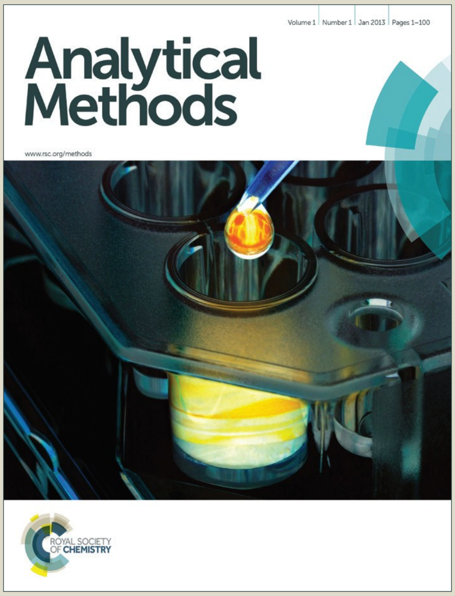
Analytical Methods

Accepted Manuscript



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Development of a multi-residue method for 58 pesticides in soil using QuEChERS and gas chromatography-tandem mass spectrometry

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ABSTRACT

This study developed a method for simultaneous determination of 58 pesticides in soil including those from organochlorine, organophosphorus, pyrethroid, carbamate and triazole classes and others commonly used in agricultural practice. The procedure was based on the quick, easy, cheap, effective, rugged and safe (QuEChERS) sample preparation method. The choice of the buffer, type of the extract solvent, shaking time and a dispersive solid phase extraction (d-SPE) clean-up were optimized. The analysis was performed using gas chromatography-tandem mass spectrometry (GC-MS/MS). Validation experiments were performed in spiked soil samples. The average recoveries at 5 μg kg^{-1} and 50 μg kg^{-1}

spiking levels ranged from 69% to 119% with relative standard deviation (RSD) below 20%. The method limits of quantification (LOQ) ranged from 0.1 μg kg^{-1} to 5 μg kg^{-1}. The correlation coefficients (R^2) were higher than 0.9961 in the linearity range of 0.25-500 μg kg^{-1} for all the pesticides. The optimized method was then applied to the test of real soil samples collected from three regions in China, demonstrating the feasibility of the method.

Key words: Pesticides multi-residue; Soil; QuEChERS; GC-MS/MS.

Abbreviations:

QuEChERS, quick, easy, cheap, effective, rugged and safe;
d-SPE, dispersive solid phase extraction;
GC-MS/MS, gas chromatography-tandem mass spectrometry;
RSD, relative standard deviation;
LOQ, limits of quantification;
R^2, correlation coefficients;
OCPs, organochlorine pesticides;
SPE, solid-phase extraction;
LLE, liquid-liquid extraction;
PSA, primary and secondary amine;
EI, electron ionization;
MRM, multiple reaction monitoring;
LOD, limits of detection;

MEs, matrix effects.

1 Introduction

As an essential cultivating additions, pesticides play an important role in modern agriculture. Hundreds of them are commonly used in current agricultural practices. [1] They can protect plants from disease, weeds and insect damage. [2] But, to obtain a higher agricultural productivity, pesticides were commonly with an extensive use. [3] Most of the pesticides have not been exploited by plants directly and then migrated into soil and water, causing the soil and water contaminations and creating potential threats on non-target organisms and human health. [1, 4, 5] Although organochlorine pesticides (OCPs) such as DDT and its isomers have been banned years ago in China, they still can be found in soil samples due to their persistence.[3] Until now, there are no residue limit standards for pesticide residues in soil except for HCH in China. Thus, it is of great importance for monitoring these pesticides in soil to protect the environment and human health. [6]

Because of the wide diversity of chemical classes and the different physicochemical properties, an optimal extraction process of sample preparation before the determination is necessary. [7] Several common extraction methods for soil samples have been recently established, including Soxhlet extraction (SOX), [8-12] shaking, [13] ultrasonic assisted extraction (UAE), [9, 14]microwave assisted extraction (MAE), [8, 9, 12, 15] solid liquid extraction (SLE), [11, 16] supercritical fluid extraction (SFE) and pressurized liquid extraction (PLE). [12, 15, 17, 18] After extraction, clean-up are commonly performed by solid-phase extraction (SPE) and liquid-liquid extraction (LLE). [18-20] [21] The most popular clean-up method is based on SPE. Although these methods are acknowledged to be effective, there are some drawbacks such as time and solvent consuming, large amount usage of hazardous chemicals organic solvents such as dichloromethane and n-hexane and requirement of expensive apparatus and consumables. [21]

A method named QuEChERS (quick, easy, cheap, effective, rugged and safe) was first introduced for pesticide residues analysis in plant origin samples by Anastassiades *et al.* [22] There are two kinds of standard methods for QuEChERS regarding to the extract buffer: the AOAC Offical Method, [23, 24] which use acetate buffer, and the CEN method, [25]which use citrate buffer. Since Lesueur first used QuEChERS methods in soil samples,[3] the QuEChERS procedure has been increasingly applied for the extraction of organic compounds from environmental samples. This method was based on a salting out extraction with magnesium sulfate and sodium chloride. [26] The majority of studies for soil samples used acetonitrile as an extraction solvent, and followed by a d-SPE as the clean-up procedure, which uses anhydrous magnesium sulfate to remove the excess water and sorbents to remove interfering substance from the organic extract in a centrifuge tube.[7, 27] Additionally, it is easy and rapid for clean extracts to be obtained for the multi-residue analysis and consumes less solvent compared to SPE.

