

World-Wide Data of Organochlorine Pesticide in Agricultural Soils

Subjects: Soil Science

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Soil constitutes the central environmental compartment that, primarily due to anthropogenic activities, is the recipient of several contaminants. Among these are organochlorine pesticides (OCPs), which are of major concern, even though they were banned decades ago due to their persistence and the health effects they can elicit. Soil pollution by OCPs should be an essential aspect of the characterization of whole soil quality, considering that a significant percent of soils on a global scale are in the borderline of suitability for cultivation and pertinent activities. The latter, to an extent, is attributed to the presence of organic contaminants, especially those of persistent chemical natures.

Keywords: American ; Asian ; African ; Organochlorine pesticides ; European countries

1. Introduction

Organochlorine pesticides (OCPs) are persistent organic pollutants (POPs) extensively used in agriculture to control insect pests in a broad variety of crops. POPs are a cluster of toxic, bio-accumulative, bio-magnified, and persistent compounds with a likelihood of long-distance movement in the environment ^[1]. OCPs are synthetic compounds with boundless chemical stability. They are considered as egregious environmental contaminants responsible for ecological instability around the globe ^[2]. OCPs, such as dichlorodiphenyltrichloroethane (DDT) and dieldrin, were among the first synthetic insecticides developed and used worldwide. Although their use was discontinued worldwide, their persistence and their extensive historical use has left numerous sites with raised soil concentrations, which require remediation.

OCPs are hydrophobic compounds with very high adsorption coefficients, meaning a considerable number of them can be adsorbed and strongly bound to soil particles through agricultural procedures ^[3]. They remain in the surface layers of soils upon adsorption without leaching down the soil profile and persist in the soil, having half-lives ranging from months to years ^[4].

OCPs were the leading chemicals used in the control of brown Muridae species, which are the most destructive insect pests in cocoa trees ^[2]. Despite being banned worldwide, OCPs are still available in many countries via illegal routes ^[3]. High global demands for OCPs in agricultural practice, in opposition to environmental regulations, were due to their excellent efficacy in pest control and cost-effectiveness ^[5].

OCPs, including hexachlorocyclohexanes (HCHs), DDTs, aldrin, dieldrin, endrin, chlordane, heptachlor, and hexachlorobenzene (HCB), have been related to causing cancer, injury to the nervous system, generative disorders, and disturbance of the immune system in humans ^[6]. Some of them are extremely toxic and have a large variety of chronic effects, including endocrine dysfunction, mutagenesis, and carcinogenesis, while others are supposed to act as endocrine disruptors affecting hormone function ^[7]. In 2001, the Stockholm Convention on Persistent Organic Pollutants (POPs) was signed and came into force in 2004. OCPs were listed in the Stockholm Convention as persistent organic pollutants (POPs) that are to be banned by the United Nations Environment Program (UNEP) ^{[8][9]}.

Aldrin, HCB, chlordane, dieldrin, endrin, heptachlor, mirex (MRX), and toxaphene were obliterated internationally under the 2001 Stockholm Convention. Furthermore, chlordecone and HCHs were added to the convention in 2009, whereas endosulfan was added later in 2013. DDT remains available for vector control, as it has been approved by the World Health Organization, but is otherwise banned. In agriculture, OCPs have acted as insecticides, acaricides and fumigants to control pests in a variety of crops. In the field of public health, they have played a pivotal role in eliminating certain parasitic diseases such as malaria ^{[10][11]}.

Environmental pollution with OCPs may be associated with point sources (industrial emissions and waste plant effluents) or, more commonly, with diffuse sources (atmospheric transport and deposition), which are the most important pathways

for their transportation to distant sites [12].

Soils and sediments possess various microenvironmental conditions that impact air and water exchange and post-depositional procedures. Soil pollution increases worries regarding soil utilities, biodiversity, and food security but also regarding the off-site transportation of pollutants via wind- and water-forced erosion. Such off-site transportation may harm the function of sink ecosystems and correspond to further exposure paths to soil pollutants for humans and other non-target organisms [13].

Regardless of the numerous consequences of soil pollution, the monitoring of pesticide residues in soil is not required in many countries, in contrast to water monitoring [13]. Furthermore, large-scale worldwide studies on soil pollution via pesticide residues are rare and are often restricted to one single pesticide or to only a few compounds [14]. Various studies have previously described the allocation of currently used and of no-longer-approved pesticides in soil at the national or regional levels, but the various sampling periods, several sampling strategies, numerous analytical methods, and various analyte lists among these studies avert a complete impression of the distribution of pesticides residues worldwide [12][13][14][15][16][17].

From soil-monitoring programs and studies, those with the theme of OCP monitoring in soil, the manufacturing of which is totally banned globally, have been brought into consideration. Subsequently, there were no other complete studies on OCP soil monitoring comprising extensive characteristic sampling locations in American countries. In Europe, monitoring surveys were started in 1990 in Spain [17]. In the following years, outcomes from more complete studies were issued, which represented the whole EU [13]. In Asia, and especially in China and India, an adequate number of monitoring studies have been implemented, which was only a few considering the vast expanse of the countries and the continent. In Africa, fewer monitoring results are available than in other areas, as studies have only covered limited positions. With regard to Oceania, no published studies have been identified.

2. European Countries

Research on soil monitoring regarding OCPs residues does not have an extensive record in Europe. The most recent and complete study within Europe with regard to the analysis of currently used and banned pesticides including OCPs has been carried out recently by Silva et al. [13]. A total of 317 soil samples from 11 different European countries with the greatest portion of agricultural areas had been examined. In total, 21 OCPs were considered, including aldrin, α -chlordane, γ -chlordane, chlordecone, o,p'-DDD, p,p'-DDD, o,p'-DDE, p,p'-DDE, o,p'-DDT, p,p'-DDT, dieldrin, α - and β -endosulfan, endosulfan sulfate, endrin, α -, β -, and γ -HCH, heptachlor, and heptachlor epoxide along with pentachlorobenzene. The most frequently detected OCP and with the highest maximum content was p,p'-DDE (a metabolite of DDT). Its detection frequency was 23% (72 out of 317 soil samples) with a median content of 20 $\mu\text{g kg}^{-1}$ and a maximum content of 310 $\mu\text{g kg}^{-1}$. o,p'-DDD, p,p'-DDT, and dieldrin were also detected with the highest concentrations of 40 $\mu\text{g kg}^{-1}$, 10 $\mu\text{g kg}^{-1}$, and 60 $\mu\text{g kg}^{-1}$, respectively, with detection frequencies of 7%, 7%, and 5%, respectively. The detection frequencies of p,p'-DDD and α -chlordane were 3% and 1%, respectively. The detection frequencies of γ -chlordane, o,p'-DDE, o,p'-DDT, heptachlor, and HCB were below 1% in all examined soils.

Italy carried out large-scale studies for the determination of OCPs in soil. One study inclusively interpreted the contamination level of 24 organochlorine pesticides (OCPs), including α -, β -, γ -, and δ -HCH, p,p'-DDE, p,p'-DDD, o,p'-DDT, o,p'-DDE, o,p'-DDD, p,p'-DDT, HCB, α -endosulfan, β -endosulfan, endosulfan sulfate, cis-chlordane, trans-chlordane, cis-nonachlor, trans-nonachlor, aldrin, dieldrin, endrin, heptachlor, MRX, and methoxychlor, in the soils was performed in Benevento, located in southern Italy [18]. Sixty-four surface soil samples (0–5 cm) were collected from the whole region of Benevento Province between December 2014 and February 2015. Quantifiable amounts of OCPs were detected in all examined soil samples, while HCBs and DDTs were the most frequently detected compounds, contributing up to 73.5% to the total concentration of OCPs. The concentrations of DDTs varied from not detected to 16.4 $\mu\text{g kg}^{-1}$, while p,p'-DDT and p,p'-DDE were the predominant compounds. The p,p'-DDD/p,p'-DDE ratio was found to be only > 1 in three soils, indicating the aerobic degradation of p,p'-DDT. The p,p'-DDT/p,p'-DDE ratio varied from 0.0010 to 9.6, indicating the occurrence of aged DDT. Taking into account the o,p'-DDT/p,p'-DDT ratio of all examined soil samples, the researchers rejected the possibility of the 'dicofol-type DDT'. With regard to HCHs, their concentration levels ranged from not detected to 0.72 $\mu\text{g kg}^{-1}$, while β -HCH was the amplest isomer, contributing to 35.2% of the total HCHs, followed by α -HCH (32.1%), γ -HCH (26.1%), and δ -HCH (6.59%) [18]. The α -HCH/ γ -HCH ratio ranged from 0.076 to 1.91, suggesting that HCHs come from both technical HCH and LND. However, the α -HCH/ β -HCH ratio in all soils was lower than that of technical-grade HCHs, excluding the risk of the fresh input of technical HCH. HCB was noted as the most frequently detected OCP, with a detection frequency up to 96.9%, while the concentration level varied between not detected to 4.15 $\mu\text{g kg}^{-1}$. The researchers proposed that the possible source of HCB emissions to the environment include its use as a

pesticide, byproducts of chemical manufacturing processes, and waste incineration [18]. Endosulfan concentration levels ranged from not detected to $1.49 \mu\text{g kg}^{-1}$. The detection frequencies of α -endosulfan, β -endosulfan, and endosulfan sulfate were 6.25%, 14.1%, and 45.3%, respectively, indicating that endosulfan residues in soil are mainly derived from historical uses. The chlordane concentration in the studied soils varied from not detected to $0.096 \mu\text{g kg}^{-1}$, while its detection frequency followed the order: cis-Nonachlor (35.9%), cis-chlordane (9.38%), trans-chlordane (6.25%), trans-nonachlor (4.69%), and heptachlor (0%) [18]. Based on the results, the researchers suggested that the recent application of technical-grade heptachlor and chlordane seems to be not possible. However, as heptachlor is rapidly transformed into heptachlor epoxide and other metabolites, additional studies are needed for the examination of heptachlor degradation products. Finally, the concentration of drin compounds varied from not-detected to $0.37 \mu\text{g kg}^{-1}$. Among them, dieldrin was the most frequently detected compound, followed by aldrin and endrin.

Another study was performed in the Campanian Plain in southern Italy for the determination of OCPs, including HCH isomers (α - β - γ - and δ -HCH) and DDTs (p,p'-DDE, p,p'-DDD, o,p'-DDT, and p,p'-DDT), in 119 soil samples collected from April to May 2011 [19]. The residual levels of HCHs varied between 0.03 and $17.3 \mu\text{g kg}^{-1}$, while, for DDTs, they varied from 0.08 to $1231 \mu\text{g kg}^{-1}$, indicating that DDT residues in soil are significantly higher than HCHs. Regarding HCHs, the analysis results revealed that β -HCH is the main isomer conducting to 57.7% of the total HCHs, followed by γ -HCH, δ -HCH, and α -HCH. In the case of DDTs, p,p'-DDE and p,p'-DDT were noticed to be the dominant compounds with maximum concentrations of $589 \mu\text{g kg}^{-1}$ and $962 \mu\text{g kg}^{-1}$, accounting for 44.1% and 48.0% of total DDTs, respectively. The ratio of α -HCH/ β -HCH and p,p'-DDT/p,p'-DDE in the area indicates the historical past uses of both OCPs.

An additional study was performed in an area located in central Italy that included four administrative zones (Lazio, Marche, Tuscany, and Umbria), as well as in southern Italy, which consisted of seven zones (Abruzzo, Apulia, Basilicata, Calabria, Campania, Molise, and Sicily) for the determination of the status, regional sources, and pollution levels of 24 OCPs, including HCHs (α -HCH, β -HCH, γ -HCH, and δ -HCH), DDTs (o,p'-DDT, p,p'-DDT, o,p'-DDD, p,p'-DDD, o,p'-DDE, and p,p'-DDE), chlordanes (cis- and trans-chlordanes), heptachlor, heptachlor epoxide, aldrin, endrin, dieldrin, endrin aldehyde, endrin ketone, α -endosulfan, β -endosulfan, endosulfan sulphate, HCB, and methoxychlor, in urban and agricultural areas [20]. One hundred and forty-eight topsoil samples were collected between April and September 2016. The OCP concentrations varied between not detected and $1043.98 \mu\text{g kg}^{-1}$ in urban soils and from not detected to $1914.1 \mu\text{g kg}^{-1}$ in rural soils. The predominant OCP was endosulfan, with a 44.42% detection frequency, followed by DDTs, with a detection frequency of 17.6%, drins (15.75%), methoxychlor (12.17%), HCHs (6.08%), chlordane-related compounds (3.53%), and HCB (0.55%) in urban areas. In the case of agricultural soils, detection frequencies followed the order: drins (39.46%) > DDTs (29.94%) > methoxychlor (18.22%) > endosulfan (5.12%) > HCHs (5.06%) > chlordanes (1.40%) > HCB (0.79%). Regarding the DDT concentration levels, it was observed that their total concentration fluctuated from not detected to $56.97 \mu\text{g kg}^{-1}$ in soils from urban areas and from not detected to $632.95 \mu\text{g kg}^{-1}$ in agricultural soils. In urban areas, the most predominant DDT isomer was p,p'-DDT, followed by p,p'-DDE, o,p'-DDD, o,p'-DDT, o,p'-DDE, and o,p'-DDD. In agricultural areas, the predominant compound was p,p'-DDT, with a detection frequency of 49.43%, followed by p,p'-DDE (29.96%), o,p'-DDT (9.32%), p,p'-DDD (6.17%), o,p'-DDD (3.64%), and o,p'-DDE (1.49%). The ratio of o,p'-DDT/p,p'-DDT demonstrated a wide range of values ranging from 0.0002 to 214 in urban soils and from 0.008 to 16.06 in rural soils. Consequently, the outcomes point towards a dominance of the historical application of technical DDT with the exclusion of some potential recent use of DCF in some urban areas. The ratio of p,p'-DDT/(p,p'-DDE + p,p'-DDD) was used to distinguish historical and recent DDT applications. In this case, this ratio presented a considerable range from 0.0014 to 55.02 for urban soils and from 0.006 to 40.42 for agricultural soils. It can be seen that residues of DDT for this survey could be related to a combined impact from historical and recent (illegal) applications. The illegal applications of DDT or DCF are most significant in urban areas. HCH (sum of α -HCH, β -HCH, γ -HCH, and δ -HCH) concentrations varied from not detected to $25.08 \mu\text{g kg}^{-1}$ in urban areas and from not detected to $47.27 \mu\text{g kg}^{-1}$ in agricultural areas. β -HCH was the predominant isomer in all cases, which accounted for 60.25% in urban soils and 48.31% in agricultural soils. The indicative ratio of α -HCH/ γ -HCH was used to distinguish the application of LND or technical HCH. In this case, the ratio of α -HCH/ γ -HCH varied between 0.06 and 568 in urban soils and from 0.09 to 78.19 in rural soils. A total of 22% of the soils demonstrated a ratio of α -HCH/ γ -HCH over 4.64; thus, the residues could probably be linked to applications of technical DDT. The α -HCH/ β -HCH ratio was used to identify the HCH source. This ratio varied from 0.002 to 822 in urban samples and from 0.005 to 180 in agricultural soils, indicating both historical and recent (illegal) applications of technical HCH in the study area. The total concentration of drins (aldrin, dieldrin, endrin, endrin aldehyde, and endrin ketone) fluctuated from not detected to $82.5 \mu\text{g kg}^{-1}$ in urban soils and from not detected to $1212 \mu\text{g kg}^{-1}$ in agricultural soils. Among drins, endrin ketone was the principal compound, accounting for 80.28% in urban areas and 93.71% in rural areas. Endrin ketone is the last photodegradation product of both endrin and endrin aldehyde, which is difficult to degrade further. The existence of drins may reveal that their residues in soils are primarily due to historical applications. The total concentrations of chlordanes (sum of cis-chlordane, trans-chlordane, heptachlor, and heptachlor epoxide) varied from not

detected to $12.46 \mu\text{g kg}^{-1}$ in urban areas and from not detected to $12.46 \mu\text{g kg}^{-1}$ in agricultural areas. Heptachlor epoxide was the predominant compound with detection frequencies of 58.73% in urban areas and 67.56% in agricultural areas. The heptachlor/heptachlor epoxide ratio in both urban and rural soils indicated the historical application of the commercial chlordane. The total endosulfan (sum of α -endosulfan, β -endosulfan and endosulfan sulfate) concentration varied from not detected to $904.21 \mu\text{g kg}^{-1}$, accounting for 44.32% of the total OCPs in urban areas, and from not detected to 92.99 ng g^{-1} , accounting for 5.12% of total OCPs in agricultural areas. The α -endosulfan/ β -endosulfan ratio was used to decide the age of their residues in soil. In this case, this ratio ranged from 0.05 to 312.9 in urban areas and from not detected to 40 in agricultural areas. However, endosulfan sulfate was the dominant compound in rural regions. The researchers attributed their findings to the recent (illegal) use of technical endosulfan in urban areas, while historical applications were the source of residues in rural areas. HCB concentration varied from 0.01 to $2.39 \mu\text{g kg}^{-1}$ in urban soils and from not detected to $13.37 \mu\text{g kg}^{-1}$ in rural soils. The researchers recommended that HCB could be partly linked to the input of technical HCH or LND in the study area. The concentrations of methoxychlor oscillated from not detected to $53 \mu\text{g kg}^{-1}$ in urban areas and from not detected to $521 \mu\text{g kg}^{-1}$ in rural areas.

