent referring to the most frequent pesticides (n ≥ 10). These values are based on the references cited in **Table 1**.

The pesticide names in bold are in the 2013/39/EU directive target list with specific MRLs; the ratio parent/residues is presented in italic style.

Table 3. Average values (ng/L) of the most frequent pesticides, quantified in water samples.

Another worth to mention aspect is that the concentrations of the herbicides, chlortoluron, and terbuthylazine in France exceeded ~300 and ~1900 ng/L, respectively, indicating an abusive application and/or improper waste treatment [34, 36]. However, none of these herbicides are included in the above referred European directive.

In Europe, the pesticides were highlighted in the Stockholm Convention list. Like DDT, aldrin, dieldrin, endrin, atrazine, HCB, HCH (gamma), heptachlor, heptachlor epoxide, mirex, and PeCB were quantified between 1996 and 2012. Average concentrations (**Figure 2**) ranged from 1.1 to 155 ng/L along these years, excluding 2004 when high concentrations of two cyclodiene pesticides (2377 ng/L for aldrin and 5156 ng/L for dieldrin) were registered in the same aquatic system (Lake Vela, Portugal) [51]. The parent/residues ratio for DDT and heptachlor reveals values above 1, indicating once again an active and abusive use of these pesticides.

Pesticides (ng/L)	BE	BG	FR	DE	GR	IT	NO	Pl	PT	RO	SP	NL	min-max
References					[29–40, 43, 45, 47–52, 54–71, 74, 75, 93]								
ΣDDT		3.7	180.5		65.8			14.1	126.7	3.0	23.6		3.0–180.5
4,4′-DDD			84.0					7.5	11.0	1.0	7.6		1.0–84.0
4,4′-DDE					30.8			0.0	19.7	1.0	3.6		0.02–30.8
4,4′-DDT		3.7	96.5		35.0			6.6	96.0	1.0	12.5		1.0–96.5
Alachlor			41.0	36.4	66.4				813.1		380.3		**36.4–813.1**
ΣCyclodienes		5.6			43.0			6.0	2174		6.4		5.6–2174.4
Aldrin		5.6			23.9			1.0	832.1		3.1		**1.0–832.1**
Dieldrin					19.2			5.0	1342		3.2		**3.2–1342**
Atrazine	213.7		95.6	18.6	67.9		0.1		459.7	77.0	30.6		0.1–459.7
Atz-desethyl			38.1	11.1	45.3				587.5		26.3		11.1–587.5
Chlorpyrifos					2.5	4.6			29.1		3.0		2.5–29.1
Chlortoluron			340.5	3.3					7.8		7.4	20.0	**3.3–340.5**
Diazinon					93.1	0.7			59.2	20.0	9.1		0.7–93.1
Dimethoate					5.2	2.3	0.0		11,650		23.7		**0.0–11,650**
Diuron	820.0		740.0	7.1			0.3		49.5		208.7		**0.3–820.0**
Endo. sulfate					19.1				55.2				19.1–55.2
Fenitrothion					3.3	2.3			77.9		151.5		2.3–151.5
HCH γ	56.0	12.8	200.0	1.3	25.7			83.4	146.6	2.6	15.7		1.3–200.0
Isoproturon	270.0		144.0	13.1			0.2		3.3		3.7	40.0	0.2–270.0
Malathion					19.4	2.7			41.8		229.1		2.7–229.1
Metolachlor	327.0		96.4	4.1			0.8		80.0		9.0		0.8–327.0
Simazine	71.9			7.7	2.7				33.5		156.9		2.7–156.9
Terbuthylazine	36.0		1950	4.1			0.3		78.9		414.0		**0.3–1950**
Terbutryn				203.4					37.4		3.7		3.7–203.4

Data are displayed by European country (BE: Belgium, BG: Bulgaria; FR: France; DE: Germany; GR: Greece; IT: Italy; NO: Norway; PL: Poland; PT: Portugal; RO: Romania; SP: Spain; NL: Netherlands) referring to the most frequent pesticides (n ≥ 10) based on the references cited in **Table 1**. Atz-desethyl: atrazine-desethyl; Endo. sulfate: endosulfan sulfate.
The pesticide names in bold are in the 2013/39/EU directive target list with specific MRLs.

