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Pesticides in Worldwide Aquatic Systems: Part II

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<http://dx.doi.org/10.5772/intechopen.73117>

Abstract

Contamination by pesticides is a worldwide problem that can greatly disturb the biota, directly and/or indirectly. Nonetheless, few efforts were done so far to present review-style publications that analyse and integrate monitoring data—in a global scale—and evaluate possible environmental risks. Herein, we assessed possible environmental risks through theoretical calculations, using worldwide data published at least during the last 17 years and considering different trophic levels and the maximum average environmental concentrations (in water) observed in each continent. Furthermore, hazard quotients—using the estimated average daily intake, theoretical maximum daily intake and the maximum residue limits—were calculated to estimate the potential risks to humans through direct consumption of molluscs, crustaceans and fish. In summary, several pesticides were quantified at concentrations capable to affect low to medium trophic level species, which through the food web can affect higher trophic levels; theoretical approaches considering the environmental mixtures showed that algae and invertebrates are the most sensitive groups. Moreover, fish and crustaceans evidenced the highest body concentrations. To evaluate a potential risk through direct consumption, human health risk assessments were done, and in spite of no direct risk, some hazard quotients indicate a potential risk for developing carcinogenic effects.

Keywords: insecticides, herbicides, fungicides, aquatic organisms, EC₅₀, LC₅₀, PNEC, ADI, EADI, MRL, hazard quotients, mollusc, crustacean, bivalve, fish, bioaccumulation, biomagnification

1. Preamble

Worldwide, several studies have shown contamination with pesticides within different matrices. Together with the data shown previously in chapter “Pesticides in Worldwide Aquatic Systems: Part I”, information such as the maximum concentrations in waters and the concentration of pesticides found in the different biological matrices were used to (i) assess eventual individual pesticide risk through the comparison with the well-established EC_{50}/LC_{50} for aquatic organisms, (ii) predict the environmental risk from pesticide mixtures found in each continent and (iii) assess the potential risk for human health when consuming molluscs, crustaceans and fish with the quantified concentrations.

2. Aquatic organisms

Fifty-two studies were used, where 111 different species were studied. The continent with the highest percentage of available results (quantified pesticides in different organisms) is Africa (39 species), followed by Europe (35 species), Asia (26 species) and then North and South America (nine and eight species, respectively). Here, we decided to focus on the sample type (zooplankton, molluscs, crustaceans, fish and mammals) analysed per continent and country (**Table 1**).

Continent/ country	Number of aquatic systems	Quantified pesticides	Sampling year	Sample type	av-min	av-max	av-av	References
ng/g								
Africa								
Egypt	2	14	1993	C, F	1.1–6.3	7.6–8.2	4.1–130.2	[3]
Ethiopia	1	12	2011	F	4.1	27.2	17.1	[4]
Ghana	3	6–13	2004–2015	F	1.6–79.8	2.8–154.3	1.6–120.5	[4, 5]
Kenya	1	7	2011	F	na	na	0.3	[1, 6, 7]
Nigeria	5	1–65	2003–2014	F	19.5–3618	21.5–6355	20.6–5233	[1, 7–9]
Tunisia	1	14	2010	F	14.9	39.3	22.1	[10]
Asia								
China	5	7–45	2003–2013	F, Mo, C	0.6–2.5	1.8–34.5	0.8–11.8	[11–15]
India	1	3	na	Ma	na	na	74.5	[16]
Russia		8	2012–2013	F	18.1	52.1	31.7	[17]
South Korea	1	15	na	F	na	na	2.2	[18]
Tibet	1	55	2005	F	na	na	1.0	[19]
Europe								
Baltic Sea	1	18	2003	C, F, Mo	8.1	10.8	9.4	[20]
Belgium	1	5	2001	F, Mo	1.5	7.6	4.1	[21, 22]

Continent/ country	Number of aquatic systems	Quantified pesticides	Sampling year	Sample type	av-min	av-max	av-av	References
ng/g								
Croatia	1	8	2012	Mo	0	1.4	na	[23]
Finland	1	5	2002	F	1.8	4.5	3.1	[24]
France	6	2–12	2001–2008	F, Mo	0.2–0.8	0.6–4.4	0.3–1.2	[21, 25, 26]
Italy	3	5–22	2002–2010	C, F, Mo	0.9–6.9	2.8–21.6	1.5–10.9	[10, 27, 28]
Poland	1	22	2003–2004	F	na	na	0.3	[29]
Portugal	4	1–54	2011–2013	F, Mo	4.6–7.6	27.2–72.0	0.2–18.6	[30–33]
Romania	1	72	2001	F,Z	188.3	278.4	220.3	[2]
Spain	3	3–13	1996–2015	C, F, Mo	0.1–10.4	0.8–9.0	0.3–8.0	[34–37]
North America								
California	1	19	2001	F	1.5	25.2	7.2	[38]
Canada	1	43	1999–2000	F	0.7	2.5	1.5	[39]
Greenland	1	18	1994–1995	F, Mo	0.1	0.3	0.2	[40]
Martinique Island	1	3	2003–2013	C, F, Mo	0.3	876.4	55.9	[41]
Mexico	1	15	2012–2013	F	2.1	25.5	6.3	[42]
USA	3	3–9	2004–2013	F, Mo	na	na	0.1–11.1	[43–45]
South America								
Argentina	1	6	1999	Ma	7	34.6	15.2	[46]
Brazil	3	6–42	1996–2009	F, Mo, Ma	0.1–30.1	0.1–410.7	0.1–99.8	[47–50]

Z, zooplankton; C, crustaceans; Mo, molluscs; F, fish; Ma, mammals; na, not applicable

Table 1. Pesticide concentrations [average minimum (av-min), average maximum (av-max) and average of averages (av-av) values; ng/g] fresh weight to make it; ng/g of fresh weight in aquatic organisms, presented by continent and country; the number of quantified aquatic systems, pesticides and sampling year were also added (when more than one aquatic system, a range of values are presented).

The data collected between 1993 and 2016 averaged from 0.1 to 5233 ng/g (**Table 1**). Europe is represented by 22 aquatic systems, followed by Africa, with 13, and the rest with no more than nine aquatic systems. When considering the number of pesticides quantified, Africa has more observations (382) than Europe (327) and the other continents (between 90 and 220), which is due to the higher number of species studied in Africa.

Africa stands out with average concentrations of 132 ng/g (SD 411), followed by Europe (57 ng/g, SD 271), South America (17 ng/g, SD 40) and Asia and North America (5 ng/g, SD 20). This scattered difference between concentrations is mainly due to the average values observed in Warri River (Nigeria, Africa) and in the Danube Delta (Romania, Europe) [1, 2].

Grouping data by category, insecticides prevail in 89% of biologic analyses, leaving 11% for the herbicide and fungicide categories and presenting the same pattern on all continents (**Figure 1**).

