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## **Research Article**

# Rapid determination of pesticide residues in herbs using selective pressurized liquid extraction and fast gas chromatography coupled with mass spectrometry

A selective pressurized liquid extraction and gas chromatography coupled with triple quadrupole mass spectrometer method was developed for simultaneous determination of 52 pesticide residues in medicine and food dual-purpose herbs. The developed extraction method integrated extraction and cleanup processes for sample preparation. The sorbents, 5 g Florisil and 100 mg graphitized carbon black, were placed inside the extraction cell to remove matrix interferences. Optimized conditions of selective pressurized liquid extraction were ethyl acetate as extraction solvent, 120°C of extraction temperature, 6 min of static extraction time, 50% of flush volume extracted for two cycles. An ultra inert capillary GC-MS HP-5 UI column (20 m  $\times$  0.18 mm id, 0.18  $\mu$ m) and column backflush system were used for the analysis. Multiple-reaction monitoring was employed for the quantitative analysis with electron ionization mode. All calibration curves showed good linearity ( $r^2 > 0.995$ ) within the test ranges. The average recoveries of most pesticides were from 81 to 118%. The validated method was successfully applied for the determination of pesticide residues in four herbs. The results indicate that selective pressurized liquid extraction and GC-MS/MS is a sensitive and reliable analytical method for the simultaneous determination of multiple pesticide residues in herbs.

Keywords: GC-MS/MS / Medicine and food dual-purpose herb / Pesticide residue / Selective pressurized liquid extraction DOI 10.1002/jssc.201200169



## 1 Introduction

In China, lots of traditional food and herbal products are consumed for both medicinal and food purposes. Likewise, "Let food be thy medicine and medicine be thy food" was also espoused by Hippocrates, the father of modern medicine, nearly 2500 years ago [1]. With the increasing demand for healthy benefits, a large quantity of medicine and food dualpurpose herbs (MFDPHs) are used throughout the world today [2]. However, during the herbs growing process, pesticides including organochlorine (OC), organicphosphorus (OP), pyrethroid (PYR), carbamate (CAR) and other types (OT) are frequently used as chemotherapeutants in agriculture for destroying or controlling any pests. Therefore, MFDPHs are liable to contain pesticide residues, which are

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**Abbreviations: GCB**, graphitized carbon black; **MFDPH**, medicine and food dual-purpose herb; **SPLE**, selective pressurized liquid extraction

accumulated from agricultural practices and storage period. In fact, pesticides have already been found in Chinese herbal medicines and over-the-counter herbal dietary supplements sold in the market [3]. Therefore, it is necessary to develop methods for the rapid and sensitive determination of multiple pesticide residues in MFDPHs.

In general, low content and complicated matrix are the two obstacles of the determination of pesticide residues in MFDPHs. Furthermore, the contamination of injection inlet and column by high boiling matrix compounds during GC analysis should be also considered, which could affect the chromatographic separation and reduce column life [4]. So far, a series of sample preparation methods, including liquid-liquid extraction (LLE) [5], pressurized liquid extraction (PLE) [6, 7], solid phase extraction (SPE) [8, 9], gel permeation chromatography (GPC) [10, 11], QuEChERS (quick, easy, cheap, effective, rugged, and safe) [12, 13], and solid phase micro extraction (SPME) [14, 15] have been employed for the extraction and enrichment of pesticides in Chinese herbal medicine. However, LLE-SPE and PLE-GPC are tedious and complicated since the extraction and cleanup are respective procedures. Meanwhile, LLE and GPC need a large amount of organic solvents. Although QuEChERS is a quick and easy method, the requirement of sample with more than 75% moisture is a limit [12, 16]. The SPME process is also very simple, but the recovery of this method depends on the property of SPME fiber for pesticides [14, 17].

PLE, an extraction technique under elevated temperature and pressure, has been recently used in the extraction of residual organic pollutants from different matrices such as tea, vegetables, and compost for its rapid extraction process and high extraction efficiency [18–20]. Meanwhile, PLE with different sorbents could be used as selective pressurized extraction approach. Integration of the PLE and cleanup process has also been achieved by loading sorbent at the bottom of the PLE stainless cell [21–23]. Comparing with traditional extraction and cleanup approaches (LLE-SPE, SPME, and PLE-GPC), the selective pressurized liquid extraction (SPLE) can simplify extraction step and significantly reduce extraction time and solvent consumption.

Gas chromatography coupled with triple quadrupole mass spectrometer (GC-MS/MS) has been intensively used for the determination of organic pollutants [24, 25]. The detector can focus on characteristic precursor and product ions. Typically, the multiple reaction monitoring of GC-MS/MS gives the possibility of simultaneous confirmation and quantification with excellent selectivity and sensitivity. In addition, a column backflush offered potential advantages to reduce run time and prevent high boiling contaminants to GC-MS system [26, 27].

In this paper, it is the first time to report an SPLE and GC-MS/MS method with column backflush for the determination of multiple pesticides residues in four MFDPHs including the root of *Pueraria thomsonii* Benth., *Pogostemon cablin* Benth., *Houttuynia cordata* Thunb., and *Disoscorea opposita* Thunb.

## 2 Materials and methods

## 2.1 Chemicals, materials, and standards

Ethyl acetate, *n*-hexane, cyclohexane, acetonitrile, toluene, and acetone (HPLC grade) were purchased from Merck (Darmstadt, Germany). Petroleum ether (bp 40–60°C) was purchased from Fluka Analytical (Sigma–Aldrich Corp., St. Louis, USA). Deionized water was purified through a Milli-Q synthesis system (Millipore, USA).

Primary and secondary amine (PSA) (particle size 50  $\mu$ m), Florisil (particle size 200  $\mu$ m, pestanal), octadecylsilyl packing (C<sub>18</sub>) (particle size 12  $\mu$ m), and graphitized carbon black (GCB) (particle size 45  $\mu$ m) were obtained from Supelco (Sigma–Aldrich Corp.). Diatomaceous earth was purchased from Dionex (Sunnyvale, CA, USA)

Twenty MFDPHs were collected from 11 different places (Table 3). The four pesticide-free samples including *P. thomsonii* Benth., *P. cablin* Benth., *H. cordata* Thunb., and *D. opposita* Thunb. came from Meishan, Sichuan; Nantong, Jiangsu; Yibin, Sichuan; and Dujiangyan, Sichuan, respectively. They were dried in a universal oven with forced convection (FD115, Tuttlingen, Germany) at 40°C for 2 days. The dried sample was ground using Sample Mill (model YF102,

Ruian Yongli Pharmacy Machinery Company, China). The botanical origins of the material were identified by Professor Yuecheng Li. The voucher specimens were deposited at Sichuan Provincial Institute for Food and Drug Control, Chengdu, Sichuan, China.

Pesticide standards (Table 1) were purchased from Dr. Ehrenstorfer (Augsburg, Germany), Fluka and Riedel-de-Haën (Sigma–Aldrich Corp.). The purities of the pesticide standards were from 96 to 99%. Individual pesticide stock solutions (1 mg/mL) were prepared in acetonitrile and kept at 0°C, protected from light. A mixed standard solution (0.02 mg/mL) was prepared by diluting an appropriate volume of each individual stock standard solution with acetonitrile. Internal standard triphenylphosphate (TPP) was purchased from Aldrich (Sigma–Aldrich Corp.). Individual stock internal standard solutions (0.01 mg/mL) were prepared in acetonitrile.

## 2.2 Sample preparation

## 2.2.1 Selective pressurized liquid extraction

SPLE was carried on an ASE 350 system (Dionex Company, Sunnyvale, CA, USA), fitted with 34 mL stainless steel cells. 5 g powder of sample with 500  $\mu$ L internal standard (TPP, 500 ng/mL) was mixed with diatomaceous earth in a proportion of 2:1. One cellulose filter was placed at the bottom of cell, 5 g of Florisil and 0.1 g of GCB, as cleanup adsorbents, were placed to the cell, and followed by the introduction of dispersed sample. Finally the empty space above the mixture was filled with diatomaceous earth (Fig. 1). The extraction cell was extracted under the optimum conditions: solvent, ethyl acetate; temperature, 120°C; static extraction time, 6 min; pressure, 1500 psi; flush volume, 50%; static cycle, 2. The extract was evaporated to near-dryness at 40°C using a gentle stream of nitrogen in a TurboVap LV concentration workstation (Hopkinton, MA, USA). The residue was transferred into a 5 mL volumetric flask, which was brought up to its volume with petroleum ether, and filtered through a 0.22 µm nylon membrane filter (Tianjin Jinteng Co., Ltd., China) before GC-MS/MS analysis.

# 2.2.2 PLE and gel permeation chromatography cleanup

Sample preparation was performed on an ASE 350 system and a fully automated GPC ULTRA System (LCTech, Bahnweg, Germany) as described by Wu et al. [10]. In brief, 5 g powder with 500  $\mu$ L internal standard was mixed with diatomaceous earth in a proportion of 2:1 and transferred into cells. The extraction procedure was the same as in Section 2.2.1 (without sorbents). The residue was dissolved in 10 mL cyclohexane–ethyl acetate (1:1, v/v) for injection into GPC system.

The cleanup condition of GPC system: mobile phase was cyclohexane–ethyl acetate (1:1, v/v) in isocratic mode.

