VERSITA

SAMPLE PREPARATION

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QuEChERS and soil analysis. An Overview.

Abstract

This paper reviews the Quick Easy Cheap Effective Rugged Safe (QuEChERS) methods used for the analysis of several pollutants in soil. The recent advances made with this method are discussed.The analysis of pesticide residues and other analytes in soil requires the extraction of analytes from this matrix. Following extraction, a clean-up procedure may be performed, if necessary, prior to instrumental analysis. This review considers all aspects of sample preparation, including extraction and cleanup. Several parameters are discussed in extraction optimization namely: soil type and sample amount, hydration, solvent of extraction QuEChERS content, extraction time and agglomeration prevention. In addition, method performance characteristics in soil studies are critically discussed.

Keywords

Soil • Sediment • Pesticides • QuEChERS • Trihalomethanes • Pharmaceuticals • Chlorophenols

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1. Introduction

Soil is a complex and heterogeneous matrix, containing both inorganic and organic components [1], and is often subject to intense chemical pollution. When chemical compounds reach the soil, either via direct intentional application or as a result of accidental spillage [2], many types of physicochemical interactions occur [2,3]. These include adsorption, leaching, and degradation [3]. Adsorption and leaching processes are both influenced by physicochemical properties of the soil and chemicals under consideration [3,4]. Generally, the water-soluble pesticides are more prone to leaching. This leaching process is also affected by the nature of soil. In well-drained or sandy soil, where the rate of water percolation is high, the leaching of these pesticides is also quite significant. Degradation of pesticides is also a complex phenomenon. The fate of pesticides prone to microbial degradation will be dependent upon the microbial flora present and chemical properties of soil, both of which will facilitate such degradation. Similarly, soil pH and other chemical properties beyond those previously mentioned also affect the end result of pesticide presence in the soil. Beyond the confines of the contaminated area, compounds can be transported from soils to other environmental systems, polluting natural resources and affecting ecosystems [5]. In summary, soil contamination by naturally occurring and anthropogenic organic and inorganic chemicals is a serious human health and environmental problem [3,6,7].

Due to the low concentration levels of soil pollutants, sample preparation step is needed to determine the type and quantity of pollutant present [8] and to avoid interferences and improve the sensitivity of the method. To extract contaminants from soil, a technique strong enough to extract bound residues is necessary [3]. The most common of these techniques are mechanical agitation by shaking [9,10], sonication, microwave energy, and liquid-solid extraction (e.g.: Soxhlet extraction; accelerated solvent extraction, ASE; pressurized liquid extraction, PLE; and, supercritical fluid extraction) [3]. The most popular clean-up methods are based on the solid phase extraction technique [3] using graphitized carbon black (GCB), C18 (octadecyl bonded silica) sorbent and Florisil cartridges [11]. These established methods are effective, yet time consuming and expensive [3].

The QuEChERS approach is based on a salting-out extraction with a solvent (mainly acetonitrile, ACN) followed by a dispersive solid phase extraction (d-SPE). The main steps of QuEChERS procedure are shown in Figure 1. This method is very flexible, modifiable, and is growing in popularity due to all the benefits described by its name: Quick, Easy, Cheap, Effective, Rugged and Safe. However, its effectiveness is dependent on the analyte properties, matrix composition, equipment, and analytical technique available in the laboratory [12]. Two differing standards exist with regard to the buffer type employed in QuEChERS: the American standard, AOAC [13], which involves the use of an acetate buffer; and, the European standard, EN 15662 [14], which involves the use of a citrate buffer.

The QuEChERS method is particularly popular for the determination of wide range of chemical residues, mostly pesticides in various food matrices, because of its simplicity, low

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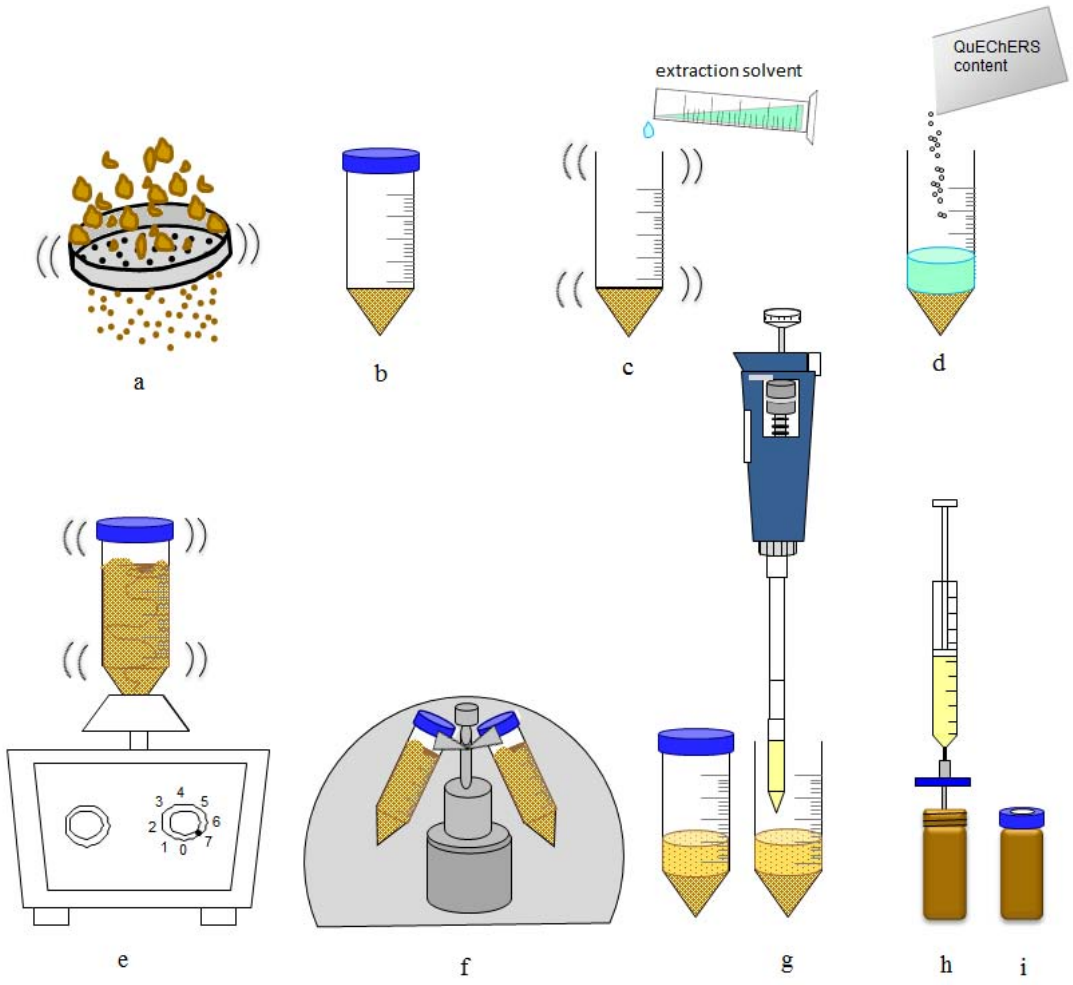

Figure 1. Steps in QuEChERS extraction. a- sieving, b-teflon tube with soil sample, c-addition of the extraction solvent and hand mix, d-addition of the QuEChERS content, e-vortex, f-centrifugation step, g-aliquot of the supernatant, h-filtration with a syringe filters, and g-vial with the extract to analysis.

cost, amenability to high throughput, and high efficiency with a minimal number of steps [11]. Other matrices, such as biological samples [15] and environmental samples (namely, soils), [16] were also studied and are increasingly analysed by this technique. Although QuEChERS has mainly been used for the determination of pesticides in soils, some other compounds, such as pharmaceuticals [15], β-lactam antibiotics [17] or veterinary drugs [18-20] have been determined using QuEChERS. The versatility of QuEChERS has been demonstrated by its acceptance outside of its traditional application areas. The composition of soils is highly variable and, as such requires the development of a procedure specific to each type [1,21]. The optimization of QuEChERS for soil and sediment analysis is the main focus of this review.

Gas and liquid chromatography (GC and LC) with mass spectrometry (MS) or tandem mass spectrometry (MS/MS) are the analytical methods commonly selected for soil pollution control, and are commonly employed after QuEChERS sample preparation.

2. Analytes

Environmental pollution has drawn public and government attention over the last few decades as a variety of new environmental contaminants have emerged [22]. This is due to the increasing introduction of new chemicals into the market [6]. The presence and migration of pollutants - mainly persistent, bioaccumulable, and toxic - may cause human toxicity if they come in contact with the food chain [22]. For this reason, pesticides in soils are studied more than any other environmental contaminants [23] largely due to their use in farming, forestry, home gardening, horticulture, and roadside [24]. Therefore, the analysis of pesticide residues in soils has become indispensable in assessing the quality of the environment.

A sample preparation method is needed for the determination of pesticides due to their low concentration levels, different chemical properties of the analytes, and the complexity of soils [8]. The QuEChERS methodology was first applied to the extraction of

pesticides from soils in 2008 by Lesueur *et al.* [16]. In this study, the authors compared different extraction methods for 24 multi-class pesticide that were commonly reported as soil pollutants in the literature. They analysed 12 GC-amenable and 12 LC-amenable herbicides (specifically, those of the dinitroaniline, phenylurea, urea, triazine and triazinone classes) and other fungicides/insecticides (in particular, those belonging to carbamate, dicarboximide, organochlorine, organophosphorus and pyrethroid) [16].

Besides, Lesueur *et al.* [16], other authors have applied the QuEChERS methodology for the extraction of the mentioned pesticides classes [1,3,24-29] and other classes such as the amide, triazinone, thiadiazine and oxadiazolone, etc. [24,26-30].

Caldas *et al.* [8] published the first study of the extraction of azoxystrobin, clomazone, and tebuconazole from soil samples using this methodology. Other works are related with novel pesticides [31-33] such as pyrimorph, pyraclostrobin and diafenthiuron. Recently, due to the impact of pesticides in health and in the environment, new agricultural practices have appeared in an attempt to reduce the quantities of applied pesticides. For instance, organic agriculture, which is a production system that only allows the use of biopesticides or ecological pesticides, which are derived from natural materials such as plants and microorganisms [5], has become more popular. The QuEChERS method was also introduced as a valid alternative for the extraction of these biopesticides [5,34], although recoveries below 50% for some of these compounds have been reported [5].

The application of QuEChERS method provides good results for the extraction of polar as well as non-polar pesticides, strengthening its diverse applicability (Table 1). High recoveries were obtained for the extraction of pesticides from soil samples applying QuEChERS methodology. Therefore, there is no reason to believe that QuEChERS could not be used for extraction of other analytes as well as pesticides from soil and sediment samples.

Consequently, this methodology was successfully applied to extraction of several other compounds from the soil namely phenols [35], diethyl aminoethyl hexanoate [36], organochlorine compounds [22], trihalomethanes [2,11,37], chlorinated compounds [11], benzene, toluene, ethylbenzene and xylenes (BTEX) [2]. The ultrasonication extraction of perfluoroalkyl substances (PFAS), five perfluororalkyl sulfonates (PFSAs), thirteen perfluoroalkyl carboxylates (PFCAs) and seven perfluororalkyl sulfonamido was cleaned up using a QuEChERS method [38]. Pharmaceutical compounds, their metabolites, and degradation products, are present in different environments, and, consequently, have emerged as contaminants. Salvia *et al.* [39] and Bragança *et al.* [21] have applied the QuEChERS method for the extraction of such compounds from soil/sediment samples with success.

The QuEChERS approach appears to have a bright future for the extraction of many compounds from soil samples.