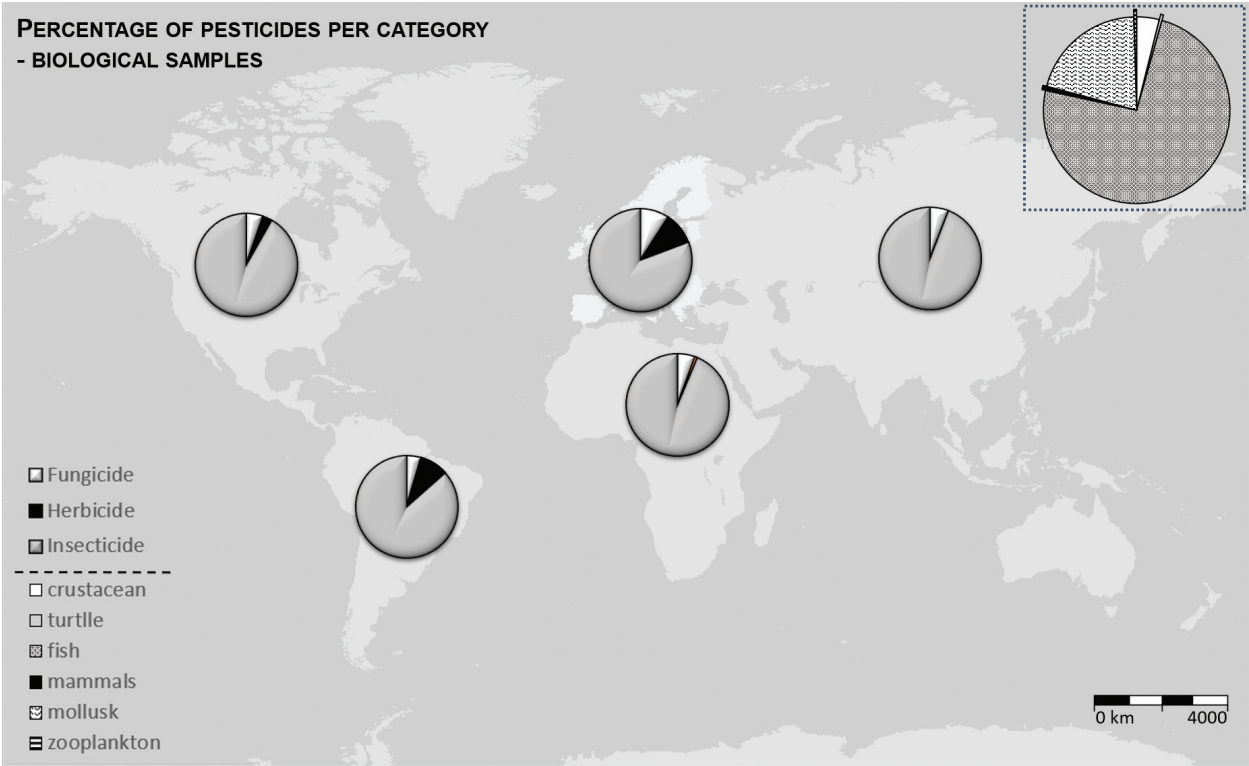


Figure 1. Representation of the quantified pesticides in organisms (%), per category, in each continent; the right upper corner pie chart represents the Metazoan lineages used worldwide.

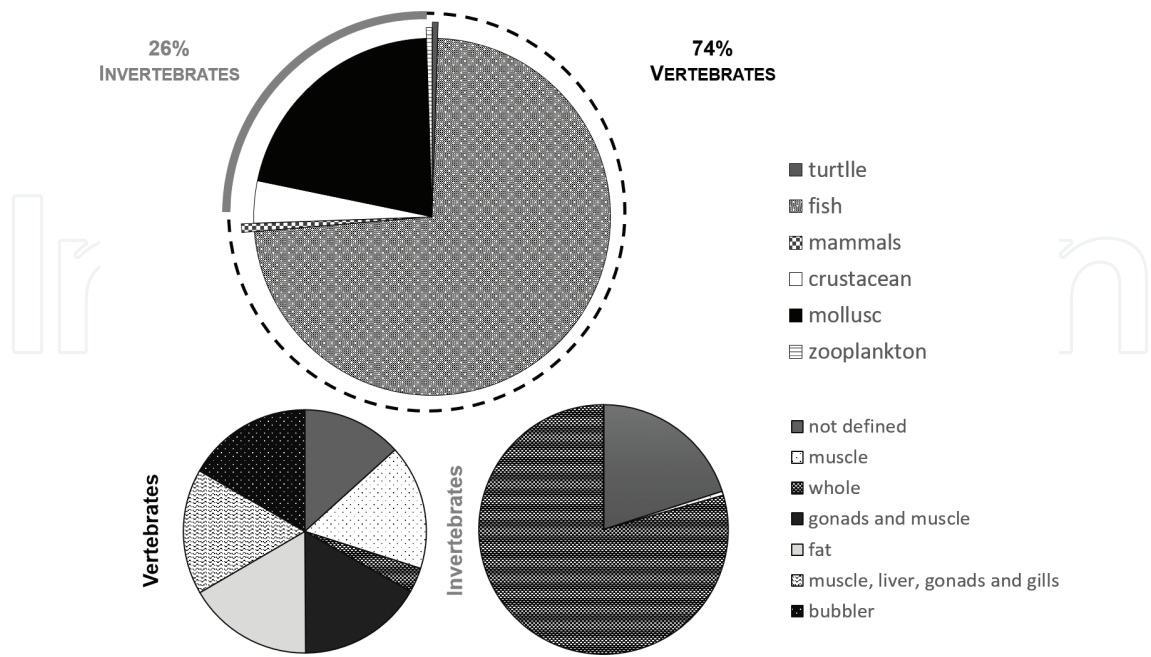


Figure 2. Representation of the quantified pesticides in organisms (%), per lineages of Metazoan, vertebrates and invertebrates and matrices.

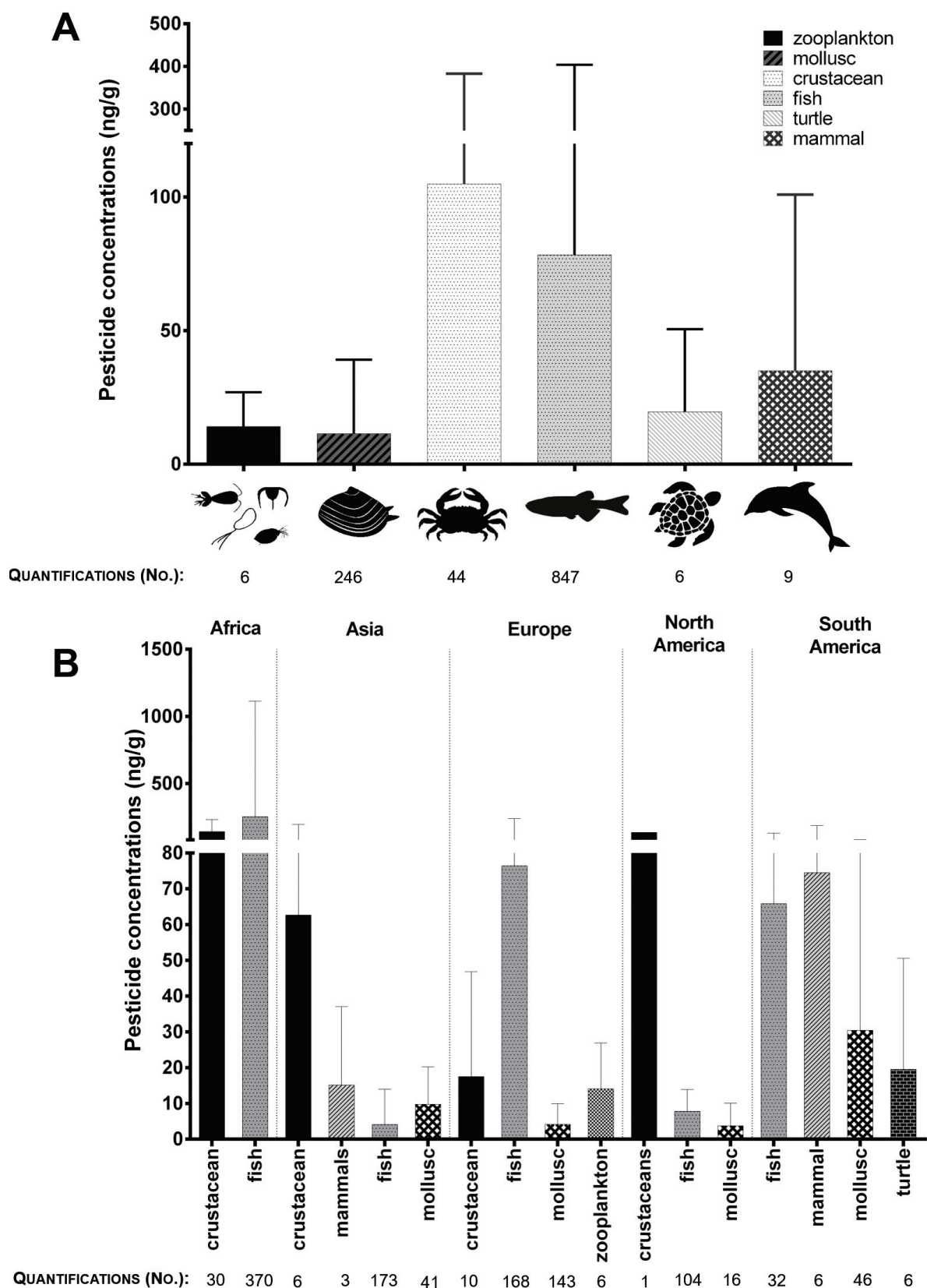


Figure 3. Average pesticide concentrations (ng/g fresh weigh) and number of quantifications per Metazoan lineage, worldwide (A) and by continent (B). The error bars represent standard deviations (SD).

