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Review Article

Analysis of pesticide residues in soil: A review and comparison of methodologies

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ABSTRACT

This work reviews recently developed methodologies for multiclass pesticide residue analysis in soil and evaluates them under the focus of Green Analytical Chemistry principles, cost and time. Different extraction, clean-up and determination techniques are highlighted. QuEChERS was found to be the dominant form of extraction reported, although extractions using pressurized fluid, ultrasound and simple solid–liquid partitioning are still widely employed. GC–MS and LC-MS remain the standard analytical techniques, with the latter becoming more prevalent due to its greater versatility in analysing different chemical classes of pesticide residues, namely poorly volatile compounds. A selection of twelve representative methods was compared using the analytical eco-scale and AGREE metrics, as well as in terms of instrumental and operational cost, and time. The analysis shows that the choice of reagents and other operational parameters are more important towards the greenness of a method than the extraction and determination techniques used, but cost and time are more dependent on the techniques themselves.

1. Introduction

Soil is an invaluable resource to life on earth. Since it is not considered renewable within the time frame of a human life, soil degradation is an important and currently pressing matter [1]. For this reason, several policy frameworks address soils. Among the UN Sustainable Development Goals (SDGs), at least seven goals directly (SDG 3, 13 and 15) or indirectly (SDG 2, 6, 11 and 12) cannot be achieved without having soil as a relevant factor [2]. In this respect, contamination from anthropogenic compounds is a significant driver in the reduction of soil quality. Among them, pesticides are some of the most important contaminants in agricultural soils, both for being widely applied and for their potential harm to various organisms (including humans) [3,4].

Pesticide residue analysis in soil is an important feature of environmental monitoring. Several recent studies have pointed out the high level of contamination from currently used pesticides in European agricultural soils [5–7]. The latent presence of some pesticides in soil after use and their degradation products is a serious environmental concern. These can contaminate the food chain, promote biomagnification, be a source of adverse health effects, negatively impact microbial communities and migrate through mechanisms such as leaching and runoff to other environmental compartments, such as water. In humans, acute pesticide toxicity (high level of exposure over a short time) is rarely a concern, but chronic exposure (small dosages over a long period) is a growing problem both for farm workers and the general population [8]. Therefore, pesticide monitoring in soil is very important from a human health perspective: to identify the source of contamination and be able to address it. Nevertheless, some pesticide residues might have low direct human toxicity, but still be very harmful to environmental systems.

Generally, contaminated soils tend to have several different hazardous compounds present [7]. These result from the broad spectrum of compounds applied and from the many degradation products that can be formed from different pesticides decomposition. Consequently, analytical methods should be able to extract and determine a wide variety of compounds. Furthermore, these contaminants are often present in very low concentrations, and a portion might be strongly bound to the soil

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Table 1
Quantitative methods for multiclass pesticide residues analysis in soil published since 2010.

Analytes	Analytical Procedure	Extraction Method	Clean up and solvent shift	Instrumental Determination	%Recovery range (%RSD range)	LOD (μg/kg)	LOQ (μg/kg)	REF
5 triazine and organophosphorous pesticide residues	SLE-HS-SPME-GC–MS	SLE with Methanol/Acetone (1:1, v/v). Centrifuged and evaporated to dryness.	Resuspended in Acetone and diluted 1:50 with 25 % (wt/v) NaCl in Water. Then HS-SPME.	GC–MS (EI-Q) with USP G27 column. 36 min runtime.	70.2–104.5 (7.0–12.8) [30 μg/kg spike]	0.08–3.14	–	[31]
10 Organophosphorous pesticide residues and Buprofezin	QuEChERS (d-SPE)-GC-NPD	QuEChERS with Acetonitrile (no Water). Then $MgSO_4$, NaCl and citrate buffer. Mixture was sonicated.	d-SPE with PSA, sonicated. Dried with rotary evaporator, redisolved in cyclohexane and filtered.	GC-NPD with USP G27 column. 44 min runtime.	45–96 (1–15) [Different spike levels, except for two analytes (poor recovery)]	0.48–12.5	1.61–41.6	[24]
98 multiclass pesticide residues	**PLE-GC–MS/MS**	PLE: two extraction cycles with ethyl acetate/Methanol (3:1, v/v) at 85 °C and 1500 Psi. Dried and redisolved in ethyl acetate.	Injected directly.	GC–MS/MS (EI-QqQ) with USP G27 column. 26 min runtime. Large volume injection.	72–108 (4–25) [10 μg/kg spike]	0.2–1.7	0.3–3.3	[32]
28 multiclass pesticide residues	**PLE-UPLC-MS/MS**		Dried under nitrogen and redisolved in 50/50 mix (v/v) of mobile phases.	UPLC-MS/MS (ESI-QqQ) with C18 column. 9.5 min runtime.	77–121 (5–27) [10 μg/kg spike]	0.2–5	0.3–10	[32]
7 organophosphorous pesticide residues	SFE-DLLME-GC-FID	Supercritical CO_2 with small ammount of Methanol modifier at 60 °C and 150Bar. Collected in Acetonitrile.	DLLME with CCl_4 as extractor (added to Acetonitrile extract), dispersed in Water. Removed and injected CCl4 phase.	GC-FID with USP G27 column. Helium as carrier gas.	80–100 (3.6–12.1) [200 μg/kg spike]	1–9	–	[33]
31 multiclass pesticide residues	SFE-GC-μECD-NPD	Supercritical CO_2 with around 15 % Methanol (w/w), at 15 MPa and 318 K, four static extractions of 10 min.	Evaporated and redisolved in ethyl acetate.	GC with flow divider connected to USP G27 column for μ-ECD, and USP G3 column for NPD	44–109 (1–24) [different spiked concentrations]	4–105100	7–17710	[34]
70 multicass pesticide residues	MAE-GC–MS	Microwave extraction with Hexane:Acetone (1:1, v/v) at 100 °C for 10 min.	Centrifuged, decanted and concentrated under nitrogen.	GC–MS (EI-Q) with USP G27 column. 42 min runtime.	75.7–119.2 (2.8–18.6) [100 μg/kg spike]	–	0.001–0.4225 mg/L (Instrumental)	[35]
7 multiclass pesticide residues	QuEChERS-LC-MS/MS	Alkaline QuEChERS with Acetonitrile and Water saturated with Ca(OH)2. Then $MgSO_4$ and NaCl, mixed. Then neutralized with Hcl, following formate buffer.	Dried Acetonitrile phase with $MgSO_4$, filtered and injected.	LC-MS/MS (ESI-QqQ) with C18 column. 20 min runtime.	72.5–113.8 (1–16.3) [2–100 μg/kg spike]	0.1–0.6	0.4–2	[36]
25 multiclass pesticide residues	PLE-UPLC-MS/MS	PLE with Acetonitrile/Water (2:1, v/v) at 100 °C and 1500 Psi.	Dried and redisolved in acidified Methanol/Water (1:1, v/v).	UPLC-MS/MS (ESI-QqQ) with C18 column. 8 min runtime	65.1–122.2 (1.7–23.4) [50 μg/kg spike]	–	0.1–2.9	[37]
25 multiclass pesticide residues	QuEChERS (d-SPE)-UPLC-MS/MS	QuEChERS with Acetonitrile and Water. Then $MgSO_4$, NaCl and citrate buffer.	d-SPE with C18.	UPLC-MS/MS (ESI-QqQ) with C18 column. 8 min runtime	79.4–113.3 (1.0–12.2) [50 μg/kg spike]	–	0.1–2.9	[37]
17 multiclass pesticide residues	**SLE-LC-MS**	Agitation for 24 h at 20 °C with Methanol/Acetone (1:1), or Methanol/water (1:1) (depending on analyte)	If Water was used, SPE with Oasis HLB. Evaporated, redisolved in Methanol and filtered. For LC-MS, diluted in Water (1:1, v/v).	LC-MS (ESI) with Luna FPF2 column. 32 min runtime.	78.7–112.2 (0.1–7) [100 μg/kg spike]	0.1–0.4	0.22–0.65	[38]
14 multiclass pesticide residues	**SLE-GC–MS**			GC–MS with USP G3 column. 32 min runtime.	74.5–105.1 (3–9) [100 μg/kg spike]	0.2–0.4	0.26–0.51	[38]

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Table 1 (*continued*)