The objective of this study was to develop and validate a fast, effective and reliable analytical procedure for 58 pesticides which are of concern in agriculture soils in China. This work involved QuEChERS extraction method, followed by d-SPE clean-up, and GC-MS/MS determination. To our knowledge, QuEChERS method combined with GC-MS/MS determination for the analysis of dozens of pesticides in agricultural soils was rarely reported. This proposed method provides an effective way for pesticide screening in soil.

2 Experimental

2.1 Chemicals and materials

Certified pesticide reference standards of high purity (>98%) were purchased from Chem Service (West Chester, PA, USA) and Dr. Ehrenstorfer (Ausberg, Germany). Acetonitrile, acetone, n-hexane, methanol, methylene chloride and ethyl acetate were HPLC grade and purchased from Fisher Scientific (Fair Lawn, NJ, USA). Water was purified using a Milli-Q (Millipore, Billerica, MA, USA) system. 50 mL volume polypropylene centrifuge tubes for initial extraction, sorbents (PSA and C18) and 15 mL volume polypropylene centrifuge tubes for d-SPE were purchased from Agilent (Agilent Technologies, Palo Alto, CA, USA). Anhydrous Magnesium sulfate was analytical grade and purchased from Sigma-Aldrich (Steinheim, Germany).

Individual stock solutions were prepared at concentrations of 100 μg mL^{-1} in ethyl acetate. A stock standard mixture was obtained from individual stock solutions in ethyl acetate with concentration of 1 μg mL^{-1}. Internal standard solution (Heptachlor epoxide, 1 μg mL^{-1}) were prepared in ethyl acetate. Solutions were stored at -20 °C until use.

2.2 Equipment

A vortex mixer (Thermo Fisher Scientific, Waltham, MA, USA), Neofuge 23R centrifuge (Heal Force LTD, Hong Kong), laboratory shaker (Jiamei CO. LTD, Jintan, China) and N-EVAP Nitrogen Evaporators (Organomation, MA, USA) were used in sample extraction.

2.3 GC-MS/MS conditions

A GC system Agilent 7890A equipped with 7693 Autosampler was interfaced to a 7000C Triple Quadrupole MS. The GC separation was achieved on HP-5 MS UI (30 m× 0.250 mm× 0.25 μm) purchased from Agilent Technologies. The column was set at a constant flow rate of 1 mL min^{-1} using helium as carrier gas. An aliquot (1.0 μL) of the sample extract was injected in splitless mode at 280 °C. Purge flow rate to split vent was set at 30 mL/min for 0.75 min (20 mL/min gas saver after 2 min). The tandem mass spectrometer was operated in EI mode. The temperature of ion source and transfer line were both set at 280 °C, electron energy was 70 eV. The GC oven temperature programme was 60 °C for 1 min raised to 120 °C at 40 °C min^{-1}, ramped to 310 °C at 5 °C min^{-1}. The total GC run time was 40.5 min divided into 11 time segments. Data acquisition (5-40.5 min) used MRM and detailed in Table 1. The MS/MS method included two optimal ion transitions for each pesticide which allowed simultaneous quantification and identification of any residues detected. Quantitation by GC-MS/MS was based on an internal standard method using the MassHunter software (B.05.00, Agilent).

2.4 Preparation of soil samples

Pesticide free soil samples were collected from agricultural areas in Tianjin, China for method development and validation. These samples were tested and shown to be absence of detectable target pesticides to influence the development of method (Fig. 1). Other soil samples were collected from Shandong (samples 1-5), Jiangsu (samples 6-9) and Liaoning (samples 10-16) province with a long history of widespread use of pesticides. Physicochemical properties of all the soil samples are given in Supplementary Information, Table S 1. After removal of litter, plant roots, and stones, pesticide free soil samples were air-dried at room temperature, mixed to homogenize. And then sieved using a 0.3 mm mesh and stored at ambient temperature prior to analysis.

