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Comparative study of organic contaminants in agricultural soils at the archipelagos of the Macaronesia☆

Andrea Acosta-Dacal [a,1], María Eugenia Hernández-Marrero [a,1], Cristian Rial-Berriel [a,1], Ricardo Díaz-Díaz [c], María del Mar Bernal-Suárez [c], Manuel Zumbado [a,b], Luis Alberto Henríquez-Hernández [a,b], Luis D. Boada [a,b], Octavio P. Luzardo [a,b,*]

[a] Toxicology Unit, Research Institute of Biomedical and Health Sciences (IUIBS), Universidad de Las Palmas de Gran Canaria, Paseo Blas Cabrera s/n, 35016, Las Palmas de Gran Canaria, Spain

[b] Spanish Biomedical Research Center in Physiopathology of Obesity and Nutrition (CIBERObn), 28029, Madrid, Spain

[c] Department of Environmental Analysis, Technological Institute of the Canary Islands, C/ Los Cactus no 68 35118, Polígono Industrial de Arinaga, Agüimes, Las Palmas, Canary Islands, Spain

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ABSTRACT

The occurrence of organic pollutants in soil is a major environmental concern. These compounds can reach the soil in different ways. Point sources, related to pesticides that are used intentionally, can be applied directly to the soil, or reach the soil indirectly due to application to the aerial parts of crops. On the other hand, non-point sources, which reach soils collaterally during irrigation and/or fertilization, or due to the proximity of plots to industrialized urban centers. Long-range transport of global organic pollutants must also be taken into account. In this study, 218 pesticides, 49 persistent organic pollutants, 37 pharmaceutical active compounds and 6 anticoagulant rodenticides were analyzed in 139 agricultural soil samples collected between 2018 and 2020 in the Macaronesia. This region comprised four inhabited archipelagos (Azores, Canary Islands, Cape Verde, and Madeira) for which agriculture is an important and traditional economic activity. To our knowledge, this is the first study on the levels of organic compound contamination of agricultural soils of the Macaronesia. As expected, the most frequently detected compounds were pesticides, mainly fungicides and insecticides. The Canary Islands presented the highest number of residues, with particularly high concentrations of DDT metabolites (p,p' DDE: 149.5 ± 473.4 ng g^{-1}; p,p' DDD: 16.6 ± 35.6 ng g^{-1}) and of the recently used pesticide fenbutatin oxide (302.1 ± 589.7 ng g^{-1}). Cape Verde was the archipelago with the least contaminated soils. Very few pharmaceutical active compounds have been detected in all archipelagos (eprinomectin, fenbendazole, oxfendazole and sulfadiazine). These results highlight the need to promote soil monitoring programs and to establish maximum residue limits in soils, which currently do not exist at either continental or local level.

1. Introduction

Macaronesia is a group of biogeographically related oceanic archipelagos located in the northeastern of the Atlantic Ocean between latitudes 15 and 39 °N (Sjö;gren, 2000). This region comprised four inhabited archipelagos: Azores, Madeira (both Portugal), the Canary Islands (Spain), and Cape Verde (Fig. 1). These islands share their volcanic origin, high zoological and botanical diversity, and mild and temperate climates throughout the year, so that tourism has become one of the main economic activities in the region, especially in the Canary Islands and Madeira (Dorta Antequera, 2020). Politically, three of these archipelagos (Azores, Madeira, and Canarias) are considered outermost regions of the European Union, while Cape Verde is a sovereign island nation. In any case, their oceanic location influences the connections, the supply of goods and services, and the economy. As a consequence, in all these archipelagos there is an important agricultural and livestock sector dedicated to self-consumption (Corral et al., 2017; Macedo et al., 2016; Santana-Cordero et al., 2017; Virgílio Cruz et al., 2013), although

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* Corresponding author. Toxicology Unit, Clinical Sciences Department, Universidad de Las Palmas de Gran Canaria, Paseo Blas Cabrera Felipe s/n, 35016, Las Palmas, Spain.

[1] These authors contributed equally to the work, and therefore should be considered indistinctly as first authors.

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there is also agricultural production for export.

These islands have a diversity of warm climates (ranging from sunny coastal deserts to cool, humid cloud forests) that allow the cultivation of a wide variety of fruits and vegetables, including tropical crops. In addition, their complicated orography makes the use of machinery and extensive agriculture difficult. In the Canary Islands, export agriculture is mainly focused on the cultivation of tomatoes and bananas grown in greenhouses, but also tropical fruits such as avocado, mango, papaya, and pineapple. Proximity agriculture (dedicated to local consumption) is in the midlands of the islands and is characterized by the coexistence of different types of crops throughout the year. The most popular crops are potatoes and sweet potatoes, figs and the exotic yam (the tuber of *Colocasia esculenta*). Agriculture in Cape Verde is hampered by its more arid climate and the occurrence of droughts. Even so, it is the main livelihood for many families. The main agricultural activity in this archipelago is gardening for home consumption, but extensive agriculture is also present and typical crops are sugar cane, bananas, or mango (Monteiro et al., 2020). Madeira's agriculture is based on the use of terraces and the use of irrigation based on the gigantic "levada" system. The types of crops vary according to altitude: at the first level are Mediterranean fruits and cereals (figs, oranges, lemons and grapes, corn, wheat, rye or barley), in the valleys grow European fruit trees (cherries, apples and plums), and at higher altitudes, tropical species (banana, sugar cane, custard apple, mango and passion fruit). In the Azores, the main crop is green maize which is used for livestock feed purposes, followed by sugar beets, potatoes and vineyards (Ragonnaud, 2015).

The Utilized Agricultural Area (UAA) of the Canary Islands is 10% of its total territory, 6.8% in Madeira, 11.2% in Cape Verde while more than half the territory of the Azores is dedicated to agricultural products (The European Network for Rural Development, 2015). However, 88% of the Azores' agriculture territory is permanent meadows and pasture used for extensive livestock farming and only 10% of the total UAA is dedicated to crops, of which 8% is maize to feed livestock and the rest is permanent crops (Ragonnaud, 2015). Thus, the Canary Islands have the largest crop area although the loss of soil and labor loss in favor of the tertiary sector. Of this, only 15% of the crops are dedicated to organic farming (MAPAMA, 2018). In fact, the Canary Islands is the Spanish region with the highest consumption of phytosanitary products, and one of those with the highest consumption of pesticides, also at the European level (Alonso González et al., 2021; Ministerio para la Transición Ecológica y el Reto Demográfico, 2016). This is probably due to the fact that agricultural land is fragmented into very small plots where several crops coexist throughout the year: vines, potatoes, fruit trees, vegetables, each with its own load of phytosanitary treatments, which are added together on the same plot of land. This coexistence of several crops on the same plot of land means that the soil of the plot is exposed to a significant load of residues of phytosanitary products, both in variety (different residues) and in quantity. Pesticides can enter soils during the aerial and ground application to crops, where they can be retained by soil materials through adsorption/desorption processes and/or be degraded (Kumari et al., 2008). In fact, parent compounds and metabolites can reach other environmental compartments by leaching, runoff and volatilization (Silva et al., 2019).

In addition to the environmental fate of commonly used pesticides, obsolete organochlorine pesticides (OCPs) are of particular interest because of their persistence and intensive use in the past. In the case of the Canary Islands, their use coincided with the more prosperous period of export agriculture in this archipelago. Before its prohibition in the 1970, DDT was used intensively in the greenhouses of extensive agriculture in these islands (Zumbado et al., 2005). As for Macaronesia, it is also interesting to note that the use of these pesticides ceased in Cape Verde much more recently than in European countries, at the end of the 2000s. OCPs belong to the well-known group of Persistent Organic Pollutants (POPs), which constitutes a large group of compounds and metabolites with high toxicity, resistance to degradation, and potential to bioaccumulate and magnify in trophic systems, properties for which they have been banned or heavily regulated (UNEP, 2004; Weber et al., 2019). These compounds could have reach the soil during their application in the past, or more recently by travelling long distances from other areas. In addition to OCPs, other POPs may reach the soil like polybrominated diphenyl ethers (PBDEs), and polychlorinated biphenyls (PCBs) used in industrial applications in the past, and polycyclic aromatic hydrocarbons (PAHs), which are by-products emitted during the incomplete combustion of organic materials, especially in anthropogenic activities (Abdel-Shafy and Mansour, 2015; Breivik et al., 2004). Due to the industrial and urban origin of these compounds, proximity to urban centers and roads is the main cause of their occurrence in the soil but they can also travel from distant areas.