Analytes	Analytical Procedure	Extraction Method	Clean up and solvent shift	Instrumental Determination	%Recovery range (%RSD range)	LOD (μg/kg)	LOQ (μg/kg)	REF
12 multiclass pesticide residues	PLE-GC-ECD	PLE with Dichloromethane/ Acetone (1:1, v/v) at 100 °C and 1500 Psi.	Evaporated and redisolved in acetone.	GC-ECD with USP G27 column. 39 min runtime.	77–106 (11–27) [different spiked concentrations]	0.9–8	3–7	[39]
18 multiclass pesticide residues	**UAE-LC-MS/MS**	Shaken for 1 h with Acetonitrile/Water (25:5, v/v), then sonicated. Centrifuged.	Diluted with Water and formic acid, filtered.	LC-MS/MS (ESI-QqQ) with C18 column. 15 min runtime.	50–134 (2–10) [50 μg/kg spike]	0.1–3.9	50	[40]
50 multiclass pesticide residues	QuEChERS (d-SPE)-LC-MS/MS	QuEChERS with Acetonitrile and Water. Then $MgSO_4$, NaCl and citrate buffer.	d-SPE with PSA and C18.	LC-MS/MS (ESI-QqQ) with C18 column. 16 min runtime.	40–92 (1–17) [50 μg/kg spike]	–	0.06–10	[29]
5 imidazolinone herbicides	SLE-UPLC-MS/MS	Shaken with basic solution (ammonium acetate 0.5 M in Water) and centrifuged.	Aqueous extract subjected to d-SPE with PSA, filtered, acidified with HCl and diluted with Water.	UPLC-MS/MS (ESI-QqQ) with C18. 3 min runtime.	70–93 (9–17) [different spiked concentrations]	1.5	5	[41]
29 multiclass pesticide residues	PLE-QuEChERS (d-SPE)-LC-HRMS/MS	PLE first with Acetone/Ethyl Acetate (30:70, v/v) at 80 °C, then Acetone/1% phosforic acid in Water (70:30, v/v) at 120 °C. Evaporated organic phase.	QuEChERS: To aqueous phase (after evaporation) added Acetonitrile, $MgSO_4$ and NH_4Cl. Collected Acetonitrile and performed d-SPE with PSA, C18 and GCB. Evaporated partially, added Methanol and filtered.	LC-HRMS/MS (ESI-LIT-Orbitrap) with C18. 27 min runtime.	70–245 (2–32)	–	0.7–25	[42]
216 multilcass pesticide residues	**QuEChERS-GC–MS/MS**	QuEChERS with Acetonitrile and Water. Then $MgSO_4$, NaCl and citrate buffer.	Evaporated with two drops of dodecane as keeper. Then redisolved in n-Hexane/Acetone (9:1 v/v) and filtered.	GC–MS/MS (EI-QqQ), with USP G27 column.	60–120 (1–15) [spike at LOQ level]	–	5–10	[20]
30 multiclass pesticide residues	**SLE-SPE-LC-MS/MS**	SLE with Methanol shaken for 4 h. Centrifuged and removed Methanol phase. Then extracted the same soil with Water for 12 h and centrifuged.	Methanol extract was evaporated. Water extract was subjected to SPE with OASIS HLB cartridge, eluted with Methanol/ Acetonitrile (1:1, v/v). Extracts were combined, evaporated to dryness and resuspended in Acetonitrile.	LC-MS/MS (ESI-QqLIT) with C18 column. Runtime: 33 min for + ESI, 17 min for -ESI.	70–106 (1–19) [10 μg/kg spike]	–	1	[30]
73 contaminants, of which 3 pesticides	QuEChERS (d-SPE)-UPLC-MS/MS	QuEChERS with Acetonitrile acidified with 1 % Acetic acid, and Water. Then $MgSO_4$ and Sodium Acetate.	d-SPE with C18.	UHPLC-MS/MS (ESI-QqLIT) with C18 column. 18 min runtime.	26–141 (0–29) [20 μg/kg spike]	–	0.1–5	[43]
46 multiclass pesticide residues	**QuEChERS-UPLC-MS/MS**	QuEChERS with Acetonitrile acidified with 1 % Ac. acid, and Water. Then $MgSO_4$ and NaAc.	Diluted with Water and acidified Acetonitrile, filterd.	UPLC-MS/MS (ESI-QqQ) with C18 column. 14 min runtime.	70–120 [5–250 μg/kg spike]	–	10	[6]
28 multiclass pesticide residues	**QuEChERS (d-SPE)-GC-HRMS/MS**		d-SPE with PSA and C18.	GC-HRMS/MS (EI-Q-Orbitrap), with TraceGOLD™ TG-OCP I (proprietary) column. 26 min runtime.		–	5	[6]

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Table 1 (*continued*)

Analytes	Analytical Procedure	Extraction Method	Clean up and solvent shift	Instrumental Determination	%Recovery range (%RSD range)	LOD (μg/kg)	LOQ (μg/kg)	REF
Glyphosate and AMPA (with isotopically labeled IS)	SLE-LC-MS/MS	SLE with KOH 0.6 M in Water, shaken for 60 min and centrifuged.	Acidified extract with HCl, then borate buffer and derivatization with FMOC-Cl for 30 min. Added formic acid, vortexed and analysed.	LC-MS/MS (ESI-QqQ) with C18. 14 min runtime.		–	50	[6]
15 organochlorine pesticide residues	QuEChERS (Magnetic d-SPE)-GC–MS	QuEChERS with Acetonitrile and Water. Then $MgSO_4$ and NaCl.	d-SPE with Fe_3O_4/Triton (magnetic) and GCB.	GC–MS (EI-Q) with USP 2 column. 47 min runtime.	86–106 (2.5–8) [spike at LOQ level]	0.11–1.85	0.34–5.45	[44]
10 organochlorines and trifluralin.	QuEChERS (d-SPE)-HS-SPME-GC–MS	QuEChERS with Acetonitrile and Water. Then $MgSO_4$, NaCl and citrate buffer.	d-SPE with PSA. Dried under nitrogen, resuspended in Methanol / aqueous NaCl solution (1:100, v/v) for HS-SPME.	HS-SPME-GC–MS (EI-Q) with PDMS/DVB SPME fiber and TraceGOLD™ TG-XLBMS (proprietary) column. 60 min runtime (SPME extraction)	67.8–169.3 (1.2–21.8) [50 μg/kg spike]	0.001–1.48	0.004–4.93	[45]
10 organochlorines and trifluralin.	**SLE-HS-SPME-GC–MS**	SLE with acetone/petroleum ether (1:1, v/v) shaken for 30 min and centrifuged. Then re-extracted with petroleum ether for 30 min.	Mixed extacts, added Acetonitrile as keeper, and evaporated to Acetonitrile volume. Then added aqueous NaCl solution for HS-SPME.		65.8–180.9 (1.3–22.4) [50 μg/kg spike]	0.005–1.16	0.02–3.85	[45]
13 multiclass pesticides and 14 other analytes	**QuEChERS (d-SPE)-UHPLC-MS/MS**	QueChERS with Water and 0.5 % formic acid in Acetonitrile. Then $MgSO_4$, NaCl and Citrate buffer.	d-SPE with C18. Evaporated and re-disolved in Acetonitrile/Water (1:9 v/v).	UHPLC-MS/MS (ESI-QqQ) with C8 column. 9.5 min runtime.	47–87 (1–20) [10 μg/kg spike]	–	0.05–0.5	[46]
12 multiclass pesticide residues	QuEChERS (d-SPE)-UHPLC-MS/MS	QuEChERS with Acetonitrile with 1 % Ac. acid, and Water. Then MgSO4 and Sodium Acetate.	Acetonitrile extract frozen at −18 °C overnight "for precipitation of the wax". Then d-SPE with PSA.	UHPLC-MS/MS (ESI-QqQ) with C18 column. 15 min runtime.	65.9–89.5 [50 μg/kg spike]	10–20	–	[47]
13 multiclass pesticides, 12 pharmaceuticals and 5 transformation products	QuEChERS (d-SPE)-UHPLC-MS/MS	QueChERS with Water and 0.5 % formic acid in Acetonitrile. Then $MgSO_4$, NaCl and Citrate buffer.	d-SPE with C18. Evaporated and re-disolved in Acetonitrile/Water (1:9 v/v).	UHPLC-MS/MS (ESI-QqQ) with C18 column. 18 min runtime.	3–99 (1–14) [50 μg/kg spike]	–	0.05–0.5	[21]
38 multiclass pesticide residues and 28 other analytes	QuEChERS-LC-MS/MS	QuEChERS with Acetonitrile acidified with 1 % Acetic acid, and Water. Then $MgSO_4$ and Sodium Acetate.	Filtered.	LC-MS/MS (ESI-QqLIT) with Core-Shell C18 column. 16 min runtime.	32–143 (6–35.5) [10 μg/kg spike]	0.01–8.15	0.04–33	[3]
34 multiclass pesticide residues	**PLE-LC-HRMS/MS**	PLE with Methanol at 80 °C and 150 Bar, in two cycles of 5 min each.	Added dodecane as keeper, evaporated, redisolved in Methanol and filtered.	LC-HRMS/MS (ESI-Q-TOF) with C18. 20 min runtime.	72–126 (1–21) [40 μg/kg spike]	–	0.01–1.25 μg/L (Instrumental)	[19]
51 multiclass pesticide residues	QuEChERS-GC–MS/MS	QuEChERS with 2.5 % formic acid in Acetonitrile (no Water). Then $MgSO_4$ and sodium citrate, sonicated and shaken.	Filtered.	GC–MS/MS (EI-QqQ) with USP G27 column. 21 min runtime.	63.4–130.7 (1.3–14.3) [20 μg/kg spike]	0.024–3.125	0.5–20	[48,49]
167 multiclass pesticide residues	QuEChERS-LC-MS/MS		Filtered and dilluted with Water.	LC-MS/MS (ESI-QqQ) with C18 column. 18 min runtime.	60–128.7 (0.9–26.6) [20 μg/kg spike]	0.024–6.25	0.5–20	[48,49]
31 multiclass pesticide residues	QuEChERS (d-SPE)-LC-MS/MS	QuEChERS. 0.1 M EDTA in Water, sonicated. Then Acetonitrile and citrate buffer. Then re-	Extracts combined then d-SPE with PSA/C18. Added DMSO as keeper, and evaporated.	LC-MS/MS (ESI-QqQ) with phenyl-hexyl column. 13.5 min runtime.	66.5–118 (3.3–27.5) [20xLOQ spike]	0.01–3	0.01–5.5	[50]

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Table 1 (*continued*)

Analytes	Analytical Procedure	Extraction Method	Clean up and solvent shift	Instrumental Determination	%Recovery range (%RSD range)	LOD (μg/kg)	LOQ (μg/kg)	REF
		extracted with more Acetonitrile.	Redisolved in Water/Methanol (8:1).					

matrix, making their extraction difficult or even impossible [9,10]. The fact that the soil itself is a very complex and variable matrix also increases the difficulty of the analysis, as it generates complex extracts that may frequently demand the use of sample clean-up procedures. All these factors play a role in the choice and development of a suitable analytical methodology.