Romanian research groups carried out numerous monitoring studies for the determination of OCPs. Soil contamination by OCPs of 17 soil samples from southeastern Romania in the lower Danube–Black Sea basin was investigated for 15 OCPs, including HCHs (α -, β -, and γ -HCH), DDTs (p,p'-DDT, o,p'-DDT, p,p'-DDD, o,p'-DDD, p,p'-DDE, and o,p'-DDE), heptachlor, chlordane, aldrin, dieldrin, endrin, and MRX [21]. Sampling was performed at two different depths of (0–5 cm) and (5–20 cm); however, the overall landscape features and different land use patterns were taken into consideration. The cyclodiene organochlorine pesticides aldrin, endrin, dieldrin, and MRX were not detected in any of the samples and depths. The total measured OCP concentrations fluctuated widely, depending on the sample location and depths. The total OCP concentration varied between $58 \mu\text{g kg}^{-1}$ dry weight (dw) and $1662 \mu\text{g kg}^{-1}$ dw for a 0–5 cm soil depth and between $6 \mu\text{g kg}^{-1}$ dw and $12,644 \mu\text{g kg}^{-1}$ dw for a soil depth of 5 to 20 cm. The most frequently detected OCPs were HCHs (α -HCH was the main compound), DDTs (p,p'-DDE was the dominant compound), and heptachlor, with concentrations ranging from 6 to $6818 \mu\text{g kg}^{-1}$ dw, 27 to $5826 \mu\text{g kg}^{-1}$ dw, and 108 to $873 \mu\text{g kg}^{-1}$ dw, respectively. The researchers concluded that the detection frequency of 65% for HCHs and 62.5% for DDTs indicates the extensive usage of these pesticides in the past [21]. Another study was performed in northeastern Romania for the determination of OCPs in soil, mosses, and tree bark samples [22]. Fifteen soil samples from forests in Moldavia were collected between August and September 2005, from a 0–5 cm soil depth for the determination of 15 OCPs including HCH isomers (α -, β -, γ -, and δ -HCH), DDT and its metabolites (p,p'-DDT, o,p'-DDT, p,p'-DDD, o,p'-DDD, p,p'-DDE, and o,p'-DDE), HCB, oxychlordane (OxC), trans-nonachlor (TN), trans-chlordane (TC), and cis-chlordane (CC). The total concentration of HCHs ranged between 1.1 and $9.8 \mu\text{g kg}^{-1}$ dw, while γ -HCH was the predominant isomer (detection frequency 64%) followed by β -, α -, and δ -HCH, with detection frequencies of 18%, 15%, and 4%, respectively [22]. The researchers attributed the determined concentrations of HCHs to long-air transport deposition volatilized from agricultural nearby fields. The sum concentration of DDTs varied between 4.4 and $79 \mu\text{g kg}^{-1}$ dw, while p,p'-DDE was the predominant compound indicating either an aerobic degradation of p,p'-DDT in soil or a long-range transport of p,p'-DDE after the conversion of p,p'-DDT following its release in the environment. The main contributors to the DDT total were p,p'-DDE and p,p'-DDT (54% and 38%, respectively) followed by p,p'-DDD, o,p'-DDT, and o,p'-DDD (5%, 2%, and 1%, respectively). The DDE/DDT ratio in the examined samples was <1 , indicating a recent illegal application of DDT in the area. Soil samples from 20 agricultural fields from Iassy, located in northeastern Romania, and 27 sites including rural (near Timisoara, Arad, Ploiesti, and Cernavoda), urban (Bucharest, Timisoara, Arad, Baia Mare, Ploiesti, and Calimanesti), industrial (Copsa Mica, and Ramnicu Valcea), and waste incineration (Timisoara and Arad) sites from all over Romania were investigated for DDT and its metabolites (DDTs), HCB, and HCHs (α -, β -, and γ -HCH) [23]. The highest concentration for HCB ($337.4 \mu\text{g kg}^{-1}$) and the sum of HCHs (α -, β -, and γ -, HCH) ($2585 \mu\text{g kg}^{-1}$) were reported for the industrial site of Ramnicu Valcea located near a factory. For all other examined sites, excluding the Iassy agricultural sites, the concentration of HCB ranged between $0.3 \mu\text{g kg}^{-1}$ and $1.9 \mu\text{g kg}^{-1}$, while the sum concentration of HCHs varied from $6.5 \mu\text{g kg}^{-1}$ to $29.2 \mu\text{g kg}^{-1}$. With regard to the Iassy agricultural areas, the concentration for HCB was in the range from not detected to $0.18 \mu\text{g kg}^{-1}$ in all examined soil samples, while the DDTs ranged from $3.5 \mu\text{g kg}^{-1}$ to $119.5 \mu\text{g kg}^{-1}$ in 18 out of 20 samples. There were two agricultural sites in the Iassy area with higher DDT concentrations, which were $492.2 \mu\text{g kg}^{-1}$ and $1331 \mu\text{g kg}^{-1}$. The researchers concluded that Iassy agricultural soil samples were less contaminated with OCPs than other Romanian sites [23].

A study was conducted in tilled agricultural fields of the southern part of Romania (Dorobantu, Calarasi farm), in either burned (the burning treatment of soils is used for cleansing) or unburned soil samples collected from the surface horizon at a depth of 25 cm for the determination of 11 OCPs (α , β and δ -HCH, heptachlor epoxide, α - and γ -chlordane, endosulfan α -, and β -, dieldrin, p,p'-DDE, and p,p'-DDD) among other soil parameters. Researchers concluded that burned soils adsorb higher quantities of organochlorine pesticides compared with unburned soils [24]. From central

Romania (Mures country), 20 soil samples were collected from 50 cm depth, between November 2004 and April 2005, from agricultural fields including apple orchards, vineyards fields, arable lands (maize, soybean, wheat, and potato fields), and greenhouses for the examination of various pesticides including OCPs. In 12 of the total 20 soil samples, OCPs were detected. DDTs were the major OCP found, while HCHs were not detected at concentrations above the limit of quantification (LOQ). The DDT and DDE concentrations in soil varied between 20 $\mu\text{g kg}^{-1}$ dw (arable agricultural fields) and 50 $\mu\text{g kg}^{-1}$ dw (apple orchards). Since soil samples were collected from 50 cm depth, the researchers considered that higher concentrations of the detected OCPs could be found in the upper soil layers and that DDT may still have been being applied in fields at the time of the study. Dieldrin was also detected, with its concentrations ranging from 27 $\mu\text{g kg}^{-1}$ to 46 $\mu\text{g kg}^{-1}$. The researchers attributed its presence to its past use [25].

A study was carried out during May 1990 for the determination of 12 OCPs, including α -HCH, β -HCH, γ -HCH (LND), δ -HCH, heptachlor, heptachlor epoxide, aldrin, dieldrin, p,p'-DDE, p,p'-DDD, p,p'-DDT, and dichlorobenzophenone, in water, soils, and earthworms along the Guadalquivir River, which runs across an agricultural area with the extensive use of pesticides in Spain [17]. The Guadalquivir basin is an economically significant area of the south of the Iberian Peninsula due to its closeness to a main metropolitan area (Cordova, Seville), which signifies the existence of several urban, commercial, and industrial locations in the district of the sampling stations. Ten soil samples were collected from the surface horizon (0–5 cm) of the studied area. The analysis results indicated the existence of HCHs and DDTs; however, aldrin, dieldrin, heptachlor, and heptachlor epoxide were not detected in any of the samples. In the analyzed soil samples, the concentration of HCHs (α -, β -, γ -, and δ -HCH) ranged from 0.66 to 2.49 $\mu\text{g kg}^{-1}$, and the detection frequencies were 50% for α -HCH, 80% for β -HCH, 70% for γ -HCH (LND), and 90% for δ -HCH. The total concentration of DDTs (p,p'-DDE, p,p'-DDD, p,p'-DDT, and dichlorobenzophenone) varied from 3.49 to 46.30 $\mu\text{g kg}^{-1}$. The analysis results reveal that p,p'-DDE and p,p'-DDD were present in all examined samples, while dichlorobenzophenone and p,p'-DDT existed in 90% and 70% of the soil samples, respectively. The reported results for OCPs in soil revealed not only significant variation but also reflect their extensive use before their ban.

Thirty-two agricultural soils were sampled during the springs of 2007 and 2008 with regard to their contamination by DDT in southwestern Spain [26]. Samples were taken from areas surrounding Doñana National Park, which contains the region of Comarca de Doñana. Soils were taken from the surface horizon (depth 10 cm), and the characteristic crops of the area were considered as follows: strawberry ($n = 11$), citrus ($n = 5$), rice ($n = 4$), cotton ($n = 3$), vineyard ($n = 3$), and olive grove ($n = 4$). In some cases, DCF treatment was allowed. Two soil samples were gathered from the park and were intended as DDT contamination background soils. DDTs were identified in all soils except for the two samples collected from the park, which were used as blank soils.

A large-scale study was conducted in Germany, covering the whole country, with regard to the determination of POPs including 8 OCPs (HCB, dieldrin, p,p'-DDT, o,p'-DDT, p,p'-DDD, o,p'-DDD, p,p'-DDE, and o,p'-DDE) in 447 soils collected from forest sites [27]. DDT residue levels were up to 4000 $\mu\text{g kg}^{-1}$ dw in forest soils from eastern Germany; in contrast, their residue levels were lower than 100 $\mu\text{g kg}^{-1}$ dw in soils from western Germany. The low DDT levels in western Germany could be explained as omnipresent background contamination. The researchers attributed DDT levels in German forest soils to historical applications based on their spatial distribution. Concerning HCB, its spatial distribution varied from below the Limit of Detection (LOD) to 24 $\mu\text{g kg}^{-1}$ dw; however, the researchers concluded that its spatial distribution is difficult to be interpreted due to its multiple potential sources, such as its application as a fungicide, as a secondary byproduct in numerous chemical synthesis processes, and as a byproduct of combustion processes if chlorine compounds are involved. Generally, the spatial distribution of low concentrations possibly reveals background contamination, while high residue levels could be attributed to the abovementioned cases. Dieldrin was detected at very low residue levels (median of 2.7 $\mu\text{g kg}^{-1}$ dw), and its existence in soils could be attributed to background contamination levels. Aldrin was analyzed; however, its levels were below the LOQ in all examined samples.

In the UK, there is inadequate information regarding the historical usage of OCP and existing residues in soils and sediments. Archived background soils and sludge-amended soils gathered from long-term agricultural experiments in the UK were examined for the determination of OCPs including HCB, endosulfan, α -HCH, β -HCH, γ -HCH, heptachlor, cis-heptachlor epoxide, trans-heptachlor epoxide, aldrin, dieldrin, endrin, trans-chlordane, cis-chlordane, cis-nonachlor, trans-nonachlor, o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT, and p,p'-DDT to determine trends over time. Thus, surface soil samples (0–23 cm) from a semirural area located 42 km north of London and soils from an untreated area (which did not receive any direct application) were collected [28]. The total OCP levels ranged from 0.1 to 10 $\mu\text{g kg}^{-1}$ dw, while γ -HCH, dieldrin, and p,p'-DDE constantly had the highest concentrations. HCB had the lowest concentration of all OCPs identified, and there was little variation among the years. A possible reason for the lack of an explicit HCB time trend could be the impact of other sources, as HCB also appears as a waste product in the production of several chlorinated products and some pesticides. Additionally, HCB emissions have been related to combustion and metallurgical processes involving

the use of chlorine [29]. The detectable DDT isomers were o,p'-DDT, p,p'-DDT, and p,p'-DDE, while the residue levels of p,p'-DDE were higher than the other DDTs. The researchers explained that their findings are inconsistent with the fact that DDE is a metabolite of DDT and that it is more persistent than the parent compound. With regard to their trend, it was concluded that all the DDT compounds exhibited the same time trend, with concentrations reaching their peak in the 1960s and then falling in the 1980s. γ -HCH is present both in technical HCH and in its pure form as LND (>99% γ -HCH). Even though information on γ -HCH use in the UK is inadequate, its application has decreased since the mid-1980s, which is reflected in the soil concentration trends. Cis- and trans-chlordane exhibited very low concentrations, with a peak in the decade of 1980. There is no documentation on its use in the UK. Among drin compounds, only dieldrin was detected. Dieldrin has been used in the past as a soil insecticide; however, it is also a metabolite of aldrin. In both the control and sludge-amended soil, o,p'-DDT, α -HCH, γ -HCH, and trans-chlordane along with dieldrin presented considerable decreases in concentrations from 1968 to 1990, and this is consistent with patterns of their use.