2.5 Extraction and clean-up procedure

An aliquot of 5 g blank soil samples were placed into 50 ml polypropylene centrifuge tube and spiked at the required fortification level by adding an appropriate volume of mixed standard solution containing 58 pesticides. Then the resulting mixture was hand-shaken gently to mix them homogeneous. After that, add 10 mL water for 30 min to hydrate soil samples before 10 mL of acetonitrile with 1% acetic acid and a ceramic homogenizer (Agilent Technologies) were added. And then the tube was shaken at 250 times/min on a shaker for 10 min. After adding 4 g anhydrous $MgSO_4$ and 1 g NaOAc into the tube, the resulting mixtures were immediate hand-shaken vigorously for 1 min and centrifuged at 2823 rcf for 5 min.

Transfer 6 mL of supernatant to a 15 mL polypropylene centrifuge tube that contained 900 mg of $MgSO_4$, 150 mg PSA and 150 mg C18. Then the extract was swirled on a vortex mixer for 1 min before centrifuged at 2823 rcf for 5 min. Transfer 2.0 mL of supernatants into a 10 mL glass centrifuge tube and add 50 µL of internal standard solution (Heptachlor epoxide, 1 µg mL^{-1}) and then concentrated to dryness under a gentle stream of nitrogen in water-bath at 40 °C. The residue was re-dissolved in 1.0 mL of ethyl acetate (1 g/mL) and filtered through a PTFE filter (0.22 µm) for GC-MS/MS analysis.

2.6 Validation of the method

Matrix matched standards were prepared by redissolving the blank soil extracts with 1.0 mL of pesticide standard solution instead of 1.0 mL of ethyl acetate.

Linearity was assessed by using matrix matched calibration curves over a wide range of concentrations 0.25-500 μg kg^{-1}. For compounds where method LOQ was higher than 0.25 μg kg^{-1}, linearity was demonstrated from LOQ to 500 μg kg^{-1}.

Recovery study was carried out to determine the method accuracy and precision. The fortification levels were 50 and 5 μg kg^{-1} and mean recovery and RSD values were based on analysis of 5 replicates at each fortification level. Recoveries were determined by comparing the peak area in the sample to peak areas of matrix-matched standards prepared at known concentration. The LOQ for each pesticide was determined as the lowest spiked concentration with 5 replicates that can be quantified with satisfactory recovery values (70-120%) and RSD≤ 20%.[28, 29]

3 Results and discussion

3.1 Sample extraction

The studied pesticides exhibit very different characteristics and physical/chemical properties such as acid-base properties, which strong influence their water-acetonitrile partition. Besides, as a complex matrix, analysis of soil requires rigorous sample preparation to obtain a repeatable and sensitive analysis. Therefore, to determine the best extraction step, the choice of the buffer, the nature of the solvent and the shaken time were studied.

In fact, the buffered system of AOAC and EN official methods are able to keep pH constant around 5. This pH value achieves satisfactory recoveries for acid-sensitive pesticides and without degradation for base-sensitive ones. In this study, these two buffers were compared, which the acetate buffer containing 1.0 g of NaOAc and 4.0 g of $MgSO_4$, and the citrate buffer containing 1.0 g of sodium citrate, 4.0 g of $MgSO_4$ and 1.0 g of NaCl, 0.5 g of sodium hydrogencitrate sesquihydrate. Besides, a no buffer method use only 4.0 g $MgSO_4$ and 1.0 g NaCl was also carried out. Average recoveries obtained from the extraction of pesticides in soils ranged between 72% and 121% (RSD≤ 19%) for AOAC buffer method. EN buffer method also obtained satisfactory recoveries (67-123%; RSD≤ 15%) except for dichlorvos (Supplementary Information, Table S 2), but the recoveries of a number of pesticides were slightly lower than AOAC method. The recoveries of most pesticides for no buffer method were not as satisfactory as those obtained with buffers. And the recoveries were lower than 70% for approximately 30% of all these pesticides, especially for dichlorvos, quintozene, p,p'-DDT, propargite and fenpropathrin, whose recoveries were blow 60%. In this context, AOAC buffer method was finally chosen for the extraction. And this buffer method has also been used to extract antibiotics in soil.[27]

The original method and most other studies used acetonitrile as the extraction solvent for soil samples. [7, 30] While there are studies that use acetone/n-hexane mixture (1:1, v/v) to extract OCPs in soil, [31] and obtained a satisfactory result. Besides, some studies used ethyl acetate to extract fluopicolide, propamocarb, penconazoles and chlorinated compound in soil matrices.[32, 33] For the development of this method, all of these solvents (acetonitrile, acetone/n-hexane (1:1, v/v), ethyl acetate) were studied and compared for extraction of pesticides in soil. Among the various tests performed, acetonitrile allowed for the highest recoveries. Therefore, acetonitrile was chosen as the organic solvent for the extraction.

