Chemical Analysis of Organochlorine Pesticide in Agricultural Soils

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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. A plethora of methods have been developed and applied for OCP analysis in environmental matrices (i.e., soil and sediment). The entire chemical analysis involves several crucial stages such as sample preparation and analyte chromatographic separation, including detection, quantification, and data analysis. Among them, the sample preparation step is considered as the most critical point to be made prior to instrumental analysis. In particular, the development of methodologies for determining pesticides in soil is a challenging task. As a result of the complexity and the physicochemical characteristics of such types of samples, two main factors should be considered: (a) the extremely low concentration of banned OCPs in soil samples. This is the reason why extremely sensitive analytical methods (including, in many cases, enrichment techniques) are required for the detection and quantification of these analytes at such levels, and (b) the strong binding of OCPs to soil.

Analytical Methods soil Organochlorine pesticides QuEChеRS extraction
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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]. The goal of this convention was to protect human health and the environment from POPs by the banning or restriction of their production.

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. Extraction Techniques Used for Solid Environmental Samples

2.1. Solvent Extraction Techniques

Various extraction and clean-up techniques for pesticide residues from soils have been reported in the literature since the 1990s. During the extraction step, many interfering compounds are co-extracted from soil samples together with the analytes.

Conventional Solvent Extraction Techniques

There are many studies that used the solvent extraction of organic analytes prior to solvent evaporation from solid samples such as environmental soil and sediment matrices, which is commonly known as solid–liquid extraction. Conventional sample preparation techniques include solvent extraction techniques such as mechanical agitation by shaking [18][19], Soxhlet extraction [20][21], as well as ultrasonic solvent extraction [22].

The shake flask method refers to the extraction of organic molecules using a mechanical shaker and some solvents. Almost ten years ago, in the study by Mao et al. in 2012, this extraction method was evaluated in the extraction of DDT pesticides from soil matrices, using five different organic solvents: ethanol, 1-propanol, and three fractions of petroleum ether. Various factors such as organic solvent concentration, wash time, temperature, mixing speed, and solution-to-soil ratio were studied, and it was proved that they could significantly affect the extraction procedure. In the same study, it was concluded that the extraction with 100 mL of petroleum ether (60–90 °C), a washing time of 180 min, a mixing speed of 100 r min^{-1}, a solution-to-soil ratio of 10:1, and a washing temperature of 50 °C were the most appropriate parameters for the extraction of DDTs from soil [23]. Since then, there have been few other studies that have referred to this technique, but in most cases, the research and assessment was conducted in conjunction with other, newer extraction techniques [24][25][26].

A second effective conventional extraction procedure for volatiles and semi-volatiles analytes from solid matrices is Soxhlet extraction (SE), which is still recommended by the US Environment Protection Agency (EPA), Food and Drug Administration (FDA), and Association of Official Analytical Chemists (AOAC) Standards Methods [27]. Generally, the minimum time needed for regular SE is normally ~8 h, where, after many cycles and significant solvent consumption, the desired compound is concentrated in the distillation flask. SE is performed with either a single solvent that is usually toluene or dichloromethane (DCM) or a mixture of solvents such as hexane/acetone, pentane/DCM, etc. As sulfur is present in the sediment and soil sample, clean-up usually involves sulfur removal via a reaction with Cu or tetrabutylammonium sulfite and the use of silica gel, Florisil ($MgSiO_3$), etc. [28]. Twenty-five years ago, Lopez-Aviala et al. were among the first to evaluate the SE procedure to determine several OCPs in soil and sediment samples [29]. Specifically, 250 mL of DCM:acetone (1:1) exchanged by 50 mL of hexane were selected as the extraction solvents following a 24 h extraction period prior to GC–ECD analysis with GC/MS confirmation. Silica gel (SG) was also used to clean individual OCPs from certain interferants [30]. Since then, many studies, including comparative approaches to other extraction techniques, have used the SE extraction method. Even recently, although SE is time-consuming, requires a large volume of organic solvents, and is difficult to modify and automate, perhaps due to the simplicity of the device and the fact that no specialized training needed, it continues to be used in this direction [31][32]. For example, in 2019, Xing et al. successfully extracted several HCHs (including α-HCH, β-HCH, γ-HCH, and δ-HCH) and other DDTs (including o,p′-DDE, p,p′-DDE, o,p′-DDD, p,p′-DDD, o,p′-DDT, and p,p′-DDT) from surface soils using 150 mL of DCM as the extraction solvent in a 24 h SE extraction procedure, prior to GC–ECD analysis [33]. Alternatively, considering the previously mentioned disadvantages of SE regarding solvent waste and time consumption, it was optimized and automated firstly in 1994, providing the commercial product known as Soxtec extraction. The latter was approved by the EPA as a standard method [28][34][35]. For OCPs, the Soxtec method was compared with a newer procedure based on QuEChERS extraction by Rashid. A. et al. in 2010. Specifically, six soil samples were collected to determine 18 OCPs, yielding results with good agreement between the two extraction methods [36].