	CI	lass	Retention time (min)	1 ime window	Dwell time (ms)	Precursor ions (1) <sup>a)</sup>	Product ions	Collide energy (eV)	Product ions	Collide energy (eV)	Precursor ions (2)	Product ions	Collide energy (eV)
2         Methamidophos         0P         5814         2         70         1410           3         Dichloross         0P         6002         2         70         1250           6         Nevinplos         0P         6002         3         70         1250           7         Netrolearbit         CAR         9,440         4         30         1260           8         Proprocarbit         CAR         9,440         4         30         1260           11         Promethoate         CAR         9,440         4         30         1260           11         Procate         CAR         9,440         4         30         1260           12         Dimonectophos         CP         10,739         5         40         2261           13         Carbofuran         CP         11,219         6         15         1640           14         Quintozene         CC         11,323         7         40         2261           14         Quintozene         CC         11,323         7         40         260           15         Diazinon         Carbofuran         CC         11,323         7 <t< td=""><td>0</td><td>AR</td><td>3.977</td><td>-</td><td>150</td><td>105.0</td><td>88.1</td><td>5</td><td>58.1</td><td>25</td><td></td><td></td><td></td></t<>	0	AR	3.977	-	150	105.0	88.1	5	58.1	25			
3         Dichlorvos         0P         6.002         2         70         185.0           7         Merolearb         CAR         9.373         3         70         127.0           8         Netrolearb         CAR         9.373         3         70         126.0           9         Sufforep         CAR         9.374         4         30         110.0           9         Sufforep         CAR         9.734         4         30         126.0           11         Phorate         CP         9.734         4         30         110.0           12         Dimethoate         CP         10.724         5         40         27.0           13         Carbofuran         CA         11.32         6         15         160.0           14         B-BHC         CC         11.32         6         15         160.0           17         Fonofora         CA         11.33         7         40         27.0           17         Fonofora         CA         11.33         7         40         25.6           18         Diarinor         CC         11.422         6         15         160.0	dophos 0	Ч	5.814	2	70	141.0	95.0	5	80.0	25			
4         Mevinphos         0P         8.002         3         70         127.0           7         Mevinphos         CAR         8.308         3         70         108.0           7         Metolearb         CAR         9.784         4         30         108.0           8         Propoxur         CAR         9.784         4         30         108.0           10         Monorotophos         0P         0.560         5         40         22.1           11         Phorate         0P         0.566         5         40         22.6           12         Dimethoate         0P         10.566         5         40         22.6           13         Carbofuran         0P         10.724         5         40         22.6           14         Phorate         0P         10.724         5         40         22.6           14         Phorate         0P         10.724         5         40         22.6           15         Dimetoration         0P         11.233         7         40         26.6           16         Unitorate         0P         11.733         7         40         26.6	os o	Ч	6.002	2	70	185.0	93.0	15	109.0	15			
5         Metalcarb         CAR $8.378$ 3         70         1080           7         Omethoate         0         9.670         4         30         1560           8         Proporcarb         0         9.670         4         30         1560           9         Sulfotep         0         0         0.022         5         40         22.11           11         Proporcarb         0         0         0.0724         5         40         22.11           11         Proporcarb         0         10.266         5         40         22.11           11         Protorate         0         10.724         6         15         164.0           12         Dimetorate         0         11.422         6         15         164.0           13         Garbofuran         0         0         11.422         6         15         164.0           14 $2.9HC         0.0C         11.342         7         40         23.69           16         Unitozente         0         11.219         6         15         164.0           16         Dinetorotacon         0         11.323     $	0 so	٩	8.002	ŝ	70	127.0	109.0	10			192.0	127.0	10
6         Isoprocarb         CAR         9.140         4         30         1560           7         Omethoate         0P         9.570         4         30         1560           9         Sufforearb         0P         9.570         4         30         1560           1         Propoxur         CAR         9.784         4         30         1560           11         Phorate         0P         10.526         5         40         22.1           12         Dimethoate         0P         10.566         5         40         22.0           13         Carbotrate         0P         11.719         6         15         164.0           14         p-BHC         0C         11.422         6         15         164.0           15         Unintozene         0P         11.793         7         40         265.0           16         Lindane         0C         11.422         6         15         164.0           16         Lindane         0C         11.422         6         15         265.0           17         Fontofor         11.422         6         15         265.0           <	rb	AR	8.378	с С	70	108.0	77.1	25	89.1	25			
7         0methoate         0P         9670         4         30         1660           8         Propoxur         CAR         9.784         4         30         100           9         Nonocrotophos         0P         10.502         5         40         120           11         Phorate         0P         10.502         5         40         120           12         Dimethoate         0P         10.502         6         15         160           13         Carbofuran         0P         10.56         5         40         2560           14         Dimethoate         0P         11.219         6         15         1610           15         Guintozene         0P         11.322         6         15         1610           16         Lindane         0C         11.323         6         15         1610           16         Duintozene         0C         11.323         7         40         2650           17         Duintozene         0C         11.363         7         40         2650           21         Duintozene         0C         11.363         7         40         2650	rb C.	AR	9.140	4	30	136.0	121.0	9			121.0	103.0	10
8         Propoxur         CAR         9.784         4         30         100           10         Monocrotophas         0P         0.562         5         40         22.1           11         Phorate         0P         10.565         5         40         26.1           12         Dimethoate         0P         10.266         5         40         26.1           13         Carbofuran         CAR         11.219         6         15         164.0           14         P.BHC         0C         11.348         6         15         26.9           15         Unintozene         0C         11.342         6         15         26.9           16         Diazinon         0P         11.351         6         15         26.9           17         Fonofos         0P         11.342         7         40         26.1           18         Diazinon         0P         11.342         7         40         26.9           21         Iprobanization         0P         11.342         7         40         26.1           22         Pentospinon         0P         11.342         1P         26.1         26.1 </td <td>ite 0</td> <td>٩</td> <td>9.670</td> <td>4</td> <td>30</td> <td>156.0</td> <td>110.0</td> <td>10</td> <td>79.0</td> <td>25</td> <td></td> <td></td> <td></td>	ite 0	٩	9.670	4	30	156.0	110.0	10	79.0	25			
9         Sufforep         0P         10.502         5         40         22.1           11         Promate         0P         10.266         5         40         22.1           12         Dimethose         0P         10.266         5         40         22.1           13         Carbofuran         0P         11.319         6         15         164.0           14 $\beta$ -BHC         0C         11.348         6         15         164.0           15         Quintozene         0C         11.342         6         15         180.0           16         Lindane         0C         11.342         7         40         266.0           17         Fondors         0C         11.342         7         40         265.0           17         Fondors         0C         11.342         7         40         266.0           18         Diazinon         0C         11.342         7         40         265.0           18         Diazinon         0C         11.342         7         40         265.0           21         Pronotization         0C         11.342         7         40         265.0	3	AR:	9.784	4	30	110.0	92.0	10	82.0	8	152.0	110.0	9
10         Monocrotophos         0P         10.566         5         40         12.70           11         Phorate         0P         10.784         5         40         2601           12         Carbofuran         CAR         11.219         6         15         1640           13         Carbofuran         CA         11.219         6         15         1640           14         3-BHC         C         11.422         6         15         1610           17         40         2.660         0         11.713         7         40         2660           18         Diazinon         0         11.713         7         40         2660           19         Chlorophall         0         11.723         6         15         1610           20         5-BHC         0         11.713         7         40         2660           21         probenfos         0         11.733         7         40         2660           22         Pentohoalinine         0         11.733         10         27.340           23         Propenfos         0         11.863         17         40         2660     <	0	٩	10.502	5	40	322.1	146.0	30	265.8	5			
11         Phorate         0P         10.724         5         40         260.1           12         Dimethoate         0P         10.724         5         40         260.1           13         Carbfuran         0P         11.319         6         15         16.40           14 $\beta$ -BHC         0C         11.328         6         15         16.40           16         Uindane         0C         11.321         6         15         26.0           13         Fonofos         0C         11.328         7         40         26.0           19         Chloraholanil         0C         11.328         7         40         26.0           21         probentos         0C         11.333         7         40         26.0           22         Pentachloraniline         0C         12.343         10         27.09         35         204.0           23         Propentos         0C         13.321         10         20         26.0           23         Pentos         13.323         10         27         20         26.0           24         probentos         0C         13.323         10         <	otophos 0	٩	10.566	5	40	127.0	109.1	10	95.0	20			
12         Dimethoate         0P         11.086         6         15         12.50           13         Carbofuran         CAR         11.219         6         15         164.0           14 $9$ -BHC         0C         11.422         6         15         164.0           16         Unintozene         0C         11.422         6         15         164.0           17         Fondos         0C         11.422         6         15         266.0           18         Diazinon         0P         11.779         7         40         266.0           21         Propontos         0P         11.779         7         40         266.0           22         Pentachloroaniline         0C         11.942         7         40         266.0           23         Propontoaniline         0C         12.566         9         35         264.0           24         Methylparathion         0C         12.566         9         35         264.0           25         Heptachlor         0C         13.343         10         26         27.19           26         Methylparathion         0C         13.343         10	0	٩	10.724	2	40	260.1	74.8	10					
13         Carbofuran         CAR         11219         6         15         164.0           14 $\beta$ -BHC         0C         11.348         6         15         181.0           16         Uninozene         0C         11.348         6         15         181.0           17         Fonofos         0C         11.342         6         15         286.9           18         Diazinon         0P         11.342         7         40         284.0           20         S-BHC         0C         11.342         7         40         286.0           21         Iprobenfos         0P         11.342         7         40         286.0           21         Iprobenfos         0P         11.342         7         40         286.0           22         Pentachloroaniline         0C         12.206         9         35         204.0           23         Propanil         0C         12.376         9         36.0         27.19           24         Mettrylparathion         0P         13.343         10         20         27.19           25         Mettrylparathion         0P         13.343         10	ate 0	P	11.086	9	15	125.0	47.0	25	79.0	5			
14 $\beta$ -BHC         0C         11.348         6         15 <b>181.0</b> 16         Uuntozene         0C         11.422         6         15 <b>236.9</b> 17         Fonofos         0C         11.551         6         15 <b>236.9</b> 18         Diazinon         0P         11.793         7         40 <b>246.0</b> 21         Iprobenfos         0C         11.863         7         40 <b>246.0</b> 21         Iprobenfos         0C         11.863         7         40 <b>246.0</b> 22         Pentachloroaniline         0C         11.863         7         40 <b>265.0</b> 23         Propani         0C         11.833         10         22 <b>204.0</b> 24         Methylparathion         0C         13.321         10         20 <b>265.0</b> 25         Metalaxyl         0T         13.333         10         20 <b>271.9</b> 26         Metalaxyl         0T         13.343         10         20 <b>265.0</b> 26         Methylparathion         0T         13.343         <	an C.	AR	11.219	9	15	164.0	149.0	10	103.9	15			
15         Quintozene         0C         11.422         6         15         236.9           17         Fondos         0         11.51         6         15         180.9           18         Diazinon         0         11.551         6         15         180.9           19         Chorthalonil         0         11.883         7         40         246.0           21         Iprobentos         0         11.942         7         40         265.9           22         Pentachloraniline         0C         11.942         7         40         265.0           23         Propanil         0C         12.284         8         70         161.0           24         Methylparathion         0C         12.566         9         35         26.0           24         Methylparathion         0C         13.343         10         20         27.19           25         Heptachlor         0C         13.343         10         29         26.0           24         Methylparathion         0F         13.343         10         20         27.19           27         Pintholos         0F         13.343         10	Ō	C	11.348	9	15	181.0	145.0	15	109.0	30	219.0	183.0	10
16         Lindane         0C         11.51         6         15         180.9           17         Fonofos         0         11.779         7         40         246.0           18<	ne 0	C	11.422	9	15	236.9	142.9	30	118.9	25			
17         Fonofos         0P         11.779         7         40 <b>246.0</b> 18         Diazinon         0P         11.863         7         40 <b>246.0</b> 20         5-BHC         0C         11.942         7         40 <b>265.0</b> 21         probentos         0C         11.942         7         40 <b>265.0</b> 22         Pentachloroaniline         0C         12.284         8         70 <b>181.0</b> 23         Propanil         0C         12.709         9         35 <b>265.0</b> 24         Methylparathion         0C         13.343         10         20 <b>261.0</b> 26         Methylparathion         0C         13.343         10         20 <b>263.0</b> 27         Propanil         0C         13.530         10         20 <b>263.0</b> 27         Propanil         0C         13.533         10         20 <b>263.0</b> 27         Pithylparathion         0C         13.533         10         20 <b>263.0</b> 27         Pithylparathion         0C         14.690	Ō	C	11.551	9	15	180.9	145.0	12	109.0	30	218.8	183.0	5