No data are available for Oceania and Antarctica; so, when citing herein “worldwide”, these continents will not appear.

Analysing data by matrix, the most common analysis occurred in fish (74%) and molluscs (20%). The remaining studies considered zooplankton, crustaceans, turtles and mammals (**Figure 1**). In total, 74% of the quantified pesticides were conducted on vertebrates and the other 26% in invertebrates (**Figure 1**). While for the latter, 80% of the quantifications were done using the whole animal, and for vertebrates, it is further divided; specific organs or tissues were used to quantify pesticides.

Many factors account for the strong bias towards vertebrates. Invertebrates are small, less complex and as a food resource almost entirely eatable, while the same is not applicable to vertebrates. Besides that, the study goal (i.e., food control or environmental/toxicological studies) also influences the type of the tissue/organ to study (muscle, liver, gonads or gills). For example, the bubbler tissue and fat are only applicable for aquatic mammals and turtles (**Figure 2**).

Results per Metazoan lineages (zooplankton, mollusc, crustacean, fish, turtles and mammals) were assessed considering the average concentrations and the number of quantifications (**Figure 3**). Average concentrations were ~11 ng/g for zooplankton and molluscs, ~35 ng/g for mammals and ~100 ng/g for crustaceans and fishes (**Figure 3A**).

Among continents, Africa presented the highest concentrations for crustaceans (142 ng/g) and fishes (253 ng/g) followed by North America (136 ng/g for crustaceans). Asia, Europe and South America included data belonging to four Metazoan lineages, with similar range of concentrations (~3 to ~76 ng/g (**Figure 3B**)).

3. Half effective and lethal concentrations (EC_{50}/LC_{50}) for aquatic organisms

It is now well established that at specific concentrations all pesticides are harmful to biota, affecting algae and plants, invertebrates and vertebrates [51]. Databases such as Pesticides Properties DataBase (PPDB) present information on the physicochemical properties, environmental fate, human health and ecotoxicological data of all active ingredients and approved pesticides [52].

In order to evaluate the worst-case scenario, the maximum average concentrations measured in waters from each continent were compared against the acute and chronic concentrations for aquatic animals, documented by the PPDB (see chapter “Part I: Pesticides in Worldwide Aquatic Systems”). On a global scale, 57 pesticides were registered at maximum average concentrations above the LC_{50} and/or EC_{50} settled for algae, invertebrates and/or fishes; among continents, Europe reported the highest number of pesticides (44 of 116), followed by Asia (14 of 42), Africa, Oceania and finally South America (6 of 24).

The most critical measured environmental concentrations (MEC) were registered for dicofol, ethion (Asia), metribuzin (Europe) and diazinon (Africa) with values from 2- to 200-folds higher than EC_{50} or LC_{50} set for invertebrates and algae.

4. Predictive aquatic risk assessment of pesticide mixtures

Despite the common occurrence of pesticides, mixtures in the environment, laws, conventions and recommendations still focus on individual standard parameters. Modelling approaches, based on available ecotoxicological information, can be used to estimate the impact of mixtures in the biota, completing this lack of information [53].

Based on the European chemical legislation REACH, the ecological risk quotient (RQ) is determined by the equation:

$$RQ \left(\frac{MEC}{PNEC} \right) = \frac{\text{Measured Environmental Concentration (MEC; mg/L)}}{\text{Predicted No Effect Concentration (PNEC; mg/L)}}$$

PNEC is derived by selecting the most sensitive trophic level—from algae, invertebrate or fish—and applying an appropriate assessment factor (AF) [52, 54]. The AF, also denoted as safety or uncertainty factor, considers intra- and inter-laboratory variation of the data, biological variance and short-term to long-term exposures, presenting stipulated values for specific conditions [55, 56]; as an example, considering the Maximum Acceptable Concentration-Quality Standards (MAC-QS) to assess short-term effects an AF = 100 should be applied [55].

The RQ values, classified from <0.01 (negligible) to >1 (significant), indicate a range of potential risks for concern, but do not inform about the specific biological end point for that organism which is representing a specific trophic level [53, 57]. For this reason, a second approach, which defines the most sensitive trophic level for that environmental concentration, should be applied [53]:

$$RQ \text{ toxic units (TU)} = \frac{MEC \text{ (mg/L)}}{EC_{50} \text{ or } LC_{50} \text{ per each trophic level (mg/L)}}$$

RQ_{TU} values are summed per trophic level (sum of the toxic units (RQ_{STU})). If both $RQ_{(MEC/PNEC)}$ and RQ_{STU} are >1, additional considerations are required [53]. Based on the two reference models—concentration addition (CA) and independent action (IA)—the RQ_{STU}/Max_{TU} can be used to predict the second tier, resulting in the maximum value from which CA may display higher toxicity values than IA [58].

In this work, the maximum of the average measured concentration of pesticides in water samples was used to assess the potential risk per continent and on a worldwide scale (**Table 2**). From a total of 144 pesticides quantified in water samples, 133 were used for ecological risk assessment (**Table 2**); the remainders, mostly isomers and metabolites, were not integrated due to lack of information on their EC_{50} and LC_{50} concentrations set for these trophic levels (algae, invertebrate and fish). The highest number of pesticides suitable for this approach are represented by insecticides ($n = 118$). In general, algae was the most sensitive group to herbicides and fungicides, with 75% and 61.5% of the cases, respectively, while invertebrates showed the highest sensitivity to insecticides (66.1%) (**Table 2**).

Globally, the $RQ_{(MEC/PNEC)}$ resulted in 43% of very high-risk cases, led by insecticides; fungicides were the least worrisome category, as most of the cases presented low or negligible risks (**Figure 4**).

	Africa	Asia	Europe	Oceania	South America	PNEC	Algae	Invert	Fish
	mg/L					(mg/L)	%		
Herbicides									
Av.	5.7E-04	8.1E-05	7.8E-03	5.7E-04	2.3E-03	2.5E-06–2.0E+00	75.0	6.25	18.8
n	5	6	38	9	7				
Insecticides									
Av.	7.7E-04	2.2E-03	2.3E-03	1.4E-05	2.9E-04	1.7E-08–1.0E+00	8.5	25.4	66.1
n	19	28	49	7	15				
Fungicides									
Av.	8.5E-05	4.5E-04	2.6E-04	1.1E-05	3.9E-05	3.0E-05–4.6E-01	61.5	0.0	38.5
n	1	8	22	3	3				

Table 2. Ecological risk assessment through the PNEC, using the maximum average concentrations of pesticides in water (mg/L), quantified in each continent; here in this table only the average values/category (Av.), the total number of pesticides (n) observed per category and continent, and the range of PNEC values are presented; data based on **Table 1** of the chapter in this book *entitled* Pesticides in worldwide aquatic systems- Part I.

The results presented above are a consequence of the highest values measured around the world. Since Europe was the continent with more values of $RQ_{(MEC/PNEC)}$, these results are mostly representative for this continent (see **Table 1**). However, this does not mean that concentrations measured on the other continents are innocuous. As observed for the number of compounds analysed per continent, Africa presented the most disturbing scenarios (52%), followed by Asia and Europe (45%) and then Oceania and South America (24%) with $RQ > 1$ (**Figure 5**).