Because of the matrix complexity, it is hard to extract compounds from soil matrices. Therefore we chose shaking as an assistant extraction produce before adding buffer salts. Shaken at 250 times/min on a shaker for 10, 20, 30, 40, 50 and 60 min were subsequently assessed. The results indicated that the time of 10 min gave satisfactorily recoveries. And the time 20 min, 30 min, 40 min, 50 min or 60 min did not increase the recoveries observably, compared to 10 min. Therefore, to obtain the best recoveries while minimizing sample preparation time, a shaking of 10 min was chosen.

3.2 Optimizing of the d-SPE clean up

An additional clean-up step was necessary to limit the presence of matrix interferents and remove the excess water. MEs (matrix effects) are common in reports on the analysis of soil. Clean-up was performed by a d-SPE approach with several most widely used sorbents, PSA and C18 with anhydrous $MgSO_4$. It was optimized according to adsorbent content in three sets: (1) 150 mg PSA+ 150 mg C18+ 900 mg of $MgSO_4$; (2) 150 mg PSA+ 900 mg of $MgSO_4$; (3) 150 mg C18+ 900 mg of $MgSO_4$. The recovery and MEs were assessed.

The ME was studied according to Equation 1 that comparing the slopes in matrix (blank soil extract) calibration solutions and pure solvent (ethyl acetate) calibration solutions.

$$\mathrm{ME}\ (\%) = (S_m/S_s - 1) \times 100\% \qquad (1)$$

S_m and S_s are the slopes in matrix and solvent. When ME (%) values were 0% no matrix effect was observed. ME (%) values between -20% and 20% were considered to be a mild matrix effect, and values between -50% and -20% or 20% and 50% were considered to be of medium matrix effect while ME values below -50% or above 50% are considered to be a strong matrix effect of signal suppression or enhancement [19].

The results indicate that most of the pesticides exhibited recoveries in the range between 70% and 120% for all the three sets (Supplementary Information, Table S 3). As can be seen in Fig. 2, most of the pesticides exhibited matrix enhancement effects. But PSA+ C18+ 900 mg of $MgSO_4$ set had a lower ME than other two sets. So set (1) with PAS + C18 + 900 mg of $MgSO_4$ was selected in the d-SPE step. In the other hand, because three out of ten pesticides had strong MEs, the matrix-matched calibration standards are indispensable for accurate quantification by GC-MS/MS in this study.

3.3 Method validation

As shown in Table 2, the GC-MS/MS response for the 58 pesticides was linear over the range tested with R^2 between 0.9961-0.9999 for all pesticides, and higher than 0.9980 for most of the pesticides. The method LOQs were between 0.1 μg kg^{-1} and 5 μg kg^{-1}.

Mean recoveries and RSD of the 58 pesticides from soil matrix are given in Table 2. Blank soil samples were spiked at 50 μg kg^{-1} and 5 μg kg^{-1} fortification levels. The results showed that mean recovery of pesticides were between 69% and 119% with RSD values at or below 20% for all the analytes except paclobutrazol (125%) and fenvalerate (122%) spiked at 5 μg kg^{-1}. The observed slightly higher recovery of paclobutrazol and fenvalerate at a concentration of 5 μg kg^{-1} might be attributable to salting-out effects. [16]

The feasibility of the method for different types of soils was assessed using three different soil samples collected from Shandong (sample 4), Jiangsu (sample 7) and Liaoning (samples 15) province. The soil samples were both fortified at 5 μg kg^{-1} and 50 μg kg^{-1}. The results (Supplementary Information, Table S 4 and Table S 5) showed that the accuracy and precision were satisfactory regardless of the type of soils.

As demonstrated above, the recoveries of different soils were generally between 60 and 120% with RSDs below 20%, except for fipronil sulfone and difenoconazole. The results indicated that the proposed method is feasible for the analysis of 58 pesticides in different types of soils.

The further validate the feasibility of this method, a traditional shaking method was conducted and compared with this proposed QuEChERS method using samples 1-16. For traditional shaking extraction method, the sample was extracted twice with one hour shaking in each time. Matrix matched calibration solution was used in both methods. These two methods had good agreement for quantitative and qualitative analysis of pesticide residues in all soil samples. However, QuEChERS method was more sensitive for some pesticides due to clean up of the extracts and a weak acid extraction buffer environment. Besides, QuEChERS was less time and solvent consuming.

The results were given in Supplementary Information, table S 6. It can be seen that, over 50% of the selected pesticides were detected in 16 samples with low residue levels. Quintozene, endosulfan-β and endosulfan sulfate were detected in sample 13 in Liaoning with concentration 4.1×10^{2} μg kg^{-1}, 80 μg kg^{-1} and 2.8×10^{2} μg kg^{-1}, respectively. Phorate sulfone, endosulfan sulfate, and chlorpyrifos were detected in sample 14 in Liaoning with concentration 1.4×10^{2} μg kg^{-1}, 1.3×10^{2} μg kg^{-1} and 2.6×10^{2} μg kg^{-1}, respectively. Besides, p,p'-DDE were found with concentration 99 μg kg^{-1} in sample 5 in Shandong province.