Metrological performance and number of compounds analysed are the factors most valued and optimized for in method development studies. However, there are also other very important variables that will be explored in this review, namely the cost and time taken per sample and accordance with Green Analytical Chemistry principles. The first two factors are pragmatic in the sense that cheaper and less time-consuming analyses would allow for better environmental monitoring. Also, instrument and qualified personnel requirements are other important variables in this category. The third factor, Green Analytical Chemistry, is a relatively new framework aimed at guiding the development and implementation of analytical methodologies in the light of Green Chemistry principles, which in general aim to eliminate or reduce the usage and generation of hazardous substances, and to be as waste and energy efficient and sustainable as possible [11].

The present study intends to review techniques for multiclass analysis of pesticide residues in soil published since 2010. Twelve representative methods employing different extraction and determination techniques were selected and compared in terms of cost, time and Green Analytical Chemistry principles.

2. Pesticide analysis in soil

Soil is a complex media with a widely varied composition. The amount of organic matter (OM) is generally between 1 and 5 % (weight) in agricultural soils, but can reach nearly 100 % for organic soils, whereas minerals of different chemical and physical composition make up the remaining bulk of the solid phase [12]. The most common soil parameters evaluated when developing and validating an analytical method for pesticides are the soil's pH, OM percentage and texture [13–16]. Both organic and mineral colloids have a profound influence on pesticide adsorption and subsequent extraction efficiency [17,18].

2.1. Extraction

Soil sampling is usually performed by hand with a trowel or an equivalent tool [3]. The sampled soil depth is normally between 0 and 20 cm [19–22], related to the depth of ploughing. After collection, the disturbed samples are typically sieved through a 2 mm mesh, separating the coarse elements from the fine earth (<2 mm) [23], which is known as the "active" part of soil. Afterwards, samples are commonly dried without direct sunlight at room temperature [24–27] or at 30–40 °C [20,21,28], but lyophilization can also be employed [27,29,30]. Table 1 presents methods for the analysis of multiclass pesticide residues in soil published since 2010. Each method was given an acronym for ease of identification.

Pesticide sorption in soil is most dependent on the solid phase, both organic and inorganic [18]. For most forms of extraction, an exact amount of water is added to the sample before the extraction solvent; It helps as co-extractant of relatively polar pesticides and competes for soil sorption sites, favouring non-polar pesticide's extraction as well [51,52]. Soil pH is also an important factor in the extraction step, especially for ionizable pesticides [53]. Often, sample clean-up techniques have to be used, especially in soils with high OM content, as matrix components can seriously hamper instrumental performance and longevity [54]. Because of soil's inherent composition variability, recoveries and other merit parameters change significantly in dependence on factors such as soil pH, OM content and texture [13]. Consequently, even a standardized procedure may need to be verified among different soil types.

The mandatory determination of recovery efficiency is troublesome in soil analysis. Due to the complexity of soil systems, varying environmental conditions and chemical nature of the pesticides, they can, over time, bind to the soil matrix through several interaction mechanisms. Some of these (especially covalent bonding to soil humus) leads to stable chemical species [9], not easily overcome by solvent extraction. Thus the simple addition of pesticide standard to a blank sample may not mimic real samples for some analytes. This issue was adequately treated in a previous review [55]. Some studies report the aging of spiked samples before extraction to better emulate real conditions, generally from 3 to 20 days, but in some cases up to 2 years [28,55]. However, no perfect way exists of addressing this analytical issue.

The European Commission's guideline SANTE/2020/12830 [56] recommends that analytical methods for pesticide analysis in soil have quantification limits (LoQ) not over 50 μg/kg. Indeed, most recovery studies for method validation use concentrations equal or under this value (Table 1). However, the same document also states that relevant ecotoxicological concentrations for the most vulnerable non-target terrestrial organism be taken into account (*e.g.* median lethal dose, no observed effect concentration) [56]. If this value is lower than the expected soil concentration for a certain application rate, then the LoQ must also be lowered.

2.1.1. Solid-liquid extraction

Solid-liquid extraction (SLE) with some form of shaking is a popular technique, which is still in use today. The simplicity and low requirements in terms of equipment make it an interesting alternative to more sophisticated extraction methods. Usually, a suitable solvent or solvent mixture is added to the sample and shaken for several hours, followed by centrifugation to remove the extract [38,57]. When water is used as extraction solvent, the extract will commonly undergo subsequent solid-phase extraction (SPE) whose function is concentration, solvent shifting (for chromatographic analysis) and clean-up [30]. However, it is costly and time intensive, especially if no automated system is used.

One of the greatest advantages of SLE is its versatility. It can be used for difficult analytes such as glyphosate and its metabolite, aminomethylphosphonic acid (AMPA), which cannot be extracted along with other pesticides in multi-residue methods due to their ionic nature [6,57]. The choice of solvent, modifiers (particularly pH control) and extraction conditions make this technique, above all others, the most adaptable. In multi-residue methods however, the high extraction time, solvent volume and frequent need for clean-up and solvent evaporation make it less desirable when compared to other techniques.

2.1.2. Pressurized liquid extraction

Pressurized liquid extraction (PLE), also known as accelerated solvent extraction or pressurized fluid extraction, has been widely applied in the analysis of pesticide residues in soil. It is an extraction technique which uses organic or aqueous solvents at increased temperature and pressure (in the range of 40–200 °C and 35–200 Bar) [58]. This