In order to evaluate the effect of the maximum average concentrations found per individual trophic level (RQ_{TU}), further evaluation should be done through RQ_{STU} (**Table 3**).

When comparing between continents, the highest RQ_{STU} ratios were attained in Europe, for algae (16.13) and fish (33.12), and in Asia for invertebrates (324.97); however, the last one is due to a punctual concentration observed in India for ethion [59]. Independently of that, the invertebrate group is the most sensitive trophic level, presenting the highest RQ_{STU} values. The same pattern is observed in the other continents except in Oceania, where the highest risk is observed for the algae (0.92) by the herbicides (**Table 3**).

The $RQ_{(MEC/PNEC)}$ and RQ_{STU} demonstrate that one or more biotest organisms are sensitive to the concentrations presented on that continent; so, the ratio $RQ_{STU}/\text{highest } RQ_{TU}$ was done, applying the highest sum among trophic levels (**Table 4**).

For each of these scenarios, the maximal possible ratio RQ_{STU}/RQ_{TU} was lower than the value given by the number of mixture of toxic components, suggesting that the possible observed toxicity is due to a low number of pesticides. As we can notice, the RQ_{STU}/RQ_{TU} ratio is very

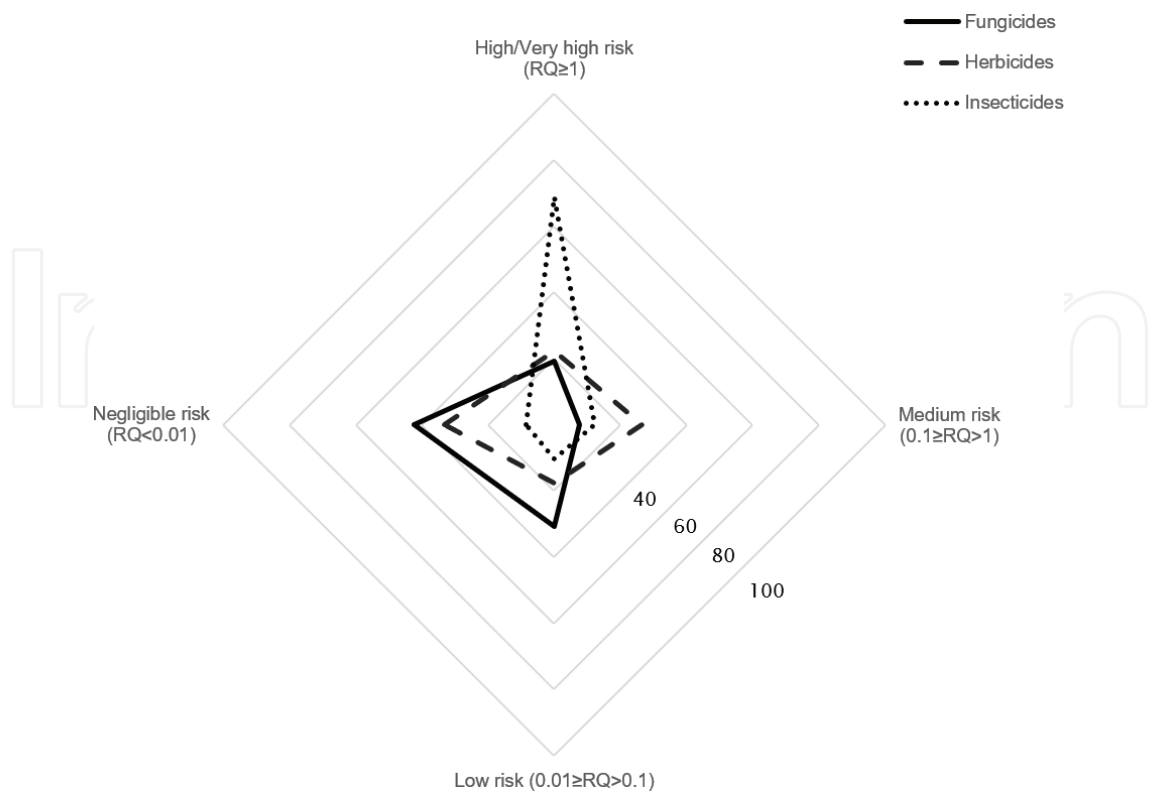


Figure 4. Distribution of pesticides per category (%), according to $RQ_{(MEC/PNEC)}$ ranking.

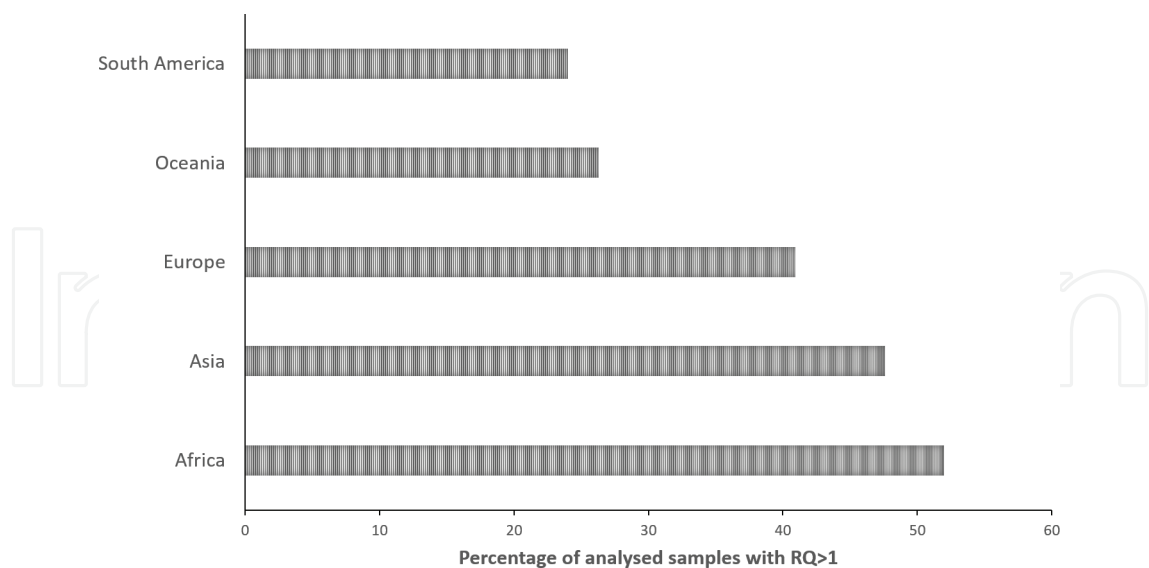


Figure 5. Percentage of $RQ_{(MEC/PNEC)}$ samples above 1, grouped by continent (total number of observations, $n = 25, 42, 110, 19, 25$ in Africa, Asia, Europe, Oceania, and South America, respectively).

	RQ _{STU}				
	Africa	Asia	Europe	Oceania	South America
Algae					
Fungicides	0.01	0.07	0.03	0.00	0.00
Herbicides	0.08	0.00	15.28	0.91	0.01
Insecticides	0.04	0.27	0.81	0.00	0.01
Total	0.13	0.34	16.13	0.92	0.02
Invertebrates					
Fungicides	0.00	0.06	0.02	0.00	0.00
Herbicides	0.57	2.91	0.19	0.00	0.02
Insecticides	8.65	322.0	18.84	0.01	3.94
Total	9.22	324.97	19.05	0.01	3.96
Fishes					
Fungicides	0.00	0.01	0.02	0.00	0.00
Herbicides	0.17	0.02	0.59	0.00	0.00
Insecticides	0.67	8.42	32.51	0.00	0.43
Total	0.84	8.45	33.12	0.00	0.43

Table 3. Sum of the toxic units per trophic level (RQ_{STU}) of each continent (with available data), organised by pesticide category; the most sensitive trophic level, per continent, is in bold.