3. Samples type and sampling

The choice of the sample treatment applied depends heavily on the complexity of the matrix [49]. The amount of contaminant that is bound to the soil varies with the type of analyte and the soil characteristics, namely organic matter content, pH, texture, mineral fraction, etc. [1]. For that reason, it is important to characterize the soil samples as these parameters can also influence the mobility and availability of the analytes [1].

The majority of the studies related to the extraction of contaminants from soils were performed in florestal, in ornamental, and in agricultural soils from diverse crop fields. There were some exceptions with the reported use of river sediments [21,27], certified reference material [2,11,16,37], sea sand [16,21], clay-loam soils [2,11,37], sludge [39], contaminated industrial soils [22] and peat cores [38]. After removing coarse particles, the soils were passed through sieve (varying the sieve opening size) to obtain a homogeneous sample.

Some of the analysed contaminants were sensitive to light and, thus, in some applications, soils were collected using dark or amber bottles [5,39] or stored away from the light [5,8]. The temperature was considered crucial in some studies, [48] where the authors performed recovery tests to determine the stability of the compounds under the storage conditions. The storage temperature ranged from -20 ºC [48] to room temperature [1].

4. QuEChERS Extraction - Optimisation of the extraction parameters

4.1 Considerations

Pollutants in water or in air generally are more easily extracted than those associated with soil. This is due to the interaction of the contaminants with the soil particles themselves. Strong chemical and physical forces may act to bind the contaminants to the soil particles. Thus, if the monitoring technique requires that the chemicals be extracted or removed from the soil prior to analysis, the efficiency of the extraction process becomes crucial to the overall success of the analysis [6]. The QuEChERS extraction method poses as an alternative method that is able to provide satisfactory and reliable results, meet the requirements of “green chemistry”, consume low amount of solvent and requires little labour and materials commonly used in laboratories [11]. Extraction aims to remove as much analyte as possible from the matrix, so it is essential to optimize the extraction parameters. Most of the publications included a specific section for optimization of the variables related to the extraction step; namely, these variables include hydration of the soil matrix, mass amount, extraction solvent, QuEChERS content, volume of extraction solvent, etc.

Modifications of the original QuEChERS procedure by using acidic-buffered extractions, adding water in order to obtain adequate moisture, or using different adsorbents in the d-SPE to remove matrix components, as described below in the clean-up section, have been used for the extraction of different types of pollutants from soil samples with good results. An overview of QuEChERS method for the extraction of several compounds from soils and sediments is presented in Table 1.

Table 1. Applications of the QuEChERS methodologies in soil sample preparation.

Compounds	Matrix characteristics	Sample treatment	Cleanup step	Recovery (%)	Spiking level	LOD and LOQ	Detection	Obs.	Ref.
Pesticides									
Anthranilic diamide (Cyantraniliprole and metabolite)	-	$Mass_{sample}$-10 g; Solvents: 10 mL of ACN Vortex with sample and wait 30' QuEChERS: 6 g $MgSO_4$, 1.5 g CH_3COONa; Vortex 2', centrifuged at 5000 rpm 2'.	50 mg PSA sorbent and 150 mg $MgSO_4$ Homogenization: Vortex 1', 5'centrifuged at 5000 rpm	77.8 - 102.5	0.01, 0.05, and 0.1 mg/kg	LOQ: 0.01 mg/kg	UPLC–MS/MS		[40]
1 Pyridinecarboxylic acids (Fluroxypyr), 1 Carboxamides (Carboxin), 1 Pyridazinones (Chloridazon), 1 Benzimidazoles (Carbendazim), 1 Pyrethroids (Cypermethrin), 1 Oxazolidinones (Clomazon), 1 Spiroketalamines (Spiroxamine), 1 Carbamates Phenmedipham, 1 Morpholines Fenpropidin	River sandy sediment	$Mass_{sample}$-4 g; 8 mL water and hand-shake and left 1 h to soak + 10 mL of ACN + 1% NH_3 QuEChERS: 2 g CH_3COONa + $MgSO_4$); Shaker 10' at 250 rpm, centrifuged at 2500 rpm 10'	2 g $MgSO_4$. Homogenization: 10' centrifuged at 2500 rpm	14-95 and <1 for Carboxin	10 ng/g	LOD: 0.1 -2 ng/g LOQ: 1 - 6 ng/g	LC-MS/MS	The sandy sediment was first pre-dried, sieved to maximum particle size smaller than 1 mm and dried at 400 °C.	[27]
14 organochlorines	The soils were collected in plastic bags (1 kg) from 10 to 20 cm in the ground used as carrot culture. Total organic carbon >2%)	$Mass_{sample}$-5 g; 3 mL water prior 7 mL ACN Vortex 1'. QuEChERS: 6 g $MgSO_4$, 1.5 g NaCl, 0.750 g Na_2Cit and 1.5 g NaCit. Vortex, ultrasonic bath 1', centrifuged at 4500 rpm for more of 10'	50 mg of PSA, 150 mg of $MgSO_4$ and 50 mg of C18 Homogenization: Vortex 1 ', centrifuged 5 ' at 4500 rpm	64-127	40, 60, and 80 µg/kg	LOD: 3.42-23.77 µg/kg and LOQ: 11.41-79.23 µg/kg	GC-ECD; (GC-MS/MS confirmation)	Samples were homogenised, sieved (2-mm mesh) and air-dried at room temperature.	[1]
	organic carbon <2.3%) The soils were collected in plastic bags (1 kg) from 10 to 20 cm in the ground used as carrot culture.			59-132	20, 40, and 100 µg/kg	LOD: 6.11-14.78 µg/kg and LOQ: 20.37-49.27 µg/kg			
1 thiourea (Diafenthiuron)	-	$Mass_{sample}$-10 g; 2 mL water prior 10 mL of ACN, vortex 1' QuEChERS: 4 g $MgSO_4$ and 1 g NaCl. Vortex 30", ultrasonic bath 2', centrifuged at 3800 rpm for 5'.	50 mg PSA and 150 mg $MgSO_4$ Homogenization: Vortex 1', 5' centrifuged at 6000 rpm	74.0– 100.0	0.02, 0.1, and 1 mg/kg	LOD:0.006 mg/kg LOQ: 0.02 mg/kg	HPLC–MS	Area of plot was 30 m^2. Samples were dried in the shade at room temperature and sieved through 40-mesh sieves.	[32]

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continued *Table 1. Applications of the QuEChERS methodologies in soil sample preparation.*

Compounds	Matrix characteristics	Sample treatment	Cleanup step	Recovery (%)	Spiking level	LOD and LOQ	Detection	Obs.	Ref.
3 alkaloids, steroid derived alkaloid (veratridine), 2 flavonoids, limonoid (azadirachtin), spynosad D, pyrethrins and piperonyl butoxide	Soil samples were taken from organic agricultural areas located.	$Mass_{sample}$-5 g; 2.5 mL water; soaking for 30'; add 5 mL ACN (1% acetic acid). Shaken 1' QuEChERS: 4 g $MgSO_4$, 4 g NaCl, 0.5 g Na_2Cit, and 1 g NaCit. Shaken 5' at 5000 rpm in the rotatory shaker.	Nylon filter (0.20 µm)	70 - 110 (nicotine and sabadine achieving < 50)	10-125 µg/kg	LOD: 1.0-5.0 µg/kg LOQ: 4.0-10.0 µg/kg	UHPLC-MS/MS	Samples were dried at room temperature in the dark during one day, and kept in brown glass bottles.	[5]
1 Anthranilic diamide (chlorantraniliprole)	Soil organic matter content and pH were 2.52 ± 0.18% and 6.2 ± 0.1, respectively.	$Mass_{sample}$-10 g; 40 mL ACN Ultrasonic bath 30', centrifuged at 8000 rpm for 3'	150 mg anhydrous $MgSO_4$, 50 mg PSA, 50 mg C18 Vortex 30", centrifuged 2' at 10000 rpm, then 0.20 mL supernatant diluted with 0.80 mL 0.1% formic acid in water.	76.9–82.4	0.002, 0.020, and 0.20 mg/kg	LOD: 0.15 µg/kg	LC–ESI–MS/MS	Surface soil (0–15 cm depth) was sampled for analysis. Three adjacent field plots with an area of 30 m^2.	[41]
1 Strobilurins (pyraclostrobin)		$Mass_{sample}$-10 g; 10 mL ACN, shaken 30' QuEChERS: 4 g $MgSO_4$ and 1g NaCl Vortex 1', centrifuge 5' at 3800 rpm.	100 mg PSA and 150 mg $MgSO_4$ Vortex 1', centrifuged 2' at 6000 rpm.	99.1-108.5	0.005, 0.05, and 0.5 mg/kg	LOD: 0.17 µg/kg LOQ: 0.57 µg/kg	LC–MS/MS	Soil dried in shade, sieved through a 40-mesh sieve. Field plots each with 30m^2 area.	[33]
1 macrocyclic lactone (emamectin benzoate)		$Mass_{sample}$-10 g; 2 mL water prior 10 mL ACN Vortex 1' QuEChERS: 4 g $MgSO_4$ and 1g NaCl Vortex 30", centrifuge for 5' at 3800 rpm.	50 mg PSA and 150 mg $MgSO_4$ Vortex 1', centrifuged 5' at 6000 rpm	75.9-97.0	0.001, 0.01, and 0.1 mg/kg	LOQ: 0.001 mg/kg	LC-ESI-MS/MS	Samples were dried in the shade at room temperature and sieved through a 40-mesh sieve. Stored at -20 ºC.	[42]
1 oxadiazine (Indoxacarb)	-	$Mass_{sample}$-15 g; 10 mL water overnight addition 30 mL ACN Shake, centrifuged for 2–3' at 15,000 rpm QuEChERS: 5–10 g NaCl and 10 g Na_2SO_4. Shook vigorously first by hand, rotospin 5', centrifuge for 3' at 2500 rpm. Decanted the upper layer 15 mL into another 50 mL centrifuge tube containing 10 g of activated sodium sulfate and again shook the contents using a rotospin for 2–3 min so as to remove even small traces of moisture.	150 mg PSA and 900 mg $MgSO_4$ and 50 mg graphitized carbon. Vortex 1', centrifuged 1' at 2500 rpm, then Transferred 4 mL into a round bottom flask and concentrated to near-dryness and added about 20 mL acetone, concentrated with a rotary vacuum evaporator at <30 ºC to completely remove ACN.	86.67-96.94	0.01, 0.05, and 0.50 mg/kg	LOD: 0.003 mg/kg LOQ: 0.01 mg/kg	GC-MS		[43]

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continued *Table 1. Applications of the QuEChERS methodologies in soil sample preparation.*