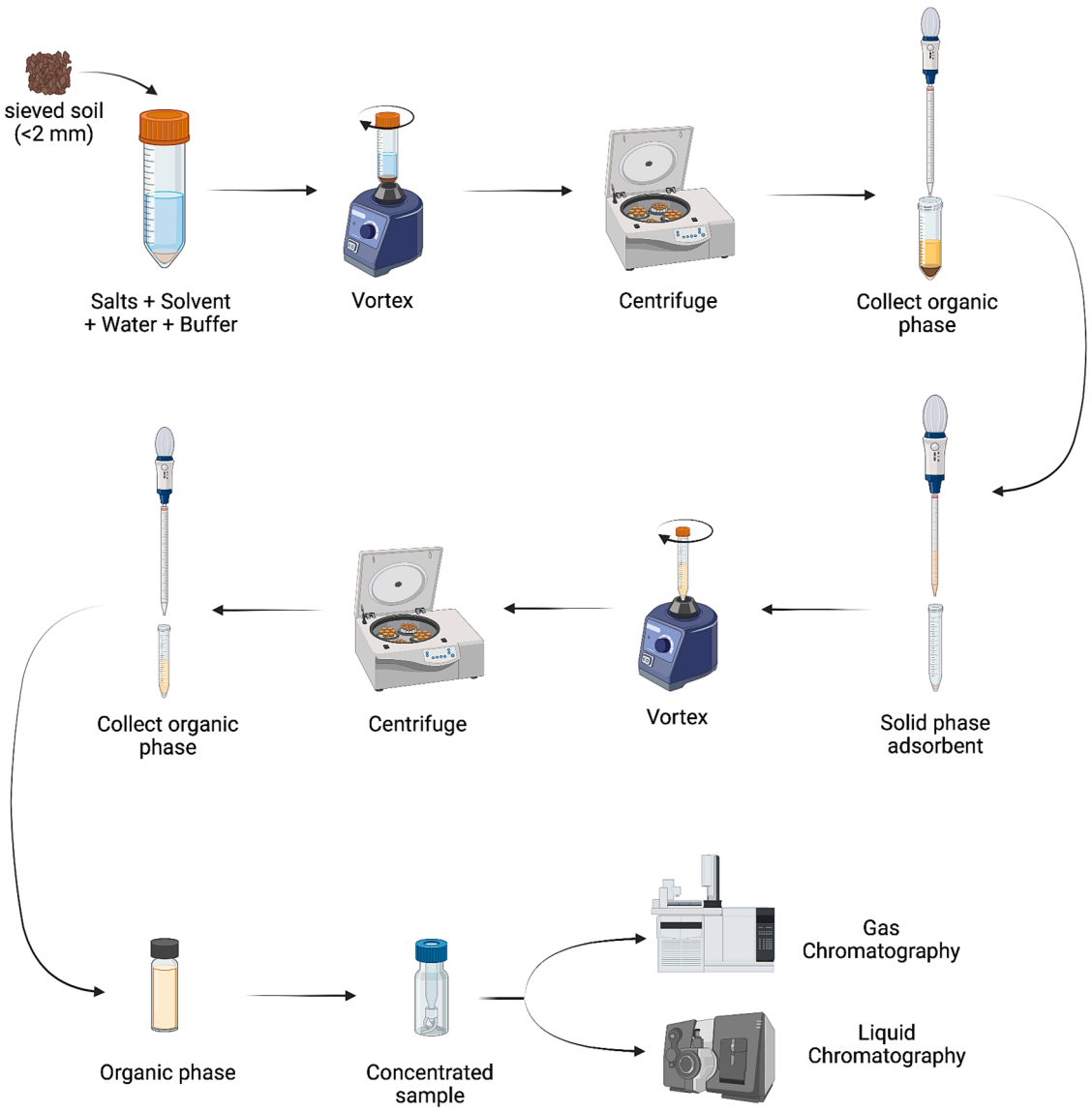

Fig. 1. Simplified scheme for QuEChERS methodology used for pesticides extraction from soil (Created with BioRender.com).

technique has seen wide acceptance due to its ease of use, speed, and effectiveness. However, equipment and operative costs remain high, and the extreme conditions may not be favourable for the extraction of some thermo-labile and sensitive analytes [59].

Pesticide extraction from soil has been performed with a variety of different solvents such as acetone, methanol and acetonitrile, but is commonly executed with a combination of solvents [19,29,32,37]. These can also be moderately acidified for better extraction and analyte stability [21]. Besides the use of organic solvents, the sample is commonly mixed with diatomaceous earth prior to PLE for drying and preventing the pressure-induced aggregation of sample particles [32]. Although this adds extra waste, diatomaceous earth itself is not toxic. The combination of low solvent volumes, semi-automation and green solvent choices make PLE a good choice for the future development of greener extraction methodologies.

2.1.3. *QuEChERS*

QuEChERS (short for Quick Easy Cheap Effective Rugged and Safe) is the commercial name given to a family of extraction methods proposed by Anastassiades *et al.* [59]. The original methodology had the purpose of overcoming limitations of routine pesticide monitoring in foodstuffs, for which a simple, cheap and fast method is essential. Since then, the method has been widely accepted by the scientific community and used in the extraction of several different analytes from various materials [60]. A general diagram of QuEChERS for soil analysis is presented in Fig. 1.

The basic method involves extraction with acetonitrile followed by the addition of salts (most commonly magnesium sulphate and sodium chloride) and centrifugation to separate the organic, aqueous and solid phases, taking advantage of the inherently high volume of water in most food samples. For soil extraction, water is added along with the acetonitrile and then partitioned in the same way [3,37,43,46]. Subsequently, the same authors and others improved the technique with the addition of a buffer to the salt mixture during the salting-out stage, to maintain the pH at around 5, which was found to be the best compromise, reducing degradation of pH sensitive analytes [61]. This has also become standard in QuEChERS for soil pesticide residue analysis, with works reporting good results with both acetate and citrate buffers.

After an aliquot of the separated organic phase is removed, it is usually subjected to a clean-up step by dispersive solid-phase extraction (d-SPE). The most commonly used adsorbents are primary-secondary amine (PSA) [24], end-capped C18 [37], or a combination of both [29], depending on the co-extractives present and the chemical nature of the analytes. Chiaia-Hernandez *et al.* reported improved recoveries for

some analytes when using a combination of PSA, end-capped C18 and graphitized carbon black (GCB), probably due to reduced ion suppression in electrospray ionization [42]. d-SPE is most commonly used for QuEChERS but has also been employed in combination with other extraction techniques such as ultrasound-assisted extraction (UAE) [21,62], and solid–liquid extraction [41].

One of the biggest advantages of QuEChERS is its low equipment requirements and cost when compared to other extraction techniques. In essence, the core method only requires a homogeneously milled or otherwise porous sample and a centrifuge. Vortex mixers are widely employed in the extraction step, but not always required [63,64]. In contrast to techniques such as supercritical-fluid extraction (SFE) or PLE, the cost and knowledge barriers to applying this methodology in routine analysis are low.

Several authors have conducted studies comparing different extraction techniques for pesticide analysis in soil (PLE, UAE, SLE and QuEChERS) and despite no technique being ideal for every analyte class, QuEChERS was always reported to be generally superior in terms of metrological parameters (especially recovery) [21,29,37,65]. Valverde *et al.* [21] tested PLE, UAE and QuEChERS for the extraction of 13 pesticides along with 17 other contaminants of emerging concern (mostly pharmaceuticals) and found PLE (no d-SPE) to be the fastest method. However, QuEChERS (with d-SPE) performed better in terms of recovery for all analytes (mean recovery of 79 % versus 46 % with PLE, 50 ng/g spike). UAE also performed well in terms of recovery (mean 62 %), but the method was tedious and labour intensive [21]. Masiá *et al.* [29] compared PLE and QuEChERS for the extraction of 50 pesticides (only the latter employing d-SPE). QuEChERS performed slightly better for soil, with a mean recovery of 76 % versus 68 % for PLE (100 ng/g spike). In total, 8 compounds had recoveries under 50 % with PLE, whereas only 3 with QuEChERS. These results seem to support the decision that given current knowledge, QuEChERS should be the first option when developing a method for multi-residue pesticide analysis in soil. However, aqueous SLE or PLE must still be used for particularly polar and ionic pesticides, not easily extracted by QuEChERS [6].

2.1.4. Other extraction methodologies.

2.1.4.1. Ultrasound-assisted extraction. The use of high-frequency mechanical waves to accelerate and improve extraction is a well-established and studied method. Ultrasound-assisted extraction (UAE) can be performed using a high-power probe, which typically allows for a more fine-grained control of ultrasound application [21,65], but is commonly performed by inserting the sample vial with the extraction solvent into an ultra-sound bath [66–68]. The application of ultrasound vibrations facilitates solvent penetration through the medium and solid–liquid mass transfer, as well as dispersing soil aggregates [69,70].

UAE is commonly performed with an organic solvent like ethyl acetate, followed by evaporation and resuspension [66]. It has also been used for extracting highly polar or ionizable pesticides with aqueous solvent mixtures, which are then *retro*-extracted via solid-phase extraction (SPE) or solid-phase micro-extraction (SPME) [68,71].

Valverde *et al.* [21] used UAE with a mixture of water and acidified acetonitrile, followed by centrifugation and subsequent dispersive-solid-phase-extraction (d-SPE) for sample clean-up, in a procedure very similar to QuEChERS, but foregoing the salting-out step. However, this method was found to be less efficient than QuEChERS itself for a variety of pesticides and pharmaceuticals [21] Other authors have used sonication with QuEChERS itself to assist in the mixing of the organic, aqueous and solid phases [24,48,72,73].

As a standalone extraction method, UAE is outperformed by other currently used methodologies because it requires several batch extractions from the same sample to obtain a good recovery, resulting in a tedious and solvent-consuming method [66].

2.1.4.2. Supercritical fluid extraction (SFE). The use of SFE in soil analysis appears to be sparse. The extraction with supercritical CO_2 usually features a certain amount of a modifier solvent (generally methanol), to improve the extraction efficiency of polar analytes [74]. Changing the pressure and temperature of the fluid can greatly modify its solvation properties. Therefore, with proper method development, SFE can exhibit great extraction selectivity [75]. Gonçalves *et al.* [28] developed and optimized an SFE-GC–MS/MS methodology to extract 20 pesticides of different chemical classes from soil, with excellent recoveries (80.4106.5 %) and good intermediate precision (4.2–15.7 %, n = 18, time span unspecified) [28]. Naeeni *et al.* [33] combined SFE with dispersive liquid–liquid microextraction (DLLME) to concentrate the sample without the time-consuming and polluting evaporation step: after SFE extraction, the collection solvent (acetonitrile) was dispersed in water and the analytes were *retro*-extracted with 17 μL of carbon tetrachloride, followed by centrifugation, after which the carbon tetrachloride layer was directly injected into the chromatographic system [33]. Although analytically relevant, this approach is complicated and labour intensive and does not address the main disadvantages of SFE in analytical extraction as a whole: it presents high cost and poor throughput when compared to techniques like QuEChERS [59]. Nevertheless, other than CO_2, SFE uses only a small volume of modifier solvent (usually) and collection solvent, which results in little waste generation.