On the other hand, the use of manure to fertilize the soil is a frequent practice in these regions (Cruz et al., 2015). In livestock farming, veterinary drugs are commonly used to treat or prevent diseases (Margalida et al., 2014). Once administered, pharmaceutical active compounds (PhACs) can be excreted in urine or feces (Díaz-Cruz and Barceló, 2005). Thus, they can end up in the soil in fertilization processes, be absorbed by the crops and cause antibiotic resistance through continuous exposure (Kaczala and E. Blum, 2015; Kim et al., 2011). PhACs are considered Compounds of Emerging Concern (CECs), a category that also includes some anticoagulant rodenticides (ARs) used for rodent pest control in sewage, cereal farming systems, or even as human pharmaceuticals for blood hypercoagulability disorders (Singer et al., 2009;

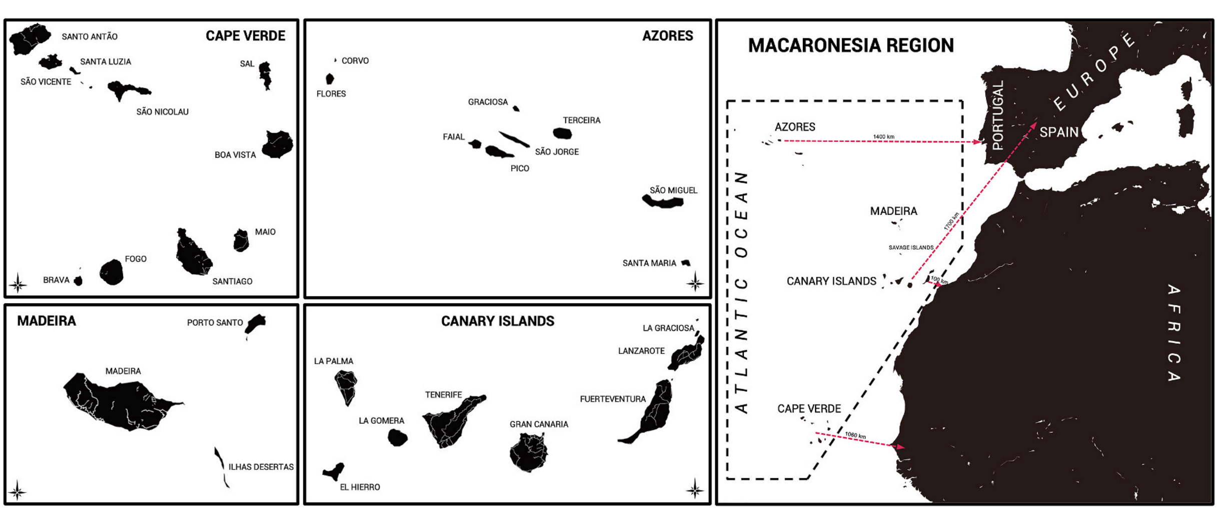

Fig. 1. Geographical location of the four inhabited archipelagos of Macaronesia.

Watt et al., 2005). ARs can reach wastewater treatment plants (WWTPs) through runoff after agricultural and livestock farming applications, solubilization of baits in urban infrastructures, or through urinary excretion from medical treatments, which is also the case of PhACs (Gómez-Canela et al., 2014; Gómez-Canela and Lacorte, 2016). If WWTPs do not have adequate tertiary treatments, some of these compounds can reach the soils through irrigation with reclaimed water, especially in regions with severe water scarcity such as the Macaronesian archipelagos (Cuthbert et al., 2014; Delgado et al., 2012) or even with the fertilization with sewage sludge, where ARs are more likely to remain due to their moderate to high octanol/water partition coefficient (K_{OW}) (André et al., 2005; Gómez-Canela et al., 2014).

It is evident from the above that the load of compounds in the soils of this region, dedicated in part to agriculture and livestock, is potentially high. Therefore, the establishment of soil monitoring programs is of utmost importance. Although some programs include recommendations for soil samples at the national level in EU countries (European Commission, 2004), there is no legislation on maximum residue limits (MRLs) in soils for pesticides or other organic compounds, except for some values for no longer approved and highly persistent and obsolete pesticides in Europe (Commission, 2010) and Spain (Presidency, 2005).

There are very few studies on pesticide residues (Acosta-Dacal et al., 2021a, 2021b; Škrbić and Đurišić-Mladenović, 2007) and other organic compounds (Acosta-Dacal et al., 2021c; Rodríguez-Ramos et al., 2019) in soils of the Canary Islands and, to our knowledge, none in the other three archipelagos. Therefore, the aim of this research was to determine the load of toxic chemicals in agricultural soils of the four inhabited archipelagos of Macaronesia. For this purpose, farms in the Canary Islands, Azores, Madeira, and Cape Verde were sampled between 2018 and 2020. Organic compounds including 218 pesticides in current or recent use, 49 POPs (18 PCBs, 12 OCPs, 11 PAHs and 8 PBDEs), and 43 CECs (6 ARs and 37 PhACs) were analyzed in these samples by validated multi-residue QuEChERS-based methods (Acosta-Dacal et al., 2021a, 2021c; 2021b; 2021d). Then, the data obtained were compared among the four archipelagos.

2. Material and methods

2.1. Analyte selection

A total of 310 chemical substances were investigated, belonging to three main groups. The first group consisted of 218 pesticides in current or recent use, selected from those included in the European Union's multiannual plan for the investigation of residues in food of plant or animal origin during the years 2020, 2021 and 2022 (Commission, 2019), but also other pesticides of environmental relevance used in this region until relatively recent times (Ruiz-Suárez et al., 2015). The second group included 49 POPs (18 PCBs, 12 OCPs, 11 PAHs and 8 PBDEs), which are traditionally detected in soils. Finally, a group of 43 CECs was also analyzed, including the most frequently detected ARs in environmental studies (Rial-Berriel et al., 2021), as well as a group of PhACs selected among the most frequent veterinary drugs used in livestock production. The complete list of compounds analyzed can be found as part of the supplementary material in Table S1.

2.2. Sample collection and location

Between 2018 and 2020, a total of 139 soil samples were collected in the four inhabited archipelagos of Macaronesia (Fig. 1). First, 65 samples were obtained in the Canary Islands. This archipelago is composed of eight inhabited islands, located south of 30°N, off the African coast and 1700 km from the Iberian Peninsula. It has a surface area of 7442 km^2 and a population of 2,153,389 inhabitants, mainly distributed between Gran Canaria and Tenerife, which are also the more industrialized islands. Samples were collected from different plots on seven of the islands: Lanzarote, Fuerteventura, Gran Canaria, Tenerife, La Palma, La Gomera y El Hierro. Thirty samples were taken in the Azores, located south 40°N, about 1400 km west of Lisbon. This archipelago is constituted by nine islands divided into three groups (eastern, central, and western) with a surface area of 2322 km^2 and 242,846 inhabitants. Sampling was concentrated in the island of Terceira, which is, together with São Miguel, the island with more agricultural activity (Ragonnaud, 2015). Twenty samples were obtained from Madeira, which is located north 30°N and 960 km from Lisbon and constituted by two main islands (Madeira and Porto Santo) and two groups of uninhabited islands (the Desertas and Selvagens islands). It has a population of 253,945 inhabitants and a surface area of 828 km^2. Samples were collected in both Madeira and Porto Santo. Finally, other 24 samples were obtained from Cape Verde, which is an African sovereign island state located south 20°N and off the coast of the mainland. It consists of 10 major and 5 minor islands separated into Barlovento and Sotavento with an area of 4033 km^2 and a population of 553,000 inhabitants. All the samples from Cape Verde were collected from the Ihla do Santiago, which is the one with more agricultural development of the archipelago (Lehotay et al., 2007) (Lehotay et al., 2007).

In each plot, at least four soil subsamples were collected at a depth of between 20 and 30 cm. The subsamples were then mixed to form a composite. Once in the laboratory, they were homogenized, air-dried at room temperature (approximately 25 °C), and sieved at 2 mm mesh prior to analysis.

2.3. Reagents, chemicals and analytical procedure

Certified stock solutions of most of the pesticides and POPs were acquired from CPA Chem (Stara Zagora, Bulgaria). Individual certified standards of ARs, PhACs and additional pesticides (purity in the range 95.2%–99.9%) were acquired from Dr. Ehrenstorfer (Augsburg, Germany), Sigma-Aldrich (Augsburg, Germany) and European Pharmacopoeia Reference Standards (Strasbourg, France). Isotopically labelled compounds (Atrazine-d5, Carbendazim-d3, Chlorpyrifos-d10, Cyromazine-d4, Diazinon-d10, Linuron-d3, Pirimicarb-d6) and PCB 200 used as procedural internal standards (P-IS) were obtained from Dr. Ehrenstorfer and Sigma-Aldrich, (99.3%–99.9% purity).

LC-MS grade methanol (MeOH), acetonitrile (ACN), acetone (Ac) and formic acid (FA, HCOOH) were purchased from Honeywell (Morristown, NJ, USA). Ammonium acetate ($NH_4CH_3CO_2$) was purchased from Fisher Scientific (Loughborough, UK). QuEChERS salts from the AOAC method (Lehotay et al., 2007) (6 g of $MgSO_4$ and 1.5 g of CH_3COONa) were purchased in commercial premixes from Agilent Technologies (Palo Alto, USA). Ultrapure water was produced in the laboratory using a Gradient A10 Milli-Q System (Millipore, Bedfore, MA, USA).

All analyses were performed using a GC System 7890B equipped with a 7693 Autosampler and Triple Quad 7010 mass spectrometer, and a 1290 Infinity II LC System coupled to a Triple Quad 6460 mass spectrometer (both from Agilent Technologies, Palo Alto, USA). All the details of the instrumental procedure and validation of the method for the quantitative determination of 218 pesticides, 7 ARs, 36 PhACs and 49 POPs in agricultural soil of different characteristics have been previously published (Acosta-Dacal et al., 2020, 2021a–d).

2.4. Statistical analysis

All statistical analyses were performed with Prism v.9.2.0 (GraphPad Software, San Diego, CA, USA). The distribution of the variables was evaluated using the Kolmogorov-Smirnov test. As expected, the data series included in this study did not follow a normal distribution and, consequently, comparisons among and between archipelagos were performed using non-parametric tests: Kruskal–Wallis test or Mann–Whitney *U* test for general and pair-wise comparisons, respectively. For statistical analyses, concentrations below the LOQ but above the LOD were assigned a random value between these two limits. Data below LOD were considered non-detected. A p-value of less than 0.05 (two-tailed) was considered statistically significant.

3. Results and discussion

In this study, 139 soil samples from farms of the Azores (30), Canary Islands (65), Cape Verde (24), and Madeira (20) were analyzed. In 100% of the plots analyzed at least 1 residue was detected and in one of them up to 77 different analytes detected above the LOD were found. In the total series a total of 2031 residues were detected, corresponding to 132 different analytes (mean = 14.61 residues per sample), which means that 42.6% of the investigated compounds were detected. Fig. 2 shows a summary of all the results obtained for the three large groups, and immediately it can be seen that in all cases the highest levels of contamination were found in the Canary Island farms, while the lowest levels were found in the Cape Verde farms.