Ultrasonic extraction (USE) is another typical extraction method that could be used as an alternative to common SE and to shaking flask extraction to extract pesticides from soil samples. As the extraction temperature and pressure are lower than the common values, is recommended for the determination of thermolabile analytes from soil samples. However, USE in general requires significant amounts of solvent and an extra separation step for residue and extraction via centrifugation or filtration. In 2006, Torr et al. applied this technique for the determination of OCPs and their metabolites from real soil samples [24]. The optimization was performed in relation to the solvent type, the amount of solvent, and the sonication time. Finally, it was proposed that the soil matrices should be extracted twice using 25 mL of a mixture of petroleum ether and acetone (1/1 *v*/*v*) incorporating 20 min of sonication to achieve satisfactory extraction efficiency. Pesticide recoveries from fortified soil samples ranged from 88% to 92%, with relative standard deviations generally below 6%. The time consumption was reduced by approximately 75% and 82% compared to the shake flask and SE methods, respectively. Furthermore, solvent reduction was near to 67% compared to SE. Even though USE is not widely used to determine OCP extraction in soils, the results strongly demonstrated that USE could be efficiently applied to extract OCPs from soils with solvent and time extraction to be scientifically reduced. Furthermore, a miniaturized ultrasonic extraction procedure was successfully developed for the determination of different OCPs in soil by Ozcan S. et al. in 2009 [37]. The parameters influencing the efficiency procedure (i.e., amount of sample, volume of extraction solvent, number of extraction steps, etc.) were optimized by using 23 experimental factorial designs. Ideally, 0.5 g of soil sample was sonicated for 5 min with 5 mL of petroleum ether and acetone mixture (1/1, *v*/*v*) in an ultrasonic bath. The extraction was repeated three times with satisfactory reproducibility at lower consumption levels of solvents and samples.

Modern Extraction Techniques

Conventional techniques, as already mentioned, use large amounts of solvents and time-consuming extraction procedures to extract low-content organic analytes from complex solid matrices. Furthermore, as the wasted solvents not only increase the analysis cost but may cause significant pollution by releasing solvents into the environment, constant changes in environmental regulations severely limit the amount of solvent usage in laboratories worldwide. For example, in the United States, an order has called for a 50–90% reduction in solvent usage in all federal laboratories [38]. Later, new extraction procedures were developed to reduce the extraction and amount of solvent required and to improve the accuracy and precision of analytes for the common extraction techniques. Over the past twenty years, some green solvent extraction techniques have been developed to mitigate these effects. Among them are ultrasound extraction (USE), microwave-assisted extraction (MAE) [39][40], accelerated solvent extraction (ASE) [41][42], supercritical fluid extraction (SFE) [41], solid phase extraction (SPE) [43], solid phase microextraction (SPME) [44], matrix solid phase dispersion extraction (MSPDE) [45][46], QuEChERS methods [24][30], and procedures such as focused ultrasound liquid extraction (FUSLE) [47][48] and pressurized liquid extraction (PLE) [42][49][50][51], which all require shorter extraction times and low amounts of solvents while sometimes providing higher recovery yields of the analytes when compared with classical extraction [52].

In recent years, the USE technique has been developed to minimize its problems and become more useful and applicable to analytical chemistry. Modified focused ultrasound liquid extraction, known as FUSLE, is based on the application of high-power focused ultrasonic waves using a micro-tip immersed directly in the extraction mixture. FUSE has been successfully optimized for the simultaneous analysis of multiple pesticides including POPs in several matrices, including soils and sediments. The variables studied during the optimization process were the percentage of maximum power, extraction time, number of cycles, extraction solvent, and sample amount [53]. In literature, the first reference to the use of the FUSE technique for the determination of OCPs in soils was made by Flores-Ramírez et al. in 2015. This group managed to successfully validate FUSE using gas chromatography–electron impact–mass spectrometry (GC-EI-MS) for the determination of 13 OCPs. In optimized conditions, FUSE was carried out with a 1 g sample using 10 mL of hexane:DCM (75:25, *v*/*v*) as an extraction solvent of for 1 min in duplicate and at 60% irradiation power at 20 °C. In addition, a cleaning procedure was followed using columns packed with Florisil. The results showed that FUSE was viable and easy to use for the detection of POPs in soils [47]. Even if only a few studies for the extraction of POPs from soils are available, it can be considered as a suitable technique.

The ASE technique, also known as PLE, or enhanced solvent extraction (ESE), is a modern comprehensive technique that has become very popular and was accepted by the US EPA (Method 3545A and 6860), the US Contract Laboratory Program (SOW OLM04.2), and ASTM (Standard Practice D-7210 and D-7567). It is also standardized for in use methods, based on ASE extraction, in China (Method GB/T 19649–2005) and in Germany (Method L00.00-34). This technique is similar in principle to SE but is performed at high temperatures in the range of 40–200 °C to enhance the speed of elution and high pressures in the range of 1000–2500 psi to keep the solvents in liquid states. Among the main advantages of ASE, as highlighted in several publications over the years, is the extraction of multi-residue pesticides and the fact that ASE can be used for a wide variety of analytes, as polar and non-polar solvents can be used for the extraction process [49][54]. Many years ago, in 1999, the extraction of pesticides from soil using the ASE technique was described by Gan et al. Soil (10 g) was shaken vigorously with 20 mL of a solvent combination of methanol:water (4:1, *v*/*v*) for 1 h. The supernatant was decanted after the mixture was centrifuged at 10.000 rpm for 15 min. The efficiency of ASE was proven to be better than that of the classical extraction methods such as SE or shake extraction using the same solvent mixture [54]. Later, several researchers tried to apply ASE to extract some OCPs from environmental solid matrices [42][54][55]. However, in 2008, the team of Vega Moreno et al. was the first that managed to determine a wide group of OCPs (α-, β-, γ-HCH, aldrin, endrin, dieldrin, p,p′-DDE, etc.) in agricultural soil samples, using a one-step ASE with gas chromatography with an electron-capture detector (ECD) [56][57]. Particular variables of ASE were studied, and they were the type of solvent, the number of cycles, temperature, time, flush volume, and pressure. The optimized conditions were: hexane:acetone (1:1), one cycle, 50 °C, 60% flush volume, and 1500 psi. This method detected thirteen OCPs in soils at low concentrations of up to 0.3 ng·kg^{-1} with satisfactory recoveries and RSD values [56]. The study by Wentao Wang et al. (2007) attempted to test the extraction efficiencies of three methods, including ASE extractions in soil samples with different total organic carbon contents. The results showed that the values obtained were comparable with the values reported by other studies and that ASE demonstrated the best extraction efficiency [53]. In the study by Lehnik-Habrink et al. (2010), the simultaneous extraction of several pesticides, including OCPs from organic forest soil, using the ASE technique with acetone/cyclohexane (2/1, *v*/*v*) followed by SPE with silica gel and GC–MS analysis, provided the highest extraction efficiency compared to other extraction techniques such as to SE, USE, and sonication [26].