Twenty-four surface soil samples (0–5 cm) were collected between September and November 1994 from the southern part of Poland, specifically from the cities Kraków, Katowice, and Chorzów, which are highly industrialized and populated, for the determination of polychlorinated biphenyls and OCPs including HCB, HCHs, DDTs, and chlordanes [30]. Samples were collected from areas close to a mine machines factory, transformer station, coal mine, along with a nearby park, garden, barren soil, city center, and near a chloro-alkali plant. In Katowice, DDTs were the predominant compounds found in the range of 23–260 $\mu\text{g kg}^{-1}$, with an average value of 110 $\mu\text{g kg}^{-1}$, followed by HCB detected in the range of 0.46–30 $\mu\text{g kg}^{-1}$; HCHs ranged from 1.1 to 11 $\mu\text{g kg}^{-1}$ and chlordanes from 1.0 to 5.8 $\mu\text{g kg}^{-1}$. DDTs were the predominant compounds in the examined soils from Kraków, ranging from 4.3 to 2400 $\mu\text{g kg}^{-1}$, followed by HCHs ranging from 0.36 to 110 $\mu\text{g kg}^{-1}$; HCB levels fluctuated from 0.19 to 9.9 $\mu\text{g kg}^{-1}$, and chlordanes varied from 0.07 to 1.9 $\mu\text{g kg}^{-1}$. The soils from the city of Katowice, the more industrialized sampling site, were more contaminated, since the DDT residue levels were one order of magnitude higher than those in Katowice, while chlordane levels were comparable with soils from Katowice. DDTs were found to be in the order of p,p'-DDT, p,p'-DDE, and p,p'-DDD, while HCHs were in the order γ -HCH > β -HCH \geq α -HCH. The α -HCH/ γ -HCH ratios indicated the use of LND in much higher rates than the technical HCH in Poland.

Soil samples from the surface horizon (0–10 cm) were collected for the determination of OCPs, including HCHs (α -, β -, γ -, δ -HCH), p,p'-DDD, p,p'-DDE, p,p'-DDT, o,p'-DDT, o,p'-DDD, o,p'-DDE, methoxychlor, heptachlor, heptachlor epoxide, endosulfan (α -, β -endosulfan, endosulfan sulfate), aldrin, HCB, cis- and trans-chlordane, dieldrin, and endrin from the northeastern part of Poland (89 samples) and Almaty-region farms (32 samples) in southeastern Kazakhstan [31]. The average total concentrations of DDT in Polish and Kazakh soil samples were 104 and 97 $\mu\text{g kg}^{-1}$, respectively. DDTs and HCHs were still the major OCPs detected in the examined soils. The p,p'-DDT/(p,p'-DDE + p,p'-DDD) ratio was used to specify whether p,p'-DDT in soils was from historical or recent input, and it varied from 0.23 to 11.41 for both countries. Specifically, this ratio fluctuated from 0.48 and 11.41 for Polish samples, indicating both historical and recent applications, and between 0.23 and 0.75 for Kazakh soils, indicating only past applications. The ratio of o,p'-DDT/ p,p'-DDT was used to discriminate whether DDT contamination was instigated by the usage of technical DDT or DCF. In this case, the ratio of o,p'-DDT/p,p'-DDT ranged between 0.11 and 0.50 for both countries; however, it was higher for Kazakh samples, showing that the fresh application of DDT was mostly introduced by DCF, while, in the case of Polish samples, it showed that the recent application of DDT was mainly introduced by the use of technical DDT. DDT levels found in the soil from northeastern Poland and southeastern Kazakhstan were normally low compared with values around the world. Despite the fact that OCPs have been restricted worldwide and for long periods of time in many countries, it remains an abundant contaminant whose environmental levels are stated not to have declined in some areas.

A study on the determination of OCPs including HCB, α -HCH, β -HCH, γ -HCH, δ -HCH, and DDTs in soils (collected from the lake catchment areas) and sediments from two high-altitude European mountain lakes, Redon in the Pyrenees (in Spain) and Ladove in the Tatra mountains (between Slovakia and Poland), was performed [42]. DDT (p,p'-DDE and p,p'-DDT) residue levels were in ranges between 1.7 and 3.4 $\mu\text{g kg}^{-1}$ and 4.5 and 13 $\mu\text{g kg}^{-1}$ in Redon and Ladove soils, respectively. HCH concentrations fluctuated between 0.08 and 0.19 $\mu\text{g g}^{-1}$ and 0.28 and 0.49 $\mu\text{g kg}^{-1}$ in Redon and Ladove soils, respectively. The difference between the two lakes possibly reveals the historic use of this pesticide in its pure form or as a technical mixture including high proportions of α -HCH. The total concentration of HCB varied from 0.15 to 0.91 $\mu\text{g kg}^{-1}$ and 0.23 to 0.33 $\mu\text{g kg}^{-1}$ in Redon and Ladove soils, respectively. The low concentrations in these mountain areas suggested a lack of pollution sources. The researchers concluded that the residues of OCPs are higher in the soils from the lakes in the Tatra mountains than in Redon, and this indicates the impact of the higher use and production of these compounds near the Tatra region. It is obvious that DDTs were the predominant OCPs in the area followed by HCB.

Topsoil samples (0–15 cm) were collected from the Plomin Power Plant (PPP) (25 samples) in Croatia and from Varaždin, an urban-industrialized area in north Croatia (16 samples), in March 2014, as well as in June and July 2013, for the determination of 13 OCPs including HCB, HCHs (α -HCH, β -HCH, and γ -HCH), DDTs (p,p'-DDE, p,p'-DDD, o,p'-DDT, and p,p'-DDT), aldrin, isodrin, heptachlor, heptachlor epoxide, and α -endosulfan [32]. HCB and p,p'-DDE were the only identified OCPs in soil samples from the Plomin Power Plant, while HCB was detected in more than 90% of the examined soils, and traces of p,p'-DDE were detected in nearly 70% of PPP soil samples. The occurrence of p,p'-DDE and the absence of the parent compound DDT revealed that there was no recent input of p,p'-DDT in soil in the vicinity of the PPP. The researcher attributed the presence of both OCPs to atmospheric transport. In Varaždin soil samples, the profile of OCPs was different than that in the soils from PPP. Varaždin city is surrounded by arable land, where pesticides are frequently used. HCB, p,p'-DDE, and p,p'-DDT were detected in more than 70% of the samples. Additionally, α -endosulfan, and γ -HCH were also identified. The total concentration of OCPs ranged from 0.86 to 21.0 $\mu\text{g kg}^{-1}$, while the total concentration of DDTs fluctuated from 0.74 to 19.9 $\mu\text{g kg}^{-1}$. The ratio of p,p'-DDE/p,p'-DDT was used as an indicator of recent or historical uses. The mean p,p'-DDE/p,p'-DDT ratio revealed a recent input of low concentrations of p,p'-DDT from the city atmosphere, probably from distant areas. HCHs were detected in more than 50% of the samples, and the γ -HCH was the only detected isomer, indicating its recent input probably through atmospheric transport. Traces of HCB were also identified, which varied from 0.05 to 1.82 $\mu\text{g kg}^{-1}$, with an average concentration of 0.08 $\mu\text{g kg}^{-1}$. The researchers attributed its existence in all analyzed samples to atmospheric transport. The researchers concluded that HCHs and DDTs were the predominant OCPs in both cases.

Various soil samples from different categories from central and southern Europe were investigated for the determination of OCPs [33]. Sampling sites were thoroughly chosen to represent a selection of background, rural, urban, and industrial areas. Samples were collected from 47 sites over a period of 5 months. Total HCH concentrations were below 1 $\mu\text{g kg}^{-1}$ in all samples, while total DDTs were from 1 to 60 $\mu\text{g kg}^{-1}$. The researchers concluded that soil samples from the examined sites were found to be a sink for DDT and for γ -HCH.

A study was conducted for the determination of OCPs, including HCB, α -HCH, β -HCH, γ -HCH, o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT, and p,p'-DDT in soils from Belgium (16 soil samples), Italy (6 soil samples), Greece (2 soil samples), and Romania (46 soil samples) [14]. Soil samples were collected from rural, urban, industrial, and waste-incineration areas. HCB residue levels were below 5.5 $\mu\text{g kg}^{-1}$ in samples from all countries; however, there were exceptions for some Romanian rural samples with concentrations up to 89.5 $\mu\text{g kg}^{-1}$. The γ -HCH/HCH ratios were similar in all countries and in urban and rural sites; however, some exceptions for Romania were observed. With regard to DDTs, their concentrations in soils varied from 0.6 to 22.4 $\mu\text{g kg}^{-1}$ in the case of Belgium, from 1.8 to 60.4 $\mu\text{g kg}^{-1}$ for Italy, 24.1 $\mu\text{g kg}^{-1}$ for Greece (two samples), and from 3.6 to 561.4 $\mu\text{g kg}^{-1}$ for Romania. The concentrations of DDT were higher in the rural sites in all countries except for Greece. The ratio of p,p'-DDT/DDTs was below 0.35 for Belgian and Italian soils, indicating the historical use of DDT. In the case of Greece and Romanian soils, this ratio was higher than 0.66, indicating more recent applications.

3. African Countries

A few studies in African countries have been dedicated to the soil monitoring of OCPs. Recent research regarding the determination of 15 OCPs, including α -, β -, and δ -HCH, HCB, LND, aldrin, dieldrin, endrin, heptachlor, heptachlor epoxide, α - and β -endosulfan, p,p'-DDE, p,p'-DDT, and chlorothalonil, was performed in Nigeria [34]. Twelve samples were collected from the plain of the Onuku River from different fields and from the surface soil horizon of 0–20 cm using a hand auger for sampling. The researchers observed high spatial distribution in most OCPs, while their individual concentrations ranged from not detected to 5250 $\mu\text{g kg}^{-1}$. The highest concentration was observed for chlorothalonil (4510 $\mu\text{g kg}^{-1}$) and p,p'-DDT (5250 $\mu\text{g kg}^{-1}$). However, the total concentration of OCPs in the examined soil samples ranged from 13,870 to 21,100 $\mu\text{g kg}^{-1}$. The researchers ascribed the low levels of most OCPs to possible run-off to the Onuku River.

Sixty-six soil samples were collected during a sampling campaign performed between February and August 2003 in rice fields in the Rufiji River Delta, a worldwide known wetland, located in the east coast of Africa in Tanzania [35]. For HCB, there was no noted significant concentration variation in the examined samples during the different sampling events, and the mean concentration was reported to be 0.4 $\mu\text{g kg}^{-1}$ dw. Among HCHs (α -HCH, β -HCH, γ -HCH, δ -HCH), γ -HCH (LND) was more frequently detected than the other isomers, and its mean determined concentration was 2.4 $\mu\text{g kg}^{-1}$ dw in samples taken during the application period and 1.3 $\mu\text{g kg}^{-1}$ dw for post-soil-application samples. Nevertheless, in soil samples, the sum concentration of HCHs revealed a substantial reduction in concentrations between surveys (4.6 to 2.7 $\mu\text{g kg}^{-1}$ dw). Residues of heptachlor, heptachlor epoxide, aldrin, keto-endrin, γ -chlordane, and dieldrin were identified in all soil samples, but concentrations ranged between 0.1 and 3.0 ng g^{-1} dw. DDTs were identified in all soil samples, while p,p'-DDE was the predominant compound, contributing to 70% of the total DDTs.

A study was conducted in former storage sites in Tanzania after 5–14 years of their clean-up for the determination of the level, composition, and allocation of OCPs in soil, including DDT, DDD, DDE, HCHs, aldrin, dieldrin, endrin, endosulfans, chlordanes, and heptachlor. Soil samples were gathered between January and April 2009 from six contaminated sites [36]. For soils with high clay content, samples were taken from two different depths: 5–10 cm and 30 cm; for sandy soils, samples were taken from 10–30 cm and at deeper depths from 50 cm and 3 m. The analysis results revealed that 27 compounds were detected in the examined samples, while the DDTs were the most frequently detected compounds, followed by HCHs, aldrin, dieldrin, endrin, endosulfans, chlordanes, and heptachlor. DDT concentrations ranged from 0.01 to 250,000 $\mu\text{g kg}^{-1}$, while p,p'-DDT was the predominant compound, and its concentration was higher than o,p'-DDT in all cases, indicating that technical DDT was the main source of contamination. HCHs (α -HCH, β -HCH, γ -HCH, and δ -HCH) were detected in most of the examined cases, with concentrations ranging from 40 to 140,000 $\mu\text{g kg}^{-1}$, while, for the rest of detected OCPs, their concentrations varied from 2900 to 3300 $\mu\text{g kg}^{-1}$. The results suggested that there were no considerable degradations/transformations in the OCPs for most of the sites. The maximum concentrations of the compounds were primarily observed in surface soil samples, and there were differences in the distribution among the sampling depths. The results reveal risks and concerns for both public health and the environment.

Soil samples from the surface horizon (0–20 cm) were collected and analyzed for the occurrence of OCPs, including β -HCH, α -HCH, δ -HCH, γ -HCH, p,p'-DDT, p,p'-DDE, p,p'-DDD, and o,p'-DDT, in three different counties in Kenya as a picture of different sections of the country, providing the chance for comparison between sites [37]. Sampling focused on areas affected by anthropogenic activities in the adjacent urban centers and agricultural areas. Fifty-two soil samples were gathered, and twenty of them were obtained from Kapsabet town, nine from Voi town, and twenty-three were taken from Nyeri town. The sampling sites from Nyeri, a city located in the central Kenya, which is well-recognized for the farming of both coffee and tea and where several manufacturing industries are set, including a soft drink bottling plant, leather products processing plant, and tea and coffee manufacturing industries, were locations affected by anthropogenic activities from nearby urban and agricultural areas. Samples were also taken from Voi, a town located on the Nairobi–Mombasa highway close to a National Park with intense farming activities. The third sampling area was in Kapsabet, the capital of Nandi County, with maize and tea industries. The total concentration of OCPs were in the range of 0.03–52.7, 0.24–24.3, and 0.06–22.4 $\mu\text{g kg}^{-1}$ for Kapsabet, Nyeri, and Voi, respectively. The predominant OCPs in the three study areas were from the HCH families. HCH (α -HCH, β -HCH, γ -HCH, and δ -HCH) concentrations varied from 0.03 to 48.1, 0.06 to 6.86, and 0.24 to 4.72 mg kg^{-1} for Kapsabet, Voi, and Nyeri, respectively, while those for DDTs fluctuated from not detected to 19.6 $\mu\text{g kg}^{-1}$, not detected to 15.5 $\mu\text{g kg}^{-1}$, and not detected to 4.68 $\mu\text{g kg}^{-1}$ in Nyeri, Voi, and Kapsabet, respectively. The residues of HCH isomers in Kapsabet were in the sequence β -HCH > α -HCH > δ -HCH > γ -HCH; however, in Nyeri and Voi, HCH isomers were in the sequence β -HCH > γ -HCH > δ -HCH > α -HCH. DDTs were present in the Nyeri soil samples, and this could be attributed to the use of pesticides containing DDT in the tea and coffee farms. In Kapsabet town, trace levels of p,p'-DDE and o,p'-DDT were detected. The identified amounts were attributed to the application of pesticides in agriculture. The concentrations of p,p'-DDE and p,p'-DDD in Voi were related to the agricultural activity. Among the DDTs, o,p'-DDT was the predominant compound in all cases. o,p'-DDT could imply that the use of technical DDT pesticides, which could have led to an increase in DDTs in the soil in Kenya. The highest concentration of HCHs was in Kapsabet (0.03–48.1 $\mu\text{g kg}^{-1}$), whereas the highest DDT concentration was in Voi (not-detected–15.5 $\mu\text{g kg}^{-1}$). Source identification revealed OCP pollution originated from the present usage of DDTs to control insect-borne diseases and from the use of LND in agriculture. The enantiomeric ratios of α -HCH/ γ -HCH were <3, indicating the use of LND, while the ratios of DDE/DDT were <1, suggesting recent input of DDT.