Table 4. Average values (ng/L) of the most frequent pesticides quantified in water samples.

3. Final considerations

Water, as the most common analyzed matrix, is usually characterized by the quantification of pesticides dissolved in the aqueous phase (after filtering). In spite of its importance, more

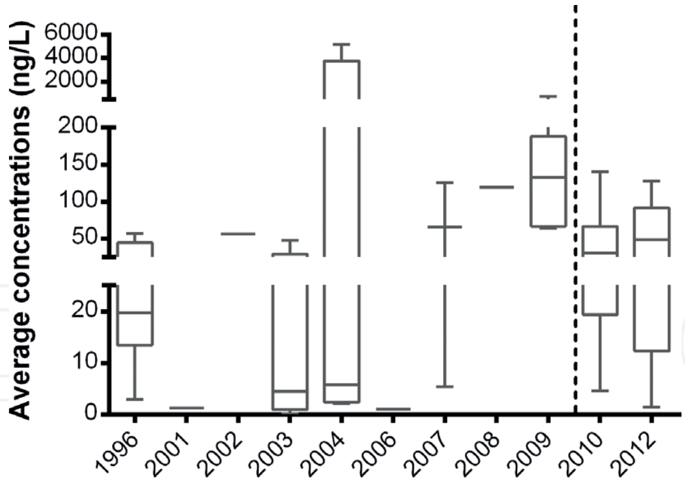

Figure 2. Representation of the priority listed pesticides average values (ng/L), quantified in water samples, collected in Europe, and displayed by sampling year (the dashed line separates the before and after the Stockholm Convention (2009).

efforts should be invested into quantifying pesticides present in the suspended particulate matter phase, since it is where most of the organic contaminants will be absorbed. In parallel, further legislative considerations should be applied. Looking at the number of different pesticides quantified per continent, Europe registered the highest number of compounds (141), which may be due to the amount of available data. Taking this in consideration together the category of the measured pesticides, insecticides were the most representative compounds, since they were measured in almost all continents, presenting also the highest number of cases above the European Legislative limits. This suggests that independently of the agricultural practices/needs, insecticides are the ones showing higher amounts in the aquatic systems. However, the highest average concentrations were registered in Asia, which can indicate an abusive usage of specific pesticides. Among continents, the continuous application of some pesticides scheduled for elimination in 2001 or 2009 by the Stockholm Convention is visible. As this study covers this transition time-frame, additional studies should be done to monitor the eradication of these substances.

In some cases, concentrations were clearly toxic to some trophic levels (acute concentrations); however, it is important to highlight that continuous exposure to medium/low levels (ng/L) may cause long-term adverse effects rippling into all trophic levels, in the likes of neurotoxicity, altered metabolism, endocrine disruption, and immunotoxicity in insects and invertebrates, passing through fish, amphibians, reptiles, and birds, and finally ending in mammals. Growth modulation, altered metabolism, and impaired photosynthesis may also occur in plants and fungi [91]. Further studies should also evaluate the impact of the main persistent metabolites, since they are the ones which persist longer in the aquatic systems.

In summary, further international discussions and pacts, such as the Stockholm Convention, should exist to alert mankind, to broadly regulate usages, monitoring, and where or when it is necessary to ban the use of these hazardous pesticides.

Acknowledgements

Partially supported by the European Regional Development Fund (ERDF) through the Operational Competitiveness Programme (COMPETE), and Operational Human Potential Programme (POPH), and by national Portuguese funds, through Foundation for Science and Technology (FCT), via project UID/Multi/04423/2013, project PTDC/MAR/70436/2006 (FCOMP-01-0124.FEDER-7382), grant (SFRH/BD/79305/2011), and grant (SFRH/BPD/120558/2016). This work was also implemented in the Framework of the Structured Program of R&D&I INNOVMAR—Innovation and Sustainability in the Management and Exploitation of Marine Resources (NORTE-01-0145-FEDER-000035), namely within the Research Line ECOSERVICES, supported by the Northern Regional Operational Programme (NORTE2020), through ERFD. Complementary funding was provided by ICBAS—U.Porto.