In another study, Xingru Zhao et al. developed a novel method to simultaneously detect eight classes of POPs, including 18 OCPs, in sediment that underwent freeze-drying and biota samples. The sample extraction was performed via ASE using a mixture of dichloromethane:hexane (1:1, *v*/*v*). In addition, in order to remove elemental sulfur acting as an interfering substance in sediment samples, further purification of the extracts with activated copper or tetrabutylammonium sulfite mixed with the extract or mounted on the top of the silica column were applied. The proposed clean-up procedure included the fractionation of extracts into two fractions with a multi-layer silica gel column, followed by further fractionation using a basic alumina column (fraction 1) and a Florisil column (fraction 2), respectively [58].

Several studies applying ASE for the extraction of OCPs can be found in the recent literature. In 2018, Chaza et al. analyzed several OCPs, including DDTs and HCHs from dried soils via ASE followed by GC–MS analysis at high levels. The levels of DDT and HCH insecticides were as follows: 29.4 and 10.1 ng g^{-1}, respectively. In their work, two successive extraction processes were applied. First, the sample was extracted with hexane/acetone (1/1 *v*/*v*) at 100 °C and pressure at 103.45 bar. Second, the extraction was performed with DCM at the same temperature and pressure at 138 bar. Finally, the two extracts were combined. To remove the sulfur, clean-up with activated copper was applied and purified in a silica column and several combinations of organic solvents [59]. Two years later, in 2020, Aleksandra Ukalska-Jaruga et al. followed the analytical procedure according to the ISO10382 standard and successfully extracted six OCPs (α-HCH, β-HCH, γ-HCH, p,p′-DDT, p,p′-DDE, and p,p′-DDD) from arable soils in Poland using a hexane:acetone mixture (70:30 *v*/*v*). The pesticides residues were determined using gas chromatography with an electron-capture detector (GC–μECD) and ranged from 0.61 to 1031.64 μg kg^{-1} [60].

MAE, also called microwave-assisted solvent extraction (MASE), uses microwave energy to heat solvents in contact with a sample and has been applied in many studies as an alternative green method for the extraction of organic pesticides from soil samples. Among the advantages of the method is the fact that it does not cause changes to the molecular structure, it is fast, and it allows for the simultaneous extraction of several compounds. Particularly, if a conventual extraction procedure is considered to take 15–30 min and requires small volumes of solvent in the range of 10–30 mL, MAE uses approximately 10 times smaller volumes. This technique was first introduced by Ganzer and Salgo in two publications in 1986 and 1987 using a domestic microwave. Onuska and Terry used microwave energy to extract OCPs from sediment samples with quantitative recoveries and without compound breakdown due to sample exposure to microwaves [29]. In 1994, Avila et al. evaluated this extraction procedure for the extraction of twenty OCPs from six types of soils and sediments, and in a subsequent study, the list of compounds was expanded to nearly a hundred OCPs and OPPs [29][61][62].

In the following years, several researchers investigated and optimized the factors influencing the performance of MAE extractions of OCP pesticides from soil samples, and many researchers were interested in comparing known extraction methods for the publication of numerous studies [53][63][64]. In 2003, Concha-Graña proposed the solvent combination of hexane:acetone (1:1) as the MAE solvent for the extraction of OCP pesticides in soil samples, arguing that the time consumed during the evaporation phase was much shorter with this solvent mixture. The extraction time was set at 10 min, and the highest power applied was set at 800 W [65]. A simple and novel analytical method for quantifying twelve persistent organic pollutants (POPs) in marine sediments was developed in 2005 by Basheer et al., using MAE and a single-step liquid-phase microextraction (LPME), hollow fiber membrane (HFM) clean-up and enrichment procedure [66]. One year later, in a study by Herbet et al. using MAE with a small volume of the same extraction solvent, followed by a clean-up step for the redissolved extracts and GC–MS/MS analysis, the successful isolation and quantitation of eleven OCPs was demonstrated in very complex solid matrices such as landfill soil samples [38]. Over the years, there have been several other reports that have used the MAE extraction technique in conjunction with other purification steps, further described below in a separate section.