Compounds	Matrix characteristics	Sample treatment	Cleanup step	Recovery (%)	Spiking level	LOD and LOQ	Detection	Obs.	Ref.
8 Triazoles	Soil (sandy loam) samples from trial plots. These matrices did not contain the target analytes.	$Mass_{sample}$-10g; 5 mL water + 10 mL ACN Shaken for 30' QuEChERS: 4 g $MgSO_4$ and 1 g NaCl Vortex 3', centrifuge for 5'.	50 mg C18 and 150 mg $MgSO_4$ Vortex 1', 5' centrifuged	81.2–106.5	5, 25, and 50 µg/kg	LOD: 0.04–1.0 µg/kg LOQ: 0.12–3.0 µg/kg	LC–MS/MS	Samples were air-dried at room temperature and kept in the dark, homogenized, and passed through a 2 mm sieve.	[44]
1 Sulfonylurea (pyrazosulfuron-ethyl)	Alluvial soil (pH value 5.83, organic material (%) 9.2, cation Exchange capacity 9.43 (cmol kg^{-1}).	$Mass_{sample}$-10 g; 4 mL water, vortex 1' 20 mL ACN (1% acetic acid) shake for 2'. QuEChERS: 6 g MgSO4 and 1.8 g of CH_3COONa Shaken as quick as possible and centrifuged for 5' at 5000 rpm	A 18 mL aliquot was filtered through a Na_2SO_4 column and dried under a stream of nitrogen.	70.8-99.0	0.1, 0.5, and 1 mg/kg	LOD: 0.05 mg/kg LOQ: 0.1 mg/kg	HPLC-UV		[12]
	Purple soil (pH value 7.13, organic material (%) 13.4, cation Exchange capacity 33.46 (cmol kg^{-1}).			83.5-86.4	0.1, 0.5, and 1 mg/kg				
1 Dinitroanaline (trifluralin)	Wind-eroded sediment	$Mass_{sample}$-10 g; 20 mL ACN, vortex 1'. QuEChERS: 4 g MgSO4, 1 g NaCl, 1 g NaCit and 0.5 g Na_2Cit Vortex 1', centrifuged for 10' at 4500 rpm.	150 mg PSA and 900 mg $MgSO_4$. Vortex 30", centrifuged 8' at 4500 rpm, then transferred 5 mL with 1 mL of ethyl acetate. Extract evaporation with N_2 flow and brought to 1.0 mL with ethyl acetate. 150 mg $MgSO_4$ was added to remove any residual water. Vortex, centrifuged for 5' at 4500 rpm.	87.18 - 93.94	500 ng/g	Estimated Method Detection Limit (EMDL) 11.41 *µg/g*	GC-ECD	60 × 45 m experimental plot was plowed. Air-dried samples were passed through a 2 mm sieve and stored at room temperature	[45]
1 Oxazolidine (clomazone), 1 phenylpyrazole (fipronil), 2 triazole and a strobilurin (azoxystrobin)	Organic matter 0.6%, and clay (w/w) 16%, pH (in KCl) 5.2.	$Mass_{sample}$-10 g; 100 µL of acetic acid and 10 mL of ACN Hand-shaken for 15", shaken for 1' with shaker QuEChERS: 1 g of NaCl, 4 g of $MgSO_4$. Hand-shaken for 15", shaker for 1' and centrifuged at 5000 rpm for 5'.	Without clean-up achieved better results	70.3-120	10, 50, 100 and 500 µg/kg	LOQ: 10-50 µg/kg	LC-APCI-MS/MS	Soils were homogenized, sieved (2 mm mesh), and air-dried at room temperature.	[8]
2 triazine, 1 carbanilate (phenmedipham), 1 benzothiazole (mefenacet), 1 chloroacetanilide (metholachlor)		$Mass_{sample}$-1.0 g; 0.5 mL water wait 20' 4 mL ACN shake for 2'. QuEChERS: 0.1 g $MgSO_4$ Shaken for 20"	0.1 g of PSA (or 0.1 g PSA + 0.1 g C18, or 0.1 g PSA + 0.03 g GCB) Shaken for 2', centrifuged 3' at 10000 rpm	75.4–98.5	4-40 µg/kg	LOD: 0.005–0.020 µg/kg LOQ: 0.017–0.067 µg/kg	UPLC-MS/MS	Samples were air-dried, sifted through 1 mm sieve and stored at room temperature	[28]

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continued *Table 1. Applications of the QuEChERS methodologies in soil sample preparation.*

Compounds	Matrix characteristics	Sample treatment	Cleanup step	Recovery (%)	Spiking level	LOD and LOQ	Detection	Obs.	Ref.
1 Acryl amide,(Pyrimorph)		$Mass_{sample}$-15 g; 9 mL water + 15 mL ACN vortex 1' QuEChERS: 6 g anhydrous $MgSO_4$ and 1.5 g CH_3COONa. Hand-shaken until well-mixed, Vortex 1' and then centrifuged 5' at 4000 rpm.	50 mg PSA and 150 mg $MgSO_4$. Shake, centrifuged 5' at 8000 rpm	86.1- 99.3	0.05, 0.1, and 1 mg/ kg	LOD: 0.05 mg/kg	HPLC-DAD	12 plots were needed and the area of each was 15 m^2. Samples were packed with polyethylene bags and kept at -20 ºC.	[31]
1 Polyamines (Dioctyldiethylenetriamine acetate)		$Mass_{sample}$-15g; 5 mL water + 15 mL ACN Shake twice for 1', and shaken for 30' in a shaker) QuEChERS: -	50 mg PSA and 150 mg $MgSO_4$ Vortex 5' at 8000 rpm	87.6-93.5	0.02, 0.1. and 1 mg/ kg	LOQ: 0.01 mg/kg	LC–MS	Soil was collected by a soil auger with depth of 0–15 cm, dried in the air under shade at 25 ± 5 ºC and screened through 40 mesh sieves.	[46]
19 Organochlorines	Pesticide free soil sample was collected from UK for use during method development and validation.	$Mass_{sample}$- 5 g; 10 mL water for 30' then added ACN (1% acetic acid), vortex 30". QuEChERS: 4 g $MgSO_4$ and 1.7 g CH_3COONa. Shaken vigorously, centrifuged 5' at 5000 □ g		70-100 (exception HCB <60)	50-200 µg/ kg	LOD: 0.3 µg/kg LOQ: 1.0 µg/kg	GC–MS/MS	Soil was air-dried at room temperature, mixed to homogenize, using pestle and mortar, passed through a 2mm sieve, stored at room temperature.	[3]
1 Organochlorine (HCB)	Two soils: a garden soil, with high organic content, a Vertisol, with a high percentage of clay, and a certified reference material RTC-CRM631 (silty clay soil)	$Mass_{sample}$- 2.5g; 1.5 mL water and vortex 1'. 2.5 mL of ethyl acetate and shake 1'. QuEChERS: 1 g $MgSO_4$ Shake 1' and then centrifuged 5' at 5000 rpm.	-	93-92	15-125 µg/ kg	LOD: 0.15 µg/kg	GC-µECD		[11]

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continued *Table 1. Applications of the QuEChERS methodologies in soil sample preparation.*

Compounds	Matrix characteristics	Sample treatment	Cleanup step	Recovery (%)	Spiking level	LOD and LOQ	Detection	Obs.	Ref.
10 Organophosphorus and a thiadiazine (buprofezin).	Soil forestall [pH (in water) = 5.99, pH (in KCl 0.1 N)= 4.78	$Mass_{sample}$-10 g; 20 mL ACN Shaken 1' QuEChERS: 4 g $MgSO_4 \cdot H_2O$ + 1 g NaCl + 1 g NaCit + 0.5 g Na_2Cit Shaken for 10", sonicated for 5' in an ultrasonic bath and then centrifuged 8' at 4,000 rpm	0.250 g PSA + 1.5 g $MgSO_4$ Shaking for a few seconds, sonicating for 1', centrifuged 10' at 4400. The dry residue was then redissolved in 1 mL of cyclohexane, a very small amount of MgSO4 was added	45 – 96	27.5-123	LOD: 0.54 – 6.54 ng/g LOQ: 1.79-21.8 ng/g	GC-NPD	Soil between 0 - 68 cm deep in the ground in the forest of Las Mercedes, La Laguna, was placed directly in plastic bags.	[24]
	Soil Ornamental [pH (in water) = 5.99, pH (in KCl 0.1 N)= 4.99					LOD: 0.68 – 12.5 ng/g LOQ: 2.27-41.6 ng/g		Soil was bought from a garden center, between 0 - 10 cm deep in the ground from an agricultural location was collected in plastic bags.	
	Soil Agricultural [pH (in water) = 4.20, pH (in KCl 0.1 N)= 3.92, Organic matter (%)= 6.71.					LOD: 0.48 – 5.71 ng/g LOQ: 1.61-19.0 ng/g		Agricultural soil was extremely acidic.	
1 Oxadiazolone (Oxadiargyl)	Soil sifted (through a 40-mesh sieve)	$Mass_{sample}$-10 g; 15 mL ACN QuEChERS: 1 g NaCl + 4 g $MgSO_4$ Shaken for 1', and then centrifuged for 5' at 2000 rpm	-	95.5-112	0.01, 0.10 and 1.00 mg/kg	LOD: 0.005 mg/kg LOQ: 0.01 mg/kg	CG-ECD		[47]
Dimethylnitrobenzene, 1 phenyl methylcarbamate (isoprocarb), 1 carbamate (carbofuran), fenaminosulf, 3 organochlorine, 1 Triazine (atrazine), 1 polychlorinated aromatic (chlorothalonil), 4 organophosphorus, 3 chloroacetanilide, 1 bridged diphenyl (dicofol), dibromobiphenyl, 2 conazole, 2 phenylpyrazole, 1 dichlorophenyl dicarboximide, 1 dithiolane (isoprothiolane), buprofezin, 1 pyrrole (chlorfenaphy), 1 anilide (oxadixyl), 1 sulfite ester (propargite), pyridaben, 5 organothiophosphate, 2 phosphoramidothioate, 2 thiadiazole organothiophosphate, 1 phenyl organothiophosphate (profenofos), 4 Pyrethroids		$Mass_{sample}$- 10 g; 4 mL water mixed and left for 30', add 20 mL ACN, shaken 1' by hand. QuEChERS: 2 g NaCl + 8 g $MgSO_4$ + 1 g Na_2Cit + 2 g NaCit Hand-shaken 1' and centrifuged 3' at 2500 rpm.	1.5 g $MgSO_4$ and 250 mg PSA Homogenization: Internal standards were added, hand-shaken 30", centrifuged for 3' at 1500 rpm. The extracts were dried under a gentle nitrogen stream. The dried residue was re-dissolved with 1 mL ACN.	70-120	10, 50 and 100 ng/g	LOD: 1.3-9.5 ng/g LOQ: 4.5-31.8 ng/g	GC-MS	The samples (up to 20 cm) were scooped into pre-cleaned glass bottles at each field plot and sediment samples (5 cm deep) from each site of the drainage channel. The samples were transported in coolers and stored in a dark room at 4°C.	[29]

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continued *Table 1. Applications of the QuEChERS methodologies in soil sample preparation.*