One study was performed for the first evaluation of the occurrence, residue levels, spatial distribution, and sources of POPs and OCPs, including aldrin, dieldrin, DDTs, endosulfan, endrin, HCHs, heptachlor, heptachlor epoxide, HCB, isodrin, methoxychlor, and MRX, in soils in the lower Nyabarongo catchment in central Rwanda [38]. One hundred and eight soil samples were collected from topsoil (5–10 cm) in fields situated along the main rivers, Nyabarongo and Nyabugogo, and their tributaries. DDTs were the most frequently detected compounds with a detection frequency of 89%, while the isomers' detection frequency followed the order p,p'-DDE > p,p'-DDT > p,p'-DDD > o,p'-DDT > o,p'-DDD, and o,p'-DDE. Dieldrin was found in 7% of samples, aldrin in 3%, and heptachlor and heptachlor epoxide (endo-) were detected in one sample each. DDT concentrations varied from 100 to 120,000 $\mu\text{g kg}^{-1}$ dw, dieldrin concentrations ranged from 0.53 to 18 $\mu\text{g kg}^{-1}$ dw, aldrin from 0.38 to 0.59 $\mu\text{g kg}^{-1}$ dw, and heptachlor from 0.14 to 0.19 $\mu\text{g kg}^{-1}$ dw. The higher DDE/DDT rate (0.22) compared to the DDD/DDT ratio (0.08) indicated the aerobic degradation of DDT as the predominant pathway. The (DDE + DDD)/DDT ratio in the examined samples varied considerably at various sampling points, amplifying different ages and sources of DDT residues in the area. Aldrin and dieldrin detection frequencies were 3% and 7%, respectively. The concentration levels for aldrin ranged from 0.38 to 0.59 $\mu\text{g kg}^{-1}$ dw and for dieldrin from 0.53 to 18 $\mu\text{g kg}^{-1}$ dw. Since dieldrin was demonstrated to have higher concentrations compared to aldrin, this suggests a current illegal application of both compounds in random places in the area and surroundings.

4. Asian Countries

China undoubtedly has the most abundant data on monitoring the OCPs in soils in Asia. One study was conducted for the determination of the concentration levels, sources, and stocks of polycyclic aromatic hydrocarbons (PAHs) and OCPs in 55 surface vegetable soils in the watershed of the Pearl River Delta, located in southern China. The area is of great economic interest as it is developing fast in industrial and agricultural activities. Soil samples were gathered during August 2005 from the surface horizon (0–20 cm) for the determination of 18 OCPs including DDTs (p,p'-isomers), HCHs, heptachlor, aldrin, heptachlor epoxide, α -endosulfan, β -endosulfan, dieldrin, endrin, endrin aldehyde, endosulfan sulfate, endrin ketone, and methoxychlor [39]. The total concentrations of HCHs varied from 0.19 to 42.3 $\mu\text{g kg}^{-1}$ in all soil samples, while the researchers attributed their existence to the agricultural activities of the area, as it was widely used in the past. Among the four HCH isomers (α -, β -, γ -, and δ -HCH), β -HCH was the predominant compound in all soil samples, and the researchers thought that this finding was attributed to its thermodynamically stable structure, with all chlorine atoms being in equatorial positions, and in addition, it is the least reactive and maximally persistent isomer, while its biodegradation is slower. The total DDT content ranged from 3.58 to 831 $\mu\text{g kg}^{-1}$, while p,p'-DDT and p,p'-DDE were the isomers detected at higher concentrations. As DDT could be transformed to DDE by soil microorganisms under aerobic conditions and DDD under anaerobic conditions, it was expected that DDE residue levels should be higher in surface soil samples, and it was confirmed by the findings in that case. Additionally, the DDT/(DDD + DDE) ratio was reported as being lower than 1 in some of the examined samples, indicating historical DDT use, while in the majority of the samples, the ratio was much higher than 1, suggesting fresh DDT application in the studied soils.

Thirty-two topsoil samples (0–15 cm) were gathered and analyzed for the determination of OCPs including HCHs (β -, γ -, δ -, and ϵ -HCH), HCB, heptachlor, heptachlor epoxide, trans-chlordane, cis-chlordane, α -endosulfan, β -endosulfan, o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT, p,p'-DDT, and MRX of arid and semiarid areas of eight prefectures of four provinces in northwest China in 2011 [40]. Soil samples were collected from urban (15 samples) and rural (14 samples) areas, as well as background sites (3 samples). The detection frequencies of total HCHs, DDTs, endosulfans, and heptachlors in the soils were up to 100%, suggesting their widespread existence in the arid and semiarid areas of northwest China, while their total concentration varied from 0.90 to 133.44 $\mu\text{g kg}^{-1}$. DDTs were demonstrated to exhibit the highest concentration in the examined soils, followed by HCHs, HCB, heptachlors, endosulfans, and chlordanes; thus, DDTs were the dominant pollutant in arid and semiarid areas of northwest China. DDT concentrations varied from 0.1 to 120.49 $\mu\text{g kg}^{-1}$, with a mean value of 12.52 $\mu\text{g kg}^{-1}$, while HCH concentrations varied from 0.17 to 9.39 $\mu\text{g kg}^{-1}$ in soils from arid and semiarid areas. The soil concentrations of HCB fluctuated from not detected to 11.71 $\mu\text{g kg}^{-1}$ with an average concentration of 1.21 $\mu\text{g kg}^{-1}$. The researchers noticed that soil concentrations for heptachlors, endosulfans, and chlordanes in arid and semiarid areas of northwest China were much lower than DDTs, HCHs, and HCB and more were uniform amongst all sites. The soil concentrations varied from 0.1 to 2.19 ng g^{-1} with an average concentration of 0.61 $\mu\text{g kg}^{-1}$ for heptachlors, from 0.01 to 0.84 $\mu\text{g kg}^{-1}$ with a mean of 0.09 $\mu\text{g kg}^{-1}$ for endosulfans, and from not detected to 0.28 $\mu\text{g kg}^{-1}$ with a mean level of 0.04 $\mu\text{g kg}^{-1}$ for chlordanes, respectively. The composition of DDTs in the examined soils followed the order: p,p'-DDT (68.5%) > o,p'-DDT (18.9%) > o,p'-DDE (7.2%) > p,p'-DDE (6.8%) > p,p'-DDD (4.0%) > p,p'-DDD (1.0%), demonstrating the dominance of p,p'-DDT. The (DDE + DDD)/DDT ratio in arid and semiarid areas of northwest China ranged from 0.06 to 0.41, indicating the recent illegal input of technical DDT. The o,p'-DDT/p,p'-DDT ratios at nearly all sampling sites were lower than 1.3, indicating that DDTs in arid and semiarid areas of northwest China were mainly from the application of DCF, a pesticide containing on average 11.4% o,p'-DDT and 1.7% p,p'-DDT. The major sources of HCHs in soil samples are mainly from the direct application of technical HCH and LND; thus, the researchers conducted composition analysis among HCH isomers to assess the potential source of HCHs using the α -HCH/ γ -HCH ratio [40]. The α -HCH/ γ -HCH ratios in the rural areas were between 0.16 and 15.5, indicating the historical use of HCH in two provinces. However, the α / γ -HCH ratio in most of the areas was less than 3, indicating the recent input of LND. Investigating HCH isomers suggests that β -HCH is the highest isomer among HCHs, accounting for 59.1% of total HCHs, followed by α -HCH (24.3%), δ -HCH (8.3%), and γ -HCH (8.2%). Higher β -HCH can be ascribed to its persistence in soil. HCB was never used in China after its ban in 1982; thus, its residues indicate activities of the chemical industry in this area. The α -endosulfan/ β -endosulfan ratio presented significant variation since it fluctuated from 0.18 to 10.85, indicating both historical uses and recent input. Technical chlordane is still being used in China against termites. The cis-chlordane/trans-chlordane ratio in the soils was less than 1, indicating that chlordane in arid and semiarid areas of northwest China was very probable due to long-range atmospheric transport. With regard to heptachlors, it was noticed that heptachlor epoxide had higher concentrations than those of heptachlor in most of soil samples, indicating historical uses of this pesticide [40].

An intensive soil-sampling program was implemented in the outskirts of Beijing, China, for the determination of HCHs (α -HCH, β -HCH, γ -HCH, and δ -HCH) and DDTs (p,p'-DDD, p,p'-DDT, p,p'-DDE, and o,p'-DDT) in shallow subsurfaces (5–30 cm depth) and deep soil layers (150–180 cm depth). Forty-seven shallow subsurface soil and forty-six deep-layer soil

samples were collected and analyzed [41]. The residue levels of HCHs in the shallow subsurface soils varied between 1.36 and 56.61 $\mu\text{g kg}^{-1}$ dw with an average concentration of 5.25 $\mu\text{g kg}^{-1}$, while the DDTs residue levels fluctuated from 0.77 to 2180 $\mu\text{g kg}^{-1}$ dw with an average concentration of 38.66 $\mu\text{g kg}^{-1}$. The concentrations of HCHs and DDTs in the deep-layer soils varied from 0.40 to 5.36 $\mu\text{g kg}^{-1}$ (average value 0.99 $\mu\text{g kg}^{-1}$) and from 0.13 to 66.98 $\mu\text{g kg}^{-1}$ (average value 0.82 $\mu\text{g kg}^{-1}$), respectively. The spatial distribution of HCHs and DDTs for both the shallow subsurface soils and deep-layer soils was comparable, with higher amounts found in the east, west, and northwest sites for both OCPs, indicating the known historical usage in the area. The percentages of HCHs in the shallow subsurface soils were as follows: β -HCH > γ -HCH > α -HCH > δ -HCH, which proved that the technical HCH had not been in use in the Beijing area for quite a long time; meanwhile, those in the deep soil layers were: γ > α - β > δ , demonstrating that γ -HCH and α -HCH had higher leaching abilities than β -HCH and δ -HCH [41]. The percentages of individual compounds in both shallow subsurface soils and deep-layer soils followed the order: p,p'-DDE > p,p'-DDT > p,p'-DDD > o,p'-DDT. The percentage of p,p'-DDE in the deep-layer soils was lower than that in the shallow subsurface soils; however, that of p,p'-DDD was higher, since DDT is likely to be dechlorinated to DDD in the anaerobic condition in the deep soil layer. Most soils included more DDE than DDT, suggesting DDT residues are from historical sources. Extremely high DDT/DDE ratios were identified in the deep layer soil, possibly because of the long-term leaching of p,p'-DDT and the retarded degradation of DDT to DDE in the deep-layer soils [41].

Another study was performed the Pearl River of China for the determination of POPs including OCPs in air, water, and soil [42]. OCPs, such as HCHs, DDT, HCB, chlordane, dieldrin, and aldrin, were extensively employed in agricultural activities in China from 1950 until 1983. Additionally, the manufacture of HCHs and DDTs in China accounted for 33% and 20% of the overall globe production, respectively. In the study area, it was assessed that the use of OCPs was about 76,000–100,000 tons annually. Sixty-three cultivated soils, including those from vegetable, banana, sugar cane, and fruit plantations, and non-cultivated soil samples were analyzed for the determination of OCPs. The analysis results indicated that DDTs and HCHs ranged from 15 to 125 $\mu\text{g kg}^{-1}$ in 70% and 2 to 30 $\mu\text{g kg}^{-1}$ in 80% of the examined soil samples, respectively, while the highest concentrations were detected in the cultivated soils. Because DDE was the predominant DDT compound in most of the samples and considering the DDE/DDT ratio, it could be suggested that an on-land weathering process took place. The higher HCH/DDT ratio in non-cultivated soils compared to cultivated soils indicates that these OCPs were mainly input from air precipitation.

Another study was performed in 2009 on 61 surface soils (0–20 cm) from paddy (33 soils), upland (22 soils), and wetland fields (6 soils) in the province around the Hongze Lake in China for the determination of organochlorine pesticides, including HCHs (α -HCH, β -HCH, γ -HCH, and δ -HCH) and DDTs (p,p'-DDD, p,p'-DDE, o, p'-DDT, and p,p'-DDT) [43]. The levels of OCPs were higher in the cultivated soils than in wetland soils, while DDTs and HCHs were the prevalent contaminants with detection frequencies 94.55% and 85.4%, respectively, though β -HCH and p, p'-DDE were the two major compounds of HCHs and DDTs, respectively. HCB was detected in 54.5% of the examined soils. The total concentration of OCPs varied from 4.80 to 219.10 $\mu\text{g kg}^{-1}$. DDT and DCF are considered the major sources of the existence of DDTs in the environment; thus, the researchers, based on the o, p'-DDT/p, p'-DDT ratio (which ranged from 0.31 to 0.45) in agricultural soil samples, indicated the possibility of the historical use of DCF in this region. The DDT/(DDD + DDE) and α -HCH/ γ -HCH ratios indicated that residues of HCHs and DDTs in soil resulted from historical past uses.

Ninety three surface soils (0–20 cm) from a vital agricultural area in Zhangzhou City, located south of the Fujian Province in China were gathered from paddy fields, vegetable lands, orchards, and tea plantations for the determination of eight OCPs, including α -HCH, β -HCH, γ -HCH, δ -HCH, p,p'-DDE, p, p'-DDD, o,p'-DDT, and p,p'-DDT [8]. DDTs and HCHs presented the highest detection frequencies, as they were detected in all examined samples, while their DDT concentrations (sum of p,p'-DDE, p,p'-DDD, o,p'-DDT, and p, p'-DDT) fluctuated from 0.64 to 78.07 $\mu\text{g kg}^{-1}$ with an average of 3.86 $\mu\text{g kg}^{-1}$; HCHs (sum of α -HCH, β -HCH, γ -HCH, and δ -HCH) ranged from 0.72 to 30.16 $\mu\text{g kg}^{-1}$ with an average of 9.79 $\mu\text{g kg}^{-1}$. Amongst HCHs, β -HCH, and δ -HCH isomers had the highest residue levels, indicating the historical usage of HCH. The total concentrations of HCHs and DDTs varied between soils from different land uses as follows: paddy fields > vegetable lands > tea plantations > orchards, and tea plantations > orchards > paddy fields > vegetable lands, respectively. The α -HCH/ γ -HCH ratio was used for the identification of contamination source (LND or technical DDT), and it was concluded that LND was widely used in the past. The (p,p'-DDE + p,p'-DDD)/p,p'-DDT ratio was used to identify the pollution source (DCF or DDT), and it was concluded that technical DDT was widely used in the past. However, the exact contribution of DCF in the total DDTs was found by the o,p'-DDT/p,p'-DDT ratio, and the contribution of dicofol-type DDT was 23% to the paddy fields, 26% to the vegetable lands, 82% to the orchards, and 66% to the tea plantations [8].