The results obtained are summarized in Tables 1–3. Those compounds with more than one usage have been classified according to their major use. To facilitate the reading of the most outstanding results, the tables do not show the results of analytes detected at trace levels and/or very low frequency (although always above the LOD of the method) and these have only been considered in the sums of each group. The following sections present and discuss the results according to these groups.

3.1. Persistent and semi-persistent organic pollutants

Forty-nine compounds considered to be persistent (18 PCBs and 12 OCPs) or semi-persistent (11 PAHs and 8 PBDEs) were analyzed, of which 40 were detected. Fig. 3 shows the sums of the POPs and the groups of POPs with the most relevant results in the study (OCPs and PAHs). As can be seen, the archipelago with the highest contamination of persistent and semi-persistent compounds is the Canary Islands, with a mean of 229.3 ± 566.1 ng g^{-1} (median = 24.5 ng g^{-1}), being the OCPs DDT (and metabolites) and dieldrin the main contributors as detailed below. Only 9.2% of the samples analyzed were free of POPs. On the other hand, the Azores presented POPs in less than half of the cases (46.7%) and with an average ten times lower than the Canary Islands ($\sum$POPs = 28.9 ± 81.1 ng g^{-1}, median = 0.0 ng g^{-1}). It is followed by Cape Verde, with concentrations of the same order ($\sum$POPs = 17.9 ± 31.5 ng g^{-1}, median = 6.5 ng g^{-1}) but with a detection frequency almost twice as high (83.3%). Finally, 75% of the Madeira samples have at least one POP but with a mean of 5.3 ± 8.9 ng g^{-1} (median = 1.6 ng g^{-1}).

Although PCBs and PBDEs are frequently found as residues on agricultural land, only PCB 153 was detected and its concentrations can be considered as trace levels in all cases (barely above the LOD). This compound is only present in the EU archipelagos, albeit at low concentrations and detection frequencies (<25%), contrary to what is usual in more industrialized regions (Gaylor et al., 2014; Hanedar et al., 2019; Jiao et al., 2016; Turrio-Baldassarri et al., 2007; Xu et al., 2019). On the other hand, all PAHs analyzed were found in both Azores and Canary Islands at low concentrations ($\sum$PAHs = 28.1 ± 80.1 ng g^{-1}, median = 0.0 ng g^{-1} and $\sum$PAHs = 29.1 ± 111.1 ng g^{-1}, median = 0.0 ng g^{-1}, respectively). Following the same trend as PCBs and PBDEs mentioned above, these compounds are usually found in much higher concentrations in agricultural soils from more industrialized and populated territories such as in India (6730 ± 7120 ng g^{-1}) (Masih and Taneja, 2006), in agricultural lands on roadsides in Shanghai, China (339 ± 594 ng g^{-1}) or even in Italy (138 ± 76.4 ng g^{-1}) (Fabietti et al., 2010). It is striking that although they were found in similar orders of magnitude in both archipelagos, the frequency of detection is higher in Azores, being double or more in some of them (Benzo[a]anthracene, Benzo[b]fluoranthene, and Chrysene and Pyrene), when the population of the Azores is ten times smaller than that of the Canary Islands and the latter have highly developed urban centers in the capital Islands (Tenerife and Gran Canaria). One possible hypothesis is that Terceira Airport is in the middle of an agricultural valley, although the number of samples is not high enough to verify the hypothesis that this could be the source of contamination. Obviously, in future studies it would be necessary to identify which areas of the island have the most contaminated soils by PAHs in the Azores.

We detected eight of these compounds in only a few Madeiran soils (5–10%), at ten times lower concentrations ($\sum$PAHs = 2.7 ± 4.2 ng g^{-1}, median = 0.0 ng g^{-1}), except for naphthalene, whose concentrations were like those in Azores, but it was detected in twice as many samples. This compound also stands out for being the only PAH found in Cape Verde with the highest concentrations, while the Canary Islands had the lowest with an almost negligible frequency of detection. Precisely, we only found significant differences for benzo[a]anthracene, benzo[b]fluoranthene, chrysene and pyrene between Azores and the other three archipelagos, and for naphthalene between the Canary Islands and the rest.

Regarding the most relevant group, OCPs, the high concentration detected in the Canary Islands of the most common DDT metabolites: p,p'-DDE, and p,p'-DDD stands out, with two samples in Gran Canaria above 1000 ng g^{-1} (1453.5 and 3426.8 ng g^{-1}). Although it is common to find these compounds in agricultural land, these concentrations are much higher than those found in other EU countries (Malusá et al., 2020; Neitsch et al., 2016; Villanneau et al., 2011), or even in India (Khuman et al., 2020) and with p,p'-DDE concentrations similar to those found in a recent study in Turkey, a country that used DDT extensively to end the control of *Anopheles* vector control (Korucu et al., 2021). These findings were consistent with a small series of samples analyzed in one of our previous articles as part of the validation of the extraction method in soils from organic and conventional vegetable farms and vineyards (Acosta-Dacal et al., 2021b) and with other previous studies conducted in the region in other matrices such as food (Luzardo et al., 2013; Rodríguez-Hernández et al., 2016), wildlife (García-Alvarez et al., 2014; Luzardo et al., 2014), or population (Henríquez-Hernández et al., 2014; Zumbado et al., 2005). Cape Verde is next with a similar frequency of detection of p,p'-DDE (>70%) but the concentrations found are ten times lower. This is interesting given that, in addition to its use to control malaria vector, farmers in Cape Verde stopped using p,p'-DDT and other organochlorine pesticides in the late 2000s, when they had been banned in Europe for more than 30 years (UNEP, 2004). However, the use of the insecticide p,p'-DDT in the Canary Islands was quite intensive when it was allowed not only because of the important role of local and export agriculture in its economy (Diaz-Diaz and Loague, 2001) but also as a

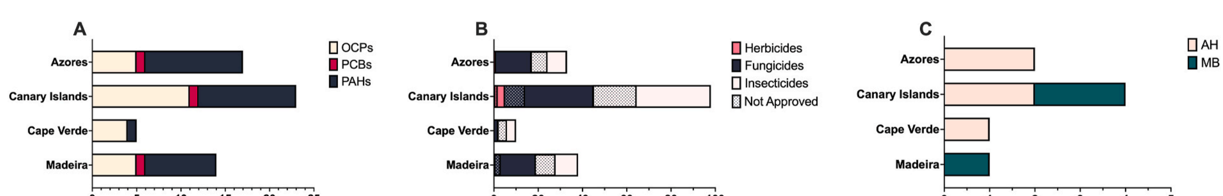

Fig. 2. Distribution of compounds detected in each archipelago (A) POPs, (B) Pesticides, and (C) PhACs. Pesticides not allowed in the European Union are specified. OCP – Organochlorine pesticides, PAH – Polycyclic aromatic hydrocarbon, PCB – Polychlorinated biphenyl, MB – microbiocide, AH – anthelminthic, F – fungicide, H – herbicide, I – insecticide (including acaricides, pesticide anthelminthic and molluscicides).

Table 1
Comparative study of the POPs detected in the four archipelagos. Concentrations are expressed in μg kg^{-1}.