3.4 Comparison of methods

The performance of the developed QuEChERS method was compared with other existing methods from the viewpoint of sample weight, solvent type, solvent volume, extraction time, recovery, LOQ (LOD) and RSD. As listed in Table 3, this proposed QuEChERS method had comparable or lower LOQs than other reported methods. Beyond that, there were some considerable advantages over the other methods: only 10 mL of acetonitrile were used, making this method safe and environmentally friendly; extraction process was simple and efficient; no special extract equipment was needed. In summary, this method enables relatively comparable accuracy and precision with those found in literature.

4. Conclusions

In this study, several experimental factors were optimized on the basis of QuEChERS method. The modified QuEChERS procedure has been adapted successfully in extracting pesticides which are generally used in agricultural practice. Sample extraction with AOAC buffer system and clean-up using PSA and C18 was found to be the optimum conditions for analysis of 58 pesticides in the soils studied. Recoveries for all analytes were acceptable with low LOQs below 5 μg kg^{-1}. The proposed method was applied in the analysis of real samples, and the results indicated that several pesticides may be found in soils several months after application. This rapid and simple method is expected to be further applied to the screen of larger number of target pesticides in agricultural soil and be essential in decision making regarding usage and environmental management of pesticides in China in the future.

Acknowledgment

This work was supported by National Natural Science Foundation of China (Grant No. 41401577).

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Figure captions:

Figure 1. GC-MS/MS chromatograms of selected compounds: (a) blank soil and (b) soil extract spiked at 100 μg kg^{-1}.

Figure 2. MEs of the comparisons between different clean-up materials in soil samples.

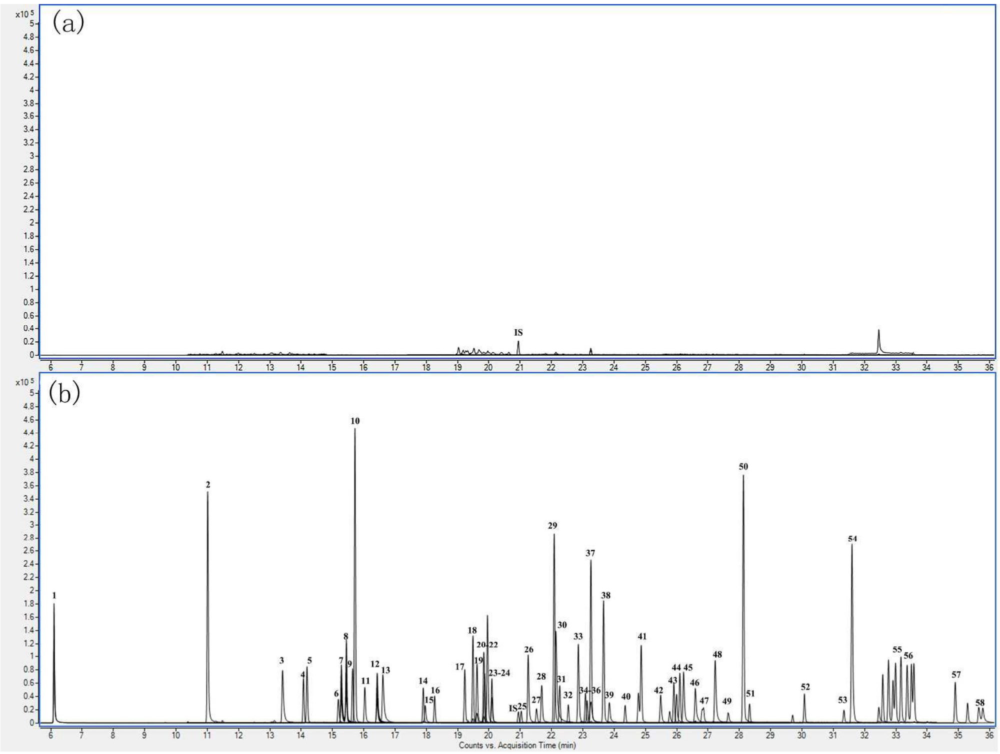


Figure 1. GC-MS/MS chromatograms of selected compounds: (a) blank soil and (b) soil extract spiked at 100 μg kg-1.
224x168mm (300 x 300 DPI)