A pertinent study was conducted in college school yards in Beijing, China for the determination of 15 OCPs including HCH (α -HCH, β -HCH, γ -HCH, and δ -HCH), heptachlor, heptachlor epoxide, chlordanes (cis and trans chlordane), endosulfans (a and b-endosulfan), p,p'-DDE, p,p'-DDD, p,p'-DDT, o,p'-DDT, HCB, and 2,4,5,6-tetrachloro-mxylene [44]. Soil samples were gathered from the surface horizon (0–20 cm) in 2006. In that research, DDTs were found to be the major soil contaminant, accounting for 93.7% of the total OCPs, followed by HCHs (2.25%) and HCBs (1.82%). Other contaminants such as chlordanes, heptachlors, and endosulfans comprised 0.51%, 1.05% and 0.79% of the 15 OCPs, respectively. The total OCP concentration varied from 21.25 ng g⁻¹ to 276.45 μ g kg⁻¹, while the total concentration of HCH (α -HCH, β -HCH, γ -HCH, and δ -HCH) varied from 0.40 to 3.72 μ g kg⁻¹ with the average value of 2.25 μ g kg⁻¹. The researchers concluded that since Beijing is in the temperate zone where pollutants cannot be easily evaporated from soil, the HCH levels in soils could be considered as unimportant pollution. Among four HCH isomers, β -HCH was the predominant compound, indicating the recent application of HCH. Based on the α -HCH/ γ -HCH ratio, it was concluded that both technical HCH and LND were used. DDTs presented the highest concentration among the other OCPs and were in the range of 0.42–76.77 μ g kg⁻¹ for p,p'-DDE, 0.67–26.59 μ g kg⁻¹ for p,p'-DDD, 0.80–163.90 μ g kg⁻¹ for o,p'-DDT, and 0.31–104.58 μ g kg⁻¹ for p,p'-DDT. Taking into account that o,p'-DDT had the highest concentration followed by p,p'-DDE, p,p'-DDT, and p,p'-DDD, as well as the o,p'-DDT/p,p'-DDT ratio, the researchers concluded recent DCF application had occurred. The (p,p'-DDE + p,p'-DDD)/p,p'-DDT ratio was quite variable, ranging from 0.12 to 294.37 μ g kg⁻¹, indicating both historical uses (70% of the samples) of DDT and recent applications. HCB ranged from 0.13 to 5.13 μ g kg⁻¹ with the average concentration of 1.78 μ g kg⁻¹. Regardless of the fact that HCB is banned, a possible source could be waste from chlorine-related industries. Chlordanes, heptachlors, and endosulfans were detected in the ranges of 0.03–0.88 μ g kg⁻¹, 0.16–4.84 μ g kg⁻¹, and 0.14–2.41 μ g kg⁻¹, respectively. Based on the detected concentrations, the researchers attributed their existence to past uses.

One study was performed with plastic shed soils and open-field agricultural soils planted primarily with corn and wheat from five provinces and one municipality of northern China, namely, Henan, Shandong, Liaoning, Jilin, Heilongjiang, and Tianjin, to examine the pollution status of soils from OCPs [45]. Twenty OCPs, including HCHs consisting of α -HCH, β -HCH, γ -HCH, and δ -HCH; DDTs, comprising o,p'-DDT, p,p'-DDT, p,p'-DDD, and p,p'-DDE; chlordanes (CDs), containing cis-chlordane and trans-chlordane; endosulfans, comprising α -endosulfan, β -endosulfan, and endosulfan sulfate; heptachlors, including heptachlor and heptachlor epoxide; and drins, containing aldrin, dieldrin, endrin, endrin ketone, and endrin aldehyde, were analyzed in 52 soil samples from plastic shed soils and 52 soil samples from the surface horizon (0–20 cm) of open-field agricultural soils collected from April to November 2018. The concentration of OCPs in the plastic shed and open-field soils were in the range of 40.1–2555 μ g kg⁻¹ and 19.1–746 μ g kg⁻¹, respectively. It is obvious that the plastic shed soils concealed considerably greater amounts of total OCPs than the adjacent open-field soils. The analysis results indicate that endosulfans, chlordanes, HCHs, and DDTs were the principal OCPs in the plastic shed soils, while only chlordanes and DDTs had substantially greater residual levels than other OCPs in the open-field soils. The detection frequencies of HCHs were more than 83% in the plastic shed soils, while β -HCH was the predominant compound with an average concentration of 27.8 μ g kg⁻¹. The detection frequencies of β -HCH and γ -HCH were below 15% in the open-field soils. Considering the ratio of α -HCH/ β -HCH, the researchers concluded that with regard to plastic shed soils, there was no likelihood of the fresh application of either HCH or LND (γ -HCH) and that the concentration of HCH isomers in open-field soils indicated historical applications. p,p'-DDT was the major constituent of DDT residues both in open-field and plastic shed soils, accounting for 65.7% and 64.0% of the total DDT residues, respectively, indicating the fresh input of DDT in agricultural soils. Cis-chlordane was the main component of chlordanes, signifying that the new application of chlordane in this area was doubtful in recent years. The α -endosulfan/ β -endosulfan ratio and the existence of endosulfan sulfate (a degradation product of endosulfan) in most of the soil samples suggests that the recent application of technical endosulfan was dubious in most sampling sites. However, there were rare cases indicating illegal recent use. Heptachlors and drins were found in low amounts and detection rates; thus, no further consideration was given.

Yu et al. summarized the results of nearly 120 studies performed between 2004 and 2018 in more than 2000 agricultural and urban soil samples, collected from 29 provinces and municipalities of China from various soil depths (<50 cm), for the determination of OCPs and PCBs with regard to their spatial and temporal distribution besides their pollution sources. Among the OCPs, the researchers were focused on DDTs (p,p'-DDE, p,p'-DDD, o,p'-DDT, and p,p'-DDT) and HCHs (α -, β -, γ -, and δ -HCH) [46]. It was noticed that the entire OCP concentration varied from 7600 to 37,331 μ g kg⁻¹, while the total concentrations of DDTs and HCHs varied from 2.9 to 26,723 μ g kg⁻¹ and from 0.4 to 2943 μ g kg⁻¹, respectively. The reported concentrations for DDTs isomers varied from: 0.05 to 139 μ g kg⁻¹ for p,p'-DDE, 0.1 to 57 μ g kg⁻¹ for p,p'-DDD, 0.05 to 505 μ g kg⁻¹ for o,p'-DDT, and 0.8 to 488 μ g kg⁻¹ for p,p'-DDT, indicating that o,p'-DDT was the predominant DDT compound. The HCH isomer concentration ranged from 0.08 to 420 μ g kg⁻¹ for α -HCH, 0.2 to 155.5 μ g kg⁻¹ for β -HCH, 0.05 to 119.3 μ g kg⁻¹ for γ -HCH, and 0.06 to 53.5 μ g kg⁻¹ for δ -HCH, indicating that α -HCH was the main compound. The researchers observed that urban soils presented higher pollution levels by OCPs compared to agricultural soils and

ascribed this finding to rapid economic growth and the development of China and that the pollution of urban soils is strongly related to industrial activities. As anticipated, the urban soils from highly industrialized Beijing had the greatest pollution level, while urban soils from remote Tibet had the lowest pollution concentration, which verifies that the levels of economic development, urbanization, and industrialization have a terrific influence on urban soil contamination. HCH levels in soils from urban areas varied from 50 to 420,200 $\mu\text{g kg}^{-1}$, while β -HCH was the major component of the four isomers in most cases. The geographical allocation reveals that soils in eastern China were more polluted than those in western China. The ratio of α -HCH/ γ -HCH in urban soils varied from 0.05 to 3.5, indicating not only historical applications but also recent uses. The ratio of α -HCH/ γ -HCH is usually used to discover the source of HCHs in the environment. The α -HCH/ γ -HCH ratio varied between 3 and 7, indicating that HCHs were derived from past applications, while α -HCH/ γ -HCH < 3 indicated recent use in the province.

It was demonstrated that forests play a significant role in the accumulation of POPs (including OCPs) in the southeast Tibetan Plateau (TP) due to the 'forest filter effect' [47]. For that reason, a study was performed for the determination of the distribution and transfer of organochlorine pesticides (OCPs) in soils of different forest types (quercous, birch, fir, and spruce dominated forests) in Mt. Shergyla, southeast Tibetan Plateau (TP), under comparable environmental and climatic conditions. HCHs, DDTs, and HCBs in the examined soils varied from below the LOD to 2.25 $\mu\text{g kg}^{-1}$ dw, from below the LOD to 10.2 $\mu\text{g kg}^{-1}$ dw, and from below the LOD to 0.95 $\mu\text{g kg}^{-1}$ dw, respectively. The researchers observed that the total concentrations of OCPs in the humus layers were considerably higher than those in the mineral layers in the four forest types. Broadleaved birch forests were demonstrated to exhibit higher DDTs concentrations, while HCHs and HCB were considerably higher in coniferous fir forests. The ratio of p,p'-DDE/p,p'-DDT was below 1 in surface soil, indicating the fresh input of DDT; however, this ratio usually rose in deeper layers, indicating the potential degradation of DDT to DDE. The researchers attributed this finding to the current use of DDTs in neighboring countries. Regarding the α -HCH/ γ -HCH ratio, it was proven to be between 3 and 7, suggesting that HCHs were mainly derived from technical HCH use [47].

One more study was conducted in Zhejiang province in eastern China for the determination of DDTs in 58 agricultural soils collected in 2006 from the surface horizon (0–20 cm) [48]. The concentration levels of DDTs varied significantly within the samples of the province, ranging from 4.0 to 530 $\mu\text{g kg}^{-1}$ dw. Among DDTs, p,p'-DDE was the prevalent compound, followed by p,p'-DDD. The low p,p'-DDT/p,p'-DDE ratios and the high o,p'-DDT/p,p'-DDT ratios indicated that there were no recent applications of DDTs; however, the fresh application of DCF, which contains DDT (o,p'-DDT in specific) was identified.

Twenty-six surface soil samples (0–20 cm) from the nature reserve of the Yellow River Delta and specifically from its entrance, the nearby coast, the roadside, and wetland were investigated for the determination of 22 OCPs, including DDTs (o,p'-DDE, o,p'-DDD, o,p'-DDT, p,p'-DDE, p,p'-DDD, and p,p'-DDT), HCHs (α -HCH, β -HCH, γ -HCH, and δ -HCH), heptachlor, heptachlor epoxide, chlordanes (cis- and trans-chlordane), endosulfans (endosulfan α - and β -), HCB, drins (aldrin, dieldrin and endrin), methoxychlor, and MRX [49]. The results indicate a significant variation in the concentration of total OCPs, as they varied from 0.01 to 10.5 $\mu\text{g kg}^{-1}$; however, DDTs (including o,p'-DDE, o,p'-DDD, o,p'-DDT, p,p'-DDE, p,p'-DDD, and p,p'-DDT) were the predominant compounds with concentrations that varied between 0.17 and 10.46 $\mu\text{g kg}^{-1}$ in the examined samples. High detection frequencies were also observed for HCHs, and their concentrations ranged between 0.28 and 1.32 $\mu\text{g kg}^{-1}$. The concentration levels of both HCHs and DDTs suggested that they were extensively used in the past. Heptachlor epoxide was the predominant compound among chlordanes, and its concentration varied between not detected and 3.53 $\mu\text{g kg}^{-1}$, with their detection being in the following order: DDTs > HCHs > chlordanes > endosulfans.

One hundred and fifty-three soils from the surface horizon (0–10 cm) around the Yellow and Bohai Seas of China, including twenty-one cities and five provinces, were collected in September 2013 for the determination of seven OCPs, including α -HCH, β -HCH, γ -HCH, δ -HCH, p,p'-DDE, p,p'-DDD, and p,p'-DDT [50]. The detection frequencies of α -HCH, β -HCH, γ -HCH, δ -HCH, p,p'-DDE, p,p'-DDD, and p,p'-DDT were 100%, 99%, 99%, 100%, 100%, 91%, and 99%, respectively. OCP concentrations in soils fluctuated from 5.89 to 179.96 $\mu\text{g kg}^{-1}$ dw with a mean value of 25.39 $\mu\text{g kg}^{-1}$ dw. Concentrations for individual compounds ranged from 0.94 to 16.89 $\mu\text{g kg}^{-1}$ dw for α -HCH, not detected to 156.12 $\mu\text{g kg}^{-1}$ dw for β -HCH, not detected to 16.17 $\mu\text{g kg}^{-1}$ dw for γ -HCH, 0.9 to 56.24 $\mu\text{g kg}^{-1}$ dw for δ -HCH, 0.43 to 91.23 $\mu\text{g kg}^{-1}$ dw for p,p'-DDE, not detected to 116.2 $\mu\text{g kg}^{-1}$ dw for p,p'-DDD, and not detected to 10.42 $\mu\text{g kg}^{-1}$ dw for p,p'-DDT. The researchers determined that the detected OCP residues had a significant relationship with orchard land-use types.

One hundred and fifty-nine soil samples from thirty forested mountain sites across China were collected from May 2012 to March 2013 from O-horizon and A-horizon and analyzed for the determination of 13 OCPs, including α -endosulfan, β -endosulfan, HCB, MRX, o,p'-DDT, pp'-DDT, o,p'-DDD, pp'-DDD, o,p'-DDE, pp'-DDE, cis-chlordane, trans-chlordane, and heptachlor [51]. DDTs (sum of all isomers) demonstrated the greatest concentrations, while p,p'-DDT was the predominant

compound in most of the samples, followed by p,p'-DDE in both the O- and A-horizons. Total DDT concentrations in the O- and A-horizons varied between 0.197 and 207 $\mu\text{g kg}^{-1}$. The HCB concentration in the O- and A-horizons ranged from 0.047 to 6.12 $\mu\text{g kg}^{-1}$ and from 0.022 to 0.748 $\mu\text{g kg}^{-1}$, respectively. Heptachlor and cis- and trans-chlordane are the main components of technical chlordane, while trans- and cis-chlordane are the most plentiful isomers in the examined samples. The concentrations of trans- and cis-chlordanes ranged from 0.008 to 0.215 $\mu\text{g kg}^{-1}$ and from 0.017 to 0.333 $\mu\text{g kg}^{-1}$ in the O-horizon and from 0.012 to 0.153 $\mu\text{g kg}^{-1}$ as well as from non-detected to 0.239 $\mu\text{g kg}^{-1}$ in the A-horizon, respectively. A-endosulfan and β -endosulfan concentrations fluctuated from not detected to 0.160 $\mu\text{g kg}^{-1}$ and not-detected to 0.097 $\mu\text{g kg}^{-1}$ in the O-horizon, respectively. Regarding the A-horizon, their concentrations ranged from not detected to 0.039 $\mu\text{g kg}^{-1}$ and from not detected to 0.185 $\mu\text{g kg}^{-1}$ in the A-horizon, respectively. MRX in the O- and A-horizon samples was detected at concentrations ranging between 0.001 and 0.029 $\mu\text{g kg}^{-1}$ and from not detected to 0.019 $\mu\text{g kg}^{-1}$, respectively. Generally, the highest concentrations appeared near agricultural zones or high consumption areas. The chiral compounds were usually non-racemic in the soils and revealed the preferential degradation of o,p'-DDT, trans and cis-chlordane in both O and A-horizons. The researchers concluded that recent and historical applications of DDT and historical uses of chlordane and endosulfan may be major sources of OCP accumulation in Chinese forest soils.