Compound	Azores (n = 30)				Canary Islands (n = 65)				Cape Verde (n = 24)				Madeira (n = 20)				*p* –Value
	Mean ± SD	Median	P25–P75	Freq. (%)	Mean ± SD	Median	P25–P75	Freq. (%)	Mean ± SD	Median	P25–P75	Freq. (%)	Mean ± SD	Median	P25–P75	Freq. (%)	
PCBs																	
PCB 153	0.1 ± 0.1	–	–	20.0	0.1 ± 0.4	–	–	23.1	–	–	–	0	0.0 ± 0.1	–	–	15.0	n.s.
OCPs																	
4,4′–Dichlorobenzophenone	0.1 ± 0.1	–	–	3.3	8.0 ± 15.5	2.2	0.6–8.7	81.5	0.7 ± 0.8	0.6	0.0–1.2	58.3	0.7 ± 2.2	–	–	15.0	<0.0001
4,4′–Dicofol	–	–	–	0	8.2 ± 27.7	–	0.0–8.7	26.2	–	–	–	0	0.8 ± 2.7	–	–	10.0	0.0006
Aldrin	–	–	–	0	0.2 ± 0.5	–	–	12.3	–	–	–	0	–	–	–	0	0.0225
Dichlorodiphenyldichloroethane (p,p' DDD)	0.1 ± 0.4	–	–	3.3	16.6 ± 35.6	–	0.0–11.4	46.2	1.0 ± 3.3	–	–	8.3	0.2 ± 0.9	–	–	5.0	<0.0001
Dichlorodiphenyldichloroethylene (p, p' DDE)	0.4 ± 1.5	–	–	13.3	149.5 ± 473.4	8.5	0.8–66.8	78.5	11.4 ± 27.5	1.6	0.5–6.5	79.2	0.7 ± 1.6	–	0.0–0.6	25.0	<0.0001
Dieldrin	–	–	–	0	15.9 ± 57.7	–	0.0–3.9	33.8	1.5 ± 2.6	–	0.0–2.3	41.7	0.1 ± 0.6	–	–	5.0	0.0001
Endosulfan alpha	0.1 ± 0.4	–	–	6.7	0.1 ± 0.5	–	–	3.1	–	–	–	0	–	–	–	0	n.s.
Endosulfan beta	0.1 ± 0.7	–	–	3.3	0.2 ± 1.4	–	–	3.1	–	–	–	0	–	–	–	0	n.s.
Endrin	–	–	–	0	0.2 ± 1.1	–	–	3.1	–	–	–	0	–	–	–	0	n.s.
Hexachlorobenzene	–	–	–	0	0.0 ± 0.2	–	–	4.6	–	–	–	0	–	–	–	0	n.s.
Hexachlorocyclohexano (beta)	–	–	–	0	0.9 ± 5.2	–	–	10.8	–	–	–	0	–	–	–	0	0.0398
PAHs																	
Acenaphthene	0.1 ± 0.3	–	–	3.3	0.0 ± 0.2	–	–	1.5	–	–	–	0	0.1 ± 0.2	–	–	5.0	n.s.
Acenaphthylene	0.1 ± 0.4	–	–	10.0	0.1 ± 0.6	–	–	4.6	–	–	–	0	–	–	–	0	n.s.
Anthracene	0.2 ± 1.0	–	–	6.7	0.5 ± 2.8	–	–	4.6	–	–	–	0	–	–	–	0	n.s.
Benzo[a]anthracene	4.1 ± 11.6	–	0.0–3.6	36.7	5.5 ± 21.0	–	–	15.4	–	–	–	0	0.2 ± 0.9	–	–	5.0	0.0022
Benzo[b]fluoranthene	7.4 ± 16.9	–	0.0–9.3	36.7	5.0 ± 15.5	–	–	13.8	–	–	–	0	0.2 ± 0.7	–	–	5.0	0.0013
Chrysene	3.7 ± 11.1	–	0.0–2.8	30.0	5.1 ± 18.0	–	–	13.8	–	–	–	0	0.1 ± 0.3	–	–	5.0	0.0118
Fluoranthene	4.9 ± 19.1	–	–	16.7	6.0 ± 27.3	–	–	10.8	–	–	–	0	–	–	–	0	n.s.
Fluorene	0.1 ± 0.4	–	–	6.7	0.1 ± 0.4	–	–	4.6	–	–	–	0	0.1 ± 0.2	–	–	10.0	n.s.
Naphthalene	1.3 ± 3.4	–	–	16.7	0.2 ± 1.3	–	–	1.5	3.2 ± 6.2	–	0.0–4.2	37.5	1.9 ± 3.1	–	0.0–3.7	35.0	<0.0001
Phenanthrene	1.5 ± 5.8	–	–	6.7	1.7 ± 8.0	–	–	6.2	–	–	–	0	0.2 ± 0.8	–	–	5.0	n.s.
Pyrene	4.8 ± 16.2	–	0.0–0.8	23.3	5.0 ± 20.7	–	–	12.3	–	–	–	0	0.1 ± 0.3	–	–	5.0	0.0458

n.s. – not significant.

Table 2
Comparative study of the recent and actual used pesticides detected in the four archipelagos. Concentrations are expressed in μg kg^{-1}.

Compound	Azores (n = 30)				Canary Islands (n = 65)				Cape Verde (n = 24)				Madeira (n = 20)				*p* –Value
	Mean ± SD	Median	P25–P75	Freq. (%)	Mean ± SD	Median	P25–P75	Freq. (%)	Mean ± SD	Median	P25–P75	Freq. (%)	Mean ± SD	Median	P25–P75	Freq. (%)	
Herbicides																	
Chlorthal dimethyl	–	–	–	0	0.0 ± 0.2	–	–	3.1	–	–	–	0	–	–	–	0	n.s.
Diflufenican	–	–	–	0	0.2 ± 1.6	–	–	1.5	–	–	–	0	–	–	–	0	n.s.
Oxyfluorfen	–	–	–	0	23.2 ± 122.5	–	–	15.4	–	–	–	0	–	–	–	0	0.0069
Pendimethalin	1.0 ± 2.6	–	–	16.7	47.8 ± 197.3	–	0.0–3.0	35.4	–	–	–	0	–	–	–	0	0.0001
Propyzamide (pronamide)	–	–	–	0	0.2 ± 1.1	–	–	7.7	–	–	–	0	–	–	–	0	n.s.
Fungicides																	
Azoxystrobin	5.4 ± 14.3	–	0.0–4.4	43.3	20.8 ± 85.0	–	0.0–0.8	35.4	–	–	–	0	–	–	–	0	0.0009
Benalaxyl	0.2 ± 0.8	–	–	13.3	8.0 ± 33.3	–	0.0–0.1	26.2	–	–	–	0	0.0 ± 0.0	–	–	5.0	0.0081
Bupirimate	–	–	–	0	0.3 ± 1.1	–	–	16.9	–	–	–	0	0.0 ± 0.0	–	–	5.0	0.0105
Cyflufenamid	0.0 ± 0.2	–	–	3.3	1.7 ± 6.2	–	–	10.8	–	–	–	0	–	–	–	0	0.0484
Cymoxanil	–	–	–	0	16.9 ± 66.8	–	–	13.8	–	–	–	0	–	–	–	0	n.s.
Cyproconazole	–	–	–	0	7.0 ± 25.5	–	–	18.5	–	–	–	0	–	–	–	0	0.0020
Cyprodinil	3.3 ± 10.4	–	0.0–1.3	26.7	15.7 ± 74.8	–	0.0–0.7	24.6	–	–	–	0	11.5 ± 34.7	–	–	20.0	n.s.
Diethofencarb	–	–	–	0	0.0 ± 0.3	–	–	3.1	–	–	–	0	–	–	–	0	n.s.
Difenoconazole	1.4 ± 4.1	–	–	13.3	22.9 ± 86.1	–	0.0–0.8	32.3	–	–	–	0	0.1 ± 0.2	–	–	15.0	0.0035
Dimethomorph	0.1 ± 0.5	–	–	10.0	21.3 ± 87.8	–	–	18.5	–	–	–	0	0.4 ± 1.6	–	–	10.0	n.s.
Dinocap	–	–	–	0	–	–	–	0	–	–	–	0	3.8 ± 9.7	–	–	15.0	0.0004
Epoxiconazole	–	–	–	0	0.0 ± 0.2	–	–	7.7	–	–	–	0	–	–	–	0	n.s.
Fenarimol	–	–	–	0	1.0 ± 3.7	–	–	21.5	–	–	–	0	0.0 ± 0.1	–	–	5.0	0.0017
Fenpropimorph	–	–	–	0	0.1 ± 0.7	–	–	4.6	–	–	–	0	–	–	–	0	n.s.
Fluazinam	–	–	–	0	0.0 ± 0.1	–	–	1.5	–	–	–	0	0.9 ± 4.1	–	–	10.0	n.s.
Fludioxonil	1.3 ± 4.5	–	–	20.0	8.0 ± 31.5	–	–	21.5	–	–	–	0	17.0 ± 57.3	–	–	15.0	n.s.
Fluopyram	1.9 ± 9.7	–	–	10.0	17.7 ± 62.2	–	–	18.5	–	–	–	0	–	–	–	0	0.0240
Flusilazole	–	–	–	0	0.0 ± 0.2	–	–	1.5	–	–	–	0	–	–	–	0	n.s.
Flutriafol	–	–	–	0	19.7 ± 61.3	–	–	13.8	–	–	–	0	–	–	–	0	0.0125
Hexaconazole	–	–	–	0	0.2 ± 1.3	–	–	1.5	–	–	–	0	–	–	–	0	n.s.
Iprodione	–	–	–	0	1.8 ± 11.9	–	–	3.1	0.2 ± 1.0	–	–	4.2	–	–	–	0	n.s.
Kresoxim methyl	–	–	–	0	0.0 ± 0.3	–	–	1.5	0.0 ± 0.1	–	–	4.2	–	–	–	0	n.s.
Linuron	0.1 ± 0.3	–	–	6.7	0.9 ± 3.9	–	–	12.3	–	–	–	0	0.2 ± 0.7	–	–	15.0	n.s.
Mandipropamid	0.7 ± 2.2	–	–	23.3	–	–	–	0	–	–	–	0	0.1 ± 0.2	–	–	20.0	<0.0001
Mefenoxam (metalaxyl-M)	0.4 ± 1.1	–	0.0–0.1	26.7	2.6 ± 13.4	–	0.0–0.3	36.9	–	–	–	0	0.1 ± 0.5	–	–	25.0	0.0058
Mepanipyrim	–	–	–	0	0.2 ± 1.7	–	–	1.5	–	–	–	0	–	–	–	0	n.s.
Metalaxyl	0.5 ± 1.2	–	0.0–0.4	43.3	3.0 ± 15.9	–	0.0–0.5	41.5	–	–	–	0	0.2 ± 0.7	–	0.0–0.2	25.0	0.0013
Metrafenone	–	–	–	0	16.7 ± 75.5	–	–	7.7	–	–	–	0	–	–	–	0	n.s.
Myclobutanil	–	–	–	0	21.2 ± 92.1	–	–	21.9	–	–	–	0	0.0 ± 0.1	–	–	5.0	0.0017
Nuarimol	–	–	–	0	0.4 ± 1.2	–	–	10.8	–	–	–	0	–	–	–	0	0.0398

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Table 2 (*continued*)