Author details

Catarina Cruzeiro[1,2,3], Eduardo Rocha[1,3] and Maria João Rocha[1,3]*

*Address all correspondence to: mjrocha@icbas.up.pt

1 Department of Microscopy, Laboratory of Histology and Embryology, ICBAS—Institute of Biomedical Sciences Abel Salazar, U.Porto—University of Porto, Porto, Portugal

2 Department of Life Sciences, CFE—Centre for Functional Ecology, University of Coimbra, Coimbra, Portugal

3 CIIMAR/CIMAR—Interdisciplinary Centre for Marine and Environmental Research, Group of Histomorphology, Pathophysiology and Applied Toxicology—Terminal de Cruzeiros do Porto de Leixões, Matosinhos, Portugal

References

[1] Agbohessi PT, Imorou Toko I, Ouédraogo A, Jauniaux T, Mandiki SNM, Kestemont P. Assessment of the health status of wild fish inhabiting a cotton basin heavily impacted by pesticides in Benin (West Africa). Science of the Total Environment. 2015;**506-507**:567-584

[2] Yamashita N, Urushigawa Y, Masunaga S, Walash MI, Miyazaki A. Organochlorine pesticides in water, sediment and fish from the Nile River and Manzala Lake in Egypt. International Journal of Environmental Analytical Chemistry. 2000;**77**(4):289-303

[3] Darko G, Akoto O, Oppong C. Persistent organochlorine pesticide residues in fish, sediments and water from Lake Bosomtwi, Ghana. Chemosphere. 2008;**72**(1):21-24

[4] Gbeddy G, Glover E, Doyi I, Frimpong S, Doamekpor L. Assessment of organochlorine pesticides in water, sediment, African cat fish and Nile tilapia, consumer exposure and

human health implications, Volta Lake. Ghana Journal of Environmental & Analitical Toxicology. 2015;**5**(4):297

[5] Otieno P, Okinda Owuor P, Lalah JO, Pfister G, Schramm KW. Monitoring the occurrence and distribution of selected organophosphates and carbamate pesticide residues in the ecosystem of Lake Naivasha, Kenya. Toxicological & Environmental Chemistry. 2015;**97**(1):51-61

[6] Sturve J, Scarlet P, Halling M, Kreuger J, Macia A. Environmental monitoring of pesticide exposure and effects on mangrove aquatic organisms of Mozambique. Marine Environmental Research. 2016;**121**:9-19

[7] Ize-Iyamu O, Asia I, Egwakhide P. Concentrations of residues from organochlorine pesticide in water and fish from some rivers in Edo State Nigeria. International Journal of Physical Sciences. 2007;**2**(9):237-241

[8] Ogbeide O, Tongo I, Ezemonye L. Risk assessment of agricultural pesticides in water, sediment, and fish from Owan River, Edo State, Nigeria. Environmental Monitoring and Assessment. 2015;**187**(10):1-16

[9] Ikpesu TO. Assessment of occurrence and concentrations of paraquat dichloride in water, sediments and fish from Warri River Basin, Niger Delta, Nigeria. Environmental Science and Pollution Research. 2015;**22**(11):8517-8525

[10] Awofolu R, Fatoki O. Persistent organochlorine pesticide residues in freshwater systems and sediments from the Eastern Cape, South Africa. Water SA. 2004;**29**(3):323-330

[11] Schulz R, Peall SKC, Dabrowski JM, Reinecke AJ. Current-use insecticides, phosphates and suspended solids in the Lourens River, Western Cape, during the first rainfall event of the wet season. Water SA. 2001;**27**(1):65-70

[12] Xue N, Xu X, Jin Z. Screening 31 endocrine-disrupting pesticides in water and surface sediment samples from Beijing Guanting reservoir. Chemosphere. 2005;**61**(11):1594-1606

[13] Shen B, Wu J, Zhao Z. Organochlorine pesticides and polycyclic aromatic hydrocarbons in water and sediment of the Bosten Lake, Northwest China. Journal of Arid Land. 2017;**9**(2):287-298

[14] Cui L, Ge J, Zhu Y, Yang Y, Wang J. Concentrations, bioaccumulation, and human health risk assessment of organochlorine pesticides and heavy metals in edible fish from Wuhan, China. Environmental Science and Pollution Research. 2015;**22**(20):15866-15879

[15] Yang D, Qi S, Zhang J, Wu C, Xing X. Organochlorine pesticides in soil, water and sediment along the Jinjiang River mainstream to Quanzhou Bay, southeast China. Ecotoxicology and Environmental Safety. 2013;**89**:59-65