18         Diazinon         0P         11.863         7         40         304.0           19         Chlorothalonil         0C         11.942         7         40         265.9           20 $\delta$ -BHC         0C         11.942         7         40         265.0           21         Iprobentos         0C         12.266         9         35         204.0           22         Pentachloroaniline         0C         12.709         9         35         265.0           23         Propanil         0C         13.021         10         20         263.0           24         Methylparathion         0C         13.343         10         20         263.0           27         Propanil         0C         13.343         10         20         263.0           27         Pitmiphos-methyl         0T         13.530         10         20         263.0           28         Mathylparathion         0T         14.487         12         161.0         263.0           29         Mathon         0T         14.487         12         16         273.0           29         Mathylparathion         0C         14.487 <t< td=""><td>0</td><td>Ч</td><td>11.779</td><td>7</td><td>40</td><td>246.0</td><td>109.1</td><td>16</td><td>137.0</td><td>5</td><td>137.0</td><td>109.0</td><td>5</td></t<>	0	Ч	11.779	7	40	246.0	109.1	16	137.0	5	137.0	109.0	5
19         Chlorothaloni         0C         11.942         7         40 <b>265.0</b> 20 $\delta$ -BHC         0C         12.566         9         35 <b>204.0</b> 21         Iprobenfos         0C         12.566         9         35 <b>206.0</b> 23         Pentachloroaniline         0C         12.566         9         35 <b>265.0</b> 24         Methylparathion         0C         13.021         10         20 <b>71.9</b> 25         Heptachlor         0C         13.375         10         20 <b>265.0</b> 27         Primiphos-methyl         0T         13.3576         10         20 <b>271.9</b> 28         Methyl-pentachlorophenyl sulfide         0C         14.817         11         70 <b>266.0</b> 29         Malathion         0P         14.83         12         70 <b>305.2</b> 31         Aldrin         0P         14.83         12         70 <b>266.0</b> 31         Aldrin         0P         14.83         12         70 <b>296.0</b> 31         Aldrin         0P         <	0	Ч	11.863	7	40	304.0	179.0	10					
20 $\delta$ -BHC         0C         12.284         8         70 <b>181.0</b> 21         Iproberfos         0P         12.566         9         35 <b>204.0</b> 22         Pentachloroaniline         0C         12.709         9         35 <b>205.0</b> 23         Propanil         0C         13.021         10         20 <b>161.0</b> 24         Methylparathion         0C         13.343         10         20 <b>263.0</b> 25         Heptachlor         0C         13.343         10         20 <b>261.0</b> 26         Methylparathion         0P         13.343         10         20 <b>263.0</b> 27         Primiphos-methyl         0T         13.550         10         20 <b>261.0</b> 29         Methyl-pentachlorophenyl sulfide         0C         14.487         11         70 <b>296.0</b> 21         Nethyl-pentachlorophenyl sulfide         0C         14.487         12         15 <b>278.0</b> 30         Chlorpyrifos         0P         14.487         12         15 <b>278.0</b> 31         Aldr	alonil 0	C	11.942	7	40	265.9	133.0	40	168.0	25			
21         Iproberifos         0P         12.566         9         35         204.0           23         Pentachloroaniline         0C         12.709         9         35         265.0           24         Methylparathion         0C         13.021         10         20         161.0           25         Heptachlor         0C         13.576         10         20         263.0           26         Methylparathion         0P         13.576         10         20         265.0           27         Pirimiphos-methyl         0T         13.576         10         20         265.0           28         Methyl-pentachlorophenyl sulfide         0C         14.091         11         70         296.0           29         Malathion         0P         14.690         12         70         296.0           30         Chlorpyrifos         0P         14.690         12         15         234.0           31         Aldrin         0P         14.690         12         15         240.0           32         Fenthion         0P         14.690         12         15         278.0           33         Isocarbophos         0P         <	Ō	с С	12.284	80	70	181.0	145.0	15	109.0	30	219.0	183.0	10
22       Pentachloroaniline       0C $12.709$ 9       35 <b>265.0</b> 23       Propanil       0C $13.021$ $10$ 20 $161.0$ 24       Methylparathion       0P $13.343$ $10$ 20 $233.0$ 25       Heptachlor       0C $13.376$ $10$ 20 $233.0$ 26       Methylparathion       0P $13.576$ $10$ $20$ $233.0$ 26       Methyl-pentachlorophenyl sulfide       0C $13.576$ $10$ $20$ $231.0$ 27       Pirimiphos-methyl       0P $14.091$ $11$ $70$ $296.0$ 29       Methyl-pentachlorophenyl sulfide       0C $14.487$ $12$ $70$ $296.0$ 30       Chlorpyrifos       0P $14.487$ $12$ $70$ $296.0$ 31       Aldrin       0P $14.487$ $12$ $70$ $296.0$ 33       Chlorpyrifos $0P$ $14.487$ $12$ $70$ $296.0$ 340 $714.04$ $11$ $70$ $297.04$	0 0	٩	12.566	6	35	204.0	91.1	10	122.0	10	204.0	171.0	2
23       Propanil       0C       13.021       10       20       161.0         24       Methylparathion       0P       13.343       10       20       263.0         25       Heptachlor       0C       13.576       10       20       263.0         26       Methylparathion       0P       13.576       10       20       26.0         27       Pirimiphos-methyl       0T       13.530       10       20       26.0         27       Pirimiphos-methyl       0P       14.091       11       70       296.0         29       Methyl-pentachlorophenyl sulfide       0C       14.487       12       15       314.0         30       Chlorpyrifos       0P       14.487       12       70       296.0         31       Aldrin       0P       14.487       12       70       265.0         31       Aldrin       0P       14.480       12       70       266.0         32       Fenthion       0P       14.480       12       70       266.0         33       Latarin       0P       14.480       12       70       266.0         33       Isocarbophos       0P <td< td=""><td>oroaniline</td><td>C</td><td>12.709</td><td>6</td><td>35</td><td>265.0</td><td>194.0</td><td>24</td><td>158.0</td><td>40</td><td>194.0</td><td>165.0</td><td>40</td></td<>	oroaniline	C	12.709	6	35	265.0	194.0	24	158.0	40	194.0	165.0	40
24       Methylparathion       0P       13.343       10       20       263.0         25       Heptachlor       0C       13.576       10       20       21.9         26       Metalaxyl       0T       13.576       10       20       21.9         27       Pirimiphos-methyl       0T       13.530       10       20       206.0         28       Methyl-pentachlorophenyl sulfide       0C       14.204       11       70       296.0         29       Malathion       0P       14.487       12       15       173.1         30       Chlorpyrifos       0P       14.690       12       15       246.0         31       Aldrin       0P       14.690       12       15       263.0         31       Aldrin       0P       14.690       12       15       263.0         33       Isocarbophos       0P       14.690       12       15       263.0         33       Isocarbophos       0P       14.690       12       15       263.0         34       0P       15.071       12       15       278.0       263.0         35       Phenthoate       0P       16.462 <td>Ō</td> <td>C</td> <td>13.021</td> <td>10</td> <td>20</td> <td>161.0</td> <td>98.8</td> <td>40</td> <td>89.9</td> <td>40</td> <td></td> <td></td> <td></td>	Ō	C	13.021	10	20	161.0	98.8	40	89.9	40			
25       Heptachlor       0C       13.576       10       20 <b>271.9</b> 26       Metalaxyl       0T       13.630       10       20 <b>206.0</b> 27       Pirimiphos-methyl       0T       13.630       10       20 <b>206.0</b> 28       Methyl-pentachlorophenyl sulfide       0C       14.204       11       70 <b>305.2</b> 29       Malathion       0P       14.487       12       15 <b>173.1</b> 30       Chlorpyrifos       0P       14.690       12       15 <b>26.0</b> 31       Aldrin       0P       14.690       12       15 <b>26.0</b> 31       Aldrin       0P       14.690       12       15 <b>263.0</b> 32       Fenthion       0P       14.690       12       15 <b>263.0</b> 33       Isocarbohos       0P       15.071       12       15 <b>263.0</b> 34       Bromophos-methyl       0P       15.071       12       15 <b>263.0</b> 35       Phenthoate       0P       15.071       12       15 <b>274.0</b> 36       Procymidone       0	arathion 0	٩	13.343	10	20	263.0	109.1	15	127.0	9	263.0	246.0	2
26         Metalaxyl         0T         13.530         10         20 <b>206.0</b> 27         Pirimiphos-methyl         0P         14.091         11         70 <b>305.2</b> 28         Methyl-pentachlorophenyl sulfide         0C         14.204         11         70 <b>305.2</b> 29         Malathion         0P         14.487         12         15 <b>173.1</b> 30         Chlorpyrifos         0P         14.690         12         15 <b>173.1</b> 31         Aldrin         0P         14.690         12         15 <b>314.0</b> 31         Aldrin         0C         14.690         12         15 <b>263.0</b> 32         Fenthion         0P         14.690         12         15 <b>263.0</b> 33         Isocarbophos         0P         15.071         12         15 <b>330.9</b> 34         Bromophos-methyl         0P         15.071         12         15 <b>360.0</b> 35         Phenthoate         0P         15.071         12         15 <b>360.0</b> 36         Procynidone         0P	lor 0	с С	13.576	10	20	271.9	236.8	25	116.9	40	274.0	239.0	20
27       Pirimiphos-methyl       0P       14.091       11       70 <b>305.2</b> 28       Methyl-pentachlorophenyl sulfide       0C       14.204       11       70 <b>296.0</b> 29       Malathion       0P       14.487       12       15 <b>173.1</b> 30       Chlorpyrifos       0P       14.487       12       15 <b>314.0</b> 31       Aldrin       0C       14.690       12       15 <b>314.0</b> 32       Fenthion       0C       14.690       12       15 <b>265.0</b> 33       Locarbophos       0C       14.690       12       15 <b>278.0</b> 34       Bromophos-methyl       0P       14.803       12       15 <b>278.0</b> 34       Bromophos-methyl       0P       15.071       12       15 <b>278.0</b> 35       Phenthoate       0P       15.363       12       15 <b>330.9</b> 36       Procymidone       0P       15.363       12       330.9 <b>274.0</b> 37       trans-Chlordane       0C       16.462       13       30 <b>233.0</b> 37 $\alpha$ -En	.0	IT	13.630	10	20	206.0	105.2	25	132.0	10			
28       Methyl-pentachlorophenyl sulfide       0C       14.204       11       70 <b>296.0</b> 29       Malathion       0P       14.487       12       15       173.1         30       Chlorpyrifos       0P       14.487       12       15       713.1         31       Aldrin       0P       14.690       12       15       24.0         31       Aldrin       0C       14.690       12       15       26.30         32       Fenthion       0P       14.690       12       15       26.30         33       Isocarbophos       0P       14.803       12       15       278.0         34       Bromophos-methyl       0P       15.071       12       15       278.0         35       Phenthoate       0P       15.363       12       15       230.9         36       Procymidone       0P       16.368       13       30       274.0         37       trans-Chlordane       0C       16.462       13       30       274.0         37       trans-Chlordane       0C       17.274       14       40       241.0         38 $\rho/r$ -DDE       0C	os-methyl 0	٩	14.091	11	70	305.2	180.2	5	289.7	10			
29       Malathion       0P $14.487$ $12$ $15$ $173.1$ 30       Chlorpyrifos       0P $14.487$ $12$ $15$ $314.0$ 31       Aldrin       0C $14.690$ $12$ $15$ $263.0$ 32       Fenthion       0C $14.690$ $12$ $15$ $263.0$ 33       Isocarbophos       0P $14.803$ $12$ $15$ $278.0$ 34       Bromophos-methyl       0P $15.071$ $12$ $15$ $278.0$ 35       Phenthoate       0P $15.363$ $12$ $15$ $330.9$ 36       Procymidone       0P $16.368$ $13$ $30$ $274.0$ 37       trans-Chlordane       0C $16.853$ $13$ $30$ $274.0$ 38 $\alpha$ -Endosulfan       0C $17.274$ $14$ $40$ $241.0$ 39 $p.p'-DDE$ 0C $17.238$ $14$ $40$ $241.0$	entachlorophenyl sulfide 0	C	14.204	11	70	296.0	262.7	15	280.6	15			
30       Chlorpyrifos       0P       14.690       12       15 <b>314.0</b> 31       Aldrin       0C       14.690       12       15 <b>263.0</b> 32       Fenthion       0C       14.690       12       15 <b>263.0</b> 33       Isocarbophos       0P       14.803       12       15 <b>278.0</b> 34       Bromophos-methyl       0P       15.071       12       15 <b>278.0</b> 35       Phenthoate       0P       15.363       12       15 <b>330.9</b> 35       Phenthoate       0P       16.368       13       30 <b>274.0</b> 36       Procymidone       0T       16.462       13       30 <b>273.0</b> 37       trans-Chlordane       0C       17.274       14       40 <b>241.0</b> 38 $\alpha$ -Endosulfan       0C       17.274       14       40 <b>241.0</b> 39 $p,p'-DDE$ 0C       17.838       14       40 <b>241.0</b>	u u	٩	14.487	12	15	173.1	0.06	15	117.1	5	173.0	127.0	4
31       Aldrin       0C       14.690       12       15       263.0         32       Fenthion       0P       14.803       12       15       278.0         33       Isocarbophos       0P       14.803       12       15       278.0         34       Bromophos-methyl       0P       15.071       12       15       230.9         35       Phenthoate       0P       15.363       12       15       330.9         36       Procymidone       0P       16.368       13       30       274.0         37       trans-Chlordane       0T       16.462       13       30       283.0         37       trans-Chlordane       0C       17.274       14       40       241.0         38 $\alpha$ -Endosulfan       0C       17.274       14       40       241.0         39 $p,p'-DDE$ 0C       17.838       14       40       241.0	ifos 0	Р	14.690	12	15	314.0	257.8	10	285.9	5			
32       Fenthion       0P       14.803       12       15 <b>278.0</b> 33       Isocarbophos       0P       15.071       12       15 <b>136.0</b> 34       Bromophos-methyl       0P       15.071       12       15 <b>330.9</b> 35       Phenthoate       0P       15.363       12       15 <b>330.9</b> 36       Procymidone       0P       16.368       13       30 <b>274.0</b> 37       trans-Chlordane       0T       16.462       13       30 <b>233.0</b> 37       trans-Chlordane       0C       16.853       13       30 <b>233.0</b> 38 $\alpha$ -Endosulfan       0C       17.274       14       40 <b>241.0</b> 39 $p,p'$ -DDE       0C       17.838       14       40 <b>241.0</b>	Ō	C	14.690	12	15	263.0	193.0	30	191.0	30	298.0	263.0	8
33       Isocarbophos       0P       15.071       12       15       136.0         34       Bromophos-methyl       0P       15.363       12       15       330.9         35       Phenthoate       0P       15.368       13       30       274.0         36       Procymidone       0T       16.368       13       30       274.0         36       Procymidone       0T       16.462       13       30       283.0         37       trans-Chlordane       0C       16.853       13       30       273.0         38 $\alpha$ -Endosulfan       0C       17.274       14       40       241.0         39 $p,p'$ -DDE       0C       17.838       14       40       241.0	0	٩	14.803	12	15	278.0	109.1	20	245.0	10			
34       Bromophos-methyl       0P       15.363       12       15       330.9         35       Phenthoate       0P       16.368       13       30       274.0         36       Procymidone       0T       16.462       13       30       283.0         37       trans-Chlordane       0T       16.462       13       30       283.0         37       trans-Chlordane       0C       16.853       13       30       283.0         38 $\alpha$ -Endosulfan       0C       17.274       14       40       241.0         39 $p_{\rho}$ <sup>o</sup> -DDE       0C       17.838       14       40       246.0	phos 0	٩	15.071	12	15	136.0	108.0	14			289.0	136.0	9
35         Phenthoate         0P         16.368         13         30 <b>274,0</b> 36         Procymidone         0T         16.462         13         30 <b>283.0</b> 37         trans-Chlordane         0C         16.853         13         30 <b>283.0</b> 37         trans-Chlordane         0C         16.853         13         30 <b>373.0</b> 38 $\alpha$ -Endosulfan         0C         17.274         14         40 <b>241.0</b> 39 $p_{,p}^{\prime}$ -DDE         0C         17.838         14         40 <b>246.0</b>	ios-methyl 0	٩	15.363	12	15	330.9	315.9	16	285.9	34	331.0	93.0	34
36         Procymidone         0T         16.462         13         30 <b>283.0</b> 37         trans-Chlordane         0C         16.853         13         30 <b>373.0</b> 38 $\alpha$ -Endosulfan         0C         17.274         14         40 <b>241.0</b> 39 $p_{,p}'$ -DDE         0C         17.838         14         40 <b>246.0</b>	ate 0	٩	16.368	13	30	274.0	121.1	10	93.0	15			
37         trans-Chlordane         0C         16.853         13         30         373.0           38 $\alpha$ -Endosulfan         0C         17.274         14         40         241.0           39 $p_{\mu}p'$ -DDE         0C         17.238         14         40         246.0	done 0	Τ	16.462	13	30	283.0	96.0	10	255.0	10	283.0	67.1	40
38 $\alpha$ -Endosulfan 0C 17.274 14 40 <b>241.0</b> 39 $p_{,p}'$ -DDE 0C 17.838 14 40 <b>246.0</b>	lordane 0	C	16.853	13	30	373.0	265.6	25	301.0	10			
39 <i>p</i> , <i>p</i> '-DDE 0C 17.838 14 40 <b>246.0</b>	ulfan 0	C	17.274	14	40	241.0	206.0	15	171.0	15			
	ō	C	17.838	14	40	246.0	176.0	30	211.0	20	248.0	176.0	30
40 Dieldrin 0C 17.882 14 40 <b>262.8</b>	Ō	C	17.882	14	40	262.8	193.2	30	227.7	25			