As an alternative to the MAE extraction technique, the Microwave-Assisted Micellar Extraction (MAME) technique, using a micellar (surfactant-rich) medium to substitute organic solvents as an extractant, has been applied to achieve the satisfactory extraction of several organic molecules from solid samples, including soil matrices, with low cost and low toxicity. However, as the micelle-rich phase is viscous and cannot be injected directly into some analysis apparatus (e.g., LC-MS/MS), an additional clean-up such as solid phase extraction (SPE) or headspace (HS)-SPME was also needed, resulting in a multi-step analytical procedure [63][67]. In 2006, Moreno et al. effectively optimized the MAME technique and studied the determination of five OCPs from several kinds of real agricultural soil samples, using a surfactant as an extractant with SPME HPLC-UV. Taking into consideration the reduction in the time and extractant required, the cost was also effectively lowered [68]. In the last decade, fewer studies have focused on the optimization and application of MAE extraction for the determination of OCPs from soils. However, there are several publications in which the MAE method was compared to other extraction methods [25][53]. MAE presented the advantages of shorter extraction time, lower solvent consumption, and greater automation with the possibility of the simultaneous determination of multiple samples. The basic advantages of MAE in comparison to other conventional and alternative methods are based on the use of high temperatures during a short period of time and low solvent volume consumes, while sometimes, MAE offers higher recoveries than SE and USE extraction techniques [52][64][69].

The SFE technique appeared in the late 1980s. There was growing interest in SFE in the early 1990s due to its numerous advantages over liquid extraction. The principle of this technique involves the use of an extractant being in its supercritical state, passing it through a contaminated matrix, solubilizing the contaminant, and transporting it to a collection solvent for analysis. Supercritical CO_2 is commonly used in SFE since it is a good extraction medium for non-polar compounds and moderately polar ones, such as OCPs. The extraction efficiency of CO_2 can be improved by adding small amounts of modifiers that interact with the matrix to promote desorption into the fluid. In addition to CO_2, supercritical N_2O could also be used both with and without modifiers. In 1996, Ling et al. evaluated the SFE extraction of 16 OCP pesticides from soil samples and studied the SFE extraction efficiency based on analyte–matrix interactions. The soil properties of TOC and pH were found to significantly influence the extraction efficiency, while moisture content (0.9% to 5.0%) did not affect the recovery results, except for the endrin aldehyde compound. Specifically, the increase in the recovery of this analyte with increasing amounts of moisture content was associated with the formation of H-bonding between the carbonyl group in the endrin aldehyde and the water molecule. In addition, the simultaneous clean-up of sulfur-containing soils using silver nitrate ($AgNO_3$) in the extraction cell proved to improve the extraction efficiency, except that the heptachlor analyte appeared to be degraded into heptachlor epoxide using $AgNO_3$. The total amount of time needed from SFE extraction to GC–ECD analysis was less than 2 h [70].

Many years later, in 2006, an experimental design approach was used to optimize the SFE extraction conditions for several pesticides, including OCPs in real soil samples from the Povoa de Varzim area, north of Portugal. A high extraction temperature was used given the high percentage of non- and semi-polar compounds, while the addition of a modifier was beneficial for the extraction of more polar pesticides. SFE has been shown to be an attractive technique for the analysis of pesticide multi-residues in soil samples, confirming a few of the previous results for persistent OCPs in the same solid environmental matrices [71]. This procedure is simple, rapid, and only requires a small number of samples and solvents. SFE was proven to be more efficient than solvent extraction, particularly for non-polar components in solid matrices such as soils, especially with high organic carbon contents, while the applicability of SFE to polar pollutants and metabolites is limited. Furthermore, SFE produces clean extracts in comparison to other extraction procedures (e.g., Sohxlet), and no additional purification is required [41]. Despite evident advantages, it was soon found that extraction conditions are strongly dependent on both the solutes and the matrix, so that parameters need to be adjusted for every new application. For example, it was reported that despite their high solubility in CO_2, the solute–matrix interactions may yield lower recoveries for OCPs than expected from solubility alone. Thus, extractions of OCPs from spiked soils were unsatisfactory, especially for soils with a high organic content [71]. Therefore, SFE is not widely adopted in official methods, and only a few analytical protocols have been reported for the multi-residue analysis of pesticides in soils based on SFE [72].

2.2. Other Extraction and Clean-Up Techniques

SPE was introduced in the 1970s, and it is still dominantly used for the extraction of organic pollutants from soil samples. Many different sorbents (which were previously conditioned by an appropriate solvent or solvent mixture) are used for the isolation of the analytes depending on the properties of the analytes and the matrix samples. The most commonly reported sorbents in pesticide extraction are reverse phase octadecyl (C18), normal-phase aminopropyl (-NH2), primary–secondary amine (PSA), anion-exchange three-methyl ammonium (SAX), and adsorbents such as graphitized carbon black (GCB). In addition, normal-phase sorbents such as Florisil, aluminum oxide (Al_2O_3), and silica (SiO_2) are usually used in combination with the previously mentioned sorbents due to their extremely polar character, and they are the proper choice for the efficient extraction of non-polar analytes in soil such as OCPs [73]. There were several studies reported regarding the extraction of OCP pesticides from environmental matrices, where SPE was used as a clean-up step in combination with several extraction techniques. For example, in 2009, Hu et al. reported the use of SPE cartridges containing 1 g of Florisil after USE for the extraction of several OCP pesticides from surface soil samples and sediments [43][74].