[16] Zhang ZL, Hong HS, Zhou JL, Huang J, Yu G. Fate and assessment of persistent organic pollutants in water and sediment from Minjiang River Estuary, Southeast China. Chemosphere. 2003;**52**(9):1423-1430

[17] Zhou R, Zhu L, Yang K, Chen Y. Distribution of organochlorine pesticides in surface water and sediments from Qiantang River, East China. Journal of Hazardous Materials. 2006;**137**(1):68-75

[18] Chen H, Zhu J, Li Z, Chen A, Zhang Q. The occurrence and risk assessment of five organophosphorus pesticides in river water from Shangyu, China. Environmental Monitoring and Assessment. 2016;**188**(11):614

[19] Zhang Z, Huang J, Yu G, Hong H. Occurrence of PAHs, PCBs and organochlorine pesticides in the Tonghui River of Beijing, China. Environmental Pollution. 2004;**130**(2):249-261

[20] Tang Z, Yang Z, Shen Z, Niu J, Cai Y. Residues of organochlorine pesticides in water and suspended particulate matter from the Yangtze River catchment of Wuhan, China. Environmental Monitoring and Assessment. 2008;**137**(1-3):427-439

[21] Li J, Li F, Liu Q. Sources, concentrations and risk factors of organochlorine pesticides in soil, water and sediment in the Yellow River estuary. Marine Pollution Bulletin. 2015;**100**(1):516-522

[22] Lin T, Li J, Xu Y, Liu X, Luo C, Cheng H, et al. Organochlorine pesticides in seawater and the surrounding atmosphere of the marginal seas of China: Spatial distribution, sources and air–water exchange. Science of the Total Environment. 2012;**435-436**:244-252

[23] Huang Y, Xu Y, Li J, Xu W, Zhang G, Cheng Z, et al. Organochlorine pesticides in the atmosphere and surface water from the equatorial Indian Ocean: Enantiomeric signatures, sources, and fate. Environmental Science & Technology. 2013;**47**(23):13395-13403

[24] Singh S, Bhutia D, Sarkar S, Rai BK, Pal J, Bhattacharjee S, et al. Analyses of pesticide residues in water, sediment and fish tissue from river Deomoni flowing through the tea gardens of Terai Region of West Bengal, India. International Journal of Fisheries and Aquatic Studies. 2015;**3**:17-23

[25] Singare PU. Distribution and risk assessment of suspected endocrine-disrupting pesticides in creek water of Mumbai, India. Marine Pollution Bulletin. 2016;**102**(1):72-83

[26] Luo X, Mai B, Yang Q, Fu J, Sheng G, Wang Z. Polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides in water columns from the Pearl River and the Macao harbor in the Pearl River Delta in South China. Marine Pollution Bulletin. 2004;**48**(11-12):1102-1115

[27] Carroll ML, Johnson BJ, Henkes GA, McMahon KW, Voronkov A, Ambrose WG Jr, et al. Bivalves as indicators of environmental variation and potential anthropogenic impacts in the southern Barents Sea. Marine Pollution Bulletin. 2009;**59**(4-7):193-206

[28] Chau NDG, Sebesvari Z, Amelung W, Renaud FG. Pesticide pollution of multiple drinking water sources in the Mekong Delta, Vietnam: Evidence from two provinces. Environmental Science and Pollution Research. 2015;**22**(12):9042-9058

[29] Loos R, Locoro G, Contini S. Occurrence of polar organic contaminants in the dissolved water phase of the Danube River and its major tributaries using SPE-LC-MS2 analysis. Water Research. 2010;**44**(7):2325-2335

[30] Direction générale des ressources naturelles et de l'environment. État des lieux des sous-bassins hydrographiques Tome I : état des lieux Sous-bassin Escaut—Lys. Incidences et évaluation du risque de non atteinte du bon état. Governmental document. Direction générale des Ressources naturelles et de l'Environment. 2005

[31] Noppe H, Ghekiere A, Verslycke T, Wulf ED, Verheyden K, Monteyne E, et al. Distribution and ecotoxicity of chlorotriazines in the Scheldt Estuary (B-Nl). Environmental Pollution. 2007;**147**(3):668-676

