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Pesticides in Worldwide Aquatic Systems: Part I

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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	ng/L			Reference
				av-min	av-max	av-av	
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),

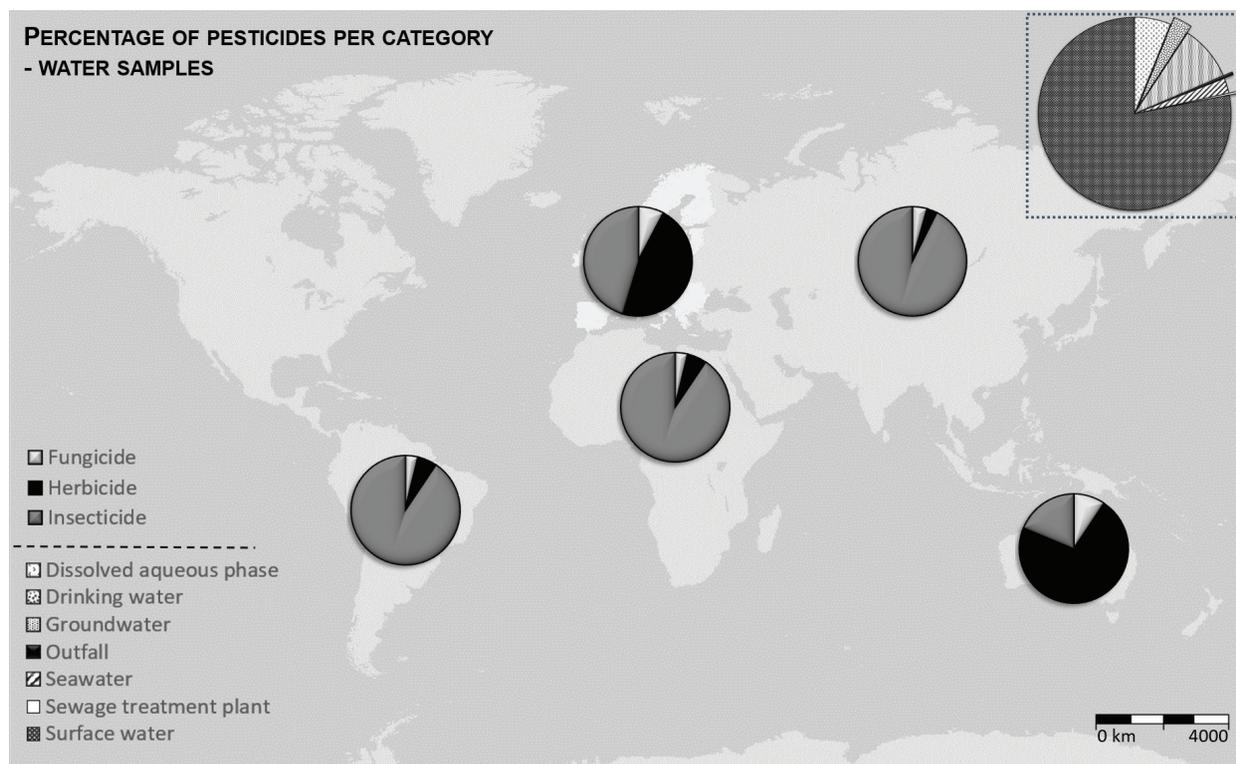


Figure 1. Representation of the quantified pesticides in water samples (%), per category, on each continent; the right upper corner figure represents the type of matrices found worldwide.

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, Σ DDT, Σ cyclodiene, chlorpyrifos, Σ endosulfan, Σ heptachlor + heptachlor epoxide, Σ HCH, and malathion were most frequent in Africa, Asia, Europe, and South America. Comparing the total average sum of these insecticides (Σ), 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 Σ ~7460 ng/L to Σ ~10,540 ng/L) among Africa, Asia, and Europe, confirming that high punctual concentrations occur in different continents. The high concentrations reported for chlorpyrifos (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 (Σ aldrin and dieldrin) were above the annual average concentrations (Σ ~5 ng/L) set by the same directive for all registered cases, presenting extremely high amounts in Portugal (Σ 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	
Σ Cyclodiene	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]
Σ Endosulfan	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]
<i>Endosulfan/Endosulfan sulfate</i>	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]
<i>Heptachlor/ heptachlor epoxide</i>	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 ($n \geq 10$). 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	PI	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
Terbutylazine	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

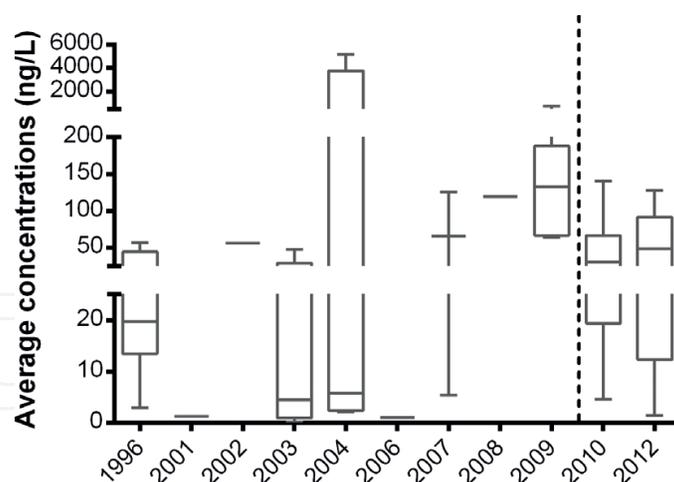


Figure 2. Representation of the priority listed pesticides average values (ng/L), quantified in water samples, collected in Europe, and displayed by sampling year (the dashed line separates the before and after the Stockholm Convention (2009)).

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.

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