In 2013, a study based on MAE using an additional SPE clean-up step was developed by Yu Liu. Twenty-three OCP pesticides were extracted from soil samples using MAE, followed by the evaporation of the solvent and purification with a silica and alumina combination column, prior to GC–ECD and GC–negative chemical ionization (NCI)-MS analysis [75]. Two years later, Shanshan et al. likewise used MAE–SPE for OCP analysis in six soil samples. The instrument was able to extract 40 solid samples in PTFE extraction vessels in a single step using a petroleum ether:acetone (1:1, *v*/*v*) solvent mixture combined with a clean-up step on a Florisil-SPE column. Satisfactory recovery, clean chromatograms, proper selectivity, and accuracy were achieved [69].

A different clean-up technique is dispersive solid phase extraction (dSPE), where the media are suspended in the sample solution to trap interferences from the solution to be able to analyze the solution for the target. More information on the use of this purification technique for the successful extraction and analysis of OCPs from soils can be found below. SPME, introduced by Pawliszyn and his coworkers as a novel and solvent-free sample pretreatment technique, is based on the redistribution of analytes between the microextraction fiber and the sample matrix [76]. SPME is an equilibrium technique where analytes are distributed between three phases, sample, gas phase, and fiber, with the advantage of simplicity, lower LOD, and reproducibility. Most of the available studies regarding the SPME technique were focused on water and to a lesser extent on soil, sediments, and air. The applications for the determination of OCPs in soil matrices are based on the preparation of soil with distilled water and the direct dipping of the SPME fiber into the produced slurry.

Researchers found that the recoveries of organic pollutants were obviously affected by the complex sample matrix. As a result, HS-SPME was utilized to determine OCP pesticides, improving selectivity and causing reductions in background adsorption and the matrix effect as the fiber is not in contact with the sample, with the advantage of a longer life for the SPME coating [38][77]. In 2006, Zhao et al. reported the SPME method for the determination of OCPs in environmental soil samples with validation results comparable to the USE extraction procedure. A very interesting observation of this group was the fact that aging the soil samples prior to spiking them with a standard solution during method validation produced samples closer to the real soil samples compared to the not-aged soil samples [44]. In the work by Carvalho et al. (2008), MAE combined with HS-SPME allotted further clean-up and pre-concentration steps, resulting in a quick and efficient procedure of sample preparation before the GC–MS determination of several OCPs in different sediment samples [64]. This combination of MAE and HS-SPME proved to be more effective than each one of these procedures acting separately as it permits the pre-concentration of analytes at the fiber and minimizes the need of a pre-clean-up of the extract from MAE, since the microextraction is performed in the headspace. In the study by Concha-Graña et al. in 2010, pressurized hot water extraction (PHWE) followed by the SPME and GC–MS methods was used for the analysis of 28 OCPs in sediment samples [78]. Alternatively, in 2014, M. Miclean et al. reported the PHWE technique in conjunction with SPE and SPME, followed by GC–ECD analysis for the determination of 19 OCPs in real soil samples collected in Cluj County, Romania [79]. Recently, in 2018, He et al. evaluated another combined approach for the determination of eight OCPs in soil, based on microwave-assisted magnetic solid phase extraction (MAE-MSPE) prior to GC–ECD analysis. The advantage of this technique was the use of novel Fe_3O_4-NH_2 MIL-101(Cr) composites as the MSPE, which aided in the selective enrichment and purification towards the targets [80]. In any case, a drawback of the technique is that minimum detection limits were achieved, as the pesticide compounds were concentrated on the SPE cartridge or (and) on the SPME fiber, and they were rapidly delivered to the column.

A miniaturized solid–liquid extraction (MISOLEX) combined with SPME as an automized clean-up procedure and GC–MS analysis was successfully validated for the quick and simple extraction of HCH and DDT from soils. In principle, the RT of an analyte was used as an indicator of its physicochemical properties [81].

Matrix solid phase dispersion (MSPD) was developed by Barker in 1989 for the extraction of solid and semi-solid samples as a new SPE-based extraction and clean-up technique that involves mixing a solid or semi-solid sample with a sorbent material (silica, alumina, Florisil, C18, etc.) to form a dry body. Then, after blending it, the body is packed into a tube and eluted with solvent to allow target analyte to be separated from the body. The most commonly used adsorbents were C8- and C18-bonded silica materials. MSPD has been reported in the past to be used for the multi-residue analysis of several pesticide classes, including OCPs [61]. Recently, this extraction and clean-up technique was reported in 2018 in the study by Wang et al. for the determination of two typical groups of OCPs, DDTs, and HCHs in farmland and bare land soil samples [45][46]. Compared with classical methods, the MSPD procedure is simple and less labor-intensive, and it allows extraction and purification in a single step using less-toxic solvents. An important practical advantage is that MSPD does not need special instruments or costly hardware. However, as with the other solid–liquid extraction methods, the LODs are worse than those obtained, for example, using LSE or even SPME [82]. Another drawback of this method is that, in many cases, large volumes of solvents are required, and an additional evaporation step is required.