Peak No.	Pesticide	Chemical class	Retention time (min)	Time window	Dwell time (ms)	Precursor ions (1) <sup>a)</sup>	Product ions	Collide energy (eV)	Product ions	Collide energy (eV)	Precursor ions (2)	Product ions	Collide energy (eV)
41	Endrin	00	18.229	15	15	263.0	227.9	20	193.0	10			
42	β-Endosulfan	00	18.392	15	15	236.9	142.8	25	118.9	30			
43	<i>p,p</i> '-DDD	00	18.486	15	15	235.0	200.0	8	199.1	15	237.0	165.0	20
44	Oxadixyl	0T	18.496	15	15	233.1	146.1	5	118.0	25			
45	<i>a,p</i> '-DDT	00	18.516	15	15	235.0	165.0	20	199.1	20	237.0	165.0	20
46	Carbophenothion	OP	18.823	15	15	157.0	45.0	15	122.1	10			
47	<i>p,p</i> '-DDT	00	18.937	15	15	235.0	165.0	20	199.1	20	237.0	165.0	20
	TPP	S	19.150	16	25	326.1	215.1	30	170.0	30			
48	Fenpropathrin	РҮВ	19.665	16	25	265.0	210.0	15	89.0	35			
49	Tetradifon	00	19.828	16	25	353.7	159.0	10	159.0	10			
50	λ-Cyhalothrin	РҮВ	20.145	16	25	197.0	161.0	10	171.0	15	181.1	152.1	30
51	Coumaphos	OP	20.897	17	25	362.1	109.0	15	225.9	15			
52	Esfenvalerate	PYR	23.031	17	25	125.0	89.1	25	99.2	25	419.0	125.0	30