Another study was performed in Wuhan, the largest city in central China, regarding the determination of 21 OCPs, including α -HCH, β -HCH, γ -HCH, δ -HCH, p,p'-DDD, p,p'-DDE, p,p'-DDT, o,p'-DDT, o,p'-DDD, o,p'-DDE, methoxychlor, heptachlor, heptachlor epoxide, α -endosulfan, β -endosulfan, aldrin, HCB, cis-chlordane, trans-chlordane, dieldrin, and endrin, in agricultural soils due to a lack of information in this area [52]. In total, 44 soil samples from rice, wheat, corn, bean, cotton, and vegetable soil were gathered from the Wuhan agricultural region in June 2009. DDTs were the predominant OCPs detected in Wuhan, and their concentrations varied from not detected to 1198 $\mu\text{g kg}^{-1}$, accounting for 77.10% of total OCPs. Among DDTs, p,p'-DDE was the predominant compound with residue levels that varied between not detected and 807.82 $\mu\text{g kg}^{-1}$, with the mean concentration of 73.38 $\mu\text{g kg}^{-1}$, followed by p,p'-DDT (mean concentration 52.74 $\mu\text{g kg}^{-1}$), o,p'-DDT (mean concentration 10.64 $\mu\text{g kg}^{-1}$), p,p'-DDD (mean concentration 9.26 $\mu\text{g kg}^{-1}$), o,p'-DDD (mean concentration 2.94 $\mu\text{g kg}^{-1}$), and o,p'-DDE (mean concentration 2.62 $\mu\text{g kg}^{-1}$) [52]. The p,p'-DDT/(p,p'-DDE + p,p'-DDD) ratio varied from 0 to 46.72; however, in 70.5% of the examined samples, it was below 1, indicating historical uses in most of the examined samples, but recent applications could not be excluded. The o,p'-DDT/p,p'-DDT ratio was used to discern whether DDT pollution was due to the usage of technical DDT or DCF, and the researchers concluded that recent DDT was primarily introduced by technical DDT. On the other hand, HCHs (sum of α -, β -, γ -, and δ -HCH) accounted for 7.83% of OCPs, and their concentration varied from not detected to 100.58 $\mu\text{g kg}^{-1}$ with the mean concentration of 15.39 $\mu\text{g kg}^{-1}$. The mean concentrations of β -HCH, δ -HCH, α -HCH, and γ -HCH were found to be 6.41, 5.14, 2.64, and 1.20 $\mu\text{g kg}^{-1}$, respectively. It is obvious that among HCHs, β -HCH was found to be the predominant isomer, indicating a lack of new HCH applications in most cases. Moreover, the α -HCH/ γ -HCH ratio ranged from 0 to 2.83, indicating historical uses of LND. Regarding chlordanes (cis and trans isomers), their residue levels varied between not detected and 7.17 $\mu\text{g kg}^{-1}$, with a mean concentration of 0.48 $\mu\text{g kg}^{-1}$. The residue levels of chlordanes (sum of cis and trans isomers) ranged from not detected to 7.17 $\mu\text{g kg}^{-1}$, with a mean concentration of 0.48 $\mu\text{g kg}^{-1}$, with cis-chlordane being the predominant compound. The concentration of heptachlors (heptachlor and heptachlor epoxide) ranged from not detected to 29.04 $\mu\text{g kg}^{-1}$ with a mean of 5.55 $\mu\text{g kg}^{-1}$, with heptachlor being the predominant compound with a concentration that varied from not detected to 28.71 $\mu\text{g kg}^{-1}$, and heptachlor epoxide being in the range of not detected to 3.65 $\mu\text{g kg}^{-1}$. Although heptachlor is metabolized in soils to heptachlor epoxide, the concentration of heptachlor was found to be higher than that of heptachlor epoxide, indicating fresh applications in most agricultural soils of Wuhan. HCB was identified in 86% of the examined soils, with a concentration that varied from not-detected to 17.77 $\mu\text{g kg}^{-1}$ with a mean concentration of 3.01 $\mu\text{g kg}^{-1}$. Since HCB exists as an impurity in some pesticides, no conclusion could be reached about its use. Endosulfan (α - and β -isomers) is still being used on cotton and other crops in China and thus was identified in the examined soils with a concentration that varied between not detected and 23.04 $\mu\text{g kg}^{-1}$, with a mean concentration of 1.28 $\mu\text{g kg}^{-1}$, while both α - and β -isomers were observed in 9% of soil samples. Metoxychlor was identified in 14% of soil samples with a concentration that varied from not detected to 169.03 $\mu\text{g kg}^{-1}$ and a mean concentration of 10.47 $\mu\text{g kg}^{-1}$. The detection frequencies for aldrin, dieldrin, and endrin were 73%, 9%, and 5%, respectively, and their concentrations ranged from not detected to 21.56 $\mu\text{g kg}^{-1}$, not detected to 16.69, and not detected to 6.12 $\mu\text{g kg}^{-1}$, respectively. The researchers attributed their existence to atmospheric depositions [52].

Allocations, sources, environmental risks, as well as environmental behaviors of 20 OCPs, including HCB, aldrin, HCHs (α -, β -, γ -, and δ -HCH), DDTs (p,p'-DDT, p,p'-DDE, p,p'-DDD, o,p'-DDT, o,p'-DDE, and o,p'-DDD), heptachlors (heptachlor, heptachlor epoxide A, and heptachlor epoxide B), chlordanes (cis-chlordane, trans-chlordane, and oxy-chlordane), and endosulfans (endosulfan- α and endosulfan- β), in riparian soils and sediments of the middle reach of the Huaihe River, a traditional agricultural area of China, were examined. The Huaihe River Basin is a conventional farming area, as well as an essential grain production center in China [53]. Riparian topsoil samples (0–5 cm) were gathered from 28 sampling

sites. All the target OCPs were identified in riparian soils, except heptachlor epoxide A, while their total concentration ranged from 1.8 to 63 $\mu\text{g kg}^{-1}$, and the average concentration was 19 $\mu\text{g kg}^{-1}$. HCHs were the predominant compounds, while α -HCH was the most prevalent HCH isomer in riparian soils, and its concentration ranged from 1.2 to 31 $\mu\text{g kg}^{-1}$ with an average concentration of 13 $\mu\text{g kg}^{-1}$, accounting for 69% of the total OCPs. Consequently, the isomeric ratio of α -HCH / γ -HCH was used to distinguish the sources of HCH, and this ratio was in the range between 1.7 and 14 with an average value of 5.9, indicating that both technical HCH and LND were used in the area. The DDT average concentration was found to be 0.4 $\mu\text{g kg}^{-1}$, accounting for 2% of the total OCPs in soils, and p,p'-DDE was the main isomer, followed by p,p'-DDD and p,p'-DDT. The ratio of (p, p'-DDE + p,p'-DDD)/p,p'-DDT was used to distinguish between fresh DDT application and historical uses. In this monitoring study, the abovementioned ratio was below 1 for only one sample, while the mean ratio for the rest of the samples was 4.6, indicating mainly historical uses. Heptachlor and heptachlor epoxide B were identified in most of the soils, and their total concentration was found to be 3.6 $\mu\text{g kg}^{-1}$, accounting for 19% of the total OCPs. Chlordanes were also identified in soils, and their total concentration was found to be 0.83 $\mu\text{g kg}^{-1}$, and oxy-chlordane was the main compound, accounting for 96% of total chlordanes. The researchers concluded that chlordanes were derived mainly from weathered chlordane. Aldrin was detected in 96% of soils, with the mean concentration of 0.53 $\mu\text{g kg}^{-1}$.

Fifty-five soil samples were gathered during May 2015 from six stations along the agricultural (twenty-one samples), backwaters (seven samples), and coastal (twenty-seven samples) transects of the southwest coast of India for the determination of 17 OCPs including α -HCH, β -HCH, γ -HCH, δ -HCH, p,p'-DDT, p,p'-DDE, p,p'-DDD, α -endosulfan, β -endosulfan, endosulfan sulfate, aldrin, dieldrin, endrin, endrin ketone, methoxychlor, heptachlor, and heptachlor epoxide. HCH, dieldrin, endrin, and endrin ketone were the most frequently identified compounds, with detection frequencies of more than 95% [54]. Generally, a declining trend in DDT, HCH, and endosulfan was noted as the study moved down south to the Indian Ocean. It should be stated that α -endosulfan was not identified in any of the samples; however, β -endosulfan was identified in some samples, and the omnipresence of endosulfan sulfate was noted. The total OCP level was at the maximum in the agricultural transect (48%), followed by the coastal (40%) and backwater transect (11%). For DDTs, endosulfans, and HCHs, the highest concentrations were observed in the agricultural transect, possibly due to historical and/or continuing usage of OCPs. HCHs (sum of α -HCH, β -HCH, γ -HCH, and δ -HCH) contributed to 15% of the total OCPs, and their concentration ranged from not detected to 123 $\mu\text{g kg}^{-1}$, with an average of 30 $\mu\text{g kg}^{-1}$. α -HCH was the predominant compound, followed by δ -HCH, γ -HCH, and β -HCH [54]. Based on the α -HCH/ γ -HCH ratio, the researchers concluded that its major source was from technical HCH. The β -HCH/(α -HCH + γ -HCH) ratio was used to reach the conclusion of ongoing HCH usage. DDTs (sum of p,p'-DDT, p,p'-DDE, and p,p'-DDD) contributed to around 5% of the total OCPs, and their concentration fluctuated between not detected to 148 $\mu\text{g kg}^{-1}$, while the highest DDT concentration was observed in the agricultural transect. The major DDT was p,p'- DDE, contributing almost 60% of the total DDT concentration, followed by p,p'-DDE (30%) and p,p'-DDD (10%). The total DDT concentration followed the order: agricultural > coastal > backwater transects. The prevalence of p,p'-DDT was noted in a few sites in agricultural and coastal transects, possibly due to its usage in vector control programs. Endosulfan (sum of α -endosulfan, β -endosulfan, and endosulfan sulfate) residues varied from not detected to 21 $\mu\text{g kg}^{-1}$, with the mean concentration of 2 $\mu\text{g kg}^{-1}$. The detection frequency of β -endosulfan and endosulfan sulfate was 13% and 35%, respectively. The contamination of endosulfan can be ascribed to historical applications in cashew plantations in the southwest coast. Endrins (sum of endrin and endrin ketone) contributed more than 50% of the total OCPs, and their concentrations ranged from not detected to 491 $\mu\text{g kg}^{-1}$, and the mean concentration was 104 $\mu\text{g kg}^{-1}$. Higher endrin ketone levels in the surface soil could be attributed to historical applications of endrin. Heptachlors (sum of heptachlor and heptachlor epoxide) contributed totally to 16% of the OCPs, while their residues fluctuated between not detected and 197 $\mu\text{g kg}^{-1}$, with an average concentration of 33 $\mu\text{g kg}^{-1}$. Heptachlor epoxide was the most frequently detected compound (>90% detection frequency) and contributed nearly 70% to heptachlors' concentration. The researchers proposed that the higher detection of heptachlor epoxide could be associated with its strong adsorption in the soil and its resistance to biodegradation. Drins (aldrin and dieldrin) along with methoxychlor contributed less than 10% of the total OCPs concentration.

One recent monitoring study was performed in Cardamom Hill Reserve, located in the southwestern Ghats of the Idukki District of Kerala, India, for the determination of 17 OCPs, including p, p'-DDE, p,p'-DDD, p,p'-DDT, α -HCH, γ -HCH, β -HCH, δ -HCH, aldrin, dieldrin, endrin, endrin aldehyde, α -endosulfan, β -endosulfan, endosulfan sulphate, heptachlor, heptachlor epoxide, and methoxychlor [4]. Twenty-two samples were randomly collected between May 2017 and 2018 from the surface horizon (0–15 cm depth) from cultivated cardamom fields. The results indicated that HCHs, DDTs, endrin, dieldrin, and endosulfan were identified in practically all soil samples, while the most frequently detected OCP was β -endosulfan, followed by endrin, p,p'-DDD, and δ -HCH. The integral concentration of OCPs in the examined soil samples varied between 6.35 $\mu\text{g kg}^{-1}$ and 118.29 $\mu\text{g kg}^{-1}$. Regarding DDT and its derivatives, p,p'-DDD was the most predominant compound ranging from below the LOQ to 43.62 $\mu\text{g kg}^{-1}$. The researchers attributed the existence of DDTs to the

extensive historical application of DDT as the concentration of its metabolites was higher than the parent compound ($(\text{DDE} + \text{DDD})/\text{DDT} < 1$). The allocation of p,p'-DDD in the study area suggests the active anaerobic degradation of DDT in soil [55]. Approximately 33% of the studied samples contained endosulfan isomers (α and β); among them, β -endosulfan was the predominant compound and its determined concentrations ranged between below the LOQ and $49.92 \mu\text{g kg}^{-1}$, while α -endosulfan and endosulfan sulfate concentrations ranged from below the LOQ to $8.499 \mu\text{g kg}^{-1}$ and below the LOQ to $5.2024 \mu\text{g kg}^{-1}$, respectively. α -Endosulfan was detected in 4.5% of the examined samples, and the researchers ascribed the existence of α -endosulfan to historical uses. The researchers attributed the existence of endosulfan sulfate to the conversion of α - and β -endosulfan into endosulfan sulfate, which is more persistent in soil than the parent compounds. The cyclodiene drin-related compounds (aldrin, dieldrin, and endrin) were detected in approximately 30% of the examined samples, while endrin was the main compound, and its concentration ranged from below the LOQ and $35.59 \mu\text{g kg}^{-1}$. Endrin aldehyde was also observed in the soil samples, ranging from below the LOQ to $32.144 \mu\text{g kg}^{-1}$. The researchers determined that endrin aldehyde exists in soils due to photochemical reactions and the biodegradation of endrin, as endrin is converted to endrin ketone and endrin aldehyde [56]. Aldrin and dieldrin were also detected in soil samples, indicating that agriculture is the core source of these compounds. HCHs were additionally found in 15.39% of the examined samples. The isomers that were identified were α -HCH, γ -HCH, and δ -HCH at 7.1%, 0.96, and 7.33% of the sum of OCPs, respectively. The researchers concluded that the contamination of the examined area is due to technical HCH because of the lower concentration of γ -HCH compared to α -HCH. The prevalence of δ -HCH isomer in the study area indicated historical applications and not current use. Aldrin, p,p'-DDE, β -HCH, heptachlor, heptachlor epoxide, and methoxychlor were not detected at concentrations above the detection limits in all samples.

Eighty-one surface soil samples (0–20 cm depth) of urban, suburban, and rural transects from the seven most important Indian cities, namely, New Delhi and Agra in the north, Kolkata in the east, Mumbai and Goa in the west, and Chennai and Bangalore in the southern part of India, were gathered and analyzed for the determination of OCPs, including o,p'-DDT, p,p'-DDE, p,p'-DDT, α -, β -, γ -, and δ -HCH, HCB, chlordanes, and endosulfans [57]. HCH concentrations were found to be between 0.01 and $60 \mu\text{g kg}^{-1}$ dw, with the greatest concentration presented in the rural site of Bangalore, followed by a rural site of Goa. β -HCH was the predominant compound followed by γ -HCH, while the $\beta\text{-HCH}/(\alpha\text{-HCH} + \gamma\text{-HCH})$ ratio was higher than 1 in 65% of the examined samples, which indicated historical uses of technical HCH. However, the use of LND could not be excluded, as in the rest of the cases, as this ratio fluctuated between 0.1 and 0.5. The DDT concentration varied between 0.4 and $124 \mu\text{g kg}^{-1}$ dw. Since 60% of DDTs consist of o,p'-DDT and p,p'-DDT, the researchers concluded that the recent use of technical DDT had occurred. However, there were cases where DDTs consisted of p,p'-DDE and p,p'-DDD, indicating historical DDT applications. The dominating p,p'-DDE compound indicates the degradation of p,p'-DDT under the tropical climate of the country. Chlordane residue levels in the examined soils varied from 0.01 to $30 \mu\text{g kg}^{-1}$ dw, while the highest concentration was detected in the rural site of Goa. Trans and cis-chlordanes contributed about 35% and 25% of total chlordanes, respectively. Endosulfans ranged from 0.01 and $237 \mu\text{g kg}^{-1}$ dw, with the highest concentration in a rural site of Goa followed by Bangalore. Endosulfan sulfate was the predominant endosulfan compound in Indian soils. In 72% of the examined soil samples, the ratio of α -endosulfan/ β -endosulfan was 2.33, indicating the recent usage of endosulfan. HCB was omnipresent in all the soil samples gathered from all seven of the major Indian cities. HCB levels could be ascribed to its usage for industrial and agricultural purposes, together with emissions from the partial incineration of waste, coal, fuel, and biomass. Total HCB concentration in Indian soil varied between 0.01 and $8 \mu\text{g kg}^{-1}$ dw, and the highest concentration was detected in Bangalore, followed by Goa. High levels of HCB were also found in soil samples, especially from the site of New Delhi near to a large-scale manufacturing unit, while in the rural site of Bangalore and Goa, it may be due to the inadequate incineration of anthropogenic waste [57].