The solid–liquid extraction with low temperature purification (SLE-LTP) could be considered as a very good alternative for the extraction of organic contaminants in solid and semi-solid matrices to emphasize the clean-up of the extracts. SLE-LTP, like all the other SLE techniques, is easier, is cheaper as it entails low solvent consumption, and has been presented in the literature to have high extraction efficiency. Recently, in 2017, Mesquita et al. studied SLE-LTP as well as liquid–liquid extraction with low-temperature purification (LLE-LTP) extraction techniques combined with the GC–MS analytical method for the determination of ten OCPs in three types of samples, including a soil matrix [83]. The two extraction methods were optimized three years earlier based on a bibliography on sewage sludge using SLE-LTP [84]. Regarding the soil matrix, due to its complexity, a key parameter studied was the homogenization time of the vial containing it, which increased from 1 min to 5 min, providing excellent recoveries around 93 to 114%. A second parameter to be considered was the volume of water for freezing the soil. While the moisture of the soil was only 2% (*w*/*w*) and as acetonitrile and water is a homogeneous system, it did not homogenize the vial in vortex before freezing, gaining recoveries that ranged from 93 to 125%.

Despite the new trends that have been appeared in pesticide residue analysis, conventional SE methods are still used for routine analysis. To overcome their identified disadvantages and retain their advantages, a different method with “Green Chemistry” characteristics has been developed, known as QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe).

QuEChERS Extraction Technique

QuEChERS present a unique combination process involving initial extraction with acetonitrile followed by an extraction/partitioning step after the addition of a salt mixture. The raw extract is cleaned-up with dSPE, with $MgSO_4$ and PSA as the sorbent. Regarding the d-SPE step (not named this at that time), sorbents were also already applied for sample clean-up, though mostly in SPE cartridges [51]. Anastassiades et al. introduced QuEChERS as a simplified version of conventional extraction methods for the determination of multi-class pesticide residues in fruits and vegetables using GC–MS and TPP as IS [85]. The original unbuffered version evolved into two official methods, the European standard EN 15662, developed by Anastassiades and co-workers, which involves the use of citrate buffer, [86] and the American standard accepted by the Association of Official Analytical Chemists (AOAC) and developed by Lehotay, which involves the use of acetate buffer [87]. Both versions lead to a pH of around 5, which corresponds to a compromise to extract the analytes of interest satisfactorily.

Subsequent adjustments were developed to make the method performance even better, especially for some difficult analytes and commodities of different origins. Specifically, a wide variety of factors were studied and evaluated regarding the sample constitution, type of extraction process, extraction time, extraction solvent, sample/solvent ratio, extraction temperature, addition of non-polar co-solvents, and/or salts and clean-up. Researchers adapting appropriate modifications to the QuEChERS method achieved the extraction of a wide range of pesticides, including highly polar pesticides as well as highly acidic and basic ones [88]. This extraction process is mainly applied for pesticides in plants and foods of animal origin and less extensively applied in several complex matrices, such as biological fluids [89], non-edible plants, and environmental samples [90][91], including soils [51][88][92]. The QuEChERS method has been applied to the extraction of pesticides from soils without clean-up [51] or with clean-up, mostly using PSA and $MgSO_4$, PSA and C18, and LLE, achieving recoveries from 53 to 128% [51]. In a recent manuscript by Leesun Kim. et al. in 2019, an overview of the current information on the QuEChERS method applied to the POP analysis of various sample matrices indicated that especially OCP analyses have mainly been limited to sample matrices with lipid content such as fish and seafood [89][90][93][94][95]. There are only a few studies having successfully used the QuEChERS method to determine OCPs in environmental matrices (e.g., water and sediment), marine products, hair, and medical plants using the modified QuEChERS methods [90][93][94]. The QuEChERS methodology was first applied to the extraction of pesticides from soils in 2008 by Lesueur et al. [96]. The application of the QuEChERS method provided good results for the extraction of polar as well as non-polar pesticides, strengthening its diverse applicability.

Based on a Scopus survey, since the development of QuEChERS in 2003, up to November 2020, among 1826 documents relating to pesticide extraction using this method, 151 papers specifically referred to OCPs. Furthermore, 368 documents referred to QuEChERS extraction from soil matrices, while only 22 documents have been published regarding OCP extraction from soils.

The QuEChERS methodology was first applied to the extraction of pesticides from soils in 2008 by Lesueur et al. [96]. Two years later, a procedure based on QuEChERS was developed for the determinations of nineteen OCPs in soil samples with different physicochemical properties. The proposed method was compared with an established procedure based on Soxhlet extraction, indicating recovery results of good agreement. QuEChERS, due to the cleaner nature of the extraction, presented lower detection limits [36].

The QuEChERS method has been applied to the extraction of pesticides from soils without clean-up [88][97] or with clean-up using sorbents, with the most widely used being PSA, C18, florisil, and their combinations, jointly with anhydrous $MgSO_4$ [51][96][97][98]. In this sense, Cvetkovic et al., to improve the overall technique performance, proposed a modification of the original method consisting of the same LLE step but using diatomaceous earth and clinoptilolite as d-SPE sorbents, which have never been used before, for the extraction of the 16 polycyclic aromatic hydrocarbons (PAHs) listed by the US EPA from soil samples. The use of the diatomaceous earth, in addition to reducing the analysis cost, in combination with acetonitrile:water (2:1) as the extraction solvent, provided the best recovery and precision results [92][99].