Compounds	Matrix characteristics	Sample treatment	Cleanup step	Recovery (%)	Spiking level	LOD and LOQ	Detection	Obs.	Ref.
1 dicarboximide (procymidone)	Beijing, clay loam, organic matter 2.3%, pH 7.3 Yantai, Sandy soil; organic matter 1.5%, pH 7.3 Baoji, loam soil, organic matter 2.6%, pH 8.1 Hohhot, black loam soil, organic matter 3.2%, pH 7.6	$Mass_{sample}$-10 g; 3 mL + 15 mL ACN (sample + ACN + water, Vortex 1') QuEChERS: 2 g NaCl Vortex 1' and centrifuged 5' at 3800 rpm	250 mg $MgSO_4$ + 50 mg PSA Vortex 1', centrifuge 2' at 6000 rpm.	82.5–92.5	0.02, 0.2 and 2 mg/kg	LOD: 1.65 mg/kg LOQ: 5.51 mg/kg	CG-MS	Soil samples were collected at 0–10 cm of the plow layer.	[48]
azadyrachtin, spinosad and rotenone	Soil	$Mass_{sample}$-5 g; 5 mL water + 100 µL acetic acid + 10 mL ACN Shaken for 5' QuEChERS: 4 g $MgSO_4$ +1 g NaCl + 0.5 g Na_2Cit + 1 g NaCit Hand-shaken for 1', centrifuged 2.5' at 4500 rpm	900 mg $MgSO_4$ + 150 mg PSA + 150 mg C-18. Vortex 1' and centrifuged 2.5' at 4500 rpm. Evaporated to dryness under N_2 flow. Re-dissolve in 0.25 mL of 0.1% ammonium acetate in methanol using ultrasonic bath. Addition of 0.25 mL of 0.1% ammonium acetate in water, then vortexed.	83-104	0.01, 0.05, and 0.1 mg/kg	LOD: 0.0018-0.0027 mg/kg LOQ: 0.006-0.009 mg/kg	UPLC/MS/MS		[34]
4 Triazine, benzimidazole (carbendazim), 3 organophosphate, 7 phenylurea, 1 Pyrethroids (deltamethrin), 2 organochlorine, 1 benzoylphenylurea (flufenoxuron), 1 triazinone (metamitron), 1 benzothiazole (methabenzthiazuron), 1 urea (pencycuron), 1 dinitroaniline (trifluralin) and 1 dichlorophenyl dicarboximide (vinclozoline).	EUROSOIL 7 [pH $CaCl_2$= 4.4, organic matter= 11.52, SO26 [pH $CaCl_2$= 4.6, organic matter= 1.81, Sea sand [pH $CaCl_2$= 5.5, sand (w/w%) = 100]	$Mass_{sample}$-10 g; 20 mL ACN QuEChERS: 4 g $MgSO_4$, 1 g NaCl, 1 g NaCit and 0.5 g Na_2Cit	150 mg Bondesil-PSA and 950 mg $MgSO_4$	27.3-120.9	500 ng/g	LOD: 0.02-88 ng/g LOQ: 0.08-292 ng/g	GC-MS and HPLC-MS/MS	The soils have been selected since they represent 24% of the arable land in Austria.	[16]
1 Triazine (atrazine), 1 phenylpyrazole (fipronil), 2 Organoclorine	Dry sediment	$Mass_{sample}$-10 g; 10 mL ACN QuEChERS: 4 g $MgSO_4$, 1 g NaCl, centrifuged 1' at 3000 rpm	SPE cartridge containing 330 mg PSA, 330 mg C18 and a 1 cm layer of $MgSO_4$ with 3 mL of ACN. Then, in the column SPE, the extract was passed and collected.	74-115	0.02, 0.05, and 0.5 mg/kg	LOD: 0.003-0.02 mg/kg LOQ: 0.01-0.05 mg/kg	GC–MS-SIM		[25]

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continued *Table 1. Applications of the QuEChERS methodologies in soil sample preparation.*

Compounds	Matrix characteristics	Sample treatment	Cleanup step	Recovery (%)	Spiking level	LOD and LOQ	Detection	Obs.	Ref.
8 Triazoles	These matrices did not contain the target analytes.	$Mass_{sample}$-10 g; 10 mL ACN Shake 30´ in a water bath shaker QuEChERS: 4 g $MgSO_4$, 1 g NaCl, Vortex 3`, centrifuged 5' at 2599xg	150 mg $MgSO_4$ and 50mg C18 Vortex 1´, centrifuged at 2077xg RCF for 5´.	76.4-108.1	5, 25, and 50 mg/kg	LOD: 0.04-1 µg/kg LOQ: 0.12-3 µg/kg	LC–MS/MS	Sandy loam samples from trial plots were obtained. The samples were air-dried at room temperature, homogenized, and passed through a 2 mm sieve.	[30]
14 Organoclhorine, 1 methoxyacrylate strobilurin (Azoxystrobin), 2 Pyrethroids, 1 pyrimidine (Bupirimate), 3 organothiophosphates, 3 anilinopyrimidine, 1 anilide (Fenhexamid), 2 aryloxyphenoxypropionic, 1 pyrrole (Fludioxinil), 2 dichlorophenyl dicarboximide, 1 carbamate (Methiocarb), 2 conazole, 1 dinitroaniline (Pendimetaline), 1 phenylsulfamide (Tolylfluanid) and dicarboximide (Vinclozolin)	Two types of soils from intensive agricultural areas working under IPM systems and organic farming (OF) during 3 consecutive years (2009–2011).	$Mass_{sample}$-5 g; 3 mL water + 10 mL ACN Vortex 1` QuEChERS: 4 g $MgSO_4$, 1 g NaCl, 1 g NaCit and 0.5 g $Na_2Cit$ Vortex 3`, ultrasonic bath 5`, centrifuged 5' at 3000 rpm	d-SPE: 150 mg PSA, 150 mg MgSO4, and 50 mg C18 vortex 1`, centrifuged 5' at 4000 rpm	67-148	10, 50, 100, and 300 µg/kg	LOD: 1.5-7.6 µg/kg	GC-MS/MS		[26]
			DPX: 150 mg PSA, 150 mg MgSO4, and 50 mg C18	70-151					
Pharmaceuticals									
Ibuprofen; Hydroxyibuprofen; Carboxyibuprofen.	Soils samples – different OC content Type -agricultural to sediments	$Mass_{sample}$: 5 g; 3 mL of water (pH 2.5, adjusted with hydrochloric acid) and 7 mL of ACN with 1% acetic acid; QuEChERS: 4 g of MgSO4, 1 g of NaCl, 1 g of NaCit and 0.50 g of Na_2Cit. Vortex 4 min and ultrasonic bath 4 min.		79.5-101	100, 200, and 300 µg/kg	LOD: 1.83 to 6.10 µg/kg LOQ: 6.10 to 22.4 µg/kg	LC–FLD		[21]

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continued *Table 1. Applications of the QuEChERS methodologies in soil sample preparation.*

Compounds	Matrix characteristics	Sample treatment	Cleanup step	Recovery (%)	Spiking level	LOD and LOQ	Detection	Obs.	Ref.
14 veterinary products: sulphanilamide; sulfadiazine; sulfathiazole; sulfameter; trimethoprim; sulfadimidine; sulfabenzamide; sulfadimethoxine; erythromycin; tylosin; roxithromycin; penicillin G; dicyclanil; phenicol florfenicol. 11 hormonal steroids: androstenedione; testosterone; progesterone; norethindrone, gestodene; levonorgestrel; oestriol; oestrone; 17β-oestradiol; 17α-oestradiol; 17α-ethynyloestradiol. 6 human contaminant: Paracetamol; sulfamethoxazole; fluvoxamine, carbamazepine; ibuprofen; bisphenol A.	Clay-loam soil that was not treated with manure or sludge was used for optimisation. Containing 32.4% clay, 45.1% loam, 22.5% sand and 2.99% organic matter. Soils collected between March to July 2010 in France were analysed	Procedure inspired by QuEChERS ACN extraction: 10 mL water and 15 mL of ACN; Acetate buffer; Shake 3 min at 750 rpm (SPEX Sample Prep)	SPE	40–110 For most of the compounds	1.5, 50, and 500 ng/g	LOD: 0.004-7ng/g LOQ: 0.013-17 ng/g	LC–MS/MS		[39]
Perfluoroalkyl substances									
5 perfluororalkyl sulfonates (PFSAs): 13 perfluoroalkyl carboxylates (PFCAs): 7 perfluororalkyl sulfonamido	Ombrotrophic peat bogs	Extracted by ultrasonication	QuEChERS MixI (4 g of $MgSO_4$, 1 g of NaCl, 0.5 g of NaCit,·and 1 g of Na_2Cit). Mix V (containing 0.15 g of CHROMABOND Diamino with 0.9 g of $MgSO_4$ and 45 mg of carbon) Ultrasonic-bath 15'.	98±17 (on average)	--------	LOD: 3.8-141 ng/kg LOQ 11-282 ng/kg	HPLC-MS/MS	QuEChERS method modified	[38]

continued *Table 1. Applications of the QuEChERS methodologies in soil sample preparation.*

Compounds	Matrix characteristics	Sample treatment	Cleanup step	Recovery (%)	Spiking level	LOD and LOQ	Detection	Obs.	Ref.
Organochlorines (chlorobenzenes, chlorophenols, chlorinated hydrocarbons and chlorinated olefins)									
1,2-Dichloroethylene; cis 1,2-dichloroethane; 1,2-dichloropropane; trichloroethylene; tetrachloroethylene; 1,1,2,2-tetrachloroethane; chorobenzene; cumene; phenol; 2-chlorophenol; 1,3-dichlorobenzene; 1,4-dichlorobenzene; 1,2-dichlorobenzene; hexachloroethane; 1,3,5-trichlorobenzene; 2,4-dichlorophenol; 4-chlorophenol; 1,2,4-trichlorobenzene; 2,6-dichlorophenol; hexachlorobutadiene; 1,2,3-trichlorobenzene; 1,2,3,5-tetrachlorobenzene; 1,2,4,5-tetrachlorobenzene; 2,4,6-trichlorophenol; 2,4,5-tricholorophenol; 1,2,3,4-tetrachlorobenzene; pentachlorobenzene; 2,3,4,6-tetrachlorophenol; α-HCH; hexachlorobenzene; β-HCH; lindane; pentachlorophenol; δ-HCH	Peat sample	$Mass_{sample}$:2 g 15 mL dichloromethane QuEChERS: 4 g $MgSO_4$, 1 g NaCl, 1 g NaCit and 0.5 g Na_2Cit Vortex vigorously 1’		60-100	100, 500, and 1000 µg/kg	LOD: 2.1 to 653.30 µg/kg LOQ: 6.9 to 2117.0 µg/kg	GC-MS	Compared to ASE extraction	[22]
Diethyl aminoethyl hexanoate	Soil	$Mass_{sample}$:10 g 10 mL ACN. Vortex 1’. QuEChERS: NaCl (1 g) and $MgSO_4$ (4 g) – Vortex 0.5’, centrifuged 5’ at 3,800 rpm	50 mg PSA and 150 mg $MgSO_4$ Vortexed 0.5’ and centrifuged 3’ at 5,000 rpm.	89.4–103.3	0.005, 0.02, 0.1, and 1 mg/kg	LOQ: 0.005 mg/kg	GC–MS	Extraction in pakchoi and cotton also study	[36]
Trihalomethanes and BTEX									
4 Trihalomethanes: Chloroform; bmodichloromethane; dibromochloromethane; bromoform; BTEX	Two different natural soils: -Public garden soil -Vertisol	$Mass_{sample}$:5 g 3 mL of water + 2.5 mL of Ethyl acetate QuEChERS: 2 g anhydrous $MgSO_4$		65-76	50, 100, 150, 200, 300 500 µg/kg	LOD: 0.2-15µg/kg LOQ: 0.5-45 µg/kg	PTV-GC–MS (large-volume injection-fast GC-MS)	Simplified version of QuEChERS	[2]

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continued *Table 1. Applications of the QuEChERS methodologies in soil sample preparation.*