A study was performed in March 2014 in an agricultural area in Kumluca, a region of Antalya on the Mediterranean coast of Turkey, for the determination of 22 OCPs including: α -HCH, β -HCH, γ -HCH, δ -HCH, heptachlor, heptachlor epoxide, α -chlordane, γ -chlordane, trans-nonachlor, cis-nonachlor, endosulfan isomers (α -, β -endosulfan, and endosulfan sulfate), p,p'-DDE, p,p'-DDD, p,p'-DDT, endrin, aldrin, dieldrin, endrin aldehyde, endrin ketone, and methoxychlor, as well as PCBs in air and soil [58]. The climatic feature of that area is a usual Mediterranean climate, which is characterized by hot and humid summer and rainy and wet winters. Thirty-four soil samples were gathered from three different soil depths: 0–15 cm, 15–30 cm, and 30–45 cm. The total concentration of OCPs in soil samples varied between not detected and $28.1 \mu\text{g kg}^{-1}$ dw. Eighteen OCPs were detected in the studied soil samples, while their detection frequencies ranged from 2.94% to 91.2%. DDTs were the most frequently detected OCPs; among them, p,p'-DDE was the most prevalent compound. Based on the DDT/DDE ratio, the researchers attributed the existence of p,p'-DDE to historical past uses in most (27 cases) of the examined soils. However, there were three cases with DDT/DDE ratios of 1.33, 1.14, and 2.27, indicating recent uses of DDT. Endosulfans distinguished in concentrations ranged from not detected to $13.8 \mu\text{g kg}^{-1}$ dw, while endosulfan sulfate was the most predominant compound in most sampling sites. The dominance of endosulfan sulfate in

most of the soil samples presents a high degree of degradation of parent isomers, which might stem from older usage. The ratio of α -/ β -endosulfan in all studied soil samples varied from 0.327 to 1.20. The lower α -/ β -endosulfan ratios might be an indication of fresh endosulfan applications. The levels of HCHs in the examined soil samples ranged from not detected to $0.041 \mu\text{g kg}^{-1} \text{ dw}$, whilst γ -HCH was the principal compound. The isomer β -HCH was only detected in one sample. The ratios of α -HCH/ γ -HCH of soil samples ranged between 0.250 and 1.57; thus, the researchers concluded that in the examined sites, normally, LND was used in the past. The total concentrations of chlordanes (α - and γ -chlordane, trans- and cis-nonachlor) in soil ranged from not detected to $0.121 \mu\text{g kg}^{-1} \text{ dw}$ [58]. Their relative contribution was trans-nonachlor, γ -chlordane, α -chlordane, and cis-nonachlor. The ratio of γ -chlordane/ α -chlordane ranged from 0.500 to 3.75; thus, the researcher attributed the existence of chlordanes to historical uses of technical chlordane. The total concentration of heptachlor and heptachlor epoxide varied from not detected to $0.095 \mu\text{g kg}^{-1} \text{ dw}$, indicating primarily past uses with some fresh contributions of technical chlordane. With regard to the drin derivatives, aldrin and endrin ketone were not detected in any of the samples, while dieldrin and endrin aldehyde were rarely detected. Endrin was distinguished in 38.2% of soil samples, while the total drin concentration ranged from not detected to $0.604 \mu\text{g kg}^{-1} \text{ dw}$. Due to the absence of endrin's degradation products, the researchers attributed the existence of endrin to recent applications [58].

There was a shortage of research on OCP residues in the soils of Hong Kong until 2000. However, 66 soil samples were gathered during December 2000 from the New Territories, Kowloon, Hong Kong Island, and Lantau Island for the determination of 16 OCPs including DDTs, HCHs, HCB, heptachlor, aldrin, endrin, dieldrin, and α - and β -endosulfan [10]. Forty-six soil samples were collected from the surface horizon (0–10 cm) encompassing five different land use patterns such as grassland, woodland, wetland, and arable as well as reclamation land, while the rest of the twenty agricultural soil samples were gathered from four sampling sites from different soil horizons and from nine soil profiles to demonstrate the depth distributions of OCPs. The analysis results demonstrate that heptachlor, aldrin, dieldrin, and β -endosulfan were not detected in any of the examined samples. HCHs (100%) and DDTs (93.47%) were the most frequently detected OCPs. Endrin, HCB, and α -endosulfan were detected in 32.6%, 11%, and 2.2% of the examined samples, respectively [10]. Endrin was detected in the examined soils at concentrations that ranged from 0.007 to $0.093 \mu\text{g kg}^{-1} \text{ dw}$. The HCB detection concentration varied from 0.007 to $0.31 \mu\text{g kg}^{-1} \text{ dw}$ but was not detected above the LOQ in arable soils. The researchers ascribed the presence of HCB in soils to waste from chlorine-related industries and not the use of HCB as a pesticide. The average concentrations of DDTs and HCHs in the examined soils were $0.52 \mu\text{g kg}^{-1} \text{ dw}$ and $6.19 \mu\text{g kg}^{-1} \text{ dw}$ accordingly. The total concentrations of DDTs in arable soils were substantially greater than those in woodland and grassland soils, indicating that DDT was primarily used for agricultural activities in Hong Kong. The researchers observed that the total concentration of HCHs in all examined soils presented insignificant variations; therefore, they attributed this finding to the comparatively higher vapor pressure of HCH, indicating that HCH is much easier to volatilize than DDT from soil to atmosphere and return to soil through dry or wet deposition after atmospheric transportation, leading to the further homogenous distribution of HCH in soils [41]. DDT (o,p' and p,p'), p,p'-DDE, and p,p'-DDD were the constituents of DDTs, with p,p'-DDE being its predominant metabolite, accounting for 78.8% of the total DDTs. Therefore, the researchers concluded that DDT's main degradation route is to DDE. The ratio of DDT/ (DDE + DDD) implied the existence of aged DDT in most soils of Hong Kong; however, fresh applications were assessed in very rare cases. HCH (α -, β -, and γ -HCH) was detected in soil, with β -HCH being the predominant compound accounting for 95.8–100% of the total HCH concentration. Additionally, the ratio of α -HCH to γ -HCH in the examined soil was like the ratio of technical HCH, which meant it could be assumed that historical uses of technical HCH was its main source; however, the historical usage of LND (γ -HCH) could not be excluded. Regarding the depth distribution of HCHs and DDTs, the researchers observed that for HCH, the concentration increased with soil depth, while the DDT concentration acted oppositely. The researchers' findings are in line with other research, indicating higher vertical mobility in soil profiles for HCH than for DDTs due to differences in their solubility. The researchers mentioned that p,p'-DDE and α -HCH and β -HCH were the main constituents of DDT and HCH, respectively, in the whole soil profile, indicating that the DDT and HCH of the various soil levels were completely undergoing the aged phase [10].

Another study was conducted in three provinces in Pakistan for the determination of OCPs, including HCHs, heptachlors, dieldrin, endrin, and DDTs, in soil and water from the vicinity of selected obsolete pesticide stores in Pakistan [59]. Between 1960 and 1970, a large amount of OCPs was imported in Pakistan for malaria suppression, locust management, and the control of crop pest infestation during the green revolution in the country. Additionally, DDT and HCH were manufactured locally. Soil samples were collected from obsolete pesticide storehouses and courtyards. Thirty-one soil samples were generally gathered from extremely contaminated locations from the vicinity of obsolete pesticide storehouses and courtyards and specifically from Northwest Frontier Province (5 samples), from Punjab (14 samples), and from Sindh (12 samples). DDTs, LND, and heptachlor were the most frequently identified compounds in all examined soil samples, while DDT and its metabolites were detected in almost 100% of soil samples. p,p'-DDT was the predominant

DDT compound, followed by o,p'-DDT, p,p'-DDE, and p,p'-DDD. Dieldrin and endrin were distinguished in 29% and 16% soil samples, with an average concentration of $3000 \mu\text{g kg}^{-1}$ and $5000 \mu\text{g kg}^{-1}$, respectively. The total OCP concentration ranged from: 247,000 to 9,157,000 $\mu\text{g kg}^{-1}$ in the soils from Northwest Frontier Province, 214,000–10,892,000 $\mu\text{g kg}^{-1}$ in soils from Punjab province, and 86,000–113,800 $\mu\text{g kg}^{-1}$ in soils from Sindh province. The researchers observed that obsolete pesticide stores were in bad conditions and posed a threat to human health and the environment; thus, further research into the decontamination of these sites is required [59].

Another study was conducted at an obsolete pesticide dumping ground and the associated areas in Hyderabad City of Pakistan for the determination of 13 OCPs, including DDTs (p,p'-DDE, o,p'-DDE, p,p'-DDD, o,p'-DDD, p,p'-DDT, and o,p'-DDT), chlordanes (cis and trans chlordane), HCB, heptachlor, and HCHs (α -HCH, β -HCH, and γ -HCH), in surface soils [60]. Twenty soil samples from the surface horizon (0–5 cm) were collected from different land use types including pesticide burial ground (seven samples), industrial (four samples), residential (four samples), and background soils (five samples). With regard to pesticide burial ground soils, DDTs were the most frequently detected chemicals and in higher residue levels (77–21,200 $\mu\text{g kg}^{-1}$), while p,p'-DDE (40.2%) and p,p'-DDT (29.5%) were the predominant compounds, followed by HCHs (43–4090 $\mu\text{g kg}^{-1}$), with α -HCH being the dominant component, then chlordanes (0.5–577 $\mu\text{g kg}^{-1}$), HCB (1.3–100 $\mu\text{g kg}^{-1}$), and heptachlor (0.1–28 $\mu\text{g kg}^{-1}$). The most frequently detected OCPs were p,p'-DDE, p,p'-DDEm, and α -HCH with the mean residue levels for p,p'-DDE, p,p'-DDT, and α -HCH being 2212 $\mu\text{g kg}^{-1}$, 615 $\mu\text{g kg}^{-1}$, and 1960 $\mu\text{g kg}^{-1}$, respectively. Generally, the distribution of OCPs revealed significant variations in all types of sampling sites. The researchers concluded that land use plays an essential role in controlling the distribution pattern of OCPs in soil, as various land use types have different physiochemical properties and OCP levels also vary in agreement with it [60].

Twenty-seven soil samples were gathered and analyzed for the determination of OCPs, including HCHs (α -HCH, β -HCH, γ -HCH, and δ -HCH), DDTs (o,p', p,p'-DDE, o,p', p,p'-DDD, and o,p', p,p'-DDT), endosulfans (α -endosulfan, β -endosulfan, and endosulfan sulfate), HCB, heptachlor, and heptachlor epoxide, from nine dumping sites in Pakistan within 200–500 m or 1–2 km distances from waste dumping sites [61]. The total concentration of OCPs in surface soil of waste dumping sites of Pakistan fluctuated between 4.2 and 30.44 $\mu\text{g kg}^{-1}$, and the mean concentration was 13.79 $\mu\text{g kg}^{-1}$, following the order: DDTs > HCHs > endosulfans > HCB > heptachlors. The average concentration of DDTs, HCHs, endosulfans, HCB, and heptachlors were 6.49 $\mu\text{g kg}^{-1}$, 3.5 $\mu\text{g kg}^{-1}$, 2.65 $\mu\text{g kg}^{-1}$, 1.12 $\mu\text{g kg}^{-1}$, and 0.93 $\mu\text{g kg}^{-1}$, respectively. The total DDT concentration varied between 0.16 and 25.66 $\mu\text{g kg}^{-1}$, while the occurrence of DDTs was in the order: p,p'-DDD > o,p'-DDT > p,p'-DDT > o,p'-DDD and p,p'-DDE > o,p'-DDE. In most of the sampling sites, p,p'-DDD was identified with a mean value of 18.8 $\mu\text{g kg}^{-1}$. The detection frequency of DDT isomers was 100%, except for p, p'-DDE, which had a detection frequency of 35.8% [61]. The researchers attributed the existence of the higher concentration of DDT metabolites in the examined soils to the subtropical weather in Pakistan that increased the rate of the transformation of the parent DDT into its metabolites. For differentiating the contribution of DCF from technical DDT, the o, p'-DDT/ p, p'-DDT ratio was employed, indicating the use of DCF in most cases, the use of both DCF and DDT in few cases, and the use of technical DDT in some other cases. The p, p'-DDT/(p,p'-DDE + p,p'-DDD) ratio suggested both recent and historical use. The DDE/DDD ratio was used as an indicator for assessing the degradation pathway of DDT. In the examined soils, both anaerobic and aerobic degradation was identified. The total concentration of HCHs (sum of isomers α -HCH + β -HCH + γ -HCH + δ -HCH) varied from 0.81 to 14.94 $\mu\text{g kg}^{-1}$, while the order of HCHs isomers was as follows: α -HCH > β -HCH > γ -HCH > δ -HCH. The detection frequency of HCHs was 100%, except for δ -HCH, which had a detection frequency of 62%; thus, its contribution to the total HCH pollution was lower than the other isomers. The α -HCH/ γ -HCH and β -HCH/ (α -HCH + γ -HCH) ratios were used to distinguish the contamination source and input history. Based on the abovementioned ratios, both LND and technical HCH were used, while historical uses and recent applications of HCH were identified. The total endosulfan concentration fluctuated between 0.10 and 9.62 $\mu\text{g kg}^{-1}$, while the occurrence of its isomers followed the order: endosulfan sulfate > α -endosulfan > β -endosulfan. It was noticed that β -endosulfan had a 100% detection frequency, whereas endosulfan sulfate had the lowest detection frequency of 30.8% among endosulfan isomers. The α -endosulfan/ β -endosulfan ratio was used for assessing historical or fresh applications. Both cases were identified. The heptachlor concentration varied between 0.11 and 3.69 $\mu\text{g kg}^{-1}$. The heptachlor epoxide/heptachlor ratio was used to estimate the age of heptachlor; thus, recent application was identified [61].

HCB was identified in the range of 0.01 to 5.87 $\mu\text{g kg}^{-1}$, and its existence was ascribed as a by-product during manufacturing processes or as an impurity in various chlorinated pesticides, including LND.