Continent	No. of compounds (toxic/total)	RQ _{TU}	ΣRQ _{STU}		
			Algae	Invert	Fishes
Africa	13/25	Parathion methyl	8.05	9.22	1.15
Asia	10/21	Ethion	221.42	8.45	1.47
Europe	9/22	Deltamethrin	20.11	33.12	1.65
Oceania	5/19	Diuron	0.79		0.92
South America	6/25	Cypermethrin	2.47	3.96	1.61

Table 4. Second tier, using RQ_{STU} and the highest RQ_{TU} per trophic level and continent.

similar among continents; however, the number of toxic compounds per total, where Africa presents a significant number (52%) when compared to the others, should be also considered (**Table 4**).

5. Human health risks

Dietary pesticide risks can be estimated through well-established indices and defined and used by US Environmental Protection Agency (EPA) [60], European Food Safety Authority (EFSA)

and European Union Directives [61, 62]. Realistic predictions involve several parameters, such as pesticide residue intake (PRI), as the one reported by Food and Agriculture Organisation (FAO) [63]:

$$\text{PRI} = \text{Pesticide Concentration (mg/kg)} \times \text{Acceptable Consumption Rate (kg/capita/day)}$$

The acceptable daily intake (ADI) estimates the amount of a substance in food that can be ingested daily over a lifetime without appreciable health risk to the consumer [64]:

$$\text{ADI (mg/kg/day)} = \frac{\text{No observed Effect Level (NOEL)}}{\text{Safety Factor}}$$

The estimated average daily intake (EADI), according to EPA, should be less than the established ADI values [64]:

$$\text{EADI} \left(\frac{\text{mg bw}}{\text{kg day}} \right) = \frac{\text{PRI}}{\text{Standard Body Weight}}$$

The theoretical maximum daily intake (TMDI) represents the maximum concentration of a pesticide residue (mg/kg) legally permitted in food [64]:

$$\text{TMDI} = \text{Consumption Rate (kg/capita/day)} \times \text{Maximum Residue Limits (MRLs)}$$

When no specific MRL is published, a 0.01 mg/kg value is applied [8]. Additionally, hazard quotients (HQs)—which measure the potential exposure for developing non-carcinogenic health effects—may be calculated using several assumptions [65].

EADI may be divided by the acute reference dose (ARfD, mg/kg/day) [14]—which is derived from the no-observed-adverse-effect levels (NOAEL) and based on studies of short time exposures (1–7 days) [66], by ADI, for long intake periods, and by TMDI, which is advised by EFSA to calculate the potential risks of unintentional compounds, such as pollutants.

In the chapter Part I: Pesticides in Worldwide Aquatic Systems, the levels/categories of pesticides per continent/country are displayed. The maximum average concentrations shown in *Part I* were used here to assess human health risks. Data are summarised in **Table 5**.

Continent	Molluscs	Invertebrates	Fishes
Africa	—	1.6E + 00 (30)	5.2E + 00 (370)
Asia	3.2E-01 (41)	1.0E-02 (3)	9.0E-02 (173)
Europe	6.0E-02 (143)	1.4E-01 (10)	4.0E + 00 (168)
North America	1.0E-02 (16)	1.4E-01 (1)	3.0E-02 (104)
South America	1.8E-01 (46)	—	1.7E-01 (32)

Table 5. Average maximum concentrations (mg/kg) found per continent and by group of aquatic animals (mollusc, invertebrates and fishes) and the total number of cases used in each case (between brackets).

	Continent/pesticide	MEC	EADI	MRL	TMDI	ADI	ARfD	HQ			
								EADI/	EADI/	EADI/	EADI/
								MRL	TMDI	ADI	ARfD
Mollusc	Asia										
	HCH (gamma)	2.9E-03	2.9E-06	2.0E-02	1.1E-03	8.0E-03	3.0E-04	0	0.02	0.08	0
	HCH (sigma)	3.2E-01	3.1E-04	1.0E-02	5.7E-04	—	—	0.03	0.09	0.21	—
	Heptachlor epoxide	5.8E-04	5.8E-07	4.0E-03	2.3E-04	1.0E-04	—	0	0.07	0.08	—
	Methoxychlor	2.2E-03	2.2E-06	1.0E-02	5.7E-04	1.0E-01	5.0E-03	0	0.55	—	—
	Europe										
	Cyanazine	3.6E-02	3.6E-05	1.0E-02	5.8E-04	2.0E-03	—	0	0.04	0.09	—
	Endrin	1.8E-02	1.8E-05	5.0E-02	2.9E-03	2.0E-04	3.0E-04	0	0.06	0.14	—
	HCH (gamma)	7.7E-03	7.7E-06	2.0E-02	1.2E-03	8.0E-03	3.0E-04	0	0.05	0.16	0.01
	Parathion ethyl	9.2E-03	9.2E-06	5.0E-02	2.9E-03	6.0E-04	5.0E-03	0	0.1	0.06	0
	Phosmet	4.2E-02	4.1E-05	1.0E-01	5.8E-03	1.0E-02	4.5E-02	0	0.05	0.15	0
	Procymidone	1.5E-02	1.5E-05	1.0E-02	5.8E-04	2.8E-03	1.2E-02	0	0.06	0	0
	Propazine	1.4E-02	1.4E-05	1.0E-02	5.8E-04	2.0E-02	1.7E-02	0	0.06	0.02	—
	Propyzamide	1.2E-02	1.2E-05	1.0E-02	5.8E-04	2.0E-02	7.5E-02	0	0.07	0.01	0
	Simetryn	1.3E-02	1.2E-05	1.0E-02	5.8E-04	2.5E-02	—	0	0.08	0	0
	Terbutylazine	2.4E-02	2.4E-05	1.0E-02	5.8E-04	4.0E-03	8.0E-03	0	0.08	0	0
	Terbutryn	9.5E-03	9.5E-06	1.0E-02	5.8E-04	1.0E-01	1.0E-03	0	0.09	0.05	0.01
	Tetrachlorvinphos	4.5E-02	4.5E-05	1.0E-02	5.8E-04	5.0E-02	3.0E-02	0	0.11	—	0.01
	South America										
	Mirex	2.6E-05	8.3E-09	1.0E-02	2.5E-04	—	2.0E-04	0	0.53	0.54	—
	Pentachlorobenzene	8.3E-05	2.6E-08	1.0E-02	2.5E-04	1.7E-02	—	0	0.11	0.01	0.19

	Continent/pesticide	MEC	EADI	MRL	TMDI	ADI	ARfD	HQ			
								EADI/ MRL	EADI/ TMDI	EADI/ ADI	EADI/ ARfD
Crustacean	Africa										
	ΣDDD,DDE,DDT	2.5E+00	1.2E-03	1.0E+00	2.9E-02	5.0E-03	—	0	0.04	0.24	—
	Chlordane (alpha)	3.0E-02	1.5E-05	2.0E-03	5.9E-05	5.0E-04	—	0.01	0.25	0.03	—
	Chlordane (gamma)	5.5E-01	2.6E-04	1.0E-02	2.9E-04	5.0E-04	—	0.03	0.9	0.53	—
	Hexachlorobenzene	3.6E-02	1.7E-05	1.0E-02	2.9E-04	6.0E-04	8.0E-04	0	0.06	0.03	0.02
	Nonachlor (beta)	1.9E-02	9.2E-06	6.0E-03	1.8E-04	—	—	0	0.05	—	—
	North America										
	Chlordecone	1.4E-01	9.9E-05	1.0E-02	5.8E-04	—	—	0.01	0.17	—	—
Fish	Africa										
	ΣAldrin + dieldrin	1.2E+00	5.6E-04	6.0E-03	1.8E-04	1.0E-04	3.0E-03	0.09	3.19	5.62	0.19
	ΣDDD,DDE,DDT	3.5E+00	1.7E-03	1.0E+00	2.9E-02	5.0E-03	—	0	0.06	0.34	—
	Atrazine	6.3E-01	3.1E-04	1.0E-02	2.9E-04	2.0E-02	1.0E-01	0.03	1.04	0.02	0
	Carbofuran	2.2E-01	1.1E-04	2.0E-02	5.9E-04	1.5E-04	1.5E-04	0.01	0.18	0.71	0.71
	Chlordane (alpha)	1.8E-01	8.7E-05	2.0E-03	5.9E-05	5.0E-04	—	0.04	1.48	0.17	—
	Chlordane (gamma)	1.2E-01	5.8E-05	1.0E-02	2.9E-04	5.0E-04	—	0.01	0.2	0.12	—
	ΣEndosulfan	8.6E-01	4.2E-04	5.0E-02	1.5E-03	6.0E-03	2.0E-02	0.01	0.28	0.07	0.02
	Endrin	4.5E-01	2.2E-04	5.0E-02	1.5E-03	2.0E-04	3.0E-04	0	0.15	1.09	0.73
	Endrin aldehyde	3.3E+00	1.6E-03	1.0E-02	2.9E-04	2.0E-04	3.0E-04	0.16	5.37	7.89	5.26
	HCH (alpha)	1.9E+00	9.0E-04	2.0E-01	5.9E-03	—	—	0	0.15	—	—