2.1.4.3. Dispersive liquid–liquid microextraction (DLLME). This technique is most suited for the extraction of relatively hydrophobic compounds from aqueous solutions. However, it has been used for solvent shifting and concentration in soil extraction. It consists in adding a mixture of a dispersive solvent (*e.g.* acetonitrile or methanol) and an extraction solvent (*e.g.* dichloromethane, chloroform) to the aqueous solution. Through mixing or sonication, fine droplets of the extraction solvent are formed, resulting in a high contact area and efficient extraction. After centrifugation, the dense extraction solvent can easily be removed from the bottom phase [33].

Watanabe and Seike [13] have used DLLME in conjunction with solid–liquid extraction. The method involved extraction of soil with an aqueous solution for 24 h, followed by dispersion of a 6:1 (v/v) solution of dichloromethane/acetonitrile into the aqueous extract and centrifugation. This could be a viable alternative to costly and time-consuming SPE, also providing concentration and solvent shifting. However, it is not as versatile as SPE, due to having very strict requirements in terms of solvent choice, and also being a time-consuming process, involving several steps. Furthermore, most analytes extracted by aqueous SLE would not be readily soluble in the dichloromethane phase, making this technique's scope limited. Also, the use of toxic chlorinated solvents should be mitigated.

2.1.4.4. Microwave-assisted extraction (MAE). MAE has been used for the extraction of several pesticide classes from soils [22,35,76,77] and has proven to be fast and efficient, albeit extracts tend to require some form of clean-up due to the frequent presence of interferents [22]. Microwave irradiation increases both temperature and pressure in a controlled manner inside a static, sealed vial, which reduces the volume of solvent needed. Extracts are generally removed manually after cool-down, unlike PLE, for example, which collects the extract automatically. MAE requires a polar solvent to receive the energy from the microwave radiation, although a new form of proprietary stir-bar can circumvent this problem by receiving the microwave energy itself [78]. Several different solvent mixtures have been used, such as hexane–acetone (1:1, v/v) [35,76] and acetonitrile [77]. Fuentes *et al.* used water-acetonitrile and water-methanol mixtures along with hexane in the extraction cell for the analysis of different pesticide classes, which allowed for a simple removal of the hexane layer once the extraction was completed [16,22]. Furthermore, they used only 1 g of soil sample and 6 mL of extraction solvent, obtaining very good recovery RSD's, which

highlights MAE's potential for miniaturization [22]. However, this particular application only seems suitable for non-polar pesticides. Zhang *et al.* compared MAE against PLE, UAE and Soxhlet for the extraction of 70 multiclass pesticide residues and found it to perform comparably well [35].

2.1.4.5. Solid-phase microextraction (SPME). In general, SPME is not the most suitable technique for environmental pesticide analysis except for aqueous samples, where the fibre can be immersed [79]. As most pesticides are not sufficiently volatile, headspace sampling is only possible for a small subset of compounds and direct immersion in soil slurry is often impracticable, due to fibre degradation. Doong and Liao [80] used Headspace-SPME (HS-SPME) followed by gas-chromatography and electron capture detection (GC-ECD) for the determination of 18 organochlorine pesticides, by making a slurry of soil and water and extracting from the headspace. This approach is considered green: having a small number of analytical steps and being fully automatable, advantages not shared by most other extraction techniques. However, it could not be used for the analysis of most currently used pesticides, due to their low volatility. HS-SPME for quantitative purposes is also controversial among the scientific community [81].

SPME can also be used in combination with solid–liquid extraction or UAE as an alternative to SPE for concentration and solvent elimination. Lambropoulou [71] performed UAE with a 95:5 (v/v) mixture of water/acetone, followed by immersion SPME. However, the contact with organic solvents (even in small concentrations) is known to reduce the fibre lifetime. Yet, this approach could be viable for some analytes. Đurović *et al.* [31] extracted soil with a mixture of methanol-acetone, followed by evaporation to dryness, resuspension in acetone and dilution (1:50) in water with 25 % (wt/v) NaCl and performed HS-SPME with a polydimethylsiloxane (PDMS) fibre, thus avoiding extended contact with the organic solvent. However, this approach still suffers from the need for analyte volatility.

2.2. Instrumental determination

There are many factors which permitted the fast increase in the sophistication of analytical instruments witnessed in the last decades, most important of which is the advance of computational power. Whereas in the 1970's a chromatogram was directly printed on thermal paper from which little information was obtainable, nowadays a chromatograph coupled to a high-resolution mass spectrometer can acquire upwards of 20 spectra *per* second, allowing for subsequent isolation of *m/z* fragmentation traces with four or more decimal places of precision. Furthermore, as instrument prices drop, mass spectrometers have become prevalent in both academia and industry. Nowadays many analyses must use mass spectrometry as no other detector will reach the limits of detection and confirmatory identification required by law [82,83].

2.2.1. Gas chromatography

The first pesticides to raise widespread environmental concern were non-polar organochlorines (DDT, aldrin, etc.), which are easily determined by standard capillary gas chromatography (GC) and indeed literature can be found as far back as the year 1964 [84] describing pesticide analysis in soil by GC. The increased use of highly polar and ionic herbicides, such as glyphosate and 2,4-D as well as the development of high-performance liquid chromatography coupled to mass spectrometry (LC-MS) have gained this technique wider use in pesticide analysis. However, GC remains the standard method for analysis of semi-volatile and non-polar pesticides.

Nearly all recent studies employing GC for pesticide analysis in soil use (5 %-phenyl)-polymethylsiloxane stationary phases (USP G27), or their equivalents (DB-5 ms, for example) [20,32,64]. These phases are known for their robustness, repeatability, and better retention of moderately polar functional groups than 100 % polydimethylsiloxane, although its use has also been reported [44]. More polar phases, such as (50 %-phenyl)-polymethylsiloxane [38] or (14 % cyanopropyl-phenyl)-polymethylsiloxane [27] have been used and may be a good choice for difficult separations of polar pesticides. Proprietary columns of undisclosed phase chemistry, specific for pesticide (and related molecules) have also been reported [45].

Comprehensive multidimensional gas chromatography has been used sparsely for analysing organic compounds in soil. The vastly improved chromatographic resolution is especially useful in non-targeted analysis, where it can be coupled to a high-duty cycle mass analyser (Time-of-Flight) to resolve incredibly complex mixtures and identify unknown contaminants [85]. The technique has also been used for targeted analysis [86,87], but the increased cost and operative expertise necessary prevent it from being commonly used, as one-dimensional high-resolution gas chromatography coupled to tandem mass spectrometry tends to be sufficient in targeted analysis.

Many detectors have been used in combination with GC for soil pesticide analysis, such as electron capture (ECD), nitrogen-phosphorous (NPD) or flame ionization (FID) [20,33]. Although still used in routine analysis, most of these detectors have been phased out by the scientific community in favour of mass spectrometers. The ECD has been extensively used in the past as it has very good sensitivity for most pesticides. However, it does not provide confirmatory identification as tandem mass spectrometry [88,89]. Furthermore, the use of a radioactive material presents disposability problems for end-of-life instruments. The only downsides of MS as opposed to these detectors are the higher costs and instrument complexity, as well as being more difficult to operate, although in some cases the ECD could obtain detection limits comparable to tandem mass spectrometry [88].

High-resolution hybrid tandem mass spectrometers (Q-Orbitrap and Q-ToF) have also been applied in soil analysis [6,90]. These provide a more sensitive and accurate drop-in replacement for every function the triple quadrupole performs, whilst also introducing more sophisticated techniques, especially relevant in nontargeted analyses [91]. These new mass spectrometers generally outperform the triple quadrupole in terms of identification, but not necessarily quantification limits. Belarbi *et al.* [92] reported some improvements in LoQ when using a GC-Q-Orbitrap versus GC-QqQ for 86 of 100 pesticides analysed. The authors also noted a strong tendency for matrix-induced analyte suppression rather than enhancement in the GC-Q-Orbitrap method [92]. Due to their much higher price and comparatively slight advantages these instruments are not expected to offer a cost benefit that promotes the replacement of triple-quadrupoles in targeted pesticide analysis anytime soon.

2.2.1.1. Sample preparation and analytical considerations. Matrix effects, especially matrix-induced response enhancement, are a major concern in GC analysis which can lead to serious over-estimation of the real values within a sample [93]. As internal standards, isotopically labelled analogous for each analyte are not generally employed due to their high cost (especially in multiresidue methods), although one analyte's labelled standard is commonly used as surrogate to check if recoveries are according to those determined during validation [21,43,87]. Other compounds, such as isotopically labelled caffeine and triphenyl phosphate have been used as volumetric internal standard added just before GC analysis [20,32]. Still, the most used technique to mitigate inaccuracy is matrix-matched calibration [28,43,67]. Analyte protectants have also been used in soil pesticide analysis, albeit scarcely [22,94]. These are polar compounds (usually sugars or vegetable oils) added to the sample before chromatographic analysis, masking active sites and thus enhancing analyte response [95]. Analyte protectants are injected at high concentrations (commonly between 0.1 and 1 mg/mL) and they must have sufficient volatility to move through the column and elute (as extremely broad peaks, not detected in tandem mass-spectrometry experiments). This technique is essentially an artificial form of matrix-

Table 2
Comparative analysis of selected methods in regard to the analytical eco-scale and AGREE metrics as well as cost and.