**Figure 1.** Packing of stainless steel cell in the developed SPLE method. The contents of developed SPLE including the mixture of sample and diatomaceous (A), cellulose filter (B), graphitized carbon black (C), and Florisil (D).

Bio-Beads S-X3 (40 g) was packed in the column (300 mm  $\times$  10 mm id). The flow rate was 5 mL/min. The fraction from 8 to 20 min was collected. The collected GPC fraction was on-line evaporated to 5 mL and subjected to analysis.

### 2.2.3 Solid phase extraction

SPE was performed on GX-274 ASPEC (Gilson, Middleton, USA) as described by Yang et al. [8]. In brief, the mixture of 5 g sample with 500  $\mu$ L internal standard and 20 mL acetonitrile was vortexed for 2 min, then added 5 g sodium chloride and vortexed for 2 min again. The mixture was centrifuged for 5 min at 4000 rpm, and then 10 mL supernatant was evaporated at 40°C until nearly dryness for cleanup.

The residue was dissolved with 2 mL acetonitrile–toluene (3:1, v/v) and loaded onto a PestiCarb/NH<sub>2</sub> mixed phase SPE column (500 mg GCB and 500 mg NH<sub>2</sub>, 6 mL, Agela, China). The extract solution was passed through the columns at the flow rate of 1 mL/min. The retained analytes were eluted with 25 mL of acetonitrile–toluene (3:1, v/v) at 1 mL/min. The eluent was collected and evaporated until nearly dryness. Finally, the residues were redissolved with 2.5 mL acetone.

## 2.2.4 Solid phase microextraction

SPME was performed using manual sampling device from Supelco (Bellefonte, PA, USA) and it consisted of a holder assembly and a replaceable 100  $\mu$ m thickness polydimethylsiloxane fibers (PDMS). The extraction condition was described by Campillo et al. [15]. In brief, 5 g powder with 500  $\mu$ L internal standard was immersed in 50 mL water for 3 min. Thirty-five milliliters of the infusion and 15 mL of phosphate buffer solution were placed in 50 mL vial, which was sealed by cap after adding the magnetic stir bars. With stirring set at 1400 rpm, the PDMS fiber was totally immersed in sample solution for 40 min at 90°C. In the desorption process, the

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fiber was inserted into GC system of splitless injection mode at 280°C for 7 min. The fiber was then kept in injector for 10 min after opening the split valve, to ensure total desorption and no memory effects.

## 2.3 GC-MS/MS analysis

GC-MS/MS was carried on an Agilent 7890A gas chromatograph coupled with 7000B triple quadrupole mass spectrometer (Waldbronn, Germany). Injection was carried out using a CTC PAL sample injector and injection volume was 1 µL. All analytes were separated on a HP-5 MS UI column (20 m imes 0.18 mm id, 0.18  $\mu$ m) and a restrictor column (1.3 m imes0.180 mm id., 0.18 µm) (Agilent Technologies). Three-way splitter with analytical column in and restrictor out to mass spectrometer was used, and helium pressure was provided by auxiliary electronic pressure control (Aux EPC) at 4 psi (Supporting Information Fig. S1). The oven temperature program was: initial temperature was set at 80°C (hold 1 min), to 186°C at 12°C/min, to 190°C at 3.5°C/min, to 210°C at 4°C /min, to 280°C at 38°C/min, and hold for 6 min at 280°C. High-purity helium gas (>99.999%) was used as carrier gas with the flow rate of 1 mL/min. Backflush parameters: hold time, 5 min; inlet pressure, 1 psi; three-way splitter pressure, 60 psi; oven temperature, 280°C.

The mass spectrometer operated in electron ionization mode at 70 eV. The analyses were performed in multiple reactions monitoring (MRM) mode (Table 1). The GC–MS transfer line and mass source temperature were 300 and 230°C, respectively. The scanned mass range was set at 45–500 m/z.

## 2.4 Linearity, LOD, and LOQ

Stock solution containing 52 pesticides standards and TPP were diluted to appropriate concentrations using matrices extracted from blank MFDPHs for the construction of calibration curves. The mixed standard solutions of seven concentrations were injected in duplicates, and then the calibration curves were constructed by plotting the ratios of the peak areas of each standard to IS versus the concentration of each analyte. The LOD and LOQ under the GC-MS/MS conditions were determined at an S/N of about 3 and 10, respectively.

## 2.5 Precision and repeatability

Intra- and inter-day variations were chosen to determine the precision of the developed method. For intra-day precision, the mixed standards solution (approx. 0.1  $\mu$ g/mL) was analyzed for six replicates within 1 day, while for inter-day precision test, the solution was examined in duplicates for consecutive 6 days. Variations were expressed by RSD.

To confirm repeatability, 5 g of MFDPHs was extracted and purified by SPLE method into five replicates and determined by GC-MS/MS system as mentioned above. The RSD value was calculated as a measurement of method repeatability.

## 2.6 Accuracy

Pesticide-free samples including *P. thomsonii*, *P. cablin*, *H. cordata*, and *D. opposite* monitored by our laboratory were used as the blank matrix for spiking to determine recoveries. The recovery was used to evaluate the accuracy of the method and determine it at three different concentration levels (10, 50, and 200  $\mu$ g/kg). Three replicates were performed at each level. The percentage recoveries were calculated according to the following equation:

(total detected amount – original amount)  $\times$  100/added amount.

## 3 Results and discussion

## 3.1 Optimization of SPLE

### 3.1.1 Selection of extraction solvent

Polarity is one of the major factors that may influence extraction efficiency. In our work, four solvents including acetonitrile, ethyl acetate, n-hexane/acetone (1:1, v/v), and nhexane/ethyl acetate (4:1, v/v), were compared. PLE parameters were performed as described by Blasco et al [28]. When *n*-hexane/acetone or *n*-hexane/ethyl acetate were used as extraction solvent, the extraction efficiencies of dichlorvos, iprobenfos, and heptachlor are very low and recoveries of other pesticides are in the range of about 30-60% (Supporting Information Table S1). When acetonitrile or ethyl acetate was used as extraction solvent, the recoveries of most pesticide residues were increased significantly. However, the acetonitrile can extract more complex matrices from MFDPHs under the conditions of high temperature and pressure (Supporting Information Fig. S2). Therefore, ethyl acetate was chosen as extraction solvent in the SPLE.

### 3.1.2 Selection of sorbent

In order to achieve effective one step sample preparation, it is crucial to choose suitable sorbent for pesticide residue analysis. Four sorbents including Florisil, PSA,  $C_{18}$ , and GCB were investigated. According to previous reports, PSA and Florisil were usually used as the major sorbents in dispersive SPE for the cleanup step of pesticides in vegetables, fruits, and medicinal plants [29–31]. PSA can effectively remove saccharide, polar organic acids and lipids from food samples, while Florisil can preferentially absorb polar and low-fat components [32]. The  $C_{18}$  and GCB were usually used as auxiliary sorbents for pesticide analysis.



Figure 2. The typical total ion chromatograms of 52 pesticide residues were acquired by multiple reactions monitoring mode. Spiked Samples were performed by different methods including SPLE (A), PLE-GPC (B), SPE (C), and SPME (D).

Result showed that the extract was turbid when using PSA (0.1–5 g, six levels) alone. However, the extract became clear when the loading amount of Florisil (3–9 g, six levels) alone was >3 g. The loading amount of Florisil was >5 g; the matrix interference was not to be further reduced significantly. Therefore, 5 g Florisil was used as the major absorbent. Octadecylsilyl ( $C_{18}$ ) and GCB were used as additional sorbents to be studied. The  $C_{18}$  material can remove fat compound, but it fails to show good performance for removing the chromatographic interference and pigments. The ability of GCB is to remove planar molecules such as chlorophylls, carotiniods, and sterols. The mixture sorbents of 5 g Florisil and GCB (0.05–0.4 g) were studied at five levels. Results showed that the mixed sorbents of 5 g Florisil and

0.1 g GCB can produce clear extracts, clean chromatographic profiles, and better recoveries for the investigated pesticide residues (Supporting Information Fig. S3, Fig. 2A, Supporting Information Table S2). Therefore, 5 g Florisil and 0.1 g GCB were used as sorbents for SPLE procedure.