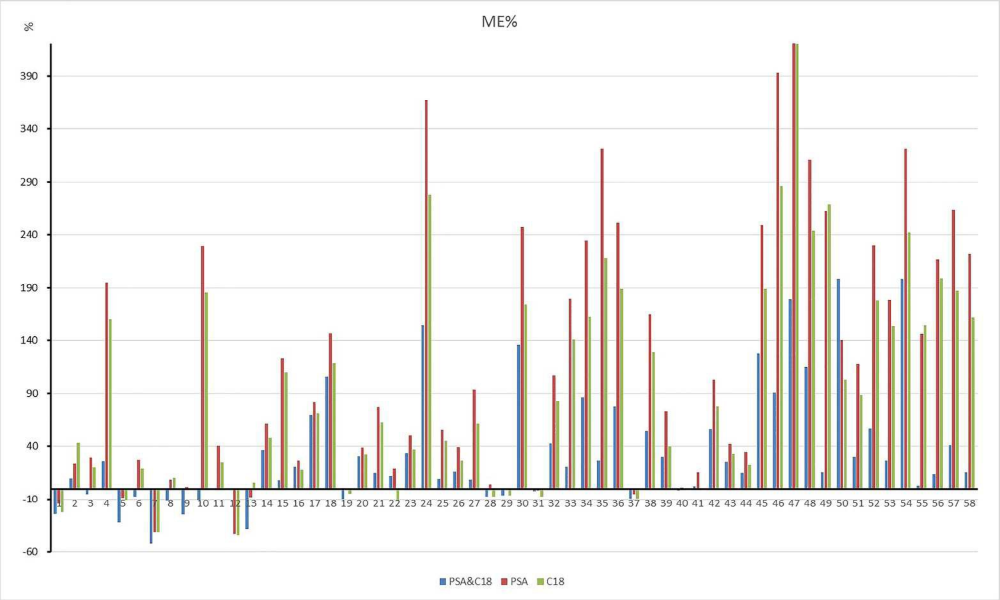


Figure 2. MEs of the comparisons between different clean-up materials in soil samples.
180x108mm (300 x 300 DPI)

Table list:

Table 1. Acquisition and chromatographic parameters for the selected pesticides.

Table 2. Validation parameters: Mean recoveries and RSD at 2 spiking levels, LOD, LOQ and linearity of pesticides.

Table 3. Comparison of methods for the determination of pesticides in soil samples.

Table 1. Acquisition and chromatographic parameters for the selected pesticides.

Numbers	Pesticides	T_R (min)	Time segment	MRM 1	CE 1	MRM 2	CE 2
1	Dichlorvos	6.11	1	109.0> 79.0	5	184.9> 93.0	10
2	Isoprocarb	11.02	2	121.0> 77.1	20	136.0> 121.1	10
3	Atrazine-desethyl	13.42	2	172.0> 94.0	15	187.0> 172.0	5
4	phorate	14.08	2	260.0> 75.0	5	230.9> 128.9	25
5	HCH-alpha	14.19	2	216.9> 181.0	5	218.9> 183.0	5
6	Atrazine	15.19	3	214.9> 58.1	10	214.9> 200.2	5
7	HCH-beta	15.29	3	181.0> 145.0	15	216.9> 181.1	5
8	HCH-gamma	15.45	3	181.0> 145.0	15	216.9> 181.0	5
9	PCNB	15.65	3	236.9> 118.9	25	236.9> 142.9	30
10	Terbufos	15.73	3	230.9> 129.0	20	230.9> 175.0	10
11	pyrimethanil	16.05	3	198.0> 156.0	10	198.0> 118.0	10
12	HCH-delta	16.44	3	181.0> 145.0	15	217.0> 181.1	15
13	Chlorothalonil	16.63	3	263.8> 168.0	25	263.8> 229.0	20
14	Acetochlor	17.91	4	222.9> 132.2	20	222.9> 147.2	5
15	Parathion-methyl	17.98	4	262.9> 79.0	30	232.9> 109.0	10
16	Alachlor	18.27	4	188.1> 160.2	10	160.0> 132.1	10
17	Phorate Sulfoxide	19.34	5	153.0> 96.9	10	121.0> 64.9	10
18	Malathion	19.50	5	172.9> 99.0	15	157.8> 125.0	5
19	Phorate Sulfone	19.63	5	124.9> 96.9	5	170.9> 143.0	5
20	Chlorpyrifos	19.84	5	196.9> 169.0	15	198.9> 171.0	15
21	Parathion	19.87	5	138.9> 109.0	5	290.9> 109.0	10
22	Dicofol	19.89	5	139.0> 111.0	15	250.9> 138.9	15
23	Triadimefon	19.96	5	208.0> 181.1	5	208.0> 111.0	20
24	Isocarbophos	20.10	5	135.9> 108.0	15	135.9> 69.0	30
IS	Heptachlor epoxide *	20.95	6	354.8> 264.9	15	352.8> 262.9	15
25	Pendimethalin	21.04	6	251.8> 162.2	10	251.8> 161.1	15
26	Fipronil Sulfide	21.26	6	351.0> 254.9	20	255.0> 228.0	15
27	Fipronil	21.53	6	366.8> 212.8	25	368.8> 214.8	25