Compound	Azores (n = 30)				Canary Islands (n = 65)				Cape Verde (n = 24)				Madeira (n = 20)				*p* –Value
	Mean ± SD	Median	P25–P75	Freq. (%)	Mean ± SD	Median	P25–P75	Freq. (%)	Mean ± SD	Median	P25–P75	Freq. (%)	Mean ± SD	Median	P25–P75	Freq. (%)	
Oxadixyl	–	–	–	0	0.3 ± 1.4	–	–	10.8	–	–	–	0	–	–	–	0	0.0398
Penconazole	0.3 ± 1.9	–	–	3.3	0.8 ± 4.4	–	–	18.5	–	–	–	0	0.2 ± 0.5	–	0.0–0.2	25.0	0.0200
Prochloraz	0.0 ± 0.1	–	–	3.3	0.6 ± 2.6	–	–	9.2	–	–	–	0	–	–	–	0	n.s.
Procymidone	–	–	–	0	2.6 ± 11.6	–	0.0–0.4	24.6	–	–	–	0	–	–	–	0	0.0001
Pyraclostrobin	0.0 ± 0.1	–	–	6.7	5.4 ± 20.8	–	0.0–0.2	27.7	–	–	–	0	0.0 ± 0.0	–	–	5.0	0.0012
Pyrimethanil	0.2 ± 0.9	–	–	10.0	5.5 ± 28.3	–	0.0–0.1	24.6	–	–	–	0	0.0 ± 0.1	–	–	10.0	0.0162
Quinoxyfen	–	–	–	0	0.0 ± 0.0	–	–	1.5	–	–	–	0	0.1 ± 0.2	–	–	10.0	n.s.
Spiroxamine	–	–	–	0	–	–	–	0	–	–	–	0	1.4 ± 4.0	–	–	20.0	<0.0001
Tetraconazole	–	–	–	0	2.4 ± 10.9	–	–	20.0	–	–	–	0	–	–	–	0	0.0011
Triadimefon	–	–	–	0	4.3 ± 24.0	–	–	20.0	–	–	–	0	–	–	–	0	0.0011
Triadimenol	–	–	–	0	14.9 ± 40.4	–	0.0–0.7	27.7	–	–	–	0	–	–	–	0	<0.0001
Zoxamide	–	–	–	0	0.1 ± 0.6	–	–	3.1	–	–	–	0	–	–	–	0	n.s.
Phthalimide	3.1 ± 1.5	2.5	1.9–4.3	100	5.7 ± 3.9	4.3	3.2–7.4	96.9	2.3 ± 0.6	2.1	1.8–2.6	100.0	4.8 ± 4.2	6.3	0.0–7.5	60.0	<0.0001
Acaricides, anthelminthic, insecticides and molluscicides																	
Abamectine	–	–	–	0	0.5 ± 2.1	–	–	7.7	–	–	–	0	–	–	–	0	n.s.
Acephate	0.4 ± 0.2	0.4	0.0–0.5	73.3	0.1 ± 0.2	–	–	15.4	–	–	–	0	0.2 ± 0.2	–	0.0–0.4	30.0	<0.0001
Acrinathrin	–	–	–	0	0.2 ± 1.0	–	–	3.1	–	–	–	0	–	–	–	0	n.s.
Bifenthrin	0.2 ± 0.5	–	–	20.0	1.4 ± 5.0	–	0.0–0.7	33.8	–	–	–	0	–	–	–	0	0.0003
Bromopropylate	–	–	–	0	7.3 ± 38.4	–	–	21.5	–	–	–	0	–	–	–	0	0.0005
Cadusafos	–	–	–	0	0.2 ± 0.5	–	–	18.5	–	–	–	0	–	–	–	0	0.0020
Chlorantraniliprole	4.7 ± 16.7	–	0.0–0.7	26.7	30.1 ± 69.7	–	0.0–9.7	44.6	–	–	–	0	1.5 ± 6.2	–	–	10.0	<0.0001
Chlorpyrifos	2.2 ± 10.2	–	–	10.0	10.8 ± 31.7	2.8	0.8–8.0	76.9	–	–	–	0	6.4 ± 15.2	–	0.0–5.7	45.0	<0.0001
Chlorpyrifos methyl	–	–	–	0	0.1 ± 0.7	–	–	4.6	–	–	–	0	–	–	–	0	n.s.
Clothianidin	2.1 ± 5.3	–	0.0–1.0	26.7	0.2 ± 1.8	–	–	1.5	–	–	–	0	0.2 ± 0.6	–	–	10.0	0.0002
Cyfluthrin	–	–	–	0	0.4 ± 2.9	–	–	3.1	–	–	–	0	–	–	–	0	n.s.
Cyhalothrin (lambda isomer)	–	–	–	0	0.2 ± 1.2	–	–	3.1	–	–	–	0	–	–	–	0	n.s.
Cypermethrin	–	–	–	0	42.3 ± 220.1	–	0.0–7.9	47.7	–	–	–	0	–	–	–	0	<0.0001
Deltamethrin	–	–	–	0	2.4 ± 10.8	–	–	7.7	0.4 ± 1.8	–	–	4.2	–	–	–	0	n.s.
Dimethoate	–	–	–	0	0.0 ± 0.0	–	–	1.5	0.2 ± 0.7	–	–	8.3	0.0 ± 0.0	–	–	5.0	n.s.
Ethoprophos	0.0 ± 0.1	–	–	3.3	0.6 ± 2.0	–	0.0–0.3	29.2	–	–	–	0	0.0 ± 0.0	–	–	5.0	0.0002
Etofenprox	–	–	–	0	0.1 ± 0.5	–	–	6.2	–	–	–	0	–	–	–	0	n.s.
Etoxazole	–	–	–	0	0.0 ± 0.2	–	–	3.1	–	–	–	0	–	–	–	0	n.s.
Fenamiphos	–	–	–	0	0.2 ± 0.5	–	–	23.1	–	–	–	0	0.0 ± 0.0	–	–	5.0	0.0009
Fenbutatin oxide	–	–	–	0	302.1 ± 589.7	42.2	8.6–320.7	96.9	0.2 ± 0.7	–	–	8.3	–	–	–	0	<0.0001
Fenpyroximate	–	–	–	0	2.3 ± 17.0	–	–	4.6	–	–	–	0	0.0 ± 0.1	–	–	5.0	n.s.
Flubendiamide	–	–	–	0	13.8 ± 59.8	–	–	21.5	–	–	–	0	–	–	–	0	0.0005
Flufenoxuron	–	–	–	0	0.2 ± 1.0	–	–	7.7	–	–	–	0	–	–	–	0	n.s.
Fluvalinate tau	–	–	–	0	0.0 ± 0.3	–	–	1.5	–	–	–	0	–	–	–	0	n.s.
Fonofos	–	–	–	0	0.0 ± 0.1	–	–	1.5	–	–	–	0	0.1 ± 0.2	–	–	10.0	n.s.
Hexaflumuron	–	–	–	0	0.1 ± 0.4	–	–	3.1	–	–	–	0	–	–	–	0	n.s.
Hexythiazox	–	–	–	0	0.2 ± 0.5	–	0.0–0.3	29.2	0.0 ± 0.1	–	–	8.3	0.1 ± 0.3	–	–	5.0	0.0007
Imidacloprid	4.0 ± 9.9	–	0.0–1.9	40.0	43.1 ± 112.1	–	0.0–30.4	49.2	10.1 ± 14.5	4.4	0.6–14.7	83.3	0.3 ± 1.0	–	–	10.0	<0.0001
Indoxacarb	0.6 ± 1.9	–	0.0–0.5	26.7	26.2 ± 83.5	1.6	0.0–10.9	64.6	–	–	–	0	–	–	–	0	<0.0001
Lufenuron	0.0 ± 0.1	–	–	3.3	3.3 ± 9.2	–	–	23.1	–	–	–	0	–	–	–	0	0.0010

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Table 2 (*continued*)

Compound	Azores (n = 30)				Canary Islands (n = 65)				Cape Verde (n = 24)				Madeira (n = 20)				*p* –Value
	Mean ± SD	Median	P25–P75	Freq. (%)	Mean ± SD	Median	P25–P75	Freq. (%)	Mean ± SD	Median	P25–P75	Freq. (%)	Mean ± SD	Median	P25–P75	Freq. (%)	
Metaflumizone	0.3 ± 1.4	–	–	10.0	10.8 ± 61.7	–	–	13.8	–	–	–	0	–	–	–	0	n.s.
Methiocarb	–	–	–	0	0.2 ± 1.7	–	–	1.5	–	–	–	0	–	–	–	0	n.s.
Methoxyfenozide	0.0 ± 0.0	–	–	3.3	1.3 ± 7.1	–	–	20.0	–	–	–	0	–	–	–	0	0.0034
Permethrin	–	–	–	0	0.0 ± 0.2	–	–	1.5	0.3 ± 1.2	–	–	8.3	–	–	–	0	n.s.
Pirimicarb	0.2 ± 0.7	–	–	10.0	4.3 ± 20.1	–	–	20.0	1.3 ± 4.6	–	–	8.3	4.8 ± 21.6	–	–	10.0	n.s.
Pirimiphos ethyl	–	–	–	0	–	–	–	0	–	–	–	0	0.1 ± 0.4	–	–	10.0	0.0074
Propiconazole	–	–	–	0	0.1 ± 0.8	–	–	7.7	–	–	–	0	–	–	–	0	n.s.
Propoxur	–	–	–	0	–	–	–	0	0.1 ± 0.3	–	–	29.2	0.0 ± 0.0	–	–	5.0	<0.0001
Pyridaben	–	–	–	0	1.3 ± 4.7	–	–	16.9	–	–	–	0	0.0 ± 0.1	–	–	5.0	0.0114
Pyriproxifen	–	–	–	0	7.7 ± 33.4	–	–	23.1	–	–	–	0	–	–	–	0	0.0003
Spirodiclofen	–	–	–	0	0.1 ± 0.3	–	–	7.7	–	–	–	0	–	–	–	0	n.s.
Spiromesifen	–	–	–	0	1.3 ± 10.1	–	–	10.8	–	–	–	0	–	–	–	0	0.0398
Spirotetramat	–	–	–	0	3.9 ± 21.4	–	–	7.7	–	–	–	0	–	–	–	0	n.s.
Tebuconazole	0.8 ± 3.1	–	–	6.7	2.1 ± 8.0	–	–	15.4	–	–	–	0	1.5 ± 4.0	–	0.0–1.2	30.0	0.0263
Tebufenocide	–	–	–	0	0.1 ± 0.3	–	–	9.2	–	–	–	0	–	–	–	0	n.s.
Tebufenpyrad	–	–	–	0	1.1 ± 6.6	–	–	7.7	–	–	–	0	–	–	–	0	n.s.
Teflubenzuron	–	–	–	0	0.8 ± 2.2	–	–	18.5	–	–	–	0	–	–	–	0	0.0020
Tefluthrin	–	–	–	0	0.5 ± 3.2	–	–	9.2	–	–	–	0	–	–	–	0	n.s.
Tetradifon	–	–	–	0	2.2 ± 12.0	–	0.0–0.9	26.2	–	–	–	0	0.1 ± 0.6	–	–	5.0	0.0003
Thiamethoxam	5.5 ± 18.0	–	–	20.0	–	–	–	0	–	–	–	0	0.2 ± 0.6	–	–	10.0	0.0006
Fenamiphos sulfone	–	–	–	0	0.1 ± 0.2	–	–	12.3	–	–	–	0	–	–	–	0	0.0225
Fenamiphos sulfoxide	0.0 ± 0.1	–	–	3.3	0.3 ± 0.8	–	0.0–0.4	36.9	–	–	–	0	0.0 ± 0.1	–	–	5.0	n.s.
Fipronil sulfide	–	–	–	0	0.1 ± 0.7	–	–	4.6	–	–	–	0	–	–	–	0	n.s.
Methiocarb sulfoxide	0.0 ± 0.1	–	–	6.7	0.1 ± 0.5	–	–	1.5	–	–	–	0	–	–	–	0	n.s.
Oxamyl oxime	–	–	–	0	0.1 ± 0.6	–	–	3.1	–	–	–	0	–	–	–	0	n.s.
Spirotetramat-enol	–	–	–	0	4.1 ± 22.5	–	–	4.6	–	–	–	0	–	–	–	0	n.s.