Continent/pesticide	MEC	EADI	MRL	TMDI	ADI	ARfD	HQ			
							EADI/	EADI/	EADI/	EADI/
							MRL	TMDI	ADI	ARfD
HCH (beta)	2.3E+00	1.1E-03	1.0E-01	2.9E-03	—	—	0.01	0.39	—	—
HCH (gamma)	6.6E-01	3.2E-04	2.0E-02	5.9E-04	8.0E-03	3.0E-04	0.02	0.54	0.04	1.07
Heptachlor	7.4E-01	3.6E-04	4.0E-03	1.2E-04	1.0E-04	—	0.09	3.05	3.58	—
Heptachlor epoxide	2.5E-01	1.2E-04	4.0E-03	1.2E-04	1.0E-04	—	0.03	1.03	1.21	—
Hexachlorobenzene	5.4E-01	2.6E-04	1.0E-02	2.9E-04	6.0E-04	8.0E-04	0.03	0.89	0.44	0.33
Nonachlor (beta)	5.2E-02	2.5E-05	6.0E-03	1.8E-04	—	—	0	0.14	—	—
Paraquat dichloride	5.2E+00	2.5E-03	1.0E-02	2.9E-04	4.0E-03	4.0E-04	0.25	8.62	0.63	6.34
Europe										
∑Aldrin + dieldrin	1.0E-02	1.0E-05	6.0E-03	3.5E-04	1.0E-04	3.0E-03	0	0.03	0.1	0
∑DDD,DDE,DDT	5.5E+00	5.5E-03	1.0E+00	5.8E-02	5.0E-03	—	0.01	0.1	1.11	—
HCH (gamma)	6.0E-02	6.0E-05	2.0E-02	1.2E-03	8.0E-03	3.0E-04	0	0.05	0.01	0.2
Hexachlorobenzene	5.7E-02	5.7E-05	1.0E-02	5.8E-04	6.0E-04	8.0E-04	0.01	0.1	0.09	0.07
North America										
Chlordane	9.6E-03	6.9E-06	2.0E-03	1.2E-04	5.0E-04	—	0	0.06	0.01	—
Chlordane (alpha)	1.0E-02	7.2E-06	2.0E-03	1.2E-04	5.0E-04	—	0	0.06	0.01	—
Endrin	1.6E-02	1.2E-05	5.0E-02	2.9E-03	2.0E-04	3.0E-04	0	0	0.06	0.04
Heptachlor	7.7E-03	5.6E-06	4.0E-03	2.3E-04	1.0E-04	—	0	0.02	0.06	—
South America										
∑Aldrin + dieldrin	1.5E-01	4.7E-05	6.0E-03	1.5E-04	1.0E-04	3.0E-03	0.01	0.31	0.47	0.02

Continent/pesticide	MEC	EADI	MRL	TMDI	ADI	ARfD	HQ			
							EADI/	EADI/	EADI/	EADI/
							MRL	TMDI	ADI	ARfD
Endrin aldehyde	5.2E-02	1.6E-05	1.0E-02	2.5E-04	2.0E-04	3.0E-04	0	0.06	0.08	0.05
HCH (gamma)	1.6E-01	5.1E-05	2.0E-02	5.1E-04	8.0E-03	3.0E-04	0	0.1	0.01	0.17
Heptachlor	3.3E-02	1.1E-05	4.0E-03	1.0E-04	1.0E-04	—	0	0.1	0.11	—
Heptachlor epoxide	1.8E-02	5.7E-06	4.0E-03	1.0E-04	1.0E-04	—	0	0.06	0.06	—

MEC, measured environmental concentration (mg/kg); **EADI**, estimated average daily intake (mg/kg bw); **MRL**, maximum residue limit (mg/kg); **TMDI**, theoretical maximum daily intake (mg); **ADI**, acceptable daily intake (mg/kg bw/d); **ARfD**, acute reference dose (mg/kg bw/day); **fish and seafood consumption** (kg/capita/day): 0.0294 (Africa), 0.05705 (Asia), 0.05765 (Europe), 0.05833 (North America), 0.02548 (South America); **body weight** (kg): 60.7 (Africa), 57.7 (Asia), 70.8 (Europe), 80.7 (North America) and 67.9 (South America).

Table 6. Human health hazard, associated with mollusc, crustaceans and fish consumption, displayed by continent and pesticide.

The highest concentrations were observed in fish from Africa (5.2 mg/kg) and Europe (4.0 mg/kg), followed then by crustaceans in Africa (1.6 mg/kg). The highest number of cases (number of quantifications found considering all the pesticides, species and countries) was registered for fish (169 average cases), followed by molluscs (62 average cases), and finally crustaceans (11 average cases). The elevated number of fish studies is likely due to their importance as a food source.

For allowing a detailed evaluation of human health hazard, the same data is displayed by pesticide and continent and organised considering molluscs, crustaceans and fishes (**Table 6**). The food consumption rate and the average adult body weight were defined by continent [63, 64]. For the compounds endrin ketone and aldehyde, HCH (sigma and lambda), pretilachlor and pentachlorobenzene, a MRL of 0.01 mg/kg was adopted, since no specific data was found.

Focusing on the molluscs results, the MEC of 15, 52, 10 and 16 pesticides (from Asia, Europe, North America and South America, respectively) were used to calculate the HQs. Due to the low ratio values, only cases with at least one ratio value above 0.05 were presented. As we can see, none of the results proved to be harmful to human through direct consumption. In other words, none of the ratios were above 1, indicating that the calculated EADI was below the reference levels (MRL, TMDI, ADI and ARfD). The highest $HQ_{(EADI/TMDI)}$ was obtained for methoxychlor in Asia (0.55). For $HQ_{(EADI/ADI)}$, the highest ratio occurred in South America for mirex with 0.54.

Looking to the crustacean data, a total MEC of eight, two, three and one cases from Africa, Asia, Europe, North America, respectively, were analysed. The same criterion, which is the case with at least one ratio value above 0.05, was applied. High HQs for chlordane (gamma) were observed in crustaceans sampled in Africa (see **Table 6**). In spite of that, none of the ratios were above 1.

Twenty-four (Africa), 16 (Asia), 10 (Europe), 28 (North America) and 21 (South America) MEC cases were analysed considering the fish data. Once again, only HQ ratios with at least one case above 0.05 are shown. As we can see, none of the maximum average concentrations were above the MRL values; however, several $HQ > 1$ are observed in Africa, bringing potential exposure for developing carcinogenic health effects. This fact may be a result of bioaccumulation processes (where concentrations increase in higher trophic levels) and/or a higher interest in this matrix (increasing the data availability and diversity). These ratios were registered for six compounds— Σ aldrin + dieldrin, endrin aldehyde, paraquat dichloride, endrin, heptachlor and heptachlor epoxide—where the most preoccupant cases ($HQ > 3$) are for the first three pesticides cited above.