## 3.1.3 Optimization of SPLE parameters

The parameters including temperature (80, 90, 100, 110, 120, and 130°C), static extraction time (2, 4, 6, and 8 min), total flush volume (40, 50, and 60%), and number of cycles (1, 2, and 3) were studied by using univariate approach while other conditions were kept constant (temperature,  $100^{\circ}$ C; static extraction time, 4 min; flush volume, 40%, and one extraction

cycle). Fluid delivery pressure 1500 psi is a fixed parameter on ASE 350 instrument. Therefore, pressure was set at 1500 psi. The recovery of *P. thomsonii* spiked mixed standard at 50  $\mu$ g/kg level was used for evaluation of extraction efficiency. The optimization results are shown in Supporting Information Fig. S4. Considering the results, the conditions of the SPLE method proposed were temperature, 120°C; static extraction time, 6 min; flush volume, 50%; cycle, 2.

## 3.2 Comparison of SPLE, SPE, SPME, PLE-GPC, and QuEChERS

The extraction and cleanup are two important steps of sample preparation for the determination of trace pesticide residues. According to previous reports, SPE, SPME, and PLE-GPC methods were utilized to extract and clean up pesticides from different complicated matrices [8-11, 15]. In this study, the developed SPLE method was compared with SPE, SPME, and PLE-GPC. The performances of different approaches were evaluated by MRM chromatograms, S/N of investigated pesticides and recoveries. Figure 2 shows the MRM chromatograms of 52 pesticide residues extracted by different methods. Among these chromatograms, the response of SPLE is the strongest. The S/Ns of multiclass pesticides residues indicated that the sensitivities of the developed SPLE are higher than those of PLE-GPC, SPE, and SPME (Supporting Information Table S3). Table 2 shows that the recovery range of the developed SPLE is 65-121%, which is better than others. SPLE has the advantage of PLE, which can accelerate the extraction kinetics and force the solvent into matrix pores under high temperature and pressure condition. Therefore, it can provide good extraction performance. Meanwhile, the extracts of SPLE are clearer than PLE (Supporting Information Fig. S3). Comparing SPLE with PLE-GPC, SPE, and SPME, the major difference is that SPLE integrates the extraction and cleanup in one step. The sample preparation process is simplified, which leads to reduce the loss of preparation. Meanwhile, sample preparation time and organic solvent consumption are reduced, too (Supporting Information Table S4). In addition, QuEChERS method has attracted great attention for pesticide analysis studies, but the method is suitable for samples with more than 75% moisture [12, 16]. It has to be used for the dried root herbs, the sample amount may have to be reduced and water has to be added to make sample pores more accessible to the extraction solvent. In other words, the dry sample amount is reduced, which leads to decrease method sensitivity. However, SPLE method can directly extract pesticides from dried sample without moisture limit. The QuEChERS method was used to determine pesticide residues in the same P. thomsonii from Meishan, Sichuan and Yifeng, Jiangxi [33]. Results show that the contents of  $\lambda$ -Cyhalothrin extracted by QuEChERS method are lower than those of SPLE method. Therefore, the extraction performance of QuEChERS is lower than that of SPLE. In a word, SPLE is a quick, simple, and efficient sample preparation method and it could be a better choice for the pesticides analysis.

## 3.3 Optimization of GC-MS/MS

The relevant parameters including precursor ions, product ions, and collision energies were optimized to obtain optimal specificity and sensitivity. The mixed standard solution was infused by GC system into the mass spectrometer. After analyzing the full scan spectra, the precursor ion for every analyte was selected, and then subjected to collision energy voltages to generate MS/MS product ions. The choice of the precursor ion was rather based on selectivity than signal intensity. For most pesticides, ions could potentially serve as the precursor ion, but preferably ions at the higher mass range (m/z > 200) were chosen because this usually afforded the highest S/Ns for the selected product ions. Based on the confirmation of precursor ions, more than two product ions should be selected when using MS/MS analysis in accordance with relevant legislation [34]. In this work, two product ions resulting from fragmentation of one precursor ion or two product ions each resulting from two different precursor ions were monitored. But there were a few exceptions of pesticides, this was the case with phorate and diazinon, for which only one MRM transition could be recorded due to either poor intensity or insufficient specificity of the second transition.

Based on pesticides' MRM chromatogram, a timescheduled acquisition method was constructed. Finally, the developed method included 17 retention time windows, each comprising between one and seven MRM transitions. Start and end times were defined and scan time parameter was set for each segment, resulting in dwell times in the range of about between 15 and 150 ms for particular MRM transitions throughout the chromatographic run. The GC–MS/MS parameters are given in Table 1 and some typical chromatograms are shown in Fig. 2. Figure 2A shows that interfering substances (11–12 and 19–20 min) affected chromatographic separation, but the extracted ion chromatograms (EIC) could evade the problem of poor separation (Supporting Information Fig. S5).

### 3.3.2 Optimization of backflush column

Due to complex matrix of MFDPHs, the high boiling point compounds and dark brown residues will be accumulated in the liner of inlet and column head after hundreds of injections. Therefore, a backflush program was developed in the present study. Operation parameters are described in Section 2.3. Supporting Information Fig. S1 shows the diagram of column backflush system. Compared with traditional GC system, the column backflush system was added a three-way splitter coupled with electronic pressure control (EPC), and 1.3 m capillary column was used as restrictor column. When GC system was in the forward elution, the pressures of injection inlet, three-way splitter, and detector were 50 psi, 4 psi, and vacuum, respectively. The investigated compounds can pass through the inlet to MS/MS detector. The restrictor column material is the same as analytical column. Therefore, separation efficiency would not be affected by restrictor

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Table 2. Comparison of the recoveries of investigated pesticide residues using different preparation method (n = 5)