			Instrumental Cost		Operational Cost			
Method Acronym	Analytical Eco-scale	AGREE	Extraction	Determination	Extraction	Determination	Operator Time	Ref
PLE-GC–MS/MS	74	0.46	+++++	+	+++	+	+	[32]
PLE-LC-HRMS/MS	68	0.44	+++++	+++++	+++	+++	+	[19]
PLE-UPLC-MS/MS	68	0.44	+++++	+++	+++	+++	+	[32]
QuEChERS(d-SPE)-GC-HRMS/MS	79	0.41	+++	+++++	+++++	+++	+++	[6]
QuEChERS(d-SPE)-UHPLC-MS/MS	73	0.38	+++	+++	+++++	+++	+++	[46]
QuEChERS-UPLC-MS/MS	75	0.44	+++	+++	+++	+++	+	[6]
QuEChERS-GC–MS/MS	68	0.35	+++	+	+++	+	+	[20]
SLE-HS-SPME-GC–MS	79	0.46	+++	+	+	+	+++	[45]
SLE-GC–MS	81	0.46	+++	+	+	+	+++	[38]
SLE-LC-MS	72	0.44	+++	+++	+	+++	+++	[38]
SLE-SPE-LC-MS/MS	58	0.29	+++	+++	+++++	+++	+++++	[30]
UAE-LC-MS/MS	71	0.42	+++	+++	+++	+++	+++	[40]

induced response enhancement, which is controllable and reproducible. The use of analyte protectants in GC has recently been thoroughly reviewed [96]. It appears that this technique has not been widely accepted even though it is very effective at homogenizing matrix-induced response enhancement: this may be attributed to the perceived higher strain that the technique puts on instruments, due to the high concentrations used and possible contaminations from the standards (especially vegetable oils).

2.2.2. *High-Performance Liquid Chromatography*

HPLC has become critically important in pesticide analysis due to the agrochemical industry's interest in developing pesticides which are more polar, have lower volatility and are easily degradable. This development aims to mitigate some of the environmental problems that the earlier pesticides presented, such as bioaccumulation, persistence and long-range transport [97].

From an analytical perspective, polar and non-volatile compounds are not easily analysed by GC, since an expensive and time-consuming derivatization may be compulsory [98], which is not in line with green analytical chemistry principles. Reverse-phase HPLC can be used for most pesticides and a wide variety of chemical classes can be analysed in the same run [99]. Nearly all published studies use C18 column chemistry (Table 1), with either methanol/water [37,41] or acetonitrile/water [30,36,47] and formic acid modifier as mobile phases. Polar pesticides can also be analysed by hydrophilic interaction columns (HILIC), using the same mobile phases [100,101]. Especially difficult analytes such as glyphosate are often derivatized (most commonly with fluorenylmethoxycarbonyl chloride, FMOC-Cl) prior to HPLC injection in order to improve column retention [102,103]. Botero-Coy *et al.* [104] published a method for the analysis of glyphosate without derivatization by using a highly polar column. However, they also noted this column's poor robustness and rapid degradation [104].

Ultra-high performance liquid chromatography (UPLC or UHPLC) instruments have become quite common, and several studies have reported their use [6,32,37]. The higher operating pressures allow for columns with sub 2 μm particles. These are generally 2.1 mm internal diameter (i.d.) and have significantly improved chromatographic efficiency than traditional HPLC columns (over 2 μm particles). Furthermore, the small internal diameter also results in less mobile phase flow, which drastically reduces the cost and waste produced by LC-MS instruments.

For pesticide analysis, LC-MS with an electrospray ion source (ESI) is by far the most used [21,26,40,100]. Simpler detectors such as the diode-array (DAD) and fluorescence (FLD) have largely been replaced in most applications.

High resolution hybrid mass spectrometers coupled to LC have also been used in soil analysis [19,42]. As with GC-High Resolution MS, the advantages of these instruments in target analysis over QqQ are not always obvious [105,106]. However, their use allows for non-targeted (or "screening") analysis of environmental contaminants [42,91]. Q-q-TOF and Q-q-Orbitrap instruments enable the acquisition of full collision induced dissociation spectra from ESI generated precursors and thus allow tentative identification of unknowns. There has been some discussion in the scientific community as to whether non-targeted analysis is reproducible [107–109], but several studies have found it a very useful way to diagnose environmental contamination [110].

2.2.2.1. *Sample preparation and analytical considerations.*

HPLC can be used in conjunction with virtually all extraction methods for pesticide analysis in soil presented above. When the final extract is dissolved in an organic solvent (such as acetonitrile in QuEChERS) the extract is either dried under a stream of nitrogen, following re-suspension in an aqueous solvent [19,21,32,43], or diluted with water [40,64] and injected, for compatibility with reversed-phase LC eluents. Direct dilution and injection results in a simpler and greener method (as no solvent evaporation or energy expenditure is involved), but some methods require the concentration step to reach lower detection limits.

LC-MS ionization sources are prone to analyte signal suppression due to matrix co-elutants [111]. This is true even in highly selective multiple-reaction-monitoring (MRM) experiments. In order to reduce these phenomena, an adequate clean-up step is commonly employed. The use of isotopically labelled internal standards is common [48,50], as is matrix-matched calibration [36,47].

3. Multi-criteria comparison of methodologies

The wide range of techniques that evolved in environmental pesticide analysis is a sign of its importance and interest to the scientific community. However, they can also be a source of some perplexity and create a difficulty of choice. Metrological performance (Trueness, limit of quantitation, *etc.*) is often the most important factor when choosing a technique and optimizing a methodology [112], yet it is also fitting to compare them in terms of other criteria such as monetary cost, time expended and accordance with green analytical chemistry principles.

Twelve exemplary methods were selected for comparison based on a mix of currently used techniques both for extraction and determination. The methods are summarily described in Table 1 highlighted in Bold (Analytical Procedure column). Table 2 presents the results of each method for the criteria used. Methods for calculation and conventions are explained in the Supplementary Info.

3.1. *Green Analytical Chemistry*

The concept of Green Chemistry emerged in the 1990's as a framework for the development of better chemical practices. It aims to promote a chemistry which is sustainable, safe for human health and the environment [113]. Paul Anastas, one of the field's founders, also preempted to the fact that analytical chemistry is an area that could be

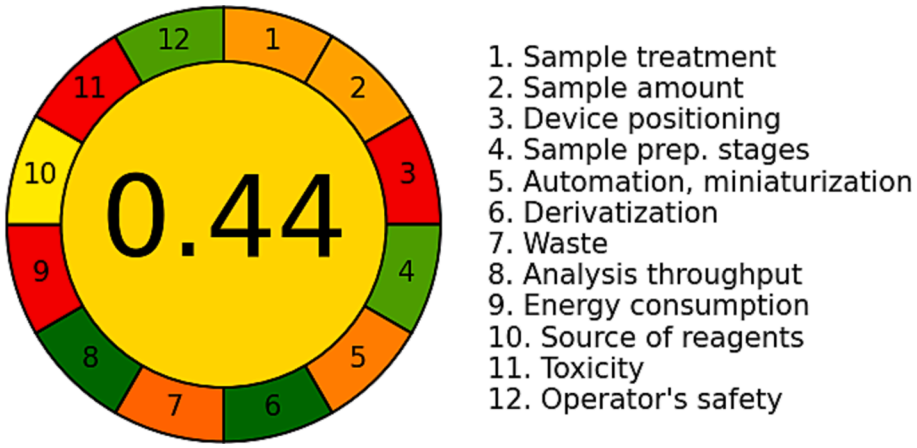

Fig. 2. Graphical representation of the AGREE metric [131].

(and has been) benefiting from the introduction of Green Chemistry Principles [113], as large amounts of hazardous solvents were often used in analytical methods [114,115]. The framework was later improved upon by the adaptation of the 12 principles of Green Chemistry to green analytical chemistry [116].

A greener method is safer for the operator and environment, faster, more efficient and often cheaper (though not necessarily related to metrological performance) [117]. In order to gauge the "greenness" of analytical methods, several methods have been developed [118,119], some of which are pictogram-based, such as the Green Analytical Procedure Index (GAPI) [120], whilst others are quantitative, providing a numerical value. Both provide a less biased evaluation than purely conceptual interpretations, enabling a better comparison of methodologies. We have chosen two quantitative metrics: Analytical eco-scale [121] and AGREE [122].

The Analytical eco-scale assumes the ideal green methodology (no solvent, minimal energy use, no toxicity, no waste) and attributes it 100 points. Then, for each deviation from the ideal (toxicity of solvents, energy use, waste generated), penalty points are attributed, reducing the overall score. Hence, the closer to 100 the score, the greener the methodology [121]. The AGREE metric closely follows the 12 principles of Green Analytical Chemistry, providing a quantifiable as well as visual way of measuring them. The principle is similar to the Analytical eco-scale, in that a maximum score of 1 represents a methodology fully compliant with the 12 principles, and deviations reduce the value. Each principle is measured separately and has the same weight on the final value (in the unaltered method). The authors [122] also developed a simple software package to assist in the calculation. Fig. 2 shows the result of the AGREE metric as per the author's software [122].