6. Final considerations

Globally, and because of these high average concentrations, several individual pesticides were quantified at levels exceeding the established LC_{50} for fish and EC_{50} for invertebrates and algae.

In addition, the review has provided clear evidence that the biological data grouped according to Metazoan lineages reached higher concentrations for fish and crustaceans (**Figure 3**). It is worth noting however that the same pattern was not verified for higher trophic levels including turtles and aquatic mammals which may be due to the lack of samples. Considering that globally, many of the data displayed a wide range of concentrations, coupled with the fact that many of the larger aquatic species are migratory; there is a need to address the pesticide problem from a global perspective.

As a complement to this work, all edible species were evaluated for dietary pesticide risks, as mollusc, crustaceans and fish. No direct human health risk was observed; however, in Africa, some hazard quotients (HQ) were above one, indicating a potential exposure for developing carcinogenic health effects.

In conclusion, the potentially harmful effects of pesticides should be considered not only locally (national/governmental institutions) but also on a global scale.

Acknowledgements

This study was 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 and project PTDC/MAR/70436/2006 (FCOMP-01-0124-FEDER-7382) and 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; Reference 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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References

- [1] 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
- [2] Covaci A, Gheorghe A, Hulea O, Schepens P. Levels and distribution of organochlorine pesticides, polychlorinated biphenyls and polybrominated diphenyl ethers in sediments and biota from the Danube Delta, Romania. *Environmental Pollution*. 2006;**140**(1):136-149
- [3] 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
- [4] Norli HR, Christiansen A, Deribe E. Application of QuEChERS method for extraction of selected persistent organic pollutants in fish tissue and analysis by gas chromatography mass spectrometry. *Journal of Chromatography A*. 2011;**1218**(41):7234-7241
- [5] Akoto O, Andoh H, Darko G, Eshun K, Osei-Fosu P. Health risk assessment of pesticides residue in maize and cowpea from Ejura, Ghana. *Chemosphere*. 2013;**92**
- [6] Omwenga I, Kanja L, Nguta J, Mbaria J, Irungu P, Ng CA. Organochlorine pesticide residues in farmed fish in Machakos and Kiambu counties, Kenya. *Cogent environmental. Science*. 2016;**2**(1):1153215
- [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 physics. 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] Yehouenou A, Pazou E, Lalèyè P, Boko M, van Gestel CAM, Ahissou H, Akpona S, et al. Contamination of fish by organochlorine pesticide residues in the Ouémé River catchment in the republic of Bénin. *Environment International*. 2006;**32**(5):594-599
- [10] Ameer WB, Trabelsi S, El Megdiche Y, Ben Hassine S, Barhoumi B, Hammami B, et al. Concentration of polychlorinated biphenyls and organochlorine pesticides in mullet (*Mugil cephalus*) and sea bass (*Dicentrarchus labrax*) from Bizerte lagoon (northern Tunisia). *Chemosphere*. 2012;**90**(9):2372-2380
- [11] 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
- [12] Jin MQ, Zhou SS, Liu WP, Zhang D, Lu XT. Residues and potential health risks of DDTs and HCHs in commercial seafoods from two coastal cities near Yangtze River estuary. *Journal of Environmental Science and Health, Part B*. 2015;**50**(3):163-174

- [13] Jiang QT, Lee TKM, Chen K, Wong HL, Zheng JS, Giesy JP, et al. Human health risk assessment of organochlorines associated with fish consumption in a coastal city in China. *Environmental Pollution*. 2005;**136**(1):155-165
- [14] Zhao Z, Zhang L, Wu J, Fan C. Distribution and bioaccumulation of organochlorine pesticides in surface sediments and benthic organisms from Taihu Lake, China. *Chemosphere*. 2009;**77**(9):1191-1198
- [15] Yang Y, Liu M, Xu S, Hou L, Ou D, Liu H, et al. HCHs and DDTs in sediment-dwelling animals from the Yangtze estuary, China. *Chemosphere*. 2006;**62**(3):381-389
- [16] Adeleye AO, Jin H, Di Y, Li D, Chen J, Ye Y. Distribution and ecological risk of organic pollutants in the sediments and seafood of Yangtze estuary and Hangzhou Bay, East China Sea. *Science of The Total Environment*. 2016;**541**:1540-1548
- [17] Tsygankov VY, Lukyanova ON, Khristoforova NK. The sea of Okhotsk and the Bering Sea as the region of natural aquaculture: Organochlorine pesticides in Pacific salmon. *Marine Pollution Bulletin*. 2016;**113**(1–2):69-74
- [18] Choi M, Lee I-S, Jung R-H. Rapid determination of organochlorine pesticides in fish using selective pressurized liquid extraction and gas chromatography–mass spectrometry. *Food Chemistry*. 2016;**205**:1-8
- [19] Yang R, Yao T, Xu B, Jiang G, Xin X. Accumulation features of organochlorine pesticides and heavy metals in fish from high mountain lakes and Lhasa River in the Tibetan plateau. *Environment International*. 2007;**33**(2):151-156
- [20] Galassi S, Bettinetti R, Neri MC, Jeannot R, Dagnac T, Bristeau S, et al. A multispecies approach for monitoring persistent toxic substances in the Gulf of Gdańsk (Baltic sea). *Ecotoxicology and Environmental Safety*. 2008;**69**(1):39-48
- [21] Schnitzler JG, Thomé JP, Lepage M, Das K. Organochlorine pesticides, polychlorinated biphenyls and trace elements in wild European sea bass (*Dicentrarchus labrax*) off European estuaries. *Science of the Total Environment*. 2011;**409**(19):3680-3686
- [22] Wille K. Analytical Approaches for Quantification of Emerging Micropollutants in the Belgian Coastal Zone Gent: Gent University; 2011
- [23] Milun V, Lušić J, Despalatović M. Polychlorinated biphenyls, organochlorine pesticides and trace metals in cultured and harvested bivalves from the eastern Adriatic coast (Croatia). *Chemosphere*. 2016;**153**:18-27
- [24] Pikkarainen A-L. Polychlorinated biphenyls and organochlorine pesticides in Baltic Sea sediments and bivalves. *Chemosphere*. 2007;**68**(1):17-24
- [25] Thomas M, Lazardtignes A, Banas D, Brun-Bellut J, Feidt C. Organochlorine pesticides and polychlorinated biphenyls in sediments and fish from freshwater cultured fish ponds in different agricultural contexts in north-eastern France. *Ecotoxicology and Environmental Safety*. 2012;**77**(0):35-44

- [26] Luna-Acosta A, Budzinski H, Le Menach K, Thomas-Guyon H, Bustamante P. Persistent organic pollutants in a marine bivalve on the Marennes-Oléron Bay and the Gironde estuary (French Atlantic Coast)—Part 1: Bioaccumulation. *Science of The Total Environment*. 2015;**514**:500-510
- [27] Ferrante MC, Clausi MT, Meli R, Fusco G, Naccari C, Lucisano A. Polychlorinated biphenyls and organochlorine pesticides in European eel (*Anguilla anguilla*) from the Garigliano River (Campania region, Italy). *Chemosphere*. 2010;**78**(6):709-716
- [28] Perugini M, Cavaliere M, Giammarino A, Mazzone P, Olivieri V, Amorena M. Levels of polychlorinated biphenyls and organochlorine pesticides in some edible marine organisms from the central Adriatic Sea. *Chemosphere*. 2004;**57**(5):391-400
- [29] 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
- [30] 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
- [31] 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
- [32] Grilo TF, Cardoso PG, Pato P, Duarte AC, Pardal MA. Organochlorine accumulation on a highly consumed bivalve (*Scrobicularia plana*) and its main implications for human health. *Science of The Total Environment*. 2013;**461–462**:188-197
- [33] Cruzeiro C, Rodrigues-Oliveira N, Velhote S, Pardal MÂ, Rocha E, Rocha MJ. Development and application of a QuEChERS-based extraction method for the analysis of 55 pesticides in the bivalve *Scrobicularia plana* by GC-MS/MS. *Analytical and Bionalytical Chemistry*. 2016;**408**:3681-3698
- [34] 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
- [35] Rodríguez-Hernández Á, Camacho M, Henríquez-Hernández LA, Boada LD, Valerón PF, Zaccaroni A, et al. Comparative study of the intake of toxic persistent and semi persistent pollutants through the consumption of fish and seafood from two modes of production (wild-caught and farmed). *Science of The Total Environment*. 2017;**575**:919-931
- [36] Sánchez-Avila J, Fernandez-Sanjuan M, Vicente J, Lacorte S. Development of a multi-residue method for the determination of organic micropollutants in water, sediment and mussels using gas chromatography–tandem mass spectrometry. *Journal of Chromatography A*. 2011;**1218**(38):6799-6811
- [37] Suárez P, Ruiz Y, Alonso A, San Juan F. Organochlorine compounds in mussels cultured in the Ría of Vigo: Accumulation and origin. *Chemosphere*. 2013;**90**(1):7-19