Nineteen OCPs in hydrated soil samples using acetonitrile and liquid–liquid partition into n-hexane achieved satisfactory recoveries [36]. In the same year, Yang et al. used this technique to determine 38 pesticides, including endosulfan I and II, in freeze-dried soil and sediment samples of a vegetable-growing area in China and achieved good reproducibility and low detection limits [100]. In 2012, Florent Rouvière et al. optimized and modified the conventional QuEChERS method for the extraction of 34 OCPs from organic peat soils. For the first time, in the extraction of the major pesticides tested, the use of a non-miscible-water solvent such as DCM was proven to be a better solvent than the commonly used acetonitrile. Moreover, clean extracts, without the need for further purification by dSPE, have been produced using PSA, which is an expensive but efficacious material. However, DCM is one of the solvents that has been avoided in recent years. At the European level, regarding the authorization of plant protection products, hazardous reagents (e.g., carcinogens, mutagens, and reproductive toxicants of category 1 and 2 according to Regulation (EC) No 1907/2006 [101]) are not permitted in risk assessment and monitoring studies [102]. At the same time the ASE extraction technique was also optimized and compared to QuEChERS. The latter was proved to be rapid, easy to use, and provided adequate recoveries [41]. In the same year, the QuEChERS method was developed by Luısa Correia-Safor et al. for the determination of 14 organochlorine pesticides in 14 soil samples from different Portuguese regions with different organic carbon contents, most of which came from carrot cultivation fields. The best recoveries were obtained when OCPs were extracted from hydrated soils (5 g/sample) with 3 mL of water and 7 mL of ACN. Afterwards, an AOAC packet and a clean-up step with PSA in combination with C18 was used [97]. In another study, the organic matter content was proven to be a key factor in the process efficiency. Generally, pesticides such as OCPs are mostly absorbed in soils rich in organic matter or clay. In particular, Lopez-Avila et al. reported lower recoveries for soils with higher contents of organic matter. As a result, it was concluded that soil matrices with higher organic carbon content have a negative effect on pesticides' recoveries, probably due to a possible sequestration [53][97][103].

Later, in 2016, Bed Salem et al., based on a previous QuEChERS method followed by GC–MS, which was validated in 2010 by Yang et al. regarding the analysis of 38 pesticides in soils [A.52 116], studied the simultaneous analysis of 16 PAHs, 12 PCBs, and 9 OCPs in sediment samples. The sample preparation was evaluated regarding the selection of the extraction solvent, the extraction technique, and the amount of sediment. The mixture of dichloromethane:acetone (DA) (1:1) using ultrasonic agitation was finally chosen for the simultaneous extraction of PAHs, PCBs, and OCPs in 5 g of frozen sediment samples. As in the study by Florent Rouvière et al. [41], the DA solvent mixture was only considered as the best extraction solvent for the simultaneous determination of all pesticides [104]. In the same year, Cheng et al. investigated the QuEChERS method combined with atmospheric pressure gas chromatography quadrupole–time-of-flight mass spectrometry (APGC-QTOF-MS) as an alternative sensitive soft ionization technique for the simultaneous determination of 15 OCPs in soil and water samples. The modified QuEChERS method used a combination of hexane with acetone (9:1 *v*/*v*) as the extraction solvent, NaCl as a partition salt, and florisil and MgSO4 as sorbents in the clean-up step [105]. Another QuEChERS method followed by d-SPE clean-up was developed by Yu et al. for the simultaneous determination of 58 pesticides from several classes, including OCPs in soil [106]. The use of the QuEChERS method combined with GC–MS/MS for the analysis of dozens of pesticides in soils was rarely reported. In this sense, a large group of 305 organic compounds, of which 49 were POPs, including 12 OCPs, were extracted and analyzed in the study by Andrea Acosta-Dacal with an easy QuEChERS extraction method with LC-MS/MS and GC–MS/MS. Then, to verify the applicability of the validated method, 81 agricultural soil samples of the Canary Islands, classified as clay loam, were used. A second study aimed to extend the use of the QuEChERS-based method for the extraction and analysis of the already-mentioned 305 organic compounds of different natures and origins to other types of soil of the agricultural land of the Canary archipelago: sandy loam, sandy clay, clay, and loamy sand [98][100][107]. This proposed method provides an effective method for pesticide screening in soil.

2.3. An Overview of the Extraction Procedures

The extraction and clean-up technique used to determine OCPs in soil matrices has been the most defining step and the weakest link in the whole analytical procedure until recently. Classical extraction techniques used to determine OCP residues in soil, although showing acceptable recovery and accuracy results, have many drawbacks. They are laborious, time-consuming (involving many steps), require large amounts of organic solvents, leading to loss of some analyte quantity, are difficult to modify and automate, etc. On account of this, upgrading the existing technique and its replacement with extraction techniques of lower environmental impact, such as SFE, SPE, SPME, MAE, ASE, QuEChERS, MSPD, FULSE, etc., is increasingly used in pesticide analysis of soil matrices and may be particularly suited to developing countries.