Compounds	Matrix characteristics	Sample treatment	Cleanup step	Recovery (%)	Spiking level	LOD and LOQ	Detection	Obs.	Ref.
4 Trihalomethanes (Chloroform, bromodichloromethane, Dibromocloromethane and Bromoform)	Two different natural soils: -Public garden soil -Vertisol	$Mass_{sample}$ 5 g 3 mL water. Vortex 1'. 2.5 mL of ethyl acetate. Vortex maximum speed 1'. QuEChERS: 2 g of $MgSO_4$, vortex 1'. Centrifuge 5' at 5000 rpm.		65-76	50, 100, 150, 200, 250, 350, and 500 µg/kg	LOD: 6-659 ng/kg LOQ: 17-1998 ng/kg	GC-µECD	Simplified QuEChERS method	[37]
2 Chlorinated pollutant compounds (Chloroform and 1,2-dichlorobenzene)	Two different natural soils: -Public garden soil -Vertisol	$Mass_{sample}$:2.5 g 1.5 mL of water, Vortex 1'. 2.5 mL of ethyl acetate, Vortex 1'. QuEChERS: 1 g $MgSO_4$ centrifuged 5' at 5000 rpm.		62-93	50-200 for CFM and 625-1562 µg/kg for 1,2-DCB	LOD: 2.2 and 1.3 (µg/kg)for CFM and 1,2-DCB	GC-µECD		[11]
Chlorophenols, alkylphenols, nitrophenols and cresols									
Nitrophenols (NTPs): 2-nitrophenol, 3-nitrophenol and 4-nitrophenol; Chlorophenols (CPs): 2-chlorophenol;4-chlorophenol; 2,4-dichlorophenol; 2,4,5-trichlorophenol; 2,4,6-trichlorophenol; pentachlorophenol Alkylphenols (APs): 4-n-nonylphenol; 4-tert-octylphenol Cresols: 2,4-dimethylphenol; 4-chloro-3-methylphenol.	Agricultural soils	$Mass_{sample}$ 10 g 10 mL of ACN (acetic acid 1%, v/v) and 5mL of water 1 h in a rotary shaker QuEChERS: 1.7 g of CH_3COONa, 6 g of $MgSO_4$ and 4 g of NaCl Shaken for 1'. 0.75 g of $MgSO_4$		65-113	10-300 µg/kg	LOD and LOQ: 1-100 µg/kg	GC- QqQ-MS/MS		[35]

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4.2 Hydration step

QuEChERS was originally developed for vegetables and fruits, which generally contain more than 75% moisture, therefore it may be necessary to adapt this methodology for dry samples [1]. The addition of water to the sample prior to the QuEChERS extraction is used to weaken interactions of the analytes within the matrix. This ensures adequate partitioning in dry samples (cereals, dried fruits, tobacco, teas, etc.), and allows for the pores in the sample to be more accessible to the extraction solvent [50].

Some authors have tested different ratios (sample:water) and compared the recoveries obtained with and without water addition [1,11,12,21,26,27]. Kvicalova *et al.* [27] tested the effect of water addition and different sample-to-water ratios (1:2 and 1:5), concluding that the best recoveries were obtained with ratio 1:2 and 4 g of soil sample. Wang *et al.* [12] also evaluated different amount of added water (0-4 mL) and, once more, better recoveries were obtained when the soil was hydrated, with 4 mL of water for 10 g of soil. Correia-Sá *et al.* [1] and Fernandes *et al.* [26] compared the extraction with a previous soil hydration (3 mL of water for 5 g of soil sample) and without water addition, the results thereof confirmed the importance of the hydration step for the success extraction of the analytes. Pinto *et al.* [11] tested 1.5 and 2.5 mL of ultra-pure water addition to the 2.5 g aliquots of garden soil. The recoveries obtained were compared using a paired t-test and no significant differences were observed. Therefore, a volume of 1.5 mL was chosen because it was enough to completely saturate the sample and provide a proper homogenization of the sample. Furthermore, Bragança *et al.* [21] studied the effect of water addition (0 mL versus 3 mL) and improved results were obtained with water addition. However, the acidification of water to pH 2.5 (adjusted with hydrochloric acid) further increased the recoveries for ibuprofen, hydroxyibuprofen, and carboxyibuprofen compounds.

Analytes may become bound to soil through physical or weak chemical bonding depending upon the nature and properties of compounds and soil. Rashid *et al.* [3] tested two different hydration procedures for the extraction of organochloride pesticides, one with 10 mL of water and the other with a 1.0 mol/L aqueous ethylenediaminetetraacetic acid disodium salt (Na_2EDTA) solution for 30 min prior to extraction to determine if the latter could facilitate the extraction of bound analytes from complex matrices. Results showed no statistical difference between the two hydration procedures and, therefore, the authors chose to use only water [3].

4.3 Ratio sample/volume

Typically sample amount is one of the studied variables. Usually, the best way to improve efficiency of an analytical method is to reduce sample size to the minimum amount and scale the method accordingly. This will provide statistically reliable results [51]. In the original QuEChERS method, the sample size was 10 g which was an advance compared to more traditional techniques that used larger sample amounts [51]. Higher sample weights or larger solvent volumes will compromise a proper homogenization due the capacity of the centrifuge tube [11].

The majority of the studies used a subsample of 10 g, but some authors choose a larger (15 g) [31,43,46] or a smaller (7.5, 5, 4, 3, 2.5 or 2 g) [1,3,5,11,21,22,26-28,34,37,52] sample size. The criterion used by the authors for choosing the best ratio was based on the most suitable dispersion and the best homogenization between the sample and the extraction solvent.

4.4 Extraction Solvent (type, volume and pH)

The choice of the solvent(s) is one of the most important decisions in any extraction. There are many aspects that have to be considered, including: the ability to cover the desired analytical spectrum (ranging from the polar to the non-polar compounds); the selectivity that can be reached during extraction; partitioning and clean-up; achieving separation from water; amenability to chromatographic separation techniques; cost; safety; environmental impact; and, handling concerns (e.g., ease of evaporation, volume transfers) [51]. ACN is the extraction solvent most commonly used due to its ability to separate easily from water when an appropriate mixture of salts (magnesium sulphate ($MgSO_4$) and sodium chloride (NaCl)) is added [51]. However, if ACN does not provide adequate recoveries, other solvents can be employed, namely: ethyl acetate, acetone and methanol (MeOH) [53].

Pinto *et al.* [11] and Wang *et al.* [12] mentioned that the main disadvantages (co-extraction of non-polar compounds such as lipids or waxes) of ethyl acetate [11] and ACN [12] may not be significant. Due to the fact that soil samples, in contrast with fruits and vegetables, do not have high contents of lipid materials, they are characterised by their mineral and organic matter fraction (mainly composed by humic substances) [11,12]. Regarding the suitability of the organic solvents for GC, Maštovská K. and Lehotay S.J. [54] evaluated and compared the possibilities of ACN, acetone, and ethyl acetate. Solvent exchange is not required before the chromatographic analysis, as the three solvents mentioned above can serve as mediums for GC injection. Leusueur *et al.* [16] investigated the effect of acetone, however, increased co-extraction of matrix interferences was observed, resulting in less clean extracts and higher limit of detection (LOD) and limit of quantification (LOQ) and demonstrating the critical need for a clean-up step [16]. Bragança *et al.* [21] extended the range of the study and different solvents were considered: ACN, MeOH, ACN–MeOH (60–40%, 50–50% and 40–60%, v/v), *n*-hexane–acetone (50–50%, v/v), ethyl acetate, and acetone. For simultaneous extraction of ibuprofen and the two metabolites, better results were obtained using ACN-MeOH (50–50%, v/v). Ethyl acetate and ACN have been studied also in the work of Pinto *et al.* (2010) [11] for the suitability of the QuEChERS extraction and for GC analysis. Regarding the recoveries obtained in the extraction process from soil samples, the two studied solvents act in a similar way for chlorinated pollutants. Better chromatographic behaviour led the authors to select ethyl acetate as the optimum extraction solvent. Rouvière *et al.* [22] compared the recoveries obtained using ACN and dichloromethane in the QuEChERS

extraction. It was concluded that dichloromethane was the best solvent extraction for chlorinated hydrocarbons, olefins, and chlorobenzenes, but hexachlorocyclohexane is most efficiently extracted with ACN. For chlorophenols, higher recoveries with ACN were obtained. However, extraction with ACN had higher relative standard deviation (RSD) ranging up to 53% because of its retention on PSA (primary secondary amine) and C18 phases. The mixture of ACN–dichloromethane (50–50% (v/v)), was also tested, but the slight increase in the recovery results was accompanied with a simultaneous increase of RSD. Thus, extraction with dichloromethane without purification by d-SPE was a good compromise between high recovery and good method precision.

Because the pKa of the compounds in question is related to solvent affinity, a pH adjustment was also studied. Bragança *et al.* [21] concluded that the pH adjustment of ACN was sufficient and more important than the acidification of the water. The best approach for QuEChERS extraction was achieved using 3 mL of purified water (with or without adjusted pH) and 7 mL of acidified ACN (1% acetic acid). Wang *et al.* [12] tested ACN versus acidified ACN (with 1% acetic acid) and MeOH as extraction solvents, achieving better recoveries for pyrazosulfuron-ethyl with the acidified ACN [12]. Kvicalova *et al.* [27] tested ACN, acidified ACN (1% acetic acid) and ACN with 1% of ammonium (NH_3). The obtained data showed that, to achieve acceptable recovery (70%–130%) for all selected compounds, it was necessary to employ a combination of two extraction procedures based on QuEChERS methodology, ACN with 1% acetic acid for chloridazon, cypermethrin, fluroxypyr and phenmedipham, and, ACN with 1% of NH_3 for carbendazim, chloridazon, clomazon, fenpropidin and spiroxamine [27].

Lehotay *et al.* [55] mentioned that the pH was an important parameter in the stability of several base-sensitive pesticides and that it was also critical for acid-sensitive pesticides, therefore, the authors developed a buffered QuEChERS method. The modifications to the original QuEChERS consisted in adding 1% acetic acid to ACN for extraction, and the use of $MgSO_4$ and CH_3COONa instead of NaCl to yield consistent pH of the procedure independent of the pH of the sample [3,12,55]. Rashid *et al.* studied organochlorines pesticides [3] and Wang *et al.* studied pyrazosulfuron-ethyl a sulfonylurea pesticide [12] using this method.

Some authors have chosen to combine the citrate buffer version or original composition with the addition of acetic acid to ACN [5,8,21,34]. Alkaloids, steroid derived alkaloid (veratridine), flavonoids, limonoid (azadirachtin), spynosad D, pyrethrins and piperonyl butoxide were analysed by Prestes [5], azadyrachtin, spinosad and rotenone pesticides were analysed by by Drozdzynski and Kowalska [34]. Caldas *et al.* [8] on the other hand, concluded that applying the original QuEChERS composition for soil samples, and using 0.1% acetic acid, led to improvement in recoveries (oxazolidine (clomazone), phenylpyrazole (fipronil), triazole and a strobilurin (azoxystrobin) pesticides), as it enabled the increase of the pesticide stability prior to analysis. The acetate buffered QuEChERS, with acidified ACN, showed advantages with respect to higher recoveries and greater stability of pH-sensitive pesticides [3,12]. Salvia *et al.* [39] studied several solvents to extract antibiotics. ACN, with 1% acetic acid, ACN with 1% NH_3 and ACN with phosphoric acid were tested (the extraction was performed with 10 mL of water and 10 mL of extraction solvent or 10 mL of 0.1 mol/L Na_2EDTA and 10 mL of extraction solvent). MeOH–based solvents were also tested, however, the authors reported that viscous extracts were obtained after evaporation, maybe due to a reaction between the salts and MeOH. Among the various tests performed, higher recoveries were obtained using ACN and acidified ACN combined with the Na_2EDTA. For the QuEChERS extraction, the authors selected ACN because the presence of EDTA reduced the efficiency of the purification step. It also offered excellent performance for the extraction of the broadest range of compounds, and also showed the least interference [39].

Nonetheless, Mei *et al.* [28], considering that the soil samples contain generally little water and their pH values are mainly stably neutral, did not deem it necessary to use the acidified ACN and a desalination step was omitted from their improved QuEChERS method.

The original QuEChERS method employs 10 g of sample to 10 mL of extraction solvent (ratio 1). According to Table 1 studies reported the use from 4 [28] to 30 mL [43] of extraction solvent.