28	Procymidone	21.69	6	96.0> 67.1	10	96.0> 53.1	15
29	o,p'-DDE	22.09	6	246.0> 176.2	30	248.0> 176.2	30
30	Paclobutrazol	22.14	6	236.0> 125.1	10	125.1> 89.0	20
31	Endosulfan-α	22.27	6	194.9> 159.0	5	194.9> 125.0	20
32	Butachlor	22.54	6	188.1> 160.2	10	236.9> 160.2	5
33	Hexaconazole	22.87	7	231.0> 175.0	10	256.0> 82.1	10
34	Isoprothiolane	23.10	7	162.1> 85.0	20	162.1> 134.0	5
35	Profenofos	23.15	7	207.9> 63.0	30	338.8> 268.7	15
36	Uniconazole	23.25	7	234.1> 165.1	10	234.1> 137.0	15
37	p,p'-DDE	23.26	7	246.1> 176.2	30	315.8> 246.0	15
38	Buprofezin	23.67	7	105.0> 77.0	20	105.0> 104.1	10
39	Fipronil Sulfone	23.85	7	383.0> 255.0	20	255.0> 228.0	15
40	Endosulfan-β	24.36	8	206.9> 172.0	15	194.9> 158.9	10
41	o,p'-DDT	24.87	8	235.0> 165.2	20	237.0> 165.2	20
42	Triazophos	25.5	8	161.2> 134.2	5	161.2> 106.1	10
43	Endosulfan sulfate	25.91	9	272.0> 237.0	15	274.0> 239.0	15
44	p,p'-DDT	26.11	9	235.0> 165.2	20	237> 165.2	20
45	Propiconazole	26.23	9	172.9>145.0	15	172.9> 74	45
46	Tebuconazole	26.61	9	250.0> 125.0	20	125.0> 89.0	15
47	Propargite	26.862	9	135.0> 107.1	10	149.9> 135.1	5
48	Epoxiconazole	27.24	9	192.0> 138.1	10	192.0> 111.0	25
49	Iprodione	27.66	9	187.0> 124.0	25	243.9> 187.0	5
50	Bifenthrin	28.14	9	181.2> 165.2	25	181.2> 166.2	10
51	Fenpropathrin	28.34	9	264.9> 210.0	10	207.9> 181.0	5
52	Cyhalothrin	30.09	10	197.0> 141.0	10	197.0> 161.0	5
53	Spirodiclofen	31.35	10	109.1> 81.1	10	109.1> 79.1	15
54	Pyridaben	31.6	10	147.2> 117.1	20	147.2> 132.2	10
55	Cyfluthrin	33.01	10	226.9> 76.9	25	198.9> 170.1	25
56	Cypermethrin	33.17	10	163.0> 91.0	10	163.0> 127.0	5
57	Fenvalerate	34.91	11	167.0> 125.1	5	224.9> 119.0	15
58	Difenoconazole	35.66	11	264.9> 202.0	20	322.8> 264.8	15

* Heptachlor epoxide was used as internal standard.

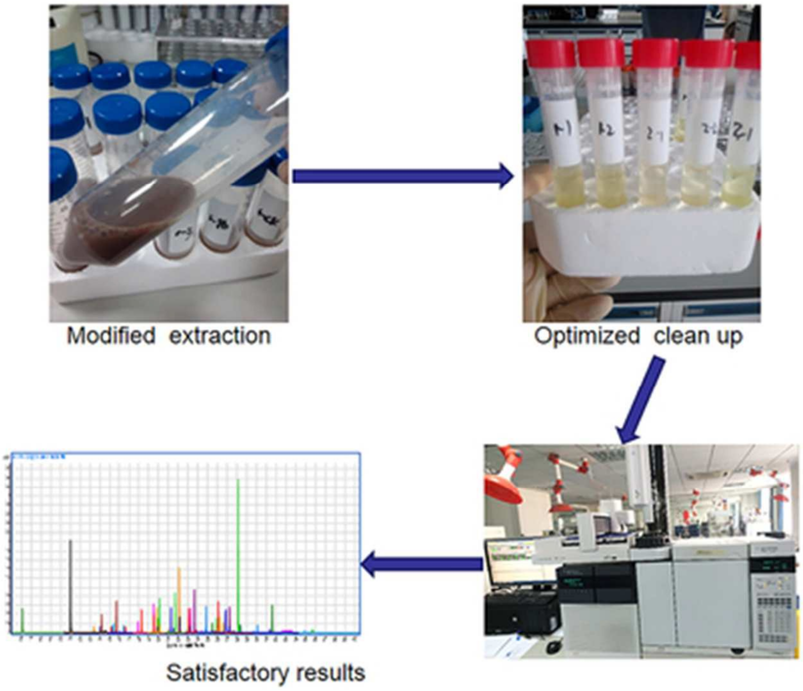
Table 2. Validation parameters: Mean recoveries and RSD at 2 spiking levels, LOD, LOQ and linearity of pesticides.

