

The presence of organochlorinated pesticides in the marine environment of the Mediterranean Sea: A Systematic Review

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Abstract Plant protection products, also known as pesticides, are chemical compounds that are used for the protection of plants against pests, weeds and diseases which affect the quantity and quality of agricultural products. The present study is a systematic review of the scientific literature regarding the scientific research on the presence of residual organochlorinated plant protection products (OCPs) concentrations in the Mediterranean Sea, which is an important semi-enclosed marine ecosystem of great biodiversity. Based on the gathered information derived from the collected and classified articles, useful conclusions, and observations are reported about research trends. Furthermore, knowledge gaps in the current research are highlighted and suggestions for future research on this topic are also discussed.

Keywords: Pesticide, organochlorine compounds, Mediterranean, organic micropollutants, persistent organic pollutants

1. Introduction

Organochlorinated plant protection products are synthetic compounds of “First Generation Pesticides” which have been banned by the relevant legislation in developed Mediterranean countries in the 1970s and 1980s due to their unique characteristics and physicochemical properties, such as lipophilicity, acute and chronic toxicity, environmental persistence, and their ability to bioaccumulate in biological tissues.

Their introduction into the environment takes place mainly through agricultural applications, and surface runoffs, whereas their deposition from the atmosphere is also an important and alternative pathway. After entering the environmental matrices, they go under slow chemical, (direct/indirect) photochemical, or biological degradation processes that are possible to take place simultaneously with other physical phenomena that determine their removal and distribution into different environmental substrates, such as adsorption, evaporation, and surface movement.

When OCPs compounds are released into the environment they can reach aquatic bodies and consequently affect the exposed aquatic organisms of flora and fauna and result in reversible or/and non-reversible disorders.

Despite the prohibition of their application, a fact that has occurred several decades ago, the presence of their residues into marine ecosystems is still monitored and reported nowadays [Carro et al., 2021; Combi et al., 2020; Necibi et al., 2020; Salvadó et al., 2019; Bajt et al., 2019; Darilmaz et al., 2019; El-Naggar et al., 2019; León et al., 2019; Milun et al., 2016]. According to the published scientific literature, the occurrence and distribution of those persistent organic pollutants in the sea is a subject on which the interest of the global scientific community is focused undiminished since the effects of their extended use are evident even today. Therefore, the aim of the present study is to carry out a systematic review concerning the scientific articles published until 31/12/2019, regarding the research of the presence of residual quantities of OCPs in the marine environment of the Mediterranean Sea.

2. Methods and materials

The systemic approach was conducted after the identification of the relevant published scientific articles by using Scopus Search (abstract and citation database). The current search was focused only on peer-reviewed journal articles that were published between January 1970 to 31 December 2019. The selection of studies was made by using the combination of terms summarized in Table 1 to specify the location (geographical limitation of Mediterranean Sea), target analytes, and type of published study. As illustrated in Table 1, the search provided a total of 1066 articles. It is important to mention that only documents which were available in English were included in this analysis. After the elimination of duplicates, and triplicates (580 articles) 486 unique entries remained in the database. Afterwards, based on review of the abstract 254 of the 486 documents were excluded due to their lack of relevance concerning either: (i) OCPs residues in terrestrial sampling areas, (ii) organochlorine compounds

not belonging in the group of pesticides, or (iii) marine environment samples originating from other geographical locations. After the inclusion of 24 additional articles that were found to be relevant with the objective of the present review and were not included in Scopus Database (either PubMed, or Google Scholar), 256 scientific articles were identified for final inclusion. Based on the full article review these articles were summarized using the following information: author (date), location of the study, type of sample, organochlorine pesticide(s) analyzed, other chemical contaminants simultaneously analyzed and primary conclusions.