[32] Litskas VD, Dosis IG, Karamanlis XN, Kamarianos AP. Occurrence of priority organic pollutants in Strymon river catchment, Greece: Inland, transitional, and coastal waters. Environmental Science and Pollution Research. 2012;**19**(8):3556-3567

[33] Miège C, Schiavone S, Dabrin A, Coquery M, Mazzella N, Berho C, et al. An in situ inter-comparison exercise on passive samplers for monitoring metals, polycyclic aromatic hydrocarbons and pesticides in surface waters. TrAC Trends in Analytical Chemistry. 2012;**36**:128-143

[34] Pesce S, Fajon C, Bardot C, Bonnemoy F, Portelli C, Bohatier J. Longitudinal changes in microbial planktonic communities of a French river in relation to pesticide and nutrient inputs. Aquatic Toxicology. 2008;**86**(3):352-360

[35] Baugros J-B, Giroud B, Dessalces G, Grenier-Loustalot M-F, Cren-Olivé C. Multiresidue analytical methods for the ultra-trace quantification of 33 priority substances present in the list of REACH in real water samples. Analytica Chimica Acta. 2008;**607**(2):191-203

[36] Taghavi L, Merlina G, Probst J-L. The role of storm flows in concentration of pesticides associated with particulate and dissolved fractions as a threat to aquatic ecosystems—case study: The agricultural watershed of save river (Southwest of France). Knowledge and Management of Aquatic Ecosystems. 2011;(400):06

[37] Gasperi J, Garnaud S, Rocher V, Moilleron R. Priority substances in combined sewer overflows: Case study of the Paris sewer network. Water Science and Technology. 2011;**63**(5):853

[38] Koal T, Asperger A, Efer J, Engewald W. Simultaneous determination of a wide spectrum of pesticides in water by means of fast on-line SPE-HPLC-MS-MS—A novel approach. Chromatographia. 2003;**57**:S93-S101

[39] Quednow K, Püttmann W. Monitoring terbutryn pollution in small rivers of Hesse, Germany. Journal of Environmental Monitoring. 2007;**9**(12):1337-1343

[40] Thomatou A-A, Zacharias I, Hela D, Konstantinou I. Determination and risk assessment of pesticide residues in lake Amvrakia (W. Greece) after agricultural land use changes in the lake's drainage basin. International Journal of Environmental Analytical Chemistry. 2012;**93**(7):780-799

[41] Golfinopoulos SK, Nikolaou AD, Kostopoulou MN, Xilourgidis NK, Vagi MC, Lekkas DT. Organochlorine pesticides in the surface waters of Northern Greece. Chemosphere. 2003;**50**(4):507-516

[42] Lambropoulou DA, Sakkas VA, Hela DG, Albanis TA. Application of solid-phase microextraction in the monitoring of priority pesticides in the Kalamas River (N.W. Greece). Journal of Chromatography A. 2002;**963**(1-2):107-116

[43] Hela DG, Lambropoulou DA, Konstantinou IK, Albanis TA. Environmental monitoring and ecological risk assessment for pesticide contamination and effects in Lake Pamvotis, northwestern Greece. Environmental Toxicology and Chemistry. 2005;**24**(6):1548-1556

[44] Mörtl M, Németh G, Juracsek J, Darvas B, Kamp L, Rubio F, et al. Determination of glyphosate residues in Hungarian water samples by immunoassay. Microchemical Journal. 2013;**107**:143-151

[45] Montuori P, Aurino S, Nardone A, Cirillo T, Triassi M. Spatial distribution and partitioning of organophosphates pesticide in water and sediment from Sarno River and Estuary, Southern Italy. Environmental Science and Pollution Research. 2015;**22**(11):8629-8642

[46] Brumovský M, Bečanová J, Kohoutek J, Thomas H, Petersen W, Sørensen K, et al. Exploring the occurrence and distribution of contaminants of emerging concern through unmanned sampling from ships of opportunity in the North Sea. Journal of Marine Systems. 2016;**162**:47-56

[47] Badach H, Nazimek T, Kaminska IA. Pesticide content in drinking water samples collected from orchard areas in central Poland. Annals of Agricultural and Environmental Medicine. 2007;**14**(1):109