Pesticides	5 μg kg^{-1}		50 μg kg^{-1}		LOQ (μg kg^{-1})	R^2
	Mean	%RSD	Mean	%RSD		
Dichlorvos	101	18	89	8	0.25	0.9964
Isoprocarb	117	9	112	8	0.25	0.9963
Atrazine-desethyl	95	15	90	9	0.5	0.9975
Phorate	81	19	82	10	0.25	0.9991
HCH-alpha	100	5	79	6	0.1	0.9982
Atrazine	111	16	85	10	0.25	0.9967
HCH-beta	95	18	85	8	0.25	0.9982
HCH-gamma	97	14	81	7	0.25	0.9983
Quintozene	95	13	74	4	1	0.9965
Terbufos	93	13	81	9	0.25	0.9961
Pyrimethanil	100	10	80	8	2	0.9967
HCH-delta	91	18	85	9	0.25	0.9969
Chlorothalonil	93	11	80	18	0.25	0.9989
Acetochlor	87	14	81	8	0.1	0.9986
Parathion-methyl	97	12	92	7	2	0.9991
Alachlor	95	5	90	10	0.5	0.9994
Phorate-sulfoxide	94	14	97	7	0.5	0.9999
Malathion	92	9	90	6	0.25	0.9997
Phorate-sulfone	91	9	88	5	1	0.9999
Chlorpyrifos	82	13	83	4	0.25	0.9994
Parathion	91	13	94	6	2	0.9989
Dicofol	111	15	99	5	0.25	0.9969
Triadimefon	88	13	103	6	0.5	0.9997
Isocarbophos	106	8	111	12	1	0.9998
Pendimethalin	88	10	93	8	0.5	0.9981
Fipronil Sulfide	104	3	100	7	0.2	0.9995
Fipronil	111	13	114	9	0.25	0.9994
Procymidone	99	11	102	10	2	0.9978
o,p'-DDE	86	17	85	5	0.1	0.9981

Paclobutrazol	125	16	116	7	0.1	0.9985
Endosulfan-α	96	9	105	8	2	0.9994
Butachlor	95	13	109	6	2	0.9999
Hexaconazole	107	6	116	9	5	0.9996
Isoprothiolane	95	11	94	7	0.25	0.9994
Profenofos	95	13	90	6	0.2	0.9994
Uniconazole	95	12	113	10	0.5	0.9999
p,p'-DDE	97	13	76	6	0.1	0.9999
Buprofezin	91	10	90	8	0.5	0.9979
Fipronil Sulfone	100	9	108	12	0.3	0.9998
Endosulfan-β	78	16	86	5	0.25	0.9974
o,p'-DDT	89	15	69	9	0.25	0.9993
Triazophos	105	10	107	6	1	0.9998
Endosulfan sulfate	96	15	84	7	0.1	0.9996
p,p'-DDT	93	13	70	7	1	0.9991
Propiconazole	91	10	88	9	4	0.9999
Tebuconazole	97	13	104	5	0.2	0.9999
Propargite	89	8	101	9	2	0.9982
Epoxiconazole	83	19	107	12	0.5	0.9998
Iprodione	94	16	92	13	0.5	0.9990
Bifenthrin	98	19	88	11	0.3	0.9999
Fenpropathrin	99	12	88	12	0.3	0.9992
Cyhalothrin	111	7	96	11	1	0.9983
Spirodiclofen	100	16	107	10	5	0.9983
Pyridaben	105	12	119	9	0.5	0.9992
Cyfluthrin	107	6	77	12	4	0.9997
Cypermethrin	104	7	92	7	5	0.9995
Fenvalerate	122	18	86	9	2	0.9980
Difenoconazole	108	15	105	12	4	0.9986

Table 3. Comparison of methods for the determination of pesticides in soil samples.

Method	Sample weight (g)	solvent type	solvent volume (mL)	Extraction time (min)	Recovery (%)	LOQ (LOD) (μg kg^{-1})	RSD (%)	References
QuEChERS	5	acetonitrile	10	0.5	43-100	0.1-2.4	≤ 20	21
QuEChERS	10	acetonitrile	15	2	83-120	(1-10)	≤ 10.2	5
QuEChERS	5	acetonitrile	10	2	79.4-113.6	0.1-2.9	≤ 12.2	17
QuEChERS	10	acetonitrile	10	19	73.8-105.7	5	≤ 16.0	29
SLE	50	acetone	150	60	67.5-113.4	1.65-33	≤ 16.0	16
PLE	15	acetonitrile	40	15	75.2-112.7	(4-5)	≤ 13.3	18
MAE	2	acetone/n-hexane (1:1)	30	4	72-120	16.5	≤ 6.86	15
Presented method	5	acetonitrile	10	10	69-125	0.1-5	≤ 20	Presented method



39x29mm (300 x 300 DPI)