Table 1. Combination of terms and keywords used for the collection of relevant data in Scopus Database

Combination of terms/keywords	Number of found documents
"Mediterranean" AND "organochlorine" AND "pesticides"	165
"Mediterranean" AND "organochlorine" AND "contamination"	100
"Mediterranean" AND "organochlorine" AND "pollution"	185
"Mediterranean" AND "organochlorine" AND "biomonitoring"	17
"Mediterranean" AND "organochlorine" AND "monitoring"	160
"Mediterranean" AND "pesticide" AND "monitoring"	250
"Mediterranean" AND "pesticide" AND "contamination"	189
TOTAL	1066

3. Results and conclusions

Overall, 256 selected articles that met the criteria of the bibliographic research were included in the present systemic review and provided relevant information for assessing the occurrence of OCPs in the marine environment of the Mediterranean Sea. Based on reported information, residual levels of these pollutants have been detected and quantified into a wide variety of matrices such as sea water, sediment, and biologic tissues substrates.

The 256 studies were afterwards grouped into three categories based on the type of the environmental sample that was collected and used for the qualitative and quantitative analytical determination of OCPs. Therefore, through the classification, 3 main databases were created that refer to water, sediment, and marine organisms' samples. In addition, the remaining articles (n=23), which did not correspond to any of the above categories fed a fourth category entitled "various" and contained either: (i) methodology, meta-analysis and review articles (n=9), (ii) air samples analysis (n=5), (iii) marine (micro)plastic debris analysis (n=4), (iv) ecotoxicity evaluation studies (n=2), and (v) studies that could not be included in the 3 main categories (n=3).

It is worth noting that many processed articles belonged to more than one category, since measurements were conducted to different marine substrates of natural marine samples (for examples water and sediment, sediments, and marine biota, etc).

According to the findings of the current review the first scientific document concerning the assessment of the occurrence of OCPs in the marine environment of Mediterranean Sea was published in 1970. Only a small number of reports (n=18) were published until 1993 (Figure 1). After 1993, an increase in the number of publications over the years was observed, that demonstrated the increased scientific interest in studying the presence and residual action of OCPs in the marine ecosystem of the Mediterranean.