5. QuEChERS Content

In QuEChERS, the initial single-phase extraction with ACN is followed by the addition of salts ($MgSO_4$ and NaCl) to induce phase separation [51]. The addition of NaCl typically leads to increased recoveries of polar compounds, but this also depends on the nature of the solvents involved in the partitioning step, and allows the control of the percentage of water in the organic phase. The use of $MgSO_4$ also has the ability to bind large amounts of water and thus significantly reduce the water phase. This also promotes partitioning of analytes into the organic layer. Nevertheless, to bind a significant fraction of water, $MgSO_4$ should be added at amounts well exceeding its saturation in water [51,53].

The AOAC 2007.01 method uses an acidification of the extraction solvent with 1% acetic acid. The addition of an anhydrous (CH_3COONa) buffer, to protect the base sensitive analytes from degradation, provides superior recovery for pH sensitive compounds [13]. The European Norm EN 15662 includes citrate buffering reagents that preserve base sensitive analytes [14]. The addition of the proper amounts and combination of salts can be used to control the percentage of water in the organic phase (and vice versa for organic solvent in the water phase). This allows for a certain degree of adjustment in the polarity of the phase [8,51].

The majority of the works applied the original composition, followed by the citrate buffer version and by the acetate version. For example, original QuEChERS content was used for extracting pesticides by Wang *et al.* [32], Zhang *et al.* [33], Wang

et al. [42], Li *et al.* [44], Temur *et al.* [8], Asensio-Ramos *et al.* [24], Shi *et al.* [47], Brondi *et al.* [25], and Li *et al.* [30] and used for extract organochlorines (chlorobenzenes, chlorophenols, chlorinated hydrocarbons and chlorinated olefins) by Jiang *et al.* [36].

The European Norm EN 15662 was used for extracting pesticides by Correia-Sá *et al.* [1], Prestes *et al.* [5], Yang *et al.* [29], Drozdzynski and Kowalska [34], Lesueur *et al.* [16], and Fernandes *et al.* [26], used for extract pharmaceuticals (ibuprofen and its major metabolites) by Bragança, *et al.* [21], used to extract perfluoroalkyl substances by Dreyer *et al.* [38], and used to extract organochlorines (chlorobenzenes, chlorophenols, chlorinated hydrocarbons and chlorinated olefins) by Rouvière *et al.* [22].

The AOAC 2007.01 method was used to extract pesticides by Sun et al. [40], Kvicalova *et al.* [27], Wang *et al.* [12], Wang *et al.* [31], and Rashid *et al.* [3] and used to extract pharmaceuticals (veterinary products, hormonal steroids and human contaminant) by Salvia *et al.* [39].

The use of only NaCl for the extraction has been applied for indoxacarb [43] and procymidone [48] analysis. On the other hand, Mei *et al.* [28] used only $MgSO_4$ for the extraction of five herbicides with small sample weight (1 g) and, thereafter, the method was then scaled, requiring only 0.1 g of $MgSO_4$. In other two studies [11,37], different salts combinations, such 1–0, 1–0.25, 1–0.50, 2–0, 2–0.25 and 2–0.50 g ($MgSO_4$–NaCl) were studied. There were no significant differences between the different combinations of the studied salts. Moreover, the addition of NaCl did not have any significant effect in the recoveries of chlorinated compounds [11] and of trihalomethanes [37] from soil samples. Due to the good recoveries obtained for the studied compounds described in the two works and also in order to simplify the new approach, 1.0 g of $MgSO_4$ was used.

Caldas *et al.* [8] optimized the salt mixture and concluded that the combinations of $MgSO_4$ and NaCl were more effective for tebuconazole and propiconazole, but for the more polar compounds (clomazone and azoxystrobin), the recoveries decreased more than 20% when 1 g of NaCl was added. Better recovery for fipronil was achieved with the exclusive use of $MgSO_4$ rather than in combination with NaCl [8]. According to Anastassiades *et al.* [8] it is proposed that added NaCl leaves less water remaining in the ACN phase. Caldas *et al.* [8] concluded that it becomes less polar and less receptive to polar compounds such as clomazone and azoxystrobin. The authors also tested the buffer approach, which was composed of acetic acid and acetate salt (AOAC Method). For three of the compounds where the buffer was used, recoveries increased. In comparison, the recoveries decreased for two others in which the buffer was not used. Therefore, the authors concluded that the combination of 4 g of $MgSO_4$, 0.1% acetic acid, and 1 g of NaCl enabled the highest recoveries for all of the compounds [8].

In the determination of chlorantraniliprole [41] in a surface soil, the extraction was also performed by liquid extraction with ACN in an ultrasonic water bath and then applied QuEChERS clean up technique, the d-SPE.

Bragança *et al.* [21] studied the influence of the extraction solvent and the QuEChERS content simultaneously for ibuprofen and metabolites (hydroxyibuprofen, carboxyibuprofen). The combination of the extraction solvent used in the AOAC 2007.01 method (1% acetic acid in ACN [13]) and the QuEChERS salts used in the EN 15662 method (citrate buffering salts [14]) was evaluated. The highest recoveries (almost 100% for the soils with 2.0 and 3.12% of organic carbon content) were obtained with this combination.

Padilla-Sánchez *et al.* [35] studied the extraction of chlorophenols, alkylphenols, nitrophenols and cresols using a mixture of CH_3COONa, $MgSO_4$ and NaCl.

6. Extraction time and Homogenization technique

Wang *et al.* [12] investigated different agitation methods: sonication and hand shaking. They also tested different timings from 2 to 15 min. Regarding homogenization and timing, the authors chose the hand shaking method for 2 min [12].

Due to the strong binding characteristics of soil, stronger conditions than shaking may be needed. Fernandes *et al.* [26] introduced a sonication step in the extraction procedure concluding that better recoveries were obtained. In another study [32], sonication time was tested in the range of 0 to 8 min. The results showed that the best recoveries were obtained with the 2 min time [32].

Bragança *et al.* [21] evaluated the extraction time from 1 to 5 min, and the maximum recovery for all the studied compounds was obtained at 4 min. To improve the extraction of hydroxyibuprofen, carboxyibuprofen, and ibuprofen in soils with higher organic matter (organic carbon of 3.12%), the authors also studied the inclusion of an additional ultrasonic bath for 4 min. The recoveries increased for all analytes.

7. Prevention of agglomeration

The formation of agglomerates is a problem that can sometimes arise in QuEChERS procedures. This can occur even with vigorous homogenization, and can compromise the extraction. QuEChERS suppliers have prescribed the use of ceramic pieces to break up salt agglomerates to facilitate sample homogenization. [50]. However, Bragança *et al.* reported that the use of ceramic pieces made no significant difference [21]. To avoid the formation of agglomerates, these authors added the QuEChERS content slowly and continuously with slow vortexing. After the addition was completed, the vortexing was performed at maximum speed, followed by 4 min homogenization and no agglomeration was noticed. Then, the sample was sonicated for 4 min, followed by the addition of acidified ACN and the rest of the procedure was executed as described previously. Good recoveries were obtained for all types of soils, with recoveries higher than 91.7% [21].

8. Clean-up

8.1 Dispersive SPE

Traditionally, a d-SPE clean-up has been utilised in studies that employ QuEChERS [8,51]. Generally, clean-up sorbents are chosen to retain the matrix components and to enable the analytes of interest to stay in the ACN phase [8]. The user is able to prepare whatever combination and amount of sorbents needed with the uses of d-SPE [8].

All studies that employ QuEChERS to extract analytes from soil or sediment samples used a d-SPE clean-up step [21, see Table 1], with some exceptions [3,5,8,12,47].

The main steps of d-SPE typically involve mixing an aliquot of the sample extract with a small amount of sorbent (PSA, C18, $MgSO_4$), followed by shaking or vortexing to distribute the d-SPE material evenly, thus making the clean-up process easier. Finally, the sorbent is separated by centrifugation, and an aliquot of the final extract is taken for analysis [1,3,12,16,24,26-34,36,40-48].

Due to the presence of a primary and secondary amine, PSA is a structure that has a high chelating effect. As a result, fatty acids and other polar compounds are typically retained in the matrix. In addition, C18 is effective as a reversed phase sorbent that traps and remove starch and sugar from some samples [8,51], and $MgSO_4$ is used to remove residual water [51].

Caldas *et al.* [8] and Wang *et al.* [12] evaluated the use of PSA and C18 sorbents, and the process showed that, for their soil samples, the different dispersive sorbents did not have a significant influence on the purification and recovery of analytes (pesticides) from the extracts. Therefore, the procedure without the clean-up step got the highest recoveries. Thus, the authors concluded that this was due to the fact that the coextractives generally removed by the sorbents (lipids, sugars, pigments, etc.) may not be present in the soil extracts; consequently, the clean-up process does not improve the recoveries [8]. Wang *et al.* [12] reported that pyrazosulfuron-ethyl from the sulfonylureas group reacted with the sorbent (PSA and C18) due to their chemical nature, resulting in low recoveries.

Pinto et al. (2010) [11] analysed the extracts obtained after the centrifugation step without conducting further clean-up. This decision was made because of the non-fatty characteristics of the soil matrices, and the high degree of selectivity and sensitivity of the micro-electron capture detector (GC-μECD). This type of analysis was duplicated by other authors [37]. Consequently, it was found that using QuEChERS without the clean-up step made the procedure simpler, faster, cheaper, and more efficient [11].

Fernandes *et al.* [26] compared the use of the d-SPE and disposable pipette extraction (DPX) (with same composition namely PSA, $MgSO_4$ and C18) as clean-up step and good recoveries were obtained with both configurations and no statistically significant differences were observed.

Mei *et al.* [28] tested different d-SPE compositions, namely the addition of 0.1 g of PSA (or 0.1 g PSA + 0.1 g C18, or 0.1 g PSA + 0.03 g GCB) adsorbent to the extract. The authors also evaluated two different methods that differ in timing of clean-up. In method 1, the clean-up step was performed after QuEChERS extraction, according to the traditional procedure [28]. In method 2, the adsorbents and anhydrous $MgSO_4$ were added during the QuEChERS extraction (in the supernatant) and not after as usual. The results demonstrated that the recoveries of both method 1 and method 2 were similar, and that the best combination of sorbent was PSA + C18. This combination obtained higher recoveries as the sorbent adsorbed minimum analytes and maximum impurities. As the method 2 was simplified it was the chosen one [28].

Another important aspect for the efficiency of the clean-up process is the standing time for the mixture of adsorbents and sample extract. Wang et al. [31] tested different timings for the d-SPE vortex, from 1 min until to 2 h with at moderate speed at 25ºC. The authors concluded that less interfering components were obtained with the purification process using 2 min vortexing or longer [31].

Asensio-Ramos et al. [24] reported that using lower sorbent amounts resulted in an important loss of chlorpyrifos, chlorpyrifosmethyl, fenamiphos, malathion, and malaoxon and poor sample clean-up, showing the importance of the optimization of sorbent amount in QuEChERS.

8.2 Other clean-up procedures

Rashid *et al.* [3] developed a simple clean-up and concentration step that is not based on d-SPE. An ACN extract was concentrated, water added, followed by liquid–liquid partitioning into *n*-hexane. Water was added prior to the partition step to facilitate the separation of the two layers. This process allowed for cleaner extracts that contained higher sample amounts (3.2 g/mL, compared to 0.5 g/mL for the standard QuEChERS method). The final extract was in *n*-hexane rather than ACN, enabling the introduction of 3 μL on the GC system instead of just 1 μL [3].

Salvia *et al.* [39] in determination of steroids, veterinary and human drugs evaluated several sorbents (PSA, PSA+C18, Florisil, silica, aluminium oxide and SAX and Strata-X SPE cartridge) jointly with anhydrous $MgSO_4$ to eliminate the excess of water. The authors concluded that the best procedure was to perform the clean-up step by a solid phase extraction (SPE) using both a strong anion-exchange cartridge and a polymeric cartridge [39].