- [38] Sapozhnikova Y, Bawardi O, Schlenk D. Pesticides and PCBs in sediments and fish from the Salton Sea, California, USA. *Chemosphere*. 2004;**55**(6):797-809
- [39] Easton MDL, Luszniak D, Von der Geest E. Preliminary examination of contaminant loadings in farmed salmon, wild salmon and commercial salmon feed. *Chemosphere*. 2002;**46**(7):1053-1074
- [40] Cleemann M, Riget F, Paulsen GB, Klungsøyr J, Dietz R. Organochlorines in Greenland marine fish, mussels and sediments. *Science of the Total Environment*. 2000;**245**(1-3):87-102
- [41] Dromard CR, Bodiguel X, Lemoine S, Bouchon-Navaro Y, Reynal L, Thouard E, et al. Assessment of the contamination of marine fauna by chlordecone in Guadeloupe and Martinique (lesser Antilles). *Environmental Science and Pollution Research*. 2016;**23**(1): 73-80
- [42] Granados-Galván IA, Rodríguez-Meza DG, Luna-González A, González-Ocampo HA. Human health risk assessment of pesticide residues in snappers (*Lutjanus*) fish from the Navachiste lagoon complex, Mexico. *Marine Pollution Bulletin*. 2015;**97**(1-2):178-187
- [43] Nilsen EB, Hapke WB, McIlraith B, Markovchick D. Reconnaissance of contaminants in larval Pacific lamprey (*Entosphenus tridentatus*) tissues and habitats in the Columbia River basin, Oregon and Washington, USA. *Environmental Pollution*. 2015;**201**:121-130
- [44] Granek EF, Conn KE, Nilsen EB, Pillsbury L, Strecker AL, Rumrill SS, et al. Spatial and temporal variability of contaminants within estuarine sediments and native Olympia oysters: A contrast between a developed and an undeveloped estuary. *Science of The Total Environment*. 2016;**557-558**:869-879
- [45] Blocksom KA, Walters DM, Jicha TM, Lazorchak JM, Angradi TR, Bolgrien DW. Persistent organic pollutants in fish tissue in the mid-continental great rivers of the United States. *Science of The Total Environment*. 2010;**408**(5):1180-1189
- [46] Durante CA, Neto EBS, Azevedo A, Crespo EA, Lailson-Brito JPOP. In the south Latin America: Bioaccumulation of DDT, PCB, HCB, HCH and Mirex in blubber of common dolphin (*Delphinus delphis*) and Fraser's dolphin (*Lagenodelphis hosei*) from Argentina. *Science of the Total Environment*. 2016;**572**:352-360
- [47] Sánchez-Sarmiento AM, Rossi S, Vilca FZ, Thijl Vanstreels RE, Monteiro SH, Vale LAS, et al. Organochlorine pesticides in green sea turtles (*Chelonia mydas*) with and without fibropapillomatosis caught at three feeding areas off Brazil. *Journal of the Marine Biological Association of the United Kingdom*. 2016;**97**(1):215-223
- [48] DMLd S, PBd C, Martinelli LA, Lanças FM, Pinto JS, Avelar WEP. Organochlorine pesticides in Piracicaba River basin (São Paulo/Brazil): A survey of sediment, bivalve and fish. *Química Nova*. 2008;**31**(2):214-219
- [49] Miranda AL, Roche H, Randi MAF, Menezes ML, Ribeiro CAO. Bioaccumulation of chlorinated pesticides and PCBs in the tropical freshwater fish *Hoplias Malabaricus*: Histopathological, physiological, and immunological findings. *Environment International*. 2008;**34**(7):939-949

- [50] Galvao P, Henkelmann B, Longo R, Lailson-Brito J, Torres JPM, Schramm K-W, et al. Distinct bioaccumulation profile of pesticides and dioxin-like compounds by mollusk bivalves reared in polluted and unpolluted tropical bays: Consumption risk and seasonal effect. *Food Chemistry*. 2012;**134**(4):2040-2048
- [51] Köhler H-R, Triebkorn R. Wildlife ecotoxicology of pesticides: Can we track effects to the population level and beyond? *Science*. 2013;**341**(6147):759-765
- [52] The Pesticide Properties DataBase (PPDB) developed by the Agriculture & Environment Research Unit (AERU) [Internet]. funded by UK national sources and through EU-funded projects. 2013 [cited 22-01-2013]. Available from: <http://sitem.herts.ac.uk/aeru/footprint/index2.htm>
- [53] Backhaus T, Faust M. Predictive environmental risk assessment of chemical mixtures: a conceptual framework. *Environmental Science & Technology*. 2012;**46**(5):2564-2573
- [54] Compound summary-toxicity [Internet]. U.S. National Library of Medicine. 2015. Available from: <https://pubchem.ncbi.nlm.nih.gov/>
- [55] Proposal for a directive of the European parliament and of the council amending directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy (2012)
- [56] Malkiewicz K, Hansson SO, Rudén C. Assessment factors for extrapolation from short-time to chronic exposure—Are the REACH guidelines adequate? *Toxicology Letters*. 2009;**190**(1):16-22
- [57] Sánchez-Bayo F, Baskaran S, Kennedy IR. Ecological relative risk (EcoRR): Another approach for risk assessment of pesticides in agriculture. *Agriculture, Ecosystems & Environment*. 2002;**91**(1-3):37-57
- [58] Silva E, Cerejeira M. Concentration addition-based approach for aquatic risk assessment of realistic pesticide mixtures in Portuguese river basins. *Environmental Science and Pollution Research*. 2014:1-10
- [59] 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
- [60] US Environmental Protection Agency (EPA). Guidelines for Ecological Risk Assessment. Washington, US: EPA; 1998
- [61] Directive 2008/105/EC of the European parliament and of the council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing council directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending directive 2000/60/EC of the European parliament and of the council, L 348/34, 2008

- [62] European Food Safety Authority (EFSA). Scientific report of EFSA- The 2011 European Union report on pesticide residues in food. Parma, Italy: Journal 2014; 2014. p. 511
- [63] Food balance/food supply - livestock and fish primary equivalent [Internet]. FAO. 2015 [cited 3–11-2015]. Available from: <http://faostat3.fao.org/>
- [64] Regulation (EC) N 396/2005 of the European Parliament and of the Council of 23 February 2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin and amending Council Directive 91/414/EEC, 2005
- [65] Herrman JL, Younes M. Background to the ADI/TDI/PTWI. *Regulatory Toxicology and Pharmacology*. 1999;**30**(2):S109-SS13
- [66] Walpole SC, Prieto-Merino D, Edwards P, Cleland J, Stevens G, Roberts I. The weight of nations: An estimation of adult human biomass. *BMC Public Health*. 2012;**12**(1):1-6

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