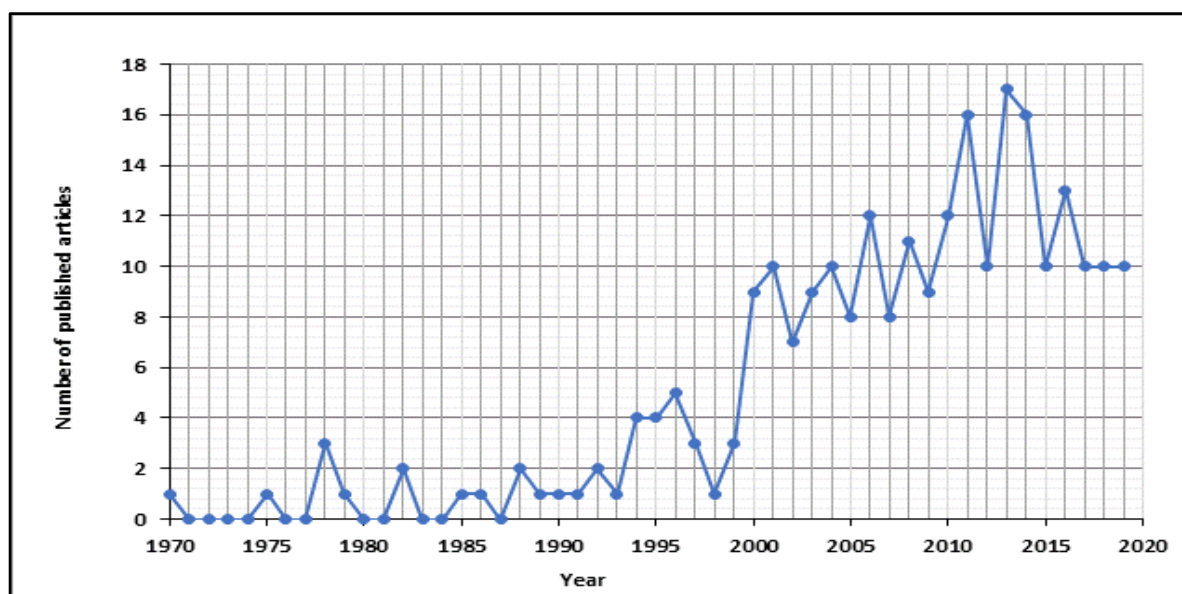


Figure 1. Number of published data vs year of publication

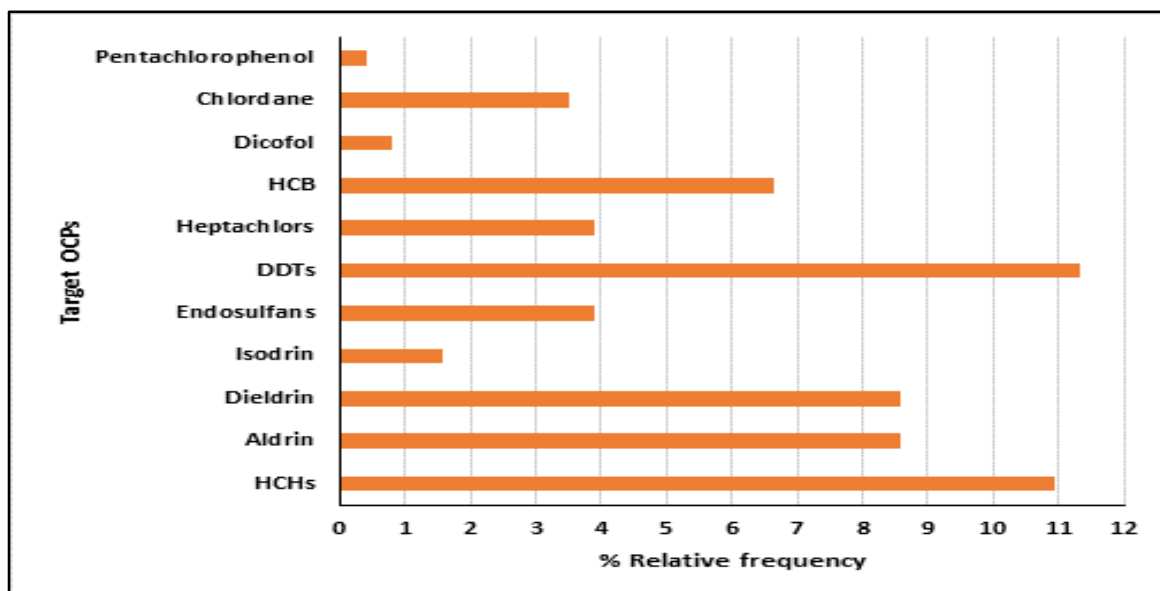


Figure 2. % Relative frequency of detection for each individual target OCPs

Overall, based on the affiliation of the first author of the selected articles it was shown that the majority of studies were conducted in Italy (n=68, 27%), followed by Spain (n=52, 20%), Greece (n=28, 11%) and Turkey (n=25, 10%), whereas a number of Mediterranean countries such as Egypt, France, Croatia, Tunisia, Germany, Israel, Portugal and several others are included with less publications (Data not shown).

Furthermore, the obtained results of present review highlighted the research trend to study the concentrations of OCPs contained in marine organisms' tissues more than in sea water or marine sediments. Hence, the global scientific interest is unquestionably focused on the analysis of marine biota samples such as fish (edible or not), cephalopods, mussels, mammals, etc) [Carro et al., 2019, Panseri et al., 2019]. Finally, it was shown that during the five decades of research HCHs (isomers of α -, β -, γ - or lindane, and δ -HCHs) are the most frequently detected organochlorine pesticides, followed by DDTs, Aldrin, Dieldrin and HCB (Figure 2).

However, and despite the extent research that has already been conducted, there is a consequent need for further monitoring to evaluate their spatial-temporal occurrence, assess dynamics, and predict the fate and distribution of those persistent toxicants in marine ecosystems. Moreover, the assessment of the chemical contamination of those vulnerable aquatic environments due to OCPs could be performed by using sensitive marine organisms as biomarkers, such as mussels.

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