A study was performed for the determination of OCPs, including HCHs (α -HCH, β -HCH, γ -HCH, and δ -HCH), DDTs (o,p'- and p,p'-DDE, -DDD, and -DDT), chlordanes (cis and trans-chlordane), HCB, heptachlor, and β -endosulfan, in the Indus River of Pakistan, which plays a critical role in the agricultural sector of the country and additionally has unique ecological significance [62]. Soil and air samples were taken from the selected sites; specifically, 38 soil samples (0–15 cm) were gathered. The total OCP residue concentration fluctuated between 0.70 and 13.47 $\mu\text{g kg}^{-1}$, while p,p'-DDE had the

highest concentration of $0.71 \mu\text{g kg}^{-1}$. The tendency of OCPs was in the following order: DDTs > HCHs > chlordanes > HCB > heptachlor > β -endosulfan. Amongst DDTs, p,p'-DDE was demonstrated to have the highest concentration (not detected to $4.76 \mu\text{g kg}^{-1}$), which suggested that DDT in soil was exposed to microbial degradation and transformation takes place into its more stable and toxic metabolite, p,p'-DDE. HCHs isomers were detected in low concentrations, and β -HCH and δ -HCH were the predominant components. Chlordanes fluctuated between not detected to $0.33 \mu\text{g kg}^{-1}$ for cis-chlordane and between not detected to $0.96 \mu\text{g kg}^{-1}$ for trans-chlordane. [62].

There is limited information about the contamination of agricultural soil by OCPs in Iran. One study was conducted between March and April 2016 in agricultural areas in southern Iran and specifically from the agricultural areas of the Dalaki and Shabankare plains of Iran. Twenty-eight soil samples were gathered from the surface horizon (0–10 cm) for the determination of OCPs, including HCH, heptachlor, DDT, chlordane, and their isomers [63]. Residues of DDTs, chlordanes, and HCHs were identified in all soil samples from both plains, while their mean concentration was determined in the following order: DDTs > chlordanes > HCH. In the Dalaki plain, the mean concentrations of the identified compounds were as follows: $0.411 \mu\text{g kg}^{-1}$ dw for HCHs (α -, β -, γ -, and δ -HCH), $4.37 \mu\text{g kg}^{-1}$ dw for DDTs (o,p'-DDE, o,p'-DDD, o,p'-DDT, p,p'-DDE, p,p'-DDD, and p,p'-DDT), and $2.04 \mu\text{g kg}^{-1}$ dw for chlordanes (trans-chlordane, cis-chlordane, heptachlor exo-epoxide, and heptachlor). In the Shabankare plain, the mean value of HCHs, DDTs, and chlordanes was measured to be $1.38 \mu\text{g kg}^{-1}$ dw, $11.99 \mu\text{g kg}^{-1}$ dw, and $1.62 \mu\text{g kg}^{-1}$ dw, respectively. The concentration tendency of OCP residues in both plains was as follows: DDT > CHL > HCH. The ratio of p, p'-DDT/(p,p'-DDE + p,p'-DDD) can be an indicator of the use of DDT. Based on the results, this ratio in Dalaki for 64.3% of the samples was less than 1 and was greater than 1 for 35.7% of the samples, indicating the historical use of DDT in most of the examined soils and recent use in some of them. In the Shabankare plain, 14.3% of the soil samples revealed the recent use of DDT, while 85.7% of the measured samples showed historical use. Taking into account the ratio of o,p'-DDT/p,p'-DDT, the researchers concluded that in both plains, 7.1% of the soil samples demonstrated the use of DDT, and 57.1% of the evaluated samples indicated that DDT was used as DCF [63]. Additionally, the ratio of p, p'-DDE/p, p'-DDD can be utilized to ascertain the relative aerobic or anaerobic conditions governing the soil environment. The researchers concluded that in Dalaki soil samples, 78.6% and 21.4% of the soil samples had aerobic and anaerobic conditions, respectively; however, in Shabankare, in all soil samples, the aerobic conditions were dominant. With regard to chlordanes, it is known that trans-chlordane decomposes faster than cis-chlordane in the environment; thus, cis-chlordane/trans-chlordane is used for the determination of the recent or historical use of this OCP. In the Shabankare and Dalaki plains, this ratio was greater than 1 in 64.3% and 21.4% of the soil, respectively, indicating historical use in most cases [63].

Ten soil samples from the surface horizon (0–20 cm) were collected twice during September 2017 and February 2018 from fields in paddy plantations situated in five locations of Machang, Kelantan of Peninsular Malaysia, for the determination of ten organochlorine pesticides, including HCHs (α -HCH, β -HCH, γ -HCH, and δ -HCH), p,p'-DDT, p,p'-DDE, p,p'-DDD, α -endosulfan, β -endosulfan, and endosulfan sulfate [64]. The presented results indicated that all HCHs isomers were identified, along with p,p'-DDT and endosulfan sulfate. HCHs concentrations varied from below the LOD to $7340 \mu\text{g kg}^{-1}$, while α -HCH was the predominant compound. Regarding p,p'-DDT, its concentration varied from 90 to $5240 \mu\text{g kg}^{-1}$ and endosulfan sulfate from below the LOD to $30 \mu\text{g kg}^{-1}$.

The central Asian Republic of Tajikistan has been an area of widespread historical agricultural pesticide use as well as large-scale burials of banned OCPs [65]. Soil samples from the surface horizon (0–10 cm) and from four rural areas of Tajikistan were gathered during a four-year study from pesticide burial sites and family farms for the determination of OCPs including DDTs (DDT, DDD, and DDE), LND isomers (α -HCH, β -HCH, γ -HCH, and δ -HCH), endosulfan isomers (α -, β -endosulfan, and endosulfan sulfate), other cyclodienes (aldrin, α - and γ -chlordanes, dieldrin, endrin, endrin aldehyde and ketone, heptachlor, and heptachlor epoxide), and methoxychlor. The sampling sites were selected to represent a variety of pesticide disposal histories and to allow for the consideration of local pesticide pollution in Tajikistan. DDT was regularly the highest measured pesticide in all four sampling areas, along with HCH isomers and β -endosulfan. Concentrations of DDD and DDE were substantially lower than the levels of DDT at each site. Heptachlor, heptachlor epoxide, methoxychlor, endrin ketone, aldrin, endrin, and endosulfan sulfate were not detected at levels above the LOD.

5. American Countries

A study to assess the contamination levels of the banned OCPs in the physical environment of Costa Rica, a country in Central America, was performed across the whole country in 2004, with sampling of air and soil samples at 23 stations. The soil-sampling sites (0–25 cm) were in protected areas, such as National Parks, Biological Reserves, and research stations, where OCPs were not used in the past and additionally reflecting not only the diverse topography (sites on the Caribbean and Pacific coast and locations with 3400 m in elevation) but also climate and soil properties. In the studied soil samples, the major DDT compounds were p,p'-DDE and p,p'-DDD with concentrations that ranged from below the LOQ

up to $1 \mu\text{g kg}^{-1}$, which could be attributed to non-agricultural background soils in protected areas [66]. Dieldrin had the highest concentration reaching up to $2.0 \mu\text{g kg}^{-1}$; however, it was detected in less than 50% of the samples. The residue levels of HCHs were normally quite low; however, γ -HCH was comparatively abundant among the other HCHs. The researchers attributed the higher γ -HCH concentrations noticed in some sampling sites to the recent use of LND in the country. DDE and DDD were only identified in 5 of the 20 samples; however, the high DDT levels clearly indicate hotspots of DDTs which were used for the elimination of malaria. Heptachlor epoxide was only detected at three sampling sites and may be related to the differential ability of soil to transform heptachlor [66].

Amongst the Latin American countries, Mexico was a major consumer of OCPs for both sanitary and agricultural purposes. For that reason, a study was performed in Mexico for the examination of the spatial distribution of OCPs including HCHs (α -HCH, β -HCH, γ -HCH, and δ -HCH), cis- and trans-chlordane, trans-nonachlor, aldrin, dieldrin, heptachlor and heptachlor epoxide, α -endosulfan, β -endosulfan and endosulfan sulfate, DDTs (p,p'-DDE, o,p'-DDE, p,p'-DDD, o,p'-DDD, p,p'-DDT, and o,p'-DDT), and toxaphenes in rural (with no agricultural activities and away from urban sites), urban, and agricultural soils. Eighteen soil samples from the surface horizon (0–5 cm) were collected from eighteen sites across nine states of Mexico during 2005 [67]. The most frequently detected OCPs were DDTs (100%), followed by toxaphenes (97%), endosulfans and chlordanes (93%), HCHs (55%), drins (21%), and heptachlors (3%). Aldrin, β -HCH, and δ -HCH were not detected in any of the samples. The DDT residue levels varied from below the LOD to $360 \mu\text{g kg}^{-1}$, while their highest concentration identified in urban soils, followed by agricultural and rural soils. It was clarified that the highest residue DDTs levels found in urban areas was due to samples taken from the endemic malaria's regions, where the highest amount of DDT was consumed during 1989 to 1999. Rural soils had a maximum DDTs residue level of $1.7 \mu\text{g kg}^{-1}$, while, in most of them, the concentration was below $0.04 \mu\text{g kg}^{-1}$. The most detectable DDT isomer was the p,p'-DDE, indicating historical uses; however, in 5 of the examined soils, p,p'-DDT concentration was higher than p,p'-DDE, indicating either recent DDT use or slower degradation rates in these soils. With regard to the DDTs, it was found that 59% of the samples contained p,p'-DDE, 48% o,p'-DDT, and 38% o,p'-DDE. Toxaphenes were considered as the sum of hepta-, octa-, and non-achlorobarnates; thus, toxaphene residue levels varied from below the LOD to $334 \mu\text{g kg}^{-1}$ in all sampling points. Higher concentrations were found in agricultural soils, followed by urban soils, while rural soils contained the lowest residue levels [67]. Endosulfan residues (α -endosulfan, β -endosulfan, and endosulfan sulfate) ranged from below the LOQ to $909 \mu\text{g kg}^{-1}$ and are the only currently used OCPs, while endosulfan sulfate was the most frequently detected compound. The highest residue levels were identified in agricultural soils, followed by urban and rural soils. Chlordanes (cis- and trans-chlordane and trans-nonachlor) residue levels varied between $0.0033 \mu\text{g kg}^{-1}$ and $2.7 \mu\text{g kg}^{-1}$, while their highest concentration was found in agricultural soils. HCHs were only detected above the LOD in some agricultural and urban soils [67].

A survey was organized in the southeastern region of Buenos Aires province in Argentina to evaluate agricultural soils as a potential source of OCPs for the aquatic biota of an adjacent pond [68]. Ten soil samples were taken between July and October 1998 at an altitude of 80 m above sea level and at two horizons (0–30 cm and 45–60 cm) for the same sampling point for the determination of OCPs including p,p'-DDT, p,p'-DDE, p,p'-DDD, γ -HCH (LND), heptachlor, heptachlor epoxide, aldrin, dieldrin, and endrin. The analysis results revealed that the total OCP concentration was higher in the lower horizon than in the upper horizon. The allocation pattern of the concentration of the OCPs in the upper horizon was: LND > heptachlor > heptachlor epoxide and DDT. In the lower horizon, the pattern was: LND > DDT > DDE > DDD > aldrin > heptachlor and heptachlor epoxide. Thus, heptachlor was limited to the upper horizon, while heptachlor epoxide, LND, DDTs, and aldrin were concentrated in the lower horizon. LND (γ -HCH) was the only OCP being used at the time of the study, and its concentration was more than 40% of the total OCPs detected in both horizons. The heptachlor epoxide average concentration found in soil was $6.7 \mu\text{g kg}^{-1}$ dw, while DDTs' highest concentration was $116.8 \mu\text{g kg}^{-1}$ dw, and it was only detected in the lower horizon of the studied soil. This was explained by its extended residence time in soils that would permit it to reach the deeper soil layer by translocation with colloids [68].

Ninety soil samples were collected randomly (grid sampling) at root level, due to fears of the possible uptake of OCPs and PCBs, from three areas (A, B, and C) in Fort Albany (on the mainland), subarctic Ontario, Canada. Samples were collected from agricultural, residential/parkland, commercial, and industrial areas and analyzed among other pollutants for OCPs including DDTs (p,p'-DDT, o,p'-DDT, p,p'-DDD, o,p'-DDD, p,p'-DDE, and o,p'-DDE), HCB (β -HCB, γ -HCB, and δ -HCB), heptachlor, heptachlor epoxide isomer B, drins (aldrin, dieldrin, endrin, and endrin aldehyde), endosulfans (α -endosulfan, β -endosulfan, and endosulfan sulfate), and methoxychlor [69]. The concentration of DDTs in soil samples presented a heterogeneous distribution with concentrations that ranged from below the LOD to $4190 \mu\text{g kg}^{-1}$.

Twenty surface soil samples (0–10 cm) collected in February 2005 from James Ross Island located in the southeast coast of the Antarctic Peninsula were collected for the determination of persistent organic pollutants including OCPs (α -HCH, β -HCH, γ -HCH, and δ -HCH), p,p'-DDE, p,p'-DDD, p,p'-DDT, HCB, and PeCB (pentachlorobenzene) [70]. The HCH

concentration ranged between 0.51 and 3.68 $\mu\text{g kg}^{-1}$, DDT between 2.41 and 7.75 $\mu\text{g kg}^{-1}$, HCB from 0.59 to 2.24 $\mu\text{g kg}^{-1}$, and PeCB from 34.9 to 171 $\mu\text{g kg}^{-1}$. The occurrence of HCB in the soil designates that the long-range atmospheric transport is the most probable source of pollution in James Ross Island.

A study was conducted in 36 Alabama agricultural soils (experimental stations and private farms) to evaluate residues of formerly used OCPs including α -HCH, γ -HCH, heptachlor, heptachlor epoxide, trans and cis-chlordane, dieldrin, p,p'-DDE, o,p'-DDE, p,p'-DDD, o,p'-DDD, p,p'-DDT, o,p'-DDT, trans-nonachlor, and toxaphenes [74]. The determined concentrations fluctuated by several orders of magnitude between farms and seemed to be log-normally distributed. Toxaphene and DDTs were demonstrated to have the highest average concentrations among other OCPs; thus, the toxaphene mean concentration was 285 $\mu\text{g kg}^{-1}$ dw, p,p'-DDE was 22.7 $\mu\text{g kg}^{-1}$, p,p'-DDT was 24.6 $\mu\text{g kg}^{-1}$, o,p'-DDT was 4.0 $\mu\text{g kg}^{-1}$, and p,p'-DDD was 2.4 $\mu\text{g kg}^{-1}$. The researchers concluded that the determined residues were not proportionate to soil organic carbon content, suggesting that residues were an indication of historical pesticide applications. The DDT/DDE ratios in six regions of the state ranged from 0.39 to 1.5, and compound ratios for chlordanes and toxaphene were different from those in the technical mixtures.

6. Overall Integration of the Studies Outcomes

In most of the studies, statistical data such as detection frequencies, arithmetic and geometric mean concentration, and concentration ranges (minimum and maximum concentrations) were available for the detected OCPs. However, the compounds studied in each monitoring survey deviated significantly. Based on the results of the monitoring studies, HCHs, DDTs, and heptachlors were the most frequently detected OCPs in soils worldwide, more than 40 years after their use was banned. This soil pollution can be due to direct exposure by their application on agricultural fields (illegal routes) or even from indirect routes via drift or runoff. Furthermore, their long half-lives have caused them to accumulate in soil historically. Examining the pesticide residues in the soil frequently is crucial to realize pesticides' fate and their occurrence in different compartments. What is evident in the examination of the OCPs in the soils is that there have not been adequate studies and programs dedicated to this issue, while the remediation of soil has not been attempted. European nations and Asian ones, to some extent, were more involved in soil pollution with OCPs, but in other parts of the world, one can easily observe an immense need for routine monitoring programs. Certainly, the future potential of soil monitoring research for OCPs is emphasized to fill the current differences in many countries.

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