Brondi *et al.* [25] also used a traditional SPE, as clean-up, with 330 mg PSA, 330 mg C18, 1 cm layer of $MgSO_4$ activated with 3 mL of ACN.

Dreyer *et al.* [38] used a modified QuEChERS clean-up method to suit the needs of peat extract clean-up and two procedures were sequentially used. After extraction, the extract was transferred to 15 mL polypropylene tubes containing 5 mL of water Milli-Q, and QuEChERS (I) (4 g of $MgSO_4$, 1 g of NaCl, 0.5 g of Na_2Cit, 1 g of NaCit). Then, supernatant ACN phases were transferred to new 1 mL PP tubes and glacial acetic acid (400 μL), and QuEChERS Mix (V) (0.15 g of CHROMABOND Diamino with 0.9 g of $MgSO_4$ and 45 mg of carbon) were added to the extract [38].

9. Method-performance characteristics

Method validation is a process that determines, through laboratory studies, whether the performance characteristics of the method meet the requirements of the intended analytical applications. Methods need to be validated or re-validated before their introduction into routine use. The process of validation of the analytical method must demonstrate that the method is suitable for its purpose. Parameters usually considered in the validation process are accuracy, precision, specificity, LOD, LOQ, linearity, range, ruggedness/robustness and applicability [56].

9.1 Accuracy (Precision and bias studies, accuracy, recovery)

In the majority of the studies related to pesticides and other pollutants extraction from soil/sediment samples (Table 1), the recovery experiments were performed for 1 to 6 levels of fortification (ranging from 1 to 2000 µg/kg) and with 3 to 10 replicates.

The results prove that QuEChERS method is adequate for pesticide determination from soils, with overall recoveries between 70–120% and with inter and intra-day studies presenting RSD below 25%. Nonetheless, some exceptions occurred.

In the study of Kvicalova *et al.* [27] the QuEChERS method (with several modifications) was compared with the Luke method. This method is based on basic conditions using the mixture of ammonia, water, and ACN. The results of this comparison showed that higher recovery for all selected compounds was observed using the combination of 2 extractions. However, very low recoveries of carboxin were obtained for all methods, confirming its rapid decomposition in solid matrices [27].

Lesueur *et al.* [16] also compared the QuEChERS method with three other methods (DIN 12393, ultrasonic extraction (USE), PLE). Only the QuEChERS and the USE methods allowed the recovery of all the substances for the three types of soils/material. The highest recoveries were obtained using the QuEChERS method and 50% of the substances satisfied the 70–120% recovery range [16]. Using European Norm DIN 12393 and PLE extraction, carbendazim and metamitron were not recovered as well as monolinuron for PLE. Carbendazim, metamitron and monolinuron were not expected to present any problem during their extraction from the materials. However, they have the lowest octanol–water partition coefficient (K_{ow}) of all the selected substances, suggesting a possibly high repartition in the water phase and as a consequence a low concentration in the analysed organic phase. Overall, the substances often reported for their strong binding to soil like lindane, trifluralin, dieldrin or deltamethrin (i.e. those with the highest organic carbon-water partition coefficient, (K_{oc})), were always recovered [16]. Additionally, it is known that OCPs have a high affinity to organic humic substances of soil matrices (high K_{ow}) with which they develop chemical bonds. Lesueur *et al.* [16] suggested that the energy produced by the ultrasonic dispersion (40 W) was too weak to break down the created bonds between organo-mineral complexes. It was also considered that this was likewise valid for chlorpyriphos, chlorpyriphos-methyl, deltamethrin and dieldrin. However, lindane has the highest water solubility in the selected group, as well as the lowest soil sorption coefficient. This would explain why there was a better recovery compared to the other organochlorine pesticides. Additionally, the secondary and tertiary amine pesticides (phenylureas, triazines, and their metabolites) tend to adsorb on the soil inter-crystalline layers of clay minerals. These minerals cannot be reached with ultrasonic vibration, making USE less efficient with these substances [16].

The authors also suggested that the soil characteristics, namely the organic matter content, affected the extraction process. The fact that the adsorption of pesticides increases with the organic matter content also played a part in the extraction. Therefore, the studied pesticides should adsorb better to the EUROSOIL 7 (11.52% of organic matter) than to its subsoil SO 26 (1.81% of organic matter), and consequently be possibly harder to desorb from the materials. However, higher recoveries were achieved with the EUROSOIL 7 than with the SO 26. This was also true for any case involving extraction in sea sand (especially for chlorpyrifos and chlorpyrifos-methyl) [16]. The authors mentioned that a possible explanation for this occurrence was the fact that the samples were dried overnight at 30 ºC. Consequently, the analytes could have built bonds to soil aggregates and solid matter that do not take place with sea sand [16].

Because OCPs have a high affinity to soils with organic matter Correia-Sá *et al.* [1] launched a study of the recoveries for two groups of soils HS and LS (high and low organic matter). The results proved that the organic matter has influence in the extraction, and the average recoveries obtained for the HS soils were lower than for LS soils [1].

In a study conducted by Asensio-Ramos *et al.* [24] the QuEChERS method was applied to three different types of soil for the extraction of a group of pesticides. The authors concluded that the recovery values were highly dependent on the type of soil analysed [24], a conclusion also mentioned by Correia-Sá *et al.* [1]. The recovery for the ornamental soil was typically lower than for the other two soils, likely due to the high amount of organic matter and a resulting high percentage of organic components (fulvic and humic acids) that could have affected the extraction efficiency of the pesticides under study. For the majority of pesticides, the organic matter content is the most important soil property affecting the degree of adsorption [24]. In regards to the recoveries of malathion and its breakdown product (malaoxon) in the ornamental and the forest soils, recovery percentages were lower (between 9 and 29%) for the ornamental soil. For the forest soil, however, results were inconsistent as variable recovery was observed for the two concentrations tested. Malathion had the shortest soil half-life (an average 4 h) of the studied pesticides. It is also understood that degradation of pesticides in soils is highly dependent the characteristics involved, and it may be possible that degradation of malathion in the forest soil occurred in an unrepeatable way [24].

Yang *et al.* [29] also reported lower recoveries (below 70%) for malathion, dicofol, phorate, and profenofos. There were also recoveries above 120%, for carbofuran, fipronil, pyridaben, cyfluthrin, fenvalerate, deltamethrin and quinalphos [29].

Prestes *et al.* [5] tested different methods for the extraction of biopesticides, namely; solid-liquid extraction (with mechanical and with sonication shaking); PLE; and QuEChERS. The recovery study for the different methods, which included the spiking of 100 µg/kg, revealed that better results were obtained when modified QuEChERS approach was used. With the exception of nicotine and sabadine, most of the compounds showed recoveries ranging from 70 to 110%. It must be highlighted that recovery values obtained with this method were higher than those obtained with previous methods. Additionally, RSD values were lower than 25%. After observation of the obtained results (in terms of recoveries and RSDs), modified QuEChERS approach was selected as the most suitable procedure for the determination of these biopesticides [5].

The QuEChERS methodology was also successfully applied to the extraction of several other types of compounds from soils as already mentioned. In general acceptable recoveries were obtained, ranging from 35 to 119% [2,11,21,22,35-39] at different concentrations, with RSD<25%.

Pinto *et al.* [11] found that the lowest obtained recovery was achieved for the most volatile compound, chloroform, meaning that volatility may interfere with the compound's extraction. In the Padilla-Sánchez *et al.* study [35] at 10 µg/kg level, some phenols did not show adequate recoveries. In the extraction of steroids, veterinary and human drugs [39] the recoveries ranged between 35% (sulfonamides) and 119% (paracetamol, sulfamethoxazole, fluvoxamine, carbamazepine, ibuprofen, and bisphenol A). However, lower recoveries were obtained for the macrolids and β-lactams (between 15 and 50%) because of their loss during the purification step [39].

In summary, the QuEChERS method was applied to several pesticides and other pollutants from several types of soil/sediments/materials; and the obtained results proved its robustness and wide applicability.

9.2 Matrix effect

As several authors have reported, the sample matrix is likely to affect the quantification of the target analytes (effect on the chromatographic or MS response). The main culprit of these occurrences is the complexity of the soils [24,57,58]. This phenomenon is called matrix effect (ME); it is highly compound-dependent and can involve either an unexpected suppression or enhancement of the analyte response induced by the co–eluting matrix [57-60]. Most of the compounds susceptible to matrix-induced enhancement are polar, capable of strong hydrogen-bonding, acids or bases [58]. In MS, the degree of ion suppression/enhancement not only varies with the sample and compound, but may also depend on the analyte concentration as well as on matrix to analyte concentration ratio [8].

ME might exert a detrimental impact on important method parameters such as LOD, LOQ, linearity, accuracy, and precision [61]. Thus, the majority of the authors perform matrix-matched calibrations [1,3,5,8,24,26,32-34,41,42,44-46] and compare the slopes obtained in the calibration using the matrix matched-standards with those obtained using the solvent standards for each analysed compound.

The ME was evaluated for analysis of pyraclostrobin showing a value of 1.046 [33]. In the analysis of trifluralin, Temur *et al.* [45] evaluated the suppression or enhancement as%, obtaining a value enhancement of 25.49%. Fernandes *et al.* [26] observed ME for α and β-HCH (Hexachlorocyclohexane), HCB (Hexachlorobenzene), endrin, o,p'-DDT (dichlorodiphenyltrichloroethane), chlorpyrifos, fludioxonil, iprodione, malathion, methiocarb, and pendimetaline, in a group of 36 multiclass pesticides. No ME was observed for the other compounds but a matrix matched calibration was performed for all compounds [26].

Li *et al.* [44] also used ESI-MS, and studied the ME for each enantiomer of fenbuconazole and its metabolites. The signal enhancements for the six target compounds were typically observed in the soil matrix extracts with the slope of calibration lines in matrix vs. solvent ratios in the range of 1.287–1.623 [44]. Asensio-Ramos *et al.* [24] studied the extraction of pesticides in three different types of soils, and showed significant ME with respect to the standards in cyclohexane, except for buprofezin, whose calibration curves in cyclohexane and in the ornamental soil extract were comparable [24]. Prestes *et al.* [5] also concluded that ME was a major drawback for quantitative trace determination of analytes using ultra-high performance liquid chromatography (UHPLC)- MS/MS. The authors considered a slope ranging from 0.8 to 1.2 in the suppression or enhancement effect to tolerable. On the other hand, values lower than 0.8 or higher than 1.2 indicated a strong ME. The results showed that tolerable ME was observed for most of the selected compounds, with the exception of nicotine, pyrethrin I (signal suppression), cevadine, and degueline (signal enhancement). Therefore, matrix matched calibration was used for quantification purposes [5]. Caldas *et al.* [8] conducted an assessment with ME in relation to the QuEChERS extraction and APCI (atmospheric pressure chemical ionization) source. Considering percentage, no effect was observed when ME was equal to 100. The highest suppression effect was observed for fipronil with 43.2% of suppression. The matrix matched calibration was used to improve the accuracy of the quantification [8]. Drozdzynski and Kowalska [34] studied the ME for biopesticides and achieved a suppression effect of 1 to 7% in soil. However, for any analyte–matrix combination, the average relative response was in the range between 70 and 120%. Consequently, accuracy and precision parameters were obtained using an internal standard method (as well as matrix-matched-standards) for more accurate quantification [34].