[48] Tomza-Marciniak A, Witczak A. Distribution of endocrine-disrupting pesticides in water and fish from the Oder River, Poland. Acta Ichthyologica Et Piscatoria. 2010;**40**(1):1-9

[49] Palma P, Kuster M, Alvarenga P, Palma VL, Fernandes RM, Soares AMVM, et al. Risk assessment of representative and priority pesticides, in surface water of the Alqueva reservoir (South of Portugal) using on-line solid phase extraction-liquid chromatography-tandem mass spectrometry. Environment International. 2009;**35**(3):545-551

[50] Rocha MJ, Ribeiro MFT, Cruzeiro C, Figueiredo F, Rocha E. Development and validation of a GC-MS method for determination of 39 common pesticides in estuarine water—Targeting hazardous amounts in the Douro River estuary. International Journal of Environmental Analytical Chemistry. 2012;**92**(14):1587-1608

[51] Abrantes N, Pereira R, Gonçalves F. Occurrence of pesticides in water, sediments, and fish tissues in a lake surrounded by agricultural lands: Concerning risks to humans and ecological receptors. Water, Air, & Soil Pollution. 2010;**212**(1):77-88

[52] AIASS A, Stigter TY. Multi-method assessment of nitrate and pesticide contamination in shallow alluvial groundwater as a function of hydrogeological setting and land use. Agricultural Water Management. 2009;**96**(12):1751-1765

[53] Cruzeiro C, Rocha E, Pardal MÂ, Rocha MJ. Environmental assessment of pesticides in the Mondego River Estuary (Portugal). Marine Pollution Bulletin. 2016;**103**:240-246

[54] Gonçalves CM, Esteves da Silva JCG, Alpendurada MF. Evaluation of the pesticide contamination of groundwater sampled over two years from a vulnerable zone in Portugal. Journal of Agricultural and Food Chemistry. 2007;**55**(15):6227-6235

[55] Cruzeiro C, Pardal M, Rocha E, Rocha M. Occurrence and seasonal loads of pesticides in surface water and suspended particulate matter from a wetland of worldwide interest—The Ria Formosa Lagoon, Portugal. Environmental Monitoring and Assessment. 2015;**187**(11):1-21

[56] Cruzeiro C, Rocha E, Pardal MÂ, Rocha MJ. Uncovering seasonal patterns of 56 pesticides in surface coastal waters of the Ria Formosa lagoon (Portugal), using a GC-MS method. International Journal of Environmental Analytical Chemistry. 2015;**95**(14):1370-1384

[57] Cruzeiro C, Rocha E, Pardal MÂ, Rocha MJ. Seasonal-spatial survey of pesticides in the most significant estuary of the Iberian Peninsula—The Tagus River Estuary. Journal of Cleaner Production. 2016;**126**:419-427

[58] Ferencz L, Balog AA. Pesticide survey in soil, water and foodstuffs from central Romania. Carpathian Journal of Earth and Environmental Sciences. 2010;**5**(1):111-118

[59] Dirtu D, Pancu M, Minea ML, Dirtu AC, Sandu I. Occurrence and assessment of selected chemical contaminants in drinking water from Eastern Romania. Revista die Chemie. 2016;**67**(10):2059-2064

[60] Köck-Schulmeyer M, Ginebreda A, de Alda M, Barceló D. Fate and Risks of Polar Pesticides in Groundwater Samples of Catalonia. The Handbook of Environmental Chemistry. Heidelberg: Springer Berlin; 2012. pp. 1-20

[61] Quintana J, Martí I, Ventura F. Monitoring of pesticides in drinking and related waters in NE Spain with a multiresidue SPE-GC-MS method including an estimation of the uncertainty of the analytical results. Journal of Chromatography A. 2001;**938**(1-2):3-13

[62] Pérez-Carrera E, León VML, Parra AG, González-Mazo E. Simultaneous determination of pesticides, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in seawater and interstitial marine water samples, using stir bar sorptive extraction–thermal desorption–gas chromatography–mass spectrometry. Journal of Chromatography A. 2007;**1170**(1-2):82-90

[63] Postigo C, López de Alda MJ, Barceló D, Ginebreda A, Garrido T, Fraile J. Analysis and occurrence of selected medium to highly polar pesticides in groundwater of Catalonia (NE Spain): An approach based on on-line solid phase extraction–liquid chromatography–electrospray-tandem mass spectrometry detection. Journal of Hydrology. 2010;**383**(1-2):83-92