n.s. – not significant.

Table 3
Comparative study of the PhACs detected in the four archipelagos. Concentrations are expressed in μg kg^{-1}.

Compound	Azores (n = 30)				Canary Islands (n = 65)				Cape Verde (n = 24)				Madeira (n = 20)				*p* –Value
	Mean ± SD	Median	P25–P75	Freq. (%)	Mean ± SD	Median	P25–P75	Freq. (%)	Mean ± SD	Median	P25–P75	Freq. (%)	Mean ± SD	Median	P25–P75	Freq. (%)	
PhACs																	
Eprinomectin	–	–	–	0	0.0 ± 0.3	–	–	1.5	–	–	–	0	–	–	–	0	n.s.
Fenbendazole	0.1 ± 0.7	–	–	10.0	0.5 ± 4.3	–	–	6.2	–	–	–	0	–	–	–	0	n.s.
Oxfendazole	0.0 ± 0.2	–	–	6.7	0.0 ± 0.1	–	–	3.1	0.1 ± 0.3	–	–	4.2	–	–	–	0	0.0267
Sulfadiacine	–	–	–	0	0.0 ± 0.2	–	–	3.1	–	–	–	0	0.1 ± 0.1	–	–	15.0	n.s

n.s. – not significant.

way to also to stop the massive plagues of locusts that hit the islands in the 1958 or in 2004 (Canarian Weekly, 2020; Deutsche Presse Agentur, 2004). On the other hand, dieldrin was detected in the Canary Islands and Cape Verde with concentrations similar to those of p,p'-DDD in each region. In the Canary Islands, together with DDT, dieldrin was used extensively in the fields. The endrin found in small amounts in Canary Island soils may be due to small amounts of it in the commercial product (3.5%) since it was used as a preservative in the timber industry to protect it from termites and in the archipelago, there is no presence of this type of industry. Although aldrin also occurs and can be converted to dieldrin, its presence may be due to a specific use.

In addition, 4,4′-dicofol was found in 26.2% of the Canary Islands samples. Furthermore, 81.5% showed 4,4′-DBP, a degradation product of 4,4-dicofol that occurs at high temperatures, such as those of the GC-MS/MS injector (Yin et al., 2017). The use of this organochlorine acaricide was widespread in the Canary Islands until the end of the 20th century, when it was banned in 1997 by the Stockholm Convention, although it continued to be produced in Spain until 2008 (Deutsche Presse Agentur, 2004). 4,4′-Dicofol and DBP occur in Madeira with a relatively low frequency and with average concentrations ten times lower than in the Canary Islands. Likewise, 4,4′-DBP appeared in Cape Verde in more than 50% of the samples but in concentrations like those of Madeira, and in the Azores its presence was practically anecdotal. However, it is possible that 4,4′-dicofol is not the only source of DBP, since in some cases it can also be produced by fungal degradation of p, p'-DDT, chlorobenzilate or other organochlorine compounds (Acosta-Dacal et al., 2021a). Additionally, endosulfans (alpha and beta) only occurred in Azores and the Canary Islands with very low and similar detection frequencies and concentrations. Finally, hexachlorocyclohexane (beta) and low concentrations of hexachlorobenzene were also present in the Canary Islands.

Organochlorinated pesticides are, therefore, the main contributor of POPs to the agricultural soil in the Canary Islands. In addition to their local use as pesticides in the past, part of their contribution may be due to their use elsewhere, as their properties allow them to travel long distances (Villa et al., 2003). For instance, DDT is still used in some African countries to combat disease vectors such as the malaria (UNEP, 2004). Thus, DDT movements might be favored by the close distance between Africa and the Canary Islands and the frequent episodes of "calima", a meteorological phenomenon whereby dust from the Sahara desert or the Sahel is transported by wind currents from the south or southeast to the islands, as suspended dust has been shown to carry persistent pollutants (Garrison et al., 2014). However, this theory has recently lost strength, since, in a comparative study between the Canary Islands population and the closest populations on the African continent, contrary to what was expected, the Canary Islands population presented much higher blood OCPs levels than the Moroccan population. From this study it was deduced that it is very unlikely that the high levels of OCP contamination traditionally described in the Canary Islands are mainly due to the contribution from the African continent (Henríquez-Hernández et al., 2016), but probably most of the contamination is residual from the intensive use that was made in the past.

The presence of these pesticides is of particular concern today on land used for organic agriculture, since the levels of these compounds, even when they have not been used recently, in many cases prevent this type of agriculture from being certified (Fenoll et al., 2009). Furthermore, although these compounds generally tend to be retained in the soil because of their high hydrophobicity, plants of the *Cucurbitaceae* family can accumulate the POPs retained in the soil through the stem and in some cases the maximum residue limits (MRL) for dieldrin have even been exceeded (Sakai et al., 2009). Such are the levels of POPs in the Canaries, that its population has been studied on several occasions and, similarly to what we found in the soil, although PCBs levels are far from those in the EU, the levels of DDT and other organochlorine pesticides are well above the European average (Henríquez-Hernández et al., 2021, 2017; Luzardo et al., 2006).

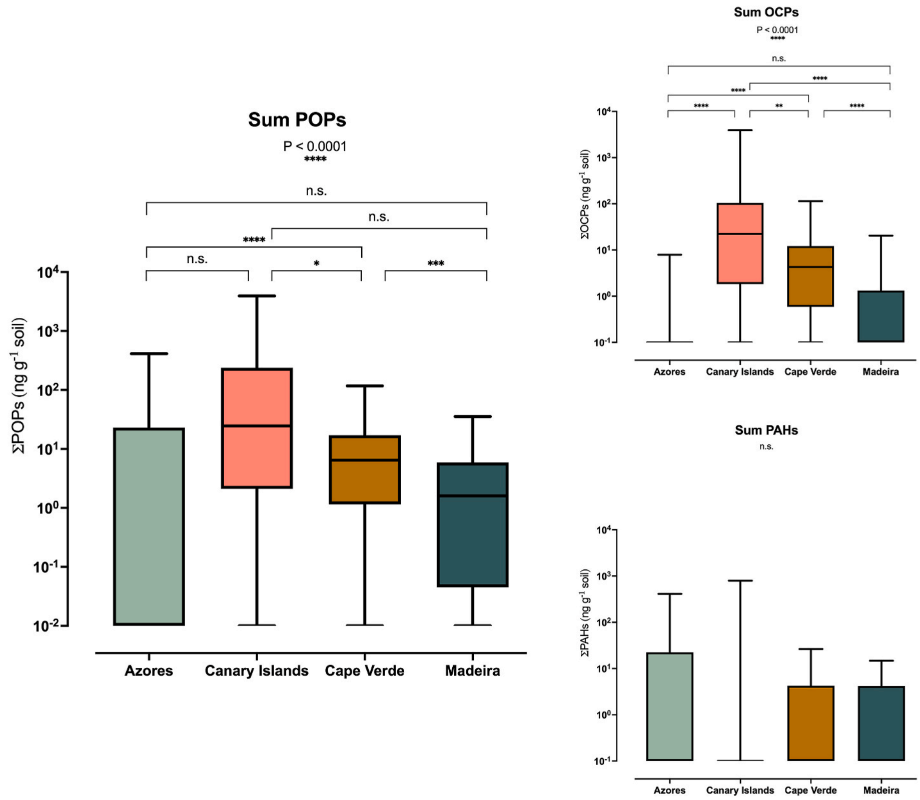

Fig. 3. Comparative study of sums of persistent and semipersistent organic pollutants, organochlorine pesticides and polycyclic aromatic hydrocarbons among archipelagos. The lines show the medians, the boxes cover the 25th to 75th percentiles, and the minimal and maximal values are shown by the ends of the bars. Significance between archipelagos is represented as: n.s. — not significant, *— $p < 0.05$; ***— $p < 0.005$; ****— $p < 0.001$.