Among them, MAE offers higher recoveries than SE and USE. Furthermore, it allows the simultaneous extraction of several compounds. However, to absorb microwaves, MAE requires polar solvents which tend to co-extract matrix interferences. SFE was proven to be more efficient than solvent extraction, particularly for apolar components in soils with high organic carbon contents, such as peat. However, due to solute–matrix interactions, only a few studies have been reported that determine OCPs in soils. ASE offers numerous advantages: it is quite a quick method which uses low amounts of solvents and allows the use of solvents with a wide range of polarities, and for this reason, it is used for the extraction of multi-residue pesticides. Moreover, the high pressure and temperature conditions enable a better penetration of the solvent into the matrix and a breaking of the intermolecular bonds [17]. As the recoveries of OCPs were affected by the complex matrix of soils, new extraction procedures have been developed or modified, with many of them followed by clean-up procedures such as SPE, SPME, etc. [69][87][97]. Among them, SLE techniques were reported in many studies with the worst LODs. On the other hand, it is remarkable that the conventional SE extraction method, also characterized by the simplicity of the device and the fact that no specialized training is needed, continues to be used in many laboratories in many studies.

QuEChERS consists of an easy alternative extraction method, able to deliver similar or better results and overcome the identified disadvantages in relation to the former methods used for the determination of OCPs in soils. QuEChERS allows for the use of different forms of LLE, SLE, SPE, and others, depending essentially on the nature of the analytes to extract and the complexity of the matrix. In the analysis of soil contaminants, Di et al. analyzed several OCPs in soils and reported that MAE and QuEChERS extraction methods generally yielded higher results compared to the USE and ASE [69].

3. Analytical Methods

Albeit multi-residue analyses have more commonly adopted liquid chromatography tandem mass spectrometry (LC–MS/MS) than gas chromatography tandem mass spectrometry (GC–MS/MS), in recent years, GC–MS/MS has increasingly been used in pesticide analysis. Various multi-residue analytical methods using GC–MS have been reported for the analysis of pesticide residues in different environmental media. In particular, OCPs as volatile or semi volatile compounds tend to be determined by GC equipped with either electron-capture (ECD) or mass spectrometry (MS) detection, unlike the analysis of other POPs, which tend to employ GC–MS/MS or LC–MS/MS [24][51][90]. In any case, the extraction of multiple pesticides including OCPs from complex environmental matrices, such as soils, remains a challenge due to their different physiochemical properties [100].

The regular use of GC–ECD for the detection of OCPs is based on its high resolution and sensitivity. Additional advantages of this detector include reduced cost of operation and the fact that it requires less technical skill to obtain reliable results. However, due to the already-mentioned complex matrices and soil interferences, the use of GC–ECD often leads to false positive results. In this sense, more selective methods such as GC–MS or even GC–MS/MS have been developed for the determination of OCPs in complex matrices in order to confirm and further determine pesticides' identity [21][109]. For example, in the study by Yu Liu, two analytical methods, GC–ECD and GC–MS with negative chemical ionization (NCI), were evaluated and compared for the measurement of 26 organochlorine pesticides. Although GC–ECD sensitivities for most of the compounds investigated were higher than those observed with the GC–NCI-MS method, the matrix interferences were obvious with GC–ECD. Consequently, GC–ECD should be used with caution in real environmental sample analysis, as the possibility of false positives associated with the GC–ECD methods may result in an overestimation of the concentrations of these banned compounds in the environment [75].

Atmospheric pressure gas chromatography (APGC) is an alternative soft ionization technique used to overcome sensitivity limitations of GC–MS methods. In particular, the APGC technique was coupled to a quadrupole-time-of-flight (QTOF) instrument by Cheng et al. for 15 OCPs in soil and water samples to identify their ionization behavior under atmospheric pressure conditions, as well as to compare the difference between EI and APGC ionization sources. Although the method was successfully applied to the analysis of those real environmental samples, there is limited research available on the application of APGC-QTOF-MS for the determination of OCPs [105].

Although methods based on liquid chromatography (LC) seem most appropriate when pesticides are thermally instable, over the years, studies have rarely examined the determination of OCP pesticides in environmental and other matrices using LC. However, several OCPs such as chlordecone, due to their physicochemical properties, do not separate well from other OCPs using conventional GC [110]. For this reason, LC-(ESI-)-MS/MS was used as an alternative to quantify chlordecone in animal tissues, drinking water, and human biological fluids [110]. Recently, in the report by Naidu. et al., the use of HPLC-UV in detecting LND and its derivatives in biological samples assisted by confirmation with matrix-assisted laser desorption/ionization (MALDI)-TOF was described [111]. Though HPLC combined with a traditional UV detector is less selective and sensitive compared to GC instruments, residues of DCF and dichlorobenzophenone (DBP) were quantified using HPLC-UV in wastewaters by Oliveira, J. L et al. [112]. In particular, the determination of OCP residues in soil matrices using the LC technique is more rarely noticed. Individually, a report is available from 2006 by Moreno et al., where MAME was optimized in conjunction to SPME-HPLC-UV for the determination of OCPs in agricultural soil samples [68].

Referring to alternative methods to avoid or reduce the required clean-up steps, expensive instrumentation, and the use of large amounts of solvents, rapid bioanalytic methods such as enzyme-linked immunosorbent assays (ELISA) have been tested individually in order to quantify few OCPs [113]. This method was used in 2002 in the study by Shivaramaiah et al. to monitor DDT/DDE residues in soil samples. The ELISA result obtained was compared against results from the GC instrumental method. Recovery values calculated using the ELISA method were comparable to that of GC, and the results indicate that the developed assay could be an alternative analytical tool for monitoring DDE [114][115].

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