Pesticides in Worldwide Aquatic Systems: Part I

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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 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 (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 |
|-------------------|--------------------------|-----------------------|---------------|--------|--------|-------|-----------|
| 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     | na    | [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] |

**Reference**

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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),

| Continent/country | Number of aquatic systems | Quantified pesticides | Sampling year | av-min | av-max | av-av | Reference |
|-------------------|--------------------------|-----------------------|---------------|--------|--------|-------|-----------|
| 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 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 Directive | References |
|-------------------|------------------------|-----------------|-----------------------------------|------------|
| 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 \( \sim 38 \text{ ng/L} \)) and lower amounts in Asia (\( \sim 4 \text{ ng/L} \)) 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 (\( \sim 1200 \text{ ng/L} \)), when compared to the other continents (\( \sim 200 \text{ ng/L} \)). Among insecticides, \( \Sigma \text{DDT}, \Sigma \text{cyclodiene}, \text{chlorpyriphos}, \Sigma \text{endosulfan}, \Sigma \text{heptachlor + heptachlor epoxide}, \Sigma \text{HCH}, \) and malathion were most frequent in Africa, Asia, Europe, and South America. Comparing the total average sum of these insecticides (\( \Sigma \)), Asia had the highest concentrations (\( \sim 10,000 \text{ ng/L} \)), followed by Africa (\( \sim 3000 \text{ ng/L} \)), Europe (\( \sim 1800 \text{ ng/L} \)), and finally, South America (\( \sim 300 \text{ ng/L} \)). 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 (\( \Sigma \sim 7460 \text{ ng/L} \)) to (\( \Sigma \sim 10,540 \text{ ng/L} \)) 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 \( \text{LC}_{50} \) and/or \( \text{EC}_{50} \) 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 \textit{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 cycloidiene pesticides (\( \Sigma \text{aldrin and dieldrin} \)) were above the annual average concentrations (\( \Sigma \sim 5 \text{ ng/L} \)) set by the same directive for all registered cases, presenting extremely high amounts in Portugal (\( \Sigma \text{cyclodienes} \sim 2174 \text{ ng/L} \)), 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 \( \text{LC}_{50} \) and/or \( \text{EC}_{50} \) 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] |
| Pesticide                  | 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     |               | [4, 7, 8, 10, 12–14, 16, 17, 19, 20, 25, 26, 32, 41, 48, 50, 51, 53, 55, 56, 68, 85] |
| Aldrin                   | 251.3                  | 16.6   | 392.1| 1.5    |         |               | [4, 7, 8, 10, 12, 19, 20, 25–27, 30, 41, 48, 50, 51, 57, 68, 76, 81] |
| 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   |         |               | [6, 8, 11, 12, 16, 19, 25–27, 32, 41, 50, 53, 55–57, 59, 64, 83–85] |
| 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    |         |               | [24, 40, 45, 47, 50, 53, 55–57, 63, 67] |
| Fenitrothion             | 77.5                   |        |      |        |         |               |                                      |
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.

| Average amounts (ng/L) | Africa | Asia | Europe | Oceania | South America | References |
|------------------------|--------|------|--------|---------|---------------|------------|
| ΣHCH                   | 1135   | 4768 | 136.1  | 41.1    |                | [2, 8, 10, 12–17, 19–23, 26, 27, 41, 48, 58, 71, 84, 85] |
| HCH α                  | 85.1   | 756.2| 24.7   |         | 8.3           | [2, 4, 10, 12–17, 19–21, 23, 26, 27, 41, 48, 58, 61, 85] |
| HCH β                  | 91.5   | 1335 | 39.1   |         | 21.0          | [4, 14, 17, 19–21, 26, 85] |
| HCH δ                  | 669.0  | 2299 | 4.5    |         |               | [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] |
| 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     |               | [1, 2, 4, 8, 10, 12, 14, 16, 17, 19, 20, 23, 26, 41, 48, 53, 55–57, 59, 85] |
| Heptachlor             | 150.6  | 24.1 | 17.7   | 0.9     |               | [8, 13, 14, 16, 17, 19, 20, 26, 41, 48, 50, 53, 57, 68, 85] |
| Heptachlor epoxide     | 430.0  | 7.0  | 16.8   | 0.7     |               | [6, 18, 40, 43, 45, 49, 50, 53, 56, 57, 63, 67, 72, 83, 92] |
| Heptachlor/ heptachlor epoxide | 0.4   | 3.4  | 1.1    | 1.2     |               | [4, 12–14, 16, 19, 35, 47, 50, 53, 56, 57] |
| Malathion              | 100.0  | 360.0| 102.7  | 42.0    |               | [4, 12–14, 16, 19, 35, 47, 50, 53, 56, 57] |
| 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.
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

| 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| 3.0–180.5 |
| 4,4′-DDD         | 84.0|      |      | 7.5 | 11.0 | 1.0  | 7.6 | 1.0 | 84.0 | 1.0–84.0 |
| 4,4′-DDE         | 30.8|      |      | 0.0 | 19.7 | 1.0  | 3.6 | 1.0 | 30.8 | 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 | 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 |
| Diethoate        | 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
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.
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