3.2. Pesticides currently or recently used

Of the 218 pesticides in current or recent use analyzed, 103 were detected: 5 herbicides, 42 fungicides, 20 acaricides, 4 anthelminthics, 42 insecticides, 1 molluscicide, and 6 metabolites (Table 2 and Fig. 4). It should be noted that some of these compounds can be classified in more than one category, since the active ingredient is used at the same time for more than one purpose (e.g., abamectin is used as an insecticide, as an acaricide and as an anthelmintic). In these cases, for statistical purposes, we have included the compound in the group in which the product is mainly used. It should also be noted that there are groups of pesticides that have been investigated which are no longer authorized in the EU, but were used, even intensively, until relatively recently. These compounds have been marked differently in Fig. 2, for all archipelagos, including Cape Verde (although the number of compounds authorized in Cape Verde and in the EU archipelagos does not coincide exactly).

3.2.1. Herbicides

Both Cape Verde and Madeira samples were free of herbicides and only 16.7% of the Azores samples showed one of them, pendimethalin. However, 44.6% of the samples from the Canary Islands had at least 1 herbicide detected, being also pendimethalin the most frequently detected (approximately one-third of the total soil samples had residues of this compound) and with the highest concentration. Oxyfluorfen followed, with half the concentration of pendimethalin, and propyzamide, diflufenican, and chlorthal dimethyl were also detected, although at much lower levels. Chlortal dimethyl is the only one that is currently not approved in the EU. However, it was detected in very few samples and residual values that may be due to its authorized use until 2010 (EU Commission, 2009). In any case, it should be noted that, due to technical limitations, we were unfortunately unable to determine the concentrations of the most widely used herbicide in the world today, glyphosate. Therefore, our results regarding herbicide contamination would only give a partial picture of the actual level of contamination, which is probably much higher than what we report here. It will certainly be interesting to conduct specific studies on glyphosate contamination in this region in the future.

3.2.2. Fungicides

The case of fungicides is particularly striking, especially in the Canary Islands, which once again stood out for their high degree of contamination. In this archipelago, up to 40 different fungicides were detected in the samples analyzed, and only 1.5% of the samples were completely free of this type of pesticide. In this archipelago, the most frequently detected compound was metalaxyl (>40% of the samples), which is highly persistent and widely used in the Canary Islands to control downy mildew. However, metalaxyl was not the fungicide reaching the highest concentrations, but difenoconazole, dimethomorph, myclobutanil, and azoxystrobin were found with the highest average concentrations (all of them above 20 ng g^{-1}). It is noteworthy that nine of the fungicides detected are not currently authorized by the European Union Commission. Thus, triadimenol, which was present in more than a quarter of the samples with an average of almost 15 ng g^{-1}, was withdrawn in 2019. This fungicide was not only used by itself, but may also come from the relatively rapid degradation in the soil of another currently banned fungicide, triadimefon (Garrison et al., 2011). However, as far as we know, triadimefon was rarely used in the Canary Islands, and furthermore it is interesting to note that this study was initiated before triadimenol was banned, the same for fenpropimorph and quinoxyfen, whose license of use in Europe ceased in 2018 and 2019. On the other hand, triadimefon was definitively banned in 2007 but it was detected in 20% of the samples. In addition to these, procymidone, fenarimol, oxadixyl, flusilazole, and hexaconazole, also banned between 2007 and 2008, were detected in low concentrations and

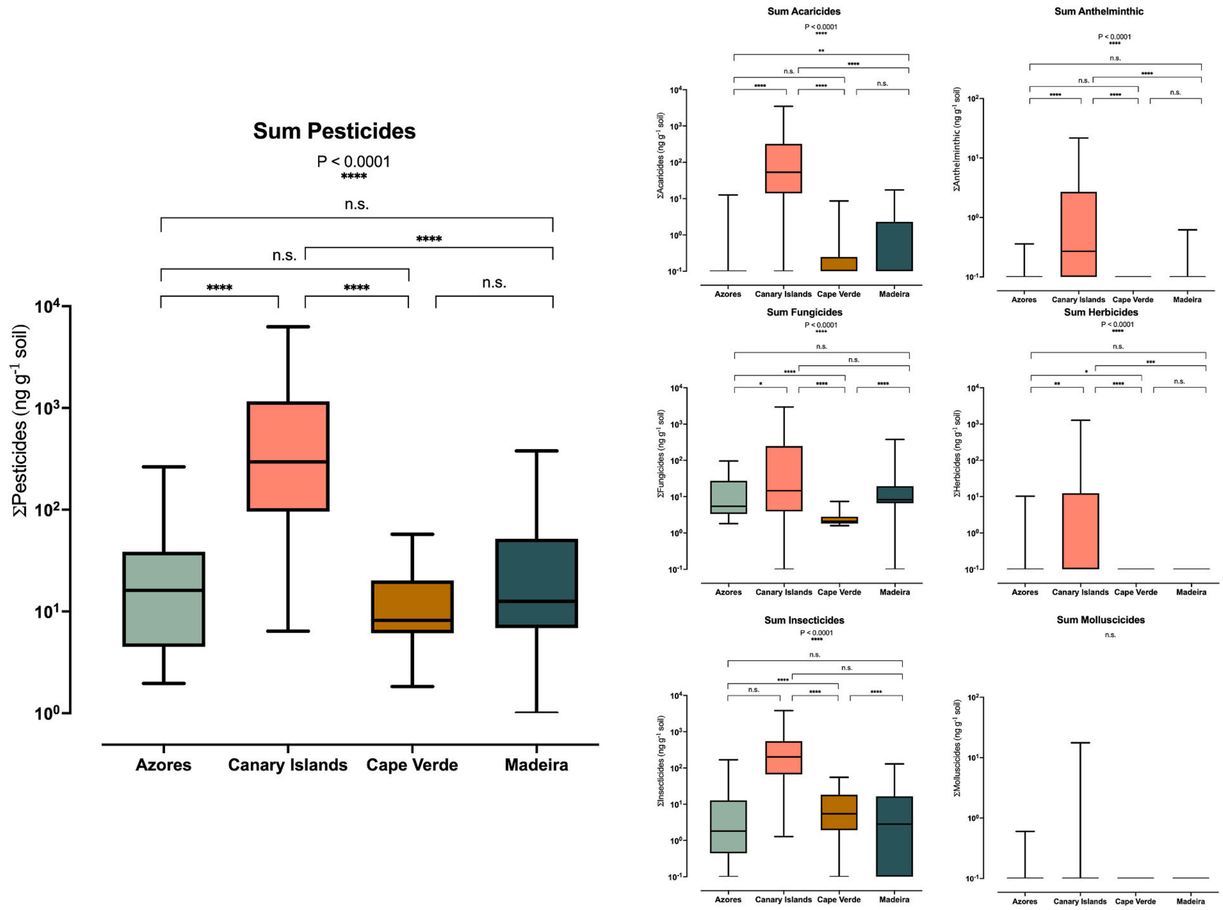

Fig. 4. Comparative study of sums of pesticides, acaricides, anthelminthic, fungicides, herbicides, insecticides and molluscicides among archipelagos. The lines show the medians, the boxes cover the 25th to 75th percentiles, and the minimal and maximal values are shown by the ends of the bars. Significance between archipelagos is represented as: n.s. — not significant, *— $p < 0.05$; ***— $p < 0.005$; ****— $p < 0.001$.

frequencies (<25%). However, triadimefon was listed as a "contaminant" in the triadimenol formulations. In fact, the residue is defined as traidimefon + triadimenol.

At the opposite extreme to the Canary Islands, we find Cape Verde, where only two fungicides were detected, in only two samples (one each): iprodione (5.08 ng g^{-1}) and kresoxim methyl (0.45 ng g^{-1}). In between we found Madeira and Azores. In Madeira, 19 fungicides were found in agricultural soil samples. Fungicides were present in 95% of the samples from this archipelago, and three of them (penconazole, metalaxyl and mefenoxam) were present in 25% of the samples analyzed. Metalaxyl is composed of two enantiomers, R and S, in a 1:1 ratio, the former being the more active component. Precisely this isomer is the main component of metalaxyl-M or mefenoxam, which allows it to be more effective than metalaxyl and the use of smaller amounts of fungicide to achieve the same effect (Monkiedje and Spiteller, 2005). Fludioxonil was the fungicide detected in the highest concentrations in Madeira, followed by cyprodinil, although with a presence of less than 20%. A fungicide banned since 2009, dinocap, was also detected in this archipelago. This fungicide is considered of low environmental persistence and has a half-life in soils of about 4–6 days (Wauchope et al., 1992), so it is very surprising to have detected it in soils several years after its prohibition. Thus, our results could reveal that this pesticide could have been misused in the three plots where it was found (at 16.6, 25.9. and 33.5 ng g^{-1}).

Finally, 16 fungicides were found in the Azores samples, azoxystrobin being the most frequently detected (together with metalaxyl). It was also the one detected in the highest concentration, although its mean concentration was four times lower than that found in the Canary Islands. In this archipelago, phthalimide deserves a special mention since, although we included this compound in the methodology mainly to determine the presence of folpet, it may not come only from folpet (Badoud et al., 2018), and this compound appeared in all samples from the Azores and Cape Verde, closely followed by the Canaries and in more than half the Madeira soils with mean concentrations of 2.3–5.7 ng g^{-1}.

3.2.3. Insecticides, acaricides, anthelmintics and molluscicides

In this section we grouped all the pesticides used to control invertebrate pests: acaricides, anthelminthics, insecticides and molluscicides. In total, 56 compounds were detected, 6 of them metabolites. Once again, Cape Verde appeared as the archipelago with the lowest number of residues, with only 4 insecticides and 4 acaricides (3 of which are also insecticides) detected in soil samples. Imidacloprid was the most detected compound (>80%), and in the highest concentrations (a maximum of 55.3 ng g^{-1}). It was followed in frequency by propoxur, although at much lower concentrations, as was the case with the rest of the compounds, which were detected in less than 10% of the samples.