[64] Sánchez-Avila J, Tauler R, Lacorte S. Organic micropollutants in coastal waters from NW Mediterranean Sea: Sources distribution and potential risk. Environment International. 2012;**46**:50-62

[65] Hildebrandt A, Guillamón M, Lacorte S, Tauler R, Barceló D. Impact of pesticides used in agriculture and vineyards to surface and groundwater quality (North Spain). Water Research. 2008;**42**(13):3315-3326

[66] Claver A, Ormad P, Rodríguez L, Ovelleiro JL. Study of the presence of pesticides in surface waters in the Ebro river basin (Spain). Chemosphere. 2006;**64**(9):1437-1443

[67] Köck M, Farré M, Martínez E, Gajda-Schrantz K, Ginebreda A, Navarro A, et al. Integrated ecotoxicological and chemical approach for the assessment of pesticide pollution in the Ebro River delta (Spain). Journal of Hydrology. 2010;**383**(1-2):73-82

[68] Salvadó V, Quintana XD, Hidalgo M. Monitoring of nutrients, pesticides, and metals in waters, sediments, and fish of a wetland. Archives of Environmental Contamination and Toxicology. 2006;**51**(3):377-386

[69] Masiá A, Campo J, Vázquez-Roig P, Blasco C, Picó Y. Screening of currently used pesticides in water, sediments and biota of the Guadalquivir River basin (Spain). Journal of Hazardous Materials. 2013;**263**(Part 1):95-104

[70] Belmonte Vega A, Garrido Frenich A, Martínez Vidal JL. Monitoring of pesticides in agricultural water and soil samples from Andalusia by liquid chromatography coupled to mass spectrometry. Analytica Chimica Acta. 2005;**538**(1-2):117-127

[71] Menchen A, JDL H, JJG A. Pesticide contamination in groundwater bodies in the Júcar River European Union Pilot Basin (SE Spain). Environmental Monitoring and Assessment. 2017;**189**(4):146

[72] Köck-Schulmeyer M, Ginebreda A, González S, Cortina JL, de Alda ML, Barceló D. Analysis of the occurrence and risk assessment of polar pesticides in the Llobregat River Basin (NE Spain). Chemosphere. 2012;**86**(1):8-16

[73] Kuster M, López de Alda MJ, Hernando MD, Petrovic M, Martín-Alonso J, Barceló D. Analysis and occurrence of pharmaceuticals, estrogens, progestogens and polar pesticides in sewage treatment plant effluents, river water and drinking water in the Llobregat river basin (Barcelona, Spain). Journal of Hydrology. 2008;**358**(1-2):112-23

[74] Masiá A, Campo J, Navarro-Ortega A, Barceló D, Picó Y. Pesticide monitoring in the basin of Llobregat River (Catalonia, Spain) and comparison with historical data. Science of The Total Environment. 2015;**503-504**:58-68

[75] Moermond C, Vos J, Verbruggen E. Environmental Risk Limits for Organophosphorous Pesticides. Netherlands: National Institute for Public Health and the Environment (RIVM); 2008 Contract No.: 601714004

[76] Allinson G, Zhang P, Bui A, Allinson M, Rose G, Marshall S, et al. Pesticide and trace metal occurrence and aquatic benchmark exceedances in surface waters and sediments of urban wetlands and retention ponds in Melbourne, Australia. Environmental Science and Pollution Research. 2015;**22**(13):10214-10226

[77] Allinson G, Allinson M, Bui A, Zhang P, Croatto G, Wightwick A, et al. Pesticide and trace metals in surface waters and sediments of rivers entering the Corner Inlet Marine National Park, Victoria, Australia. Environmental Science and Pollution Research. 2016;**23**(6):5881-5891

[78] Mitchell C, Brodie J, White I. Sediments, nutrients and pesticide residues in event flow conditions in streams of the Mackay Whitsunday Region, Australia. Marine Pollution Bulletin. 2005;**51**(1-4):23-36

[79] Birch GF, Drage DS, Thompson K, Eaglesham G, Mueller JF. Emerging contaminants (pharmaceuticals, personal care products, a food additive and pesticides) in waters of Sydney estuary, Australia. Marine Pollution Bulletin. 2015;**97**(1-2):56-66