Recovery <sup>10</sup> RSD         Recovery (%)         RSD         Image: recovery (%)         RSD         Image: recovery (%)         RSD         Image: recovery (%)         RSD         Recovery (%)         RSD         Image: recovery (%)         RSD         Image: recovery (%)         RSD         Image: recovery (%)         RSD         Image: recovery (%)         RSD         <	Pesticide	SPLE		PLE-GPC		SPE		SPME	
Methomyl         10129         8.48         96.96         27.53         79.78         21.20            Methomylos         83.45         13.26         79.27         11.08         -		Recovery <sup>a)</sup> (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Methamidophos         83.45         12.26         79.27         11.08         -	Methomyl	101.29	8.48	86.96	27.53	79.78	21.20	_b)	_
Dichlorvos         65.08         44.8         64.620         23.56         40.22         21.2         -         -           Matolacab         103.30         5.81         81.48         0.56         -         -         -         -           Isaproarab         107.25         5.81         81.48         0.56         -         -         -         -           Softene         104.85         5.81         42.88         11.60         - </td <td>Methamidophos</td> <td>83.45</td> <td>13.26</td> <td>79.27</td> <td>11.08</td> <td>_</td> <td>-</td> <td>_</td> <td>_</td>	Methamidophos	83.45	13.26	79.27	11.08	_	-	_	_
Mevinphos         73.6         7.58         68.24         4.30         -         -         -         -           Isoprocarb         103.25         4.45         76.88         555         68.33         15.93         -         -           Comethoate         64.58         5.81         42.88         11.60         -         -         -         -           Sufferp         95.64         7.84         100.30         16.35         71.06         17.42         12.27         62.27           Phorate         95.16         7.89         75.47         14.40         94.08         -         -         -           Carbofuran         109.45         7.18         100.17         12.65         81.42         12.21         11.24         11.19           Omitozare         105.73         81.81         92.52         12.38         93.43         15.50         15.57         21.95           Carbofuran         107.08         7.52         103.30         44.34         15.50         86.4         12.21         11.41           Outrozare         105.06         6.02         75.39         19.35         64.34         15.50         12.41         14.42           Diarotanon	Dichlorvos	65.08	4.48	46.60	23.56	40.22	23.12	_	_
Metolanch         103.30         5.81         8.14.9         0.56         - </td <td>Mevinphos</td> <td>78.36</td> <td>7.58</td> <td>68.24</td> <td>4.30</td> <td>_</td> <td>_</td> <td>_</td> <td>_</td>	Mevinphos	78.36	7.58	68.24	4.30	_	_	_	_
isoprocarb         107.25         4.45         76.88         5.55         68.33         15.39         -         -           Propoxur         108.45         6.34         42.28         11.50         -         -         -           Sulfotep         96.64         7.84         100.30         16.35         71.66         17.42         122.73         6.82           Dimethoats         65.19         17.84         100.30         16.35         71.66         17.42         12.73         6.82           Dimethoats         016.65         7.89         75.47         14.40         84.08         7.06         -	Metolcarb	103.30	5.81	81.49	0.56	_	_	_	_
Ometholate         94.88         5.81         42.88         11.60         -         -         -         -           Propoxar         104.85         6.34         100.30         16.35         71.66         17.42         122.73         6.82           Monocrotophos         6.619         18.71         45.55         27.44         -	lsoprocarb	107.25	4.45	76.88	5.55	68.33	15.93	_	_
Propoxur         104.85         6.34         92.28         15.78         76.75         90.96         -         -         -         6.82           Sulfotap         95.64         7.84         100.30         16.35         71.06         17.42         122.73         6.82           Monocrotophos         65.19         97.74         14.07         61.31         16.66         107.42         12.73         6.82           Dimethoat         107.63         15.64         61.84         14.13         74.40         34.08         -	Omethoate	64.58	5.81	42.98	11.60	_	_	_	_
Sulfatep         95.64         7.84         10.00         16.35         71.06         17.42         122.73         6.82           Mone crotophos         65.19         19.71         45.35         27.49         - <t< td=""><td>Propoxur</td><td>104.85</td><td>6.34</td><td>92.28</td><td>15.78</td><td>76.75</td><td>30.96</td><td>_</td><td>_</td></t<>	Propoxur	104.85	6.34	92.28	15.78	76.75	30.96	_	_
$\begin{split} \begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	Sulfotep	95.64	7.84	100.30	16.35	71.06	17.42	122.73	6.82
Phorate96.167.8975.4714.0781.2116.66130.7427.13Dimethoate107.6311.5461.8414.1374.4034.08 $\beta$ -BhC115.523.1397.9219.0384.897.06112.6111.19Quintozane105.7381.8192.5412.887.06112.6111.19Quintozane11.334.9686.1721.9274.259.30155.5721.95Fondos105.066.0275.3319.3384.3515.68122.7419.43Chorotabloni79.963.2867.2125.6760.0414.48S-BHC111.753.9986.695.2863.7212.6410.5728.46Chorotabloni79.963.22102.2113.11Pentachloroaniline113.523.3252.480.3178.5517.47Pentachloroaniline11.5250.544.0810.0542.8114.83Propani11.126.25100.2713.11Methyloparathion82.8911.5265.0514.4910.5442.8114.83Propani11.123.1680.1919.4374.798.3229.749.42Methyloparathion92.8114	Monocrotophos	65.19	19.71	45.35	27.49	_	_	_	_
Dimethoate         107.63         11.54         61.84         14.13         74.40         34.08         -         -           Carboturan         109.45         7.18         100.17         12.85         81.42         77.67         112.61         11.19           Duintozene         105.73         8.18         92.54         12.88         79.16         13.28         68.68         15.67           Lindane         111.33         4.98         68.17         21.92         74.25         9.30         155.57         21.96           Fonofos         105.06         6.02         75.39         19.93         84.34         15.50         87.46         6.25           Diaxinon         107.08         7.52         103.06         14.82         68.85         15.68         122.74         19.43           Albrothonil         79.98         3.82         67.21         25.87         60.51         12.26         106.50         12.44         67.67         2.86           Propanil         111.23         6.25         100.72         13.11         -         -         -         -         -         -         -         -         -         -         -         -         -         -	Phorate	96.16	7.89	75.47	14.07	81.31	16.66	130.74	27.13
Carbohran109.457.18100.1712.8581.4217.27 $\beta$ -BHC115.523.1397.9219.0384.897.06112.6111.19Lindane11.334.9686.1721.9274.259.30155.5721.95Fondos105.066.0275.3319.9384.3415.5087.466.22Diazinon107.087.52103.0614.8268.8515.68122.7419.43Chiorothalonil79.963.2867.2125.6760.0414.48 $\delta$ -BHC111.753.9986.685.2863.7212.6108.9115.20Jprobenfo86.1814.73116.957.847.6517.47Methylparathion82.8911.5265.0514.4115.37Methylparathion82.8911.5265.0514.4115.378.30Methylparathion82.4911.5265.0514.4374.798.3229.749.42Motalaxyl101.596.4168.6911.0542.8114.83Propanil11.613.1680.1919.4374.798.3229.749.42Methyl-pertachlorophenyl sulfide11.613.1680.1919.4374.798.3229.749.42Matinion92	Dimethoate	107.63	11.54	61.84	14.13	74.40	34.08	_	_
Dep BHC         1152         3.13         97.92         19.03         84.89         7.06         112.61         11.19           Quintozene         105.73         8.18         92.54         12.68         79.16         13.28         68.68         156.57         21.95           Fonofos         105.06         6.02         75.39         19.33         84.34         15.50         87.46         62.25           Diazinon         107.08         7.52         103.06         14.82         68.85         15.68         122.74         19.43           Chorothalonil         79.96         3.28         67.21         25.67         60.04         14.48         - </td <td>Carbofuran</td> <td>109.45</td> <td>7 18</td> <td>100 17</td> <td>12.85</td> <td>81 42</td> <td>17 27</td> <td>_</td> <td>_</td>	Carbofuran	109.45	7 18	100 17	12.85	81 42	17 27	_	_
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$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		105.73	8 18	92 54	12.68	79.16	13.00	68 68	15.67
Lindunts 111.23 10.5 06 6.02 75.39 1939 44.34 15.50 87.46 6.25 15.01 107.08 7.52 103.06 14.82 68.55 15.68 122.74 19.43 16.50 107.08 7.52 103.06 14.82 68.55 15.68 122.74 19.43 5.8 67.71 25.67 60.04 14.48 5.8HC 111.75 3.99 86.69 5.28 63.72 12.26 108.91 15.20 19.70 19.70 14.52 3.22 52.48 0.31 76.55 17.47	Lindane	111 22	4.96	86 17	21 92	74.25	9.20	155 57	21.05
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Ennotas	105.06	6.02	75 39	19.92	84 34	15 50	87.46	6 25
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$ \begin{array}{c} \text{Chindminim} & 13.30 & 3.20 & 0.721 & 2.307 & 0.0.47 & 14.40 & - & - & - \\ Berneline of the set of $	Chlorothalanil	70.06	2.02	67.21	25.67	60.03	1// /0	122.74	13.43