These two metrics were chosen for several reasons:

1. They are very well known and (along with GAPI) the most widely used green analytical chemistry metrics [119].
2. These metrics are applicable to all methods for pesticide analysis in soils described in this review and can be calculated with the data provided by the authors. Furthermore, additional data on solvents and reagents required for these calculations (such as GHS pictogram and hazard statements) are widely available in material safety data sheets. The United States National Fire Protection Association scores for example, which are required for the calculation of GAPI, can be hard to obtain for specialty chemicals such as the buffers often used in LC-MS mobile phases.
3. The result for each method is a single value which aids in comparing them directly (although it can also be too reductionistic) and significant variability in this value is obtained when comparing methods which are relatively similar.
4. The analytical eco-scale measures more precisely the hazard of every reagent used, whereas AGREE incorporates more green analytical chemistry principles (such as automation and the use of renewable chemicals). Therefore, these two metrics complement each other.

We have chosen to calculate the metrics unaltered (*i.e.* exactly as described by their authors) in order to maintain consistency and clarity. However, several values are the same for all methodologies and do not contribute to the comparison (the energy usage, for example, is given the same grade for all methods, as they all use either GC–MS or LC-MS).

The results are presented in Table 2. The lowest scoring analytical method (SLE-SPE-LC-MS/MS) involved several steps, including two sequential solid–liquid extractions (one with methanol and another with water), and an SPE stage for the aqueous extract [30]. It must be noted that if this method could be used to extract both polar and non-polar analytes, it might preclude the need for two separation methods in certain multi-residue analyses, making it the greener alternative. A more sophisticated chromatographic technique (such as LCxLC) could also permit the analysis of both polar and non-polar pesticides in a single run [123].

PLE extraction uses high amounts of diatomaceous earth (or other forms of silica), as well as disposable filters, which contribute to the overall waste. In addition, the equipment itself uses a considerable amount of energy. Still, it scored high due to most methods using relatively non-hazardous solvents and being a semiautomated technique, which increases sample throughput. Due to the high efficiency of PLE, a great number of analytes can be extracted from the same sample, an important goal in green analytical chemistry [32,116]. Furthermore, the avoidance of centrifugation reduces the number of vials used as well as time and energy spent.

The QuEChERS methods rated quite differently amongst each other. The lowest ranking method (QuEChERS-GC–MS/MS) used a small amount of hexane, which is highly hazardous [20]. The use of d-SPE did not seem to affect greatly the results, although it presents an extra step. The salts used in QuEChERS ($MgSO_4$, NaCl and citrate buffers) are all considered non-hazardous. There is a particular feature of QuEChERS which makes it potentially less environmentally conscious than the other techniques, especially considering its implementation: it produces a higher amount of plastic waste (in the form of conical tubes). This is because QuEChERS is usually performed with single use plastic centrifuge tubes which have the salts pre-weighed when bought. Although very time efficient and convenient, each sample will produce one or two (if d-SPE is used) conical tubes as waste. This type of waste is rarely considered in analytical laboratories, but it is very important [124]. Any method which employs a centrifuge will use conical plastic tubes. However, these should be washed and re-used as long as contamination and analyte carryover can be avoided.

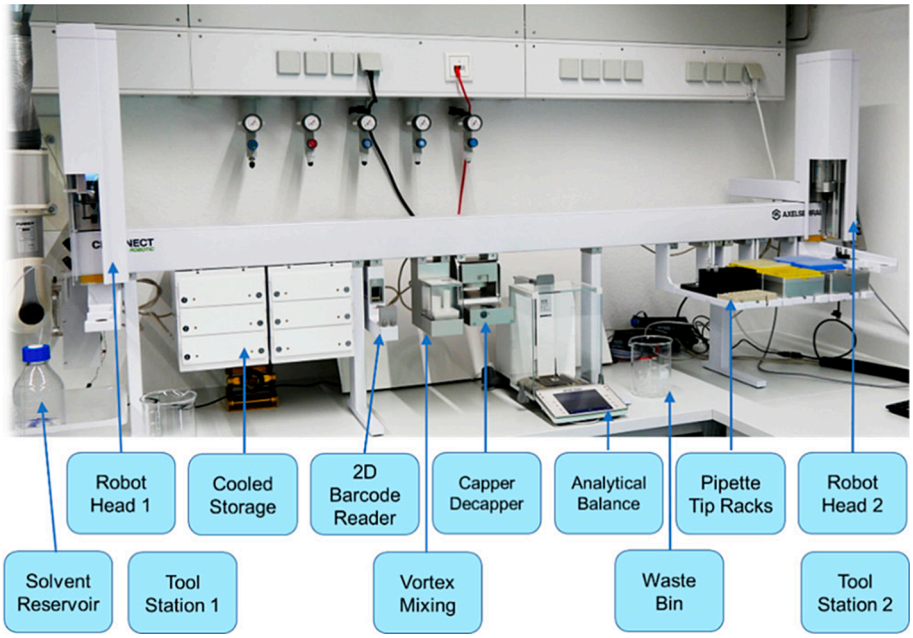

Fig. 3. Automatic multicompound working standard preparation robot (courtesy Axel Semrau GmbH). Reprinted with permission [125]. Copyright 2022 American Chemical Society.

Although GC–MS is inherently greener than LC-MS (due to less waste produced), sample preparation for GC can use highly toxic organic solvents, whereas LC is compatible with aqueous injection. Furthermore, the use of LC-MS is generally preferred to derivatization for GC–MS, in line with green analytical chemistry's principles 4, 6 and 8 (Fig. 2), especially if all target analytes can be chromatographed in a single LC-MS run alone.

In method "SLE-HS-SPME-GC–MS", the authors developed a miniaturized extraction (using only 0.5 g of soil), which ranked high in both the Analytical eco-scale and AGREE, due to the smaller volumes of solvents used, and the integration of a solvent-minimized clean-up and extraction (HS-SPME) [45]. When miniaturizing methods, there is a risk of compromising sample representativeness, especially in a highly variable material like soil, which even sieved by a 2 mm mesh will contain particles of varying sizes and densities. Sampling and sample homogenization are the critical steps to the correct application of such methods, and even when performed ideally poor repeatability and reproducibility can occur [45].

3.2. Cost and time

The cost of an analysis is seldom discussed. Instrument manufacturers are keen on guarding the prices of their products, analytical chemists only occasionally refer to costs and thus the subject of money is often buried under other considerations. This is surprising if one considers that the single most important factor for adopting an analytical procedure is availability of instrumentation or capacity (and inclination) to purchase and adopt it [112]. Instrument amortization and depreciation as well as consumable costs determine the price *per* sample analysed. From an environmental standpoint, a greater number of samples analysed (at a reduced cost) provides a far better monitoring and diagnosis.

Closely related to cost is time, which is an important consideration on two scores: less time *per* sample means more throughput (especially important with expensive instrumentation, increasing amortization rates) and less operator-time means reduced costs and possibility of human error, also increasing the analyst's throughput.

Our analysis in Table 2 provides a rough overview of the cost and time each technique entails. In terms of extraction, PLE equipment is more expensive, whilst most other methods employ cheaper shaker/vortex and centrifuges. QuEChERS will be cheaper in terms of consumables if no d-SPE is employed, but the increased strain on instruments, particularly if analysing soils with high organic matter content, will likely outweigh the benefit. The price of the technique can change greatly between buying pre-weighed kits and bulk reagents for weighing in the lab. SPE will always significantly increase cost and time expended. For chromatographic/mass spectrometric determination, LC instruments are more expensive than GC instruments with the same mass analysers, as is their running cost. Triple quadrupole instruments appear to be the ideal compromise due to their extremely good selectivity compared to single quadrupoles and midrange price. High resolution tandem mass spectrometers do not appear to provide significant metrological advantages compared to the triple quadrupole (QqQ), despite their much higher price and therefore seem to be more suited towards non-target analysis, where they excel [85,110].

4. Future Perspectives

Although analytical chemistry is a constantly evolving field, the bulk of "innovation" comprises more efficient or clever uses of existing technologies. The development of entirely new methods which break with the current paradigm is impossible to predict. Nevertheless, several recent advances from different areas of analytical chemistry could theoretically be applied to pesticide analysis in soil.

4.1. Automation

There is a constant movement towards greater automation of analytical tasks, especially in laboratories with large numbers of samples. Autosampler systems are now commonplace in nearly every instrument: their usefulness and accuracy can be attested by anyone who has had to inject a large number of samples manually. The upfront cost of automation is easily paid by less worker-hours and analytical errors. A fault from a properly validated equipment is often easier to diagnose than human error, because it's more predictable.