[80] Bainbridge ZT, Brodie JE, Faithful JW, Sydes DA, Lewis SE. Identifying the land-based sources of suspended sediments, nutrients and pesticides discharged to the Great Barrier Reef from the Tully–Murray Basin, Queensland, Australia. Marine and Freshwater Research. 2009;**60**(11):1081-1090

[81] De Gerónimo E, Aparicio VC, Bárbaro S, Portocarrero R, Jaime S, Costa JL. Presence of pesticides in surface water from four sub-basins in Argentina. Chemosphere. 2014;**107**:423-431

[82] Etchegoyen M, Ronco A, Almada P, Abelando M, Marino D. Occurrence and fate of pesticides in the Argentine stretch of the Paraguay-Paraná basin. Environmental Monitoring and Assessment. 2017;**189**(2):63

[83] Laabs V, Amelung W, Pinto AA, Wantzen M, da Silva CJ, Zech W. Pesticides in surface water, sediment, and rainfall of the northeastern Pantanal basin, Brazil. Journal of Environmental Quality. 2002;**31**(5):1636-1648

[84] Rissato SR, Galhiane MS, Ximenes VF, de Andrade RMB, Talamoni JLB, Libânio M, et al. Organochlorine pesticides and polychlorinated biphenyls in soil and water samples in the Northeastern part of São Paulo state, Brazil. Chemosphere. 2006;**65**(11):1949-1958

[85] Montory M, Ferrer J, Rivera D, Villouta MV, Grimalt JO. First report on organochlorine pesticides in water in a highly productive agro-industrial basin of the Central Valley, Chile. Chemosphere. 2017;**174**:148-156

[86] Production/crops [Internet]. FAOSTAT. 2015 [cited 28-12-2015]. Available from: http://faostat3.fao.org/

[87] Food and Agriculture Organization (FAO) of the United Nations. FAO Statistical Yearbook 2012—Africa Food and Agriculture. Accra, Ghana: FAO; 2012

[88] van den Berg L, Braun E, van der Meer J. Portugal: Urban policies or policies with an urban incidence? In: Limited AP, editor. National Policy Responses to Urban Challenges in Europe. England: Ashgate Publishing, Ltd.; 2007

[89] Branco MC, França FH, Medeiros MA, Leal JGT. Uso de inseticidas para o controle da traça-do-tomateiro e traça-das-crucíferas: um estudo de caso. Horticultura Brasileira. 2001;**19**:60-63

[90] Hunt L, Bonetto C, Resh VH, Buss DF, Fanelli S, Marrochi N, et al. Insecticide concentrations in stream sediments of soy production regions of South America. Science of the Total Environment. 2016;**547**:114-124

[91] Köhler H-R, Triebskorn R. Wildlife ecotoxicology of pesticides: Can we track effects to the population level and beyond? Science. 2013;**341**(6147):759-765

[92] Cruzeiro C, Pardal MÂ, Rodrigues-Oliveira N, Castro LFC, Rocha E, Rocha MJ. Multi-matrix quantification and risk assessment of pesticides in the longest river of the Iberian peninsula. Science of the Total Environment. 2016;**572**:263-272

[93] Pawełczyk A. Assessment of health risk associated with persistent organic pollutants in water. Environmental Monitoring and Assessment. 2013;**185**(1):497-508

[94] Executive Body of the Convention. Guidance Document on Best Available Techniques for Reducing Emissions of POPs from Major Stationary Sources Adopted on 18 December 2009. UNECE, 2009

[95] United Nations. Protocol to the 1979 convention on long-range transboundary air pollution on persistence organic pollutants—Amendments to the text and to annexes I, II, III, IV, VI and VIII to the protocol. 2009 Contract No.: C.N.555.2010.TREATIES-3

[96] Gervais G, Brosillon S, Laplanche A, Helen C. Ultra-pressure liquid chromatography-electrospray tandem mass spectrometry for multiresidue determination of pesticides in water. Journal of Chromatography A. 2008;**1202**(2):163-172

[97] Palma P, Köck-Schulmeyer M, Alvarenga P, Ledo L, López de Alda M, Barceló D. Environmental Science and Pollution Research. 2015;**22**(10):7665-7675