Martín *et al.* [37] compared ME in garden and Vertisol soils versus water sample spiked at the same concentration levels and subjected to the same extraction procedure as applied to the soil samples. The slopes for the garden and Vertisol soils were lower by 1 and 16% for the chloroform, 6 and 14% for the bromodichloromethane, 13 and 20% for dibromocloromethane,

and 19 and 27% for bromoform than for water samples. The differences can be explained by highlighting the different interactions of the compounds in the two types of soils. These soils have a complex porous structure, and contain different proportions of minerals and natural organic components. A comparison was also made between calibration curves (using standard solutions in solvent) and matrix–matched standards (in soils or in the certified reference material). This comparison was made using the same concentration range. The results showed the slopes were significantly different within these standards. In order to compensate this effect, and also for quantification purposes, the matrix-matched standard calibration was used [37]. Rouvière *et al.* [22] observed a positive ME for some of the studied compounds (tetra-, penta- and hexa-chlorobenzenes and for tri-, and tetra-chlorophenols), with results ranging from 120 to 180%.

In several studies, no significant ME was observed for chlorantraniliprole [41], herbicides group [28], ibuprofen (and its metabolites) [21], and organochlorine [11] in soil matrix. In these instance, the complex matrix-matched calibration could be avoided, and the determination method simplified.

9.3 Linearity range and Detention and Quantification Limits

For pesticides the linearity range was diverse, with some authors performing the calibration in matrix [1,3,5,8,24,26,32-34,41,42,44-46] or in solvent [12,16,26-29,31,40,43,47,48], and this may constitute a determinant fact as LODs and LOQs are matrix dependent. Regarding the LOD and LOQ, acceptable limits were obtained. These limits were generally determined according to signal-to-noise ratio, except for the work of Correia-Sá *et al.*[1], that used the Miller equation, and for Temur *et al.* [45] that determined the limit associated to the equipment (IDL) and with the matrix (EMDL).

For all the studies, related to pesticide extraction from soils applying the QuEChERS method (Table 1), a good linearity was obtained with a correlation coefficient (R^2) ≥0.99, except for diafenthiuron that presented a R^2 of 0.962 [32].

For the OCPs group the LODs ranged from 0.04 to 23.77 µg/kg and LOQs from 0.1 to 292 µg/kg [1,3,11,16,26,29]. In this group the LODs and LOQs varied substantially with the studies. Rashid *et al.* [3] presented the lowest LODs (≤0.7 µg/kg) and LOQs (≤2.4 µg/kg) for this group. As mentioned earlier, these authors developed a method that introduced a simultaneous clean-up and concentration step that resulted in cleaner, more concentrated extracts. The method also enabled the injection of greater volume on GC, leading to lower LOD and LOQ values for 19 OCPs [3]. The highest LOQ belonged to dieldrin in Leusuer *et al.* [16] study, as the authors referred this pesticide had a reported strong binding to soil, but still was always recovered. The organophosphorus group presented LODs from 0.48 to 37 µg/kg, and LOQs from 1.61 to 125 µg/kg [16,26,29,43]. In this group the values were very similar for the several studies except for chlorpyrifos-methyl that presented a LOQ between 3.29 µg/kg [24] and 125 µg/kg [16] in the different studies. For carbamates, LODs ranging from 0.020 to 2.9 µg/kg and LOQs from 0.00667 to 21.5 µg/kg were obtained [26-29]. In this group, phenmedipham was analysed in two works. [27,28], and the lowest LOQ (0.0667 µg/kg) for this pesticide was obtained in the work of Mei *et al.* [28]. The pyrethroids presented LODs ranged from 2-14 µg/kg and LOQs from 6-47 µg/kg [16,26,27,29]. Deltamethrin obtain the highest LODs (14 µg/kg) and LOQs (47 µg/kg) [29]. Finally, regarding to the biopesticides [5,34] it were obtained LODs from 1 to 5 µg/kg and LOQs from 4 to 10 µg/kg.

Good linearity was obtained ranged from 1.5 to 500 µg/kg for pharmaceuticals [21], 100 to 1000 µg/kg for organochlorines (chlorobenzenes, chlorophenols, chlorinated hydrocarbons and chlorinated olefins) [22], 5 to 1000 µg/kg for diethyl aminoethyl hexanoate [36], 50 to 1562 µg/kg to trihalomethanes and BTEX [2], and 10 to 300 µg/kg for chlorophenols, alkylphenols, nitrophenols and cresols [35]. For this group of pollutants, LOD range from 0.004 [39] to 141 [38] µg/kg and LOQ range from 0.013 [39] to 282 µg/kg [38]. Martín *et al.* [37] noted that the highly sensitive and selective detector was used to obtain LODs for the trihalomethanes (in the order of ng/kg). In comparing the obtained LOD and LOQ (1 to 100 µg/kg) for phenols to the maximum allowed by the current legislation (maximum residue limit of 10 mg/kg), it was concluded that the proposed method by Padilla-Sánchez *et al.* [35] fitted the purpose. In the Pinto *et al.* study [2], the LOD ranged from 0.2 to 15 µg/kg. This result was caused by the high volatility of some compounds. With the exception of benzene, the predicted values for all compounds exist within the prediction intervals specified in the certified reference material.

The LOD obtained for the 34 studied compounds by Rouvière *et al.* [22] were in the range of 2.1 (cumene) to 635.3 µg/kg (pentachlorophenol). LOQ values reached to 2100 µg/kg for pentachlorophenol, due to its low volatility and chromatographic profile. This method was further applied to two other soils with different properties (organics and mineral soils), and the compounds were successfully quantified in the same range. The results also showed that this method could be applied to several types of soils (mineral or organic), and was appropriate to use with volatile compounds. This option was not available with other conventional technique [22].

10. Coupling of QuEChERS to gas and liquid chromatography

The selection of instrumentation to obtain a good separation and quantification of analytes depends on sample complexity and selectivity of the extractive process. In recent years, significant advances in chromatographic instrumentation have led to substantial progress in the pollutant analysis [62] by GC and LC.

Pollutants extracted from soils by QuEChERS have been analysed by GC with nitrogen–phosphorus detection (NPD) [24], ECD [1,43,45,47], ^{63}Ni µECD [11], and MS [36]. The detector volume of µECD is 10 times smaller than any other ECD, which translates into improved sensitivity and decreases the chance

of cell contamination [11]. Additionally, GC-MS has also been used to confirm the identity of pollutants [24,43]. It is understood that MS/MS presents advantages over MS/single ion monitoring (SIM) because of its specificity and sensitivity [1,3,26].

The low pre-concentration of the compounds in the extracts has been identified as the main drawback in the QuEChERS method. Pinto *et al.* [2] were able to solve this problem by using a large-injection volume-fast GC and MS detection. Additionally, the selected SIM mode was employed to provide proper identification and a lower limit of quantitation. The programmable temperature vaporizer allows for the injection of large volumes of sample, improving the sensitivity of the method [2].

Phenol analysis by GC-MS/MS is difficult due to the polarity of some of these compounds, which result in poor chromatographic peaks. In response, Padilla-Sánchez *et al.* [35] used acetic acid anhydride with pyridine as derivatisation reagents. The final determination was carried out by GC–MS/MS.

Unfortunately, GC is inadequate for polar, thermo-labile, and low volatility compounds [23]. Polar compounds often result from pollutant transformation. Consequently, the polarity range covered by the chromatographic method must be extended, and GC analysis is less suitable for simultaneous determinination of several pollutants and their transformation products (TPs) [23]. Conveniently, parent pollutants can be analysed by either GC or LC. In comparison, TPs can only be analysed by LC because of their low volatility and higher polarity [23]. Traditionally, LC methods used common ultraviolet (UV) [12], diode array detection (DAD) [31], fluorescence (FLD) [21], or electrochemical detection (occasionally combined with post column derivatisation). An effective alternative is LC-FLD, as it has lower detection limits, is simpler, and is less expensive than MS detection [21]. However, because of the complexity of matrices, as well as low concentrations of pollutant residues present within them [63], the many applications relied on LC-MS [8,16,28,32,34,40,46].

QuEChERS extracts can be injected directly into LC or evaporation/reconstitution may be required depending on the exact chromatographic conditions employed in a given application. In the Prestes *et al.* [5] study the supernatant was filtered through syringe nylon filter prior UHPLC-MS/MS analysis. Other possible procedures were evaluated by others, different aliquots of the supernatant (18 mL (of the supernatant was filtered through a Na_2SO_4 column) [12], 2 mL [34], and 5 mL [21]) were evaporated to dryness under a stream of nitrogen [12,21,34]. The dried extract were redissolved in 500 µL of ACN [21], in 1.0 mL of MeOH [12], or in 0.5 mL of 0.1% ammonium acetate in methanol and 0.5 mL of 0.1% ammonium acetate in water [34] using vortex. Normally if no further concentration step is required only a filtration is required prior LC analysis. Generally the residues are redissolved in appropriate to the eluent phase.

Table 1 show that MS/MS detection was used in most studies and that LC has proved to be an alternative technique for determining pollutants in soil.

11. Conclusions

The QuEChERS method is becoming increasingly more popular as a new and robust procedure. QuEChERS provides high quality results with a high sample throughput. This is because a large number of samples can be extracted simultaneously, and it reduces sample handling and pre-treatment. Additionally, there is low solvent and glassware consumption, with low work and cost of analysis per sample. It satisfies requests for “green chemistry”, and instruments used in the procedure are affordable for any analytical laboratory. Therefore, it can be an interesting alternative to other existing methods. Due to its simplicity, QuEChERS is being applied in the analysis of complex matrices, and is beginning to replace traditional extraction methods.

Modified and a simplified QuEChERS approaches have been reported and several compounds (pesticides and other pollutants) were successfully extracted from soil/sediment matrices. The proposed methods have been validated allowing a reliable determination of the selected compounds with high recoveries. However, future development is needed to address more extensive validation of this method in order to extend it to a wider range of compounds that exhibit various chemical and physical properties.

Abbreviations:

ACN, Acetonitrile; AOAC, American standard; APCI, Atmospheric pressure chemical ionization; ASE, Accelerated solvent extraction; BTEX, Benzene, toluene, ethylbenzene and xylenes; C18, Octadecyl bonded silica sorbent; DAD, Diode array detection; DDT, dichlorodiphenyltrichloroethane; d-SPE, Dispersive solid phase extraction; µECD; micro-electron capture detector; EMDL, limit associated with the matrix; EN, European standard; ESI, Electro spray ionization; FLD, Fluorescence detection; GC, Gas chromatography; GCB, Graphitized carbon black; HCH, Hexachlorocyclohexane; HCB, Hexachlorobenzene; HS, High organic matter; IDL, limit associated to the equipment; Koc, Organic carbon-water partition coefficient; Kow, Octanol–water partition coefficient; LC, Liquid chromatography; LS, Low organic matter; LOD, Limit of detection; LOQ, Limit of quantification; ME, Matrix effect; MeOH, Methanol; $MgSO_4$, Magnesium sulfate; MS, mass spectrometry; MS/MS, Tandem mass spectrometry; Na_2EDTA; Ethylenediaminetetraacetic acid disodium salt; NaCl, Sodium chloride; NH_3, Ammonium; NPD, Nitrogen–phosphorus detection; SPE, Solid phase extraction; PSA, Primary secondary amine; PLE, Pressurized liquid extraction; PFAS, Perfluoroalkyl substances; PFCAs, Perfluoroalkyl carboxylates; PFSAs, Perfluororalkyl sulfonates; QuEChERS, Quick Easy Cheap Effective Rugged Safe; RSD, Relative standard desviation; SIM, Single ion monitoring; TPs, transformation products; UHPLC, Ultra-high performance liquid chromatography; USE, Ultrasonic extraction, UV, Ultraviolet detection.

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