Nowadays, robotic systems for working standards preparation and certain forms of sample extraction and clean-up can be purchased [125] (Fig. 3). The claim that these systems are "greener" must be pondered

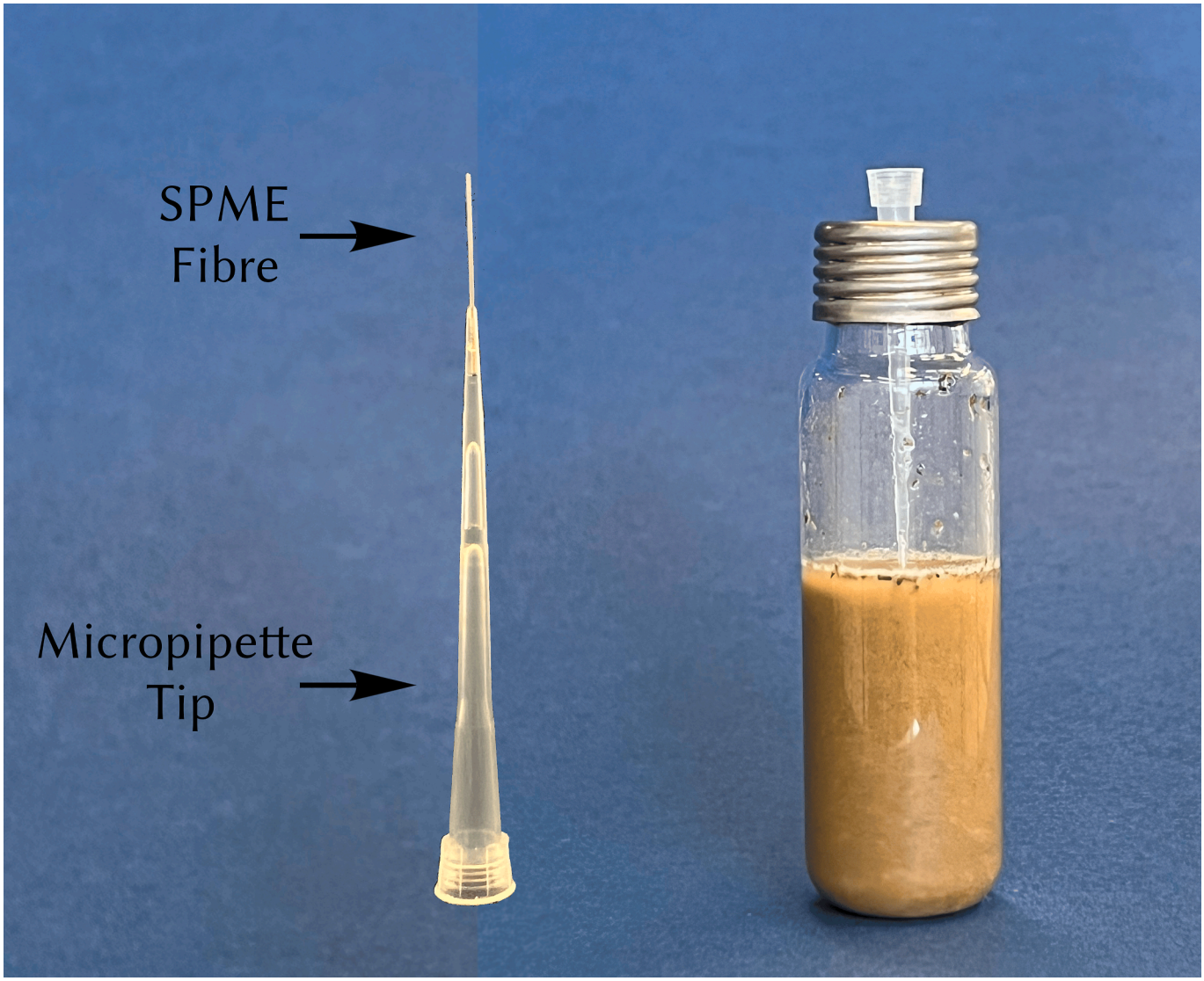

Fig. 4. SPME LC tips and a theoretical application for pesticide analysis in soil.

critically: the miniaturization of methods, reduced exposure of analysts to chemicals, increased sample throughput amongst other benefits are certainly in line with green analytical chemistry principles, but these need to be weighed against the increased energy and material use in the production and operation of such equipment, which can be substantial. Nevertheless, higher throughput and accuracy will undoubtedly result in their adoption by many laboratories.

4.2. Sample Preparation

In most methods of pesticide analysis, sample preparation involves the greatest production of waste, mostly in the form of chemicals (solvents, reagents) and disposable plastic [121,124]. Furthermore, it is often the longest and most labour-intensive step, especially since the introduction of instrument auto-samplers and automated chromatographic data processing. Therefore, sample preparation is the area with the greatest potential for development and application of greener methods.

New solid phase microextraction tips [126] (commercially called SPME LC tips) may overcome the limitation of traditional SPME for analysis of soil: small SPME fibres held to micropipette tips can be immersed in soil–water slurry and then desorbed onto an organic solvent for posterior analysis by GC–MS or LC-MS. A possible application is shown in Fig. 4. These can be used disposably because of their reduced cost (akin to SPE cartridges), and without high volumes of organic solvents.

Several studies have reported the use of switchable solvents as aids in extraction and pre-concentration of pesticides, mostly from aqueous samples [127]. These are compounds which under certain circumstances (by pH change or chemical reaction) switch from hydrophilic to hydrophobic, and vice-versa, allowing their co-dissolution in water and subsequent isolation as an organic phase. This type of switchable solvents seems to have limited application in soil analysis, but recyclable switchable solvents, which can undergo reversible chemical decomposition with temperature [128], present an interesting prospect for a greener extraction solvent, which might be theoretically decomposed and recycled, although purity and repeatability could be a problem.

4.3. Chromatography

Because both GC–MS and LC-MS are very widespread techniques with an enormous range of applications, there is abundant innovation. Although pesticide analysis in soil is not as economically significant as pharmaceutical or food analysis, new discoveries can be applied to this field with effective results.

Capillary columns with 0.25 mm i.d. are almost universally used in

all GC–MS instruments except those built specifically for fast GC. The use of narrower columns (0.18 and 0.15 mm) appears most logical for trace analysis [129], especially if a proper sample clean-up is conducted, as they give better chromatographic resolution with sharper peaks (consequently a faster separation) and require less carrier gas (also resulting in a slightly lower MS operating pressure). On the other hand, narrow-bore columns require higher head pressures and are much more susceptible to overload (particularly in splitless injections). Although 0.25 mm i.d. columns have been held as the ideal compromise for GC–MS, there is no reason why narrower columns should not be used in soil pesticide analysis, where analytes are usually present at trace levels. Indeed, this movement towards narrower columns has been seen in LC-MS, with the advent of UHPLC.

The use of helium as carrier gas in GC–MS presents a problem, since it is a limited resource with various other applications, most notably magnetic resonance imaging machines. The actual helium shortage problem has come into question [130], but even so the replacement of helium for hydrogen allows better resolution at high flow rates and it can be produced from ultra-pure water *in situ*. Unlike helium, hydrogen is reactive and can lead to reactions with the analytes. Furthermore, its lower viscosity results in less MS vacuum and consequently reduced sensitivity [131]. These effects have prevented hydrogen from replacing helium as GC–MS carrier gas, but in the future this change may be compulsory.

There is an interesting dynamic between GC and HPLC: Although GC–MS in inherently greener and mostly cheaper, due to less solvent and instrumentation demands, the rise of LC-MS instrumentation has allowed the analysis of polar and non-volatile analytes without recourse to expensive and hazardous derivatization steps. Furthermore, as LC-MS technology continues to develop (notably polarity switching and LCxLC, [123]) more classes of analytes can be determined in the same run, potentially eliminating altogether the need for GC in some analyses.

5. Conclusions

This work reviewed recently developed methods for pesticide analysis in soils and compared them in terms of cost, time and green analytical chemistry metrics. Our analysis shows that QuEChERS has revolutionized the field of sample preparation and continues to do so with new applications being published constantly. Still, other forms of extraction remain popular and indeed necessary for certain analyte classes such as the ionic pesticides glyphosate and glufosinate. In terms of instrumental determination, GC–MS and LC-MS remain the gold standard for nearly all pesticide residues, being somewhat complementary to one another, although LC-MS has asserted itself as the *de-facto* technique due to its versatility for nearly all pesticide chemical classes, with GC–MS being used increasingly only for semi-volatile pesticides which cannot be adequately quantified by LC-MS.

The accordance with Green Analytical Chemistry principles was found to be more influenced by the application than the technique itself. Any method can be made greener by clever selection of solvents, adequate miniaturization and hermitization of steps (for example). Although GC is inherently greener than LC, this comparison is meaningless for analytes which can only be chromatographed by the latter. Nevertheless, it is the choice of technique rather than its implementation which determines most of the cost and time expended in the analysis (which is also related to Green Analytical Chemistry).

It appears that pesticide analysis in soil is always downstream from food or water analysis, due to not being destined for direct human consumption. However, as an interface between mediums, soil is an extremely important and often overlooked support for life. Pesticide pollution in soils can contaminate natural systems and human food supply chains. New advances in sample preparation and analysis developed for food or water have yet to be tested in soil pesticide analysis, where they may yield simpler, greener and cheaper methods: an exciting prospect for the environmental analytical chemist.

Declaration of Competing Interest

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

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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