In the Azores, 16 residues were detected, 2 of which are metabolites of active substances. It should be noted that the most detected compound within this group in this archipelago was acephate with a median of 0.4 ng g^{-1}, even though the use of this compound has been prohibited since 2003. The half-life of this insecticide in soil can range from 3 to 6 days, and in some soils it can reach 13 days (Pinjari et al., 2012). Therefore, its appearance seems to indicate that it has been used irregularly in recent times. In fact, 7 other unapproved compounds were detected but with lower incidence (≤27%).

In the other Portuguese archipelago, Madeira, residues of 18 compounds were detected, including fenamiphos and its metabolite. The one with the highest incidence and concentration was chlorpyrifos, followed by acephate and tebuconazole. This latter insecticide is also not allowed since April 2020. Given that all the samples in which it appeared were collected in the middle of that year, our finding could be reflecting the remains of the latest applications of this pesticide. The rest of the analytes found were detected in less than 10% of the samples, 8 of which are also not licensed for use in the EU, but all of them were detected at concentrations below 1 ng g^{-1}.

Finally, 53 residues were detected in the Canary Islands, of which slightly less than half are not permitted substances according to the EU legislation. One of them, fenbutatin oxide, was detected in practically all soils and with an average concentration 20 times higher than the next one (imidacloprid) with a maximum of 3493 ng g^{-1}. In Europe, this insecticide and acaricide is not allowed since 2015. It has a high persistence due to its extremely high octanol-water partition coefficient (log Kow 12.8), negligible vapor pressure, and chemical stability, and its half-life in soils ranges between 9 months and 3.5 years, increasing with each application ((EPA), 1994; Lin et al., 2021). Therefore, some of these measurements may be due to their abuse while it was authorized. In terms of frequency, chlorpyrifos followed (detected in more than 75% of the samples) but with a median 20 times lower. As for authorized pesticides, indoxacarb, cypermethrin, chlorantraniliprole and, imidacloprid are next in both concentrations (26.2–46.1 ng g^{-1}) and frequency of detection (45–65%).

3.3. Compounds of emerging concern

Of the 43 compounds of emerging concern analyzed, only 4 PhACs were found in generally small concentrations and low detection frequencies (≤15%, Table 3). Specifically, these analytes were two antibiotics (eprinomectin and sulfadiazine) and two veterinary anthelmintics (fenbendazole and oxfendazole). All of them appeared the Canary Islands samples, with fenbendazole being present in 6.2% of the samples, one of them with 34.3 ng g^{-1}. Oxfendazole was the only PhAC detected in Cape Verde in only one sample, an antihelmintic that is also present in 10% of the samples from the Azores. Finally, sulfadiazine was only detected in 15% of the samples from Madeira.

In Spain, veterinary drugs containing oxfendazole, fenbendazole, or eprinomectin are used in livestock and farm animals, although the latter two are also used in companion animals (dogs and cats) ((AEMPS), 2018). As mentioned above, the presence of these compounds in soil may be caused by fertilization with manure or sewage sludge, soil contamination due to the existence of farms close to crops, and/or reclaimed water if these compounds reach WWTPs that do not provide the appropriate treatments capable of removing them. In both the Canary Islands and the Azores, fenbendazole was present in samples in which oxfendazole was also detected, which means that they were probably part of the same treatment.

On the other hand, although sulfadiazine is used both as a human and veterinary prescription drug ((AEMPS), 2018, 1999), its presence in Madeira is more likely to come from the use of manure than from reclaimed water, since it is only used on the island of Porto Do Santo for irrigation of parks and gardens (Delgado et al., 2012).

In the Canary Islands, some PhACs have been found together with other emerging compounds in reclaimed water at the outlet of WWTPs (Afonso-Olivares et al., 2017; Estévez et al., 2012). In this archipelago, the samples in which sulfadiazine appears come from the islands of Tenerife and La Palma. While in Tenerife part of the reclaimed water is used for crop irrigation, in La Palma it is not used (Delgado et al., 2012). Furthermore, although the use of sewage sludge was studied on the island of Gran Canaria, it is not yet used to fertilize agricultural soils in the Canary Islands (Press, 2017). Therefore, it is most likely that the origin of the PhACs found is related to livestock farming and not from irrigation.

In summary, the Canary Islands have shown more variety and concentration of CEC residues than the other three archipelagos of the Macaronesia. As mentioned, the agricultural sector in the Azores is characterized by a strong orientation towards livestock. In fact, in 2014 it had 17.2% of the total cattle herd in Portugal and they produce 35% of the milk consumed in the country (Ragonnaud, 2015). However, livestock production in the Azores is more traditional, with large extensions of meadows and pasture for feed, while in the Canary Islands livestock production follows a more industrialized model.

Be that as it may, our results indicate that PhACs are hardly present in the soils analyzed in Macaronesia compared with other regions such as in Andalucía (Spain) were 17 compounds were found at 2–15 ng g^{-1} in soils irrigated with reclaimed water (Biel-Maeso et al., 2018) or in a farm fertilized with manure in China where they found up to 949.4 ng g^{-1} of tetracyclines and 19.6 ng g^{-1} of sulfonamides, far away from the highest concentration of sulfadiazine in our study (1.6 ng g^{-1}) (Pan et al., 2019).

In summary, the results of this work provide us with an overview of pesticide uses on current crops in the four archipelagos studied. Regarding the Canary Islands, pre-emergence herbicides, fungicides to combat downy mildew, powdery mildew and botrytis, and insecticides of recent use are mainly detected. In the Azores and Madeira, the situation is like that of the Canary Islands in terms of the general overview, but with a much lower pressure of phytosanitary residues in agricultural soils. In Cape Verde, the presence of residues is very low, mainly due to the type of self-consumption agriculture, in a country with a low per capita income, with many farmers unable to afford the cost of phytosanitary products. In addition, the residues detected in soils indicate the imprint left by the past use of insecticides/acaricides such as dieldrin/DDT, dicofol, fenbutatin, chlorpyrifos, especially in the Canary Islands, where the use of some of these products has been massive.

It is interesting to note that in this research we have monitored the concentrations of a multitude of compounds, detecting more than a hundred of them, and we have discussed their probable origin, and the present or past agricultural practices leading to these levels. However, the direct consequences of the presence of these residues on environmental health (and ultimately on human health) have not been the subject of this study. Simple detection/quantification of xenobiotics in abiotic and biotic compartments does not allow us to infer the magnitude of the consequences they may have, especially when they occur as complex mixtures, as is the case here. The effects of agrochemicals on soil ecosystem components represented by microorganisms and macroinvertebrates deserve special attention. The use of pesticides against plant pests, weeds and pathogens has been shown to affect the chemical and biological fertility of soils in several cases, including a number of possible adverse effects against soil microorganisms and/or non-target organisms. In the past, classical studies evidencing the effects of pesticides on the whole soil microbial biomass and/or on soil biochemical and enzymatic activities were conducted, and contrasting results were derived, highlighting the detrimental effect in most of the studies but, in some cases, also stimulatory effects due to pesticides acting as a carbon source (Vischetti et al., 2020). Therefore, we believe that it is necessary to complete this type of studies with others in which the biological or ecological effects of these mixtures are properly evaluated.

4. Conclusions

To our knowledge, this study includes the largest number of residues studied in soil samples to date (about 310 substances simultaneously). The agricultural soils of the Canary Islands proved to be by far the most contaminated of the four archipelagos. Residues of 125 organic compounds (active substances and metabolites) were found, of which 109 were pesticides, including OCPs, with DDT metabolites, and especially DDE, standing out. This contrasts with the low levels and frequencies of detection in Cape Verde, even though in this archipelago the use of these products was permitted until much more recent times than in Europe. This is consistent with findings to date in the Canary Islands in soils and other environmental and biological samples and is clearly a consequence of intensive use in the past. As for recently used pesticides, fenbutatin oxide stands out for its high concentration and for being present in 96.7% of the sampled plots. Madeira and the Azores had less than half as many pesticides as the Canary Islands (44 and 39) and with lower concentration levels. Although these two archipelagos belong to the same country, they do not present the same pattern of pesticides due to the difference in crop types and land uses in each archipelago. This was not the case for PAHs, where the Azores presented levels like those of the Canary Islands but with a higher presence. In contrast, the soils of the only non-EU region, Cape Verde, proved to be the least contaminated. Its local character, self-consumption agriculture and much more traditional agricultural practices may have led to a very limited use of pesticides and less contamination of its soils. Finally, as for CECs, few compounds were found and in very low concentrations in all archipelagos. From our results it is possible to conclude that there is no high input during manure fertilization and/or irrigation with reclaimed water that is of concern in these regions. As mentioned, there is no European or local legislation on MRLs in soils, apart from some indications for POPs. The data obtained during the development of this work should be used to promote soil monitoring and legislation to avoid potential adverse effects of these compounds on biota, the environment, and humans. Bioremediation solutions for the most contaminated soils should also be encouraged to accelerate the transition to organic farming.

Credit author statement

Guarantor of integrity of the entire study: OPL. Study concepts and design: OPL. Literature research: AAD, MEHM, CRB, RDD, MMBS, OPL, Laboratory work: AAD, CRB, MEHM, RDD, MMBS, LDB, MZ, LAHH, OPL, Data analysis: AAD, CRB, LAHH, LDB, MZ, OPL. Statistical analysis: AAD, OPL. Manuscript preparation: AAD, MEHM, RDD, MMBS, OPL, Manuscript editing: AAD, CRB, MEHM, RDD, MMBS, LDB, MZ, LAHH, OPL.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2022.118979.

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