orbit11.733.3330.033.2.005.7212.20106.5110.2.0110.2.01Pentachloroaniline113.523.3252.480.3178.5012.0446.7628.46Propanil111.236.25100.7213.11Heptachloroaniline113.523.3252.480.3178.5012.0446.7628.46Propanil111.236.25100.7213.11Heptachlor103.625.0584.0818.0676.975.9037.4230.52Metalaxyl101.596.4168.6911.0542.8114.83Pirminybos-methyl92.8114.84103.6613.4460.1212.12293.7232.78Methyl-pentachlorophenyl sulfide111.613.1680.1919.4374.798.3229.749.42Maltrion92.3112.34103.8617.1588.239.12132.386.94Aldrin113.245.0871.9118.4166.087.5740.4916.14Fenthion101.275.9481.3910.7178.8611.99208.3422.31Isocarbophos80.7712.69133.322.6765.836.8059.5024.83Procymidone111.254.90113.6912.2183.149.15109.5727.33Isocarbophos80.7712.69 </td <td></td> <td>79.90</td> <td>0.20 2.00</td> <td>07.21</td> <td>20.07</td> <td>62 72</td> <td>14.40</td> <td></td> <td>15 20</td>		79.90	0.20 2.00	07.21	20.07	62 72	14.40		15 20
problem60.1614.7.3110.357.3410.63517.47Pentachloroaniline113.523.3252.480.3178.5012.0446.7628.46Propanil111.236.25100.7213.11Methylparathion82.8911.5265.0514.9153.7718.30Primiphos-methyl101.596.4168.6911.0542.8114.83Primiphos-methyl92.8114.84103.6613.4460.1210.21293.7232.78Methyl-pentachlorophenyl sulfide111.613.1680.1919.4374.798.3229.749.42Malathion92.3112.34103.895.8061.5614.09Choroyrifos103.276.8490.6617.1588.239.12132.386.94Aldrin11.275.9481.3910.7178.661.9920.8322.31Isocarbophos80.7712.69133.322.6762.8715.32Bromophos-methyl104.084.2983.3513.265.806.8059.5024.83Phentoate89.418.5877.0513.1171.238.61107.9820.86Prozymidone111.254.90113.6912.2183.149.15109.5727.33trans_chlordane111.69 </td <td>0-DIL</td> <td>06 10</td> <td>3.99 14 70</td> <td>00.09</td> <td>J.ZO</td> <td>03.72</td> <td>12.20</td> <td>100.91</td> <td>15.20</td>	0-DIL	06 10	3.99 14 70	00.09	J.ZO	03.72	12.20	100.91	15.20
Pentathoroannine113.523.3252.480.3176.5012.0440.7626.40Propani111.126.25100.7213.11Methylparathion82.8911.5265.0514.9153.7718.30Heptachlor103.625.0584.0818.0676.975.9037.4230.52Metalaxyl101.596.4168.6911.0542.8114.83Pirimiphos-methyl92.8114.84103.6613.4460.1210.21293.7232.78Methyl-pentachlorophenyl sulfide111.613.1680.1919.4374.798.3229.749.42Malathion92.3112.34103.895.8061.5614.09Chloryrifos103.276.8490.6617.1568.239.12132.386.94Aldrin113.245.0871.9118.4166.087.5740.4916.14Fenthion101.275.9481.3910.7178.8611.99208.3422.31Isocarbophos80.7712.6913.322.6762.8715.20Bromophos-methyl104.084.2983.3513.2658.836.8059.5024.83Phocymidone111.254.90113.6912.2183.149.1510.9227.33tras-Chlordane111.69 <td></td> <td>00.10</td> <td>14.73</td> <td>110.90</td> <td>7.84</td> <td>70.00</td> <td>17.47</td> <td>-</td> <td></td>		00.10	14.73	110.90	7.84	70.00	17.47	-	
Propani111.230.29100.7213.11Heptachlor103.625.0584.0818.0676.975.9037.4230.52 <t< td=""><td>Pentachioroaniline</td><td>113.52</td><td>3.3Z</td><td>52.48</td><td>0.31</td><td>78.50</td><td>12.04</td><td>40.70</td><td>28.40</td></t<>	Pentachioroaniline	113.52	3.3Z	52.48	0.31	78.50	12.04	40.70	28.40
$\begin{split} & \text{Methylightartition} & 82.83 & 11.32 & 65.05 & 14.91 & 53.77 & 18.30 & - & - & - \\ & - & - & - & - & - & - \\ & \text{Heptachor} & 103.62 & 5.05 & 84.08 & 18.06 & 76.97 & 5.90 & 37.42 & 30.52 \\ & \text{Metalaxyl} & 101.59 & 6.41 & 68.69 & 11.05 & 42.81 & 14.83 & - & - \\ & \text{Pirimiphos-methyl} & 92.81 & 14.84 & 103.66 & 13.44 & 60.12 & 10.21 & 293.72 & 32.78 \\ & \text{Methyl-pentachlorophenyl sulfide} & 111.61 & 3.16 & 80.19 & 9.43 & 74.79 & 8.32 & 29.74 & 9.42 \\ & \text{Malathion} & 92.31 & 12.34 & 103.89 & 5.80 & 61.56 & 14.09 & - & - \\ & \text{Chlorpyrifos} & 103.27 & 6.84 & 90.66 & 17.15 & 88.23 & 9.12 & 132.38 & 6.94 \\ & \text{Aldrin} & 113.24 & 5.08 & 71.91 & 18.41 & 66.08 & 7.57 & 40.49 & 16.14 \\ & \text{Fenthion} & 101.27 & 5.94 & 81.39 & 10.71 & 78.86 & 11.99 & 208.34 & 22.31 \\ & \text{Isocarbophos} & 80.77 & 12.69 & 133.32 & 2.67 & 62.87 & 15.32 & - & - \\ & \text{Bromophos-methyl} & 104.08 & 4.29 & 83.95 & 13.26 & 58.83 & 6.80 & 59.50 & 24.83 \\ & \text{Procymidone} & 111.25 & 4.90 & 113.69 & 12.21 & 83.14 & 9.15 & 109.57 & 27.33 \\ & \text{trans-Chordane} & 111.69 & 4.42 & 101.48 & 15.24 & 71.31 & 3.96 & 40.06 & 11.11 \\ & \alpha\text{-Endosulfan} & 114.14 & 8.22 & 91.33 & 15.19 & 76.45 & 8.42 & 45.89 & 29.23 \\ & p.p'-DDE & 111.32 & 7.18 & 73.53 & 17.15 & 70.92 & 1.63 & 67.97 & 8.88 \\ & Dieldrin & 101.15 & 7.90 & 87.90 & 19.98 & 63.92 & 3.94 & 63.09 & 28.57 \\ & \beta\text{-Endosulfan} & 88.36 & 16.87 & 75.93 & 19.33 & 76.76 & 17.99 & 76.31 & 17.14 \\ & y.pc'-DD & 104.43 & 5.94 & 100.37 & 5.86 & 56.54 & 5.90 & 29.65 & 34.14 \\ & Oxadixyl & 101.64 & 5.86 & 82.59 & 19.15 & 64.58 & 22.59 & - & - \\ & - & - & - & - & - & - & - &$	Propanii	111.23	6.25	100.72	13.11	-	-	_	-
Heptachlor103.525.0584.0818.0576.975.9037.4230.52Metalaxyl101.596.4168.6911.0542.8114.83 $-$ -Pirimiphos-methyl92.8114.84103.6613.4460.1210.21293.7232.78Mathion92.3112.34103.895.8061.5614.09Chlorynfos103.276.8490.6617.1588.239.12132.386.94Aldrin113.245.0871.9118.4166.087.5740.4916.14Fenthion101.275.9481.3910.7178.8611.99208.3422.31Isocarbophos80.7712.69133.322.6762.8715.32Bromophos-methyl104.084.2983.3513.2658.836.8059.5024.83Phenthoate89.418.5877.0513.1171.238.61107.9820.86Procynidone111.654.90113.6912.2183.149.15109.5727.33trans-Chordane111.694.4291.4315.1976.458.4245.8929.23 $\rho / DD$ 111.127.1875.5317.1570.921.6367.978.88Dieldrin101.157.9087.9319.9376.7617.9976.3117.14 $\rho / DD$ 104.435.94100.375.8656.54<	Nietnyiparatnion	82.89	11.52	65.05	14.91	53.77	18.30	-	-
Mretalaxyl101.990.4108.0911.0542.8114.83Pirimiphos-methyl92.8114.84103.6613.4460.1210.21293.7232.78Methyl-pentachlorophenyl sulfide111.613.1680.1919.4374.798.3229.749.42Malathion92.3112.34103.895.8061.5614.09Chiorpyrifos103.276.8490.6671.1588.239.12132.386.94Aldrin113.245.0871.9118.4166.087.5740.4916.14Fenthion101.275.9481.3910.7178.8611.99208.3422.31Isocarbophos80.7712.69133.322.6762.8715.32Bromophos-methyl104.084.2983.9513.2658.836.8059.5024.83Phentoate89.418.5877.0513.1171.238.61107.9820.86Procymidone111.254.90113.6912.2183.149.15109.5727.33trans-Chlordane111.694.42101.4815.2471.313.9640.0611.11 $\alpha$ -fodosulfan12.143.9486.7419.8562.771.8389.993.04Endrin101.157.9087.9019.9863.923.9463.0928.57 $\rho^{J}$ -DD104.435.9410.375	Heptachior	103.62	5.05	84.08	18.06	/6.9/	5.90	37.42	30.52
Primipnos-methyl 92.81 14.84 103.06 13.44 00.12 10.21 293.72 32.78 Methyl-pentachlorophenyl sulfide 111.61 3.16 80.19 19.43 74.79 8.32 29.74 9.42 Malathion 92.31 12.34 103.88 5.80 61.56 14.09 Chlorpyrifos 103.27 6.84 90.66 17.15 88.23 9.12 132.38 6.94 Aldrin 113.24 5.08 71.91 18.41 66.08 7.57 40.49 16.14 Fenthion 101.27 5.94 81.39 10.71 78.86 11.99 208.34 22.31 lsocarbophos 80.77 12.69 133.32 2.67 62.87 15.32 Bromophos-methyl 104.08 4.29 83.95 13.26 58.83 6.80 59.50 24.83 Phenthoate 89.41 8.58 77.05 13.11 71.23 8.61 107.98 20.86 Procymidone 111.25 4.90 113.69 12.21 83.14 9.15 109.57 27.33 trans-Chlordane 111.69 4.42 91.33 15.19 76.45 8.42 45.89 29.23 p,p'-DDE 111.32 7.18 73.53 17.15 70.92 1.63 67.97 8.88 Dieldrin 121.14 3.94 86.74 19.85 62.77 1.83 89.99 3.04 Endrin 101.15 7.90 87.90 19.98 63.92 3.94 63.09 28.57 $\beta$ -Endosulfan 88.36 16.87 75.93 19.93 76.76 17.99 76.31 17.14 p,p'-DDD 104.43 5.54 100.37 5.86 56.54 5.90 29.65 34.14 0xadixyl 101.64 5.86 82.59 19.15 64.58 22.59 0.5 (2.50 11.57) 10.57 25.33 15.51 0.55 20 2.85 34.14 0.55 10.95 7 2.53 1.55 1.55 1.55 1.55 1.55 1.55 1.55 1		101.59	6.41	68.69	11.05	42.81	14.83	-	
Methyl-pentachlorophenyl sulfide11.613.1680.1919.4374.798.3229.749.49Malathion92.3112.34103.895.8061.5614.09Chlorpyrifos103.276.8490.6617.1588.239.12132.386.94Aldrin113.245.0871.9118.4166.087.5740.4916.14Fenthion101.275.9481.3910.7178.8611.99208.3422.31Isocarbophos80.7712.69133.322.6762.8715.32Bromophos-methyl104.084.2983.9513.2658.836.8059.5024.83Phenthoate89.418.5877.0513.1171.238.61109.9727.33trans-Chlordane111.694.42101.4815.2471.313.9640.0611.11 $\alpha$ -Endosulfan114.148.2291.3315.1976.458.4245.8929.23 $\rho'$ -DD111.327.1873.5317.1570.921.6367.978.88Dieldrin121.143.9486.7419.8562.771.8389.993.04Endrin101.157.9087.9019.9863.923.9463.0928.57 $\rho'$ -DD104.435.94100.375.8656.545.9029.6534.14 $\rho_r'$ -DDT111.773.5495.3413.587	Pirimiphos-methyl	92.81	14.84	103.66	13.44	60.12	10.21	293.72	32.78
Malathon92.3112.34103.895.8061.5614.09 $ -$ Chlorpyrifos103.276.8490.6617.1588.239.12132.386.94Aldrin113.245.0871.9118.4166.087.5740.4916.14Fenthion101.275.9481.3910.7178.8611.99208.3422.31Isocarbophos80.7712.69133.322.6762.8715.32 $ -$ Bromophos-methyl104.084.2983.9513.2658.836.8059.5024.83Phenthoate89.418.5877.0513.1171.238.61107.9820.66Procymidone111.254.90113.6912.2183.149.15109.5727.33trans-Chlordane11.694.42101.4815.2471.313.9640.0611.11 $\alpha$ -Endosulfan114.148.2291.3315.1976.458.4245.8929.23 $p/r'$ -DD111.327.1873.5317.1570.921.6367.978.88Dieldrin121.143.9486.7419.8562.771.8389.993.04Endrin101.157.9087.9019.9863.923.9463.0928.57 $\beta$ -Endosulfan88.3616.8775.9319.9376.7617.9976.3117.14 $p/r$ -DD104.435.94100.375.8656.5	Methyl-pentachlorophenyl sulfide	111.61	3.16	80.19	19.43	/4./9	8.32	29.74	9.42
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Malathion	92.31	12.34	103.89	5.80	61.56	14.09	-	-
Aldrin113.245.0871.9118.4166.087.5740.4916.14Fenthion101.275.9481.3910.7178.8611.99208.3422.31Isocarbophos80.7712.69133.322.6762.8715.32Bromophos-methyl104.084.2983.9513.2658.836.8059.5024.83Phenthoate89.418.5877.0513.1171.238.61107.9820.66Procymidone111.254.90113.6912.2183.149.15109.5727.33trans-Chlordane111.694.42101.4815.2471.313.9640.0611.11 $\alpha$ -Endosulfan114.148.2291.3315.1976.458.4245.8929.23 $p,p'$ -DDE111.327.1873.5317.1570.921.6367.978.88Dieldrin121.143.9486.7419.8562.771.8389.993.04Endrin101.157.9087.9019.9863.923.9463.0928.57 $\beta$ -Endosulfan88.3616.8775.9319.9376.7617.9976.3117.14 $p,p'$ -DD104.435.94100.375.8656.545.9029.6534.14Oxadixyl101.645.8682.5919.1564.5822.59 $\rho'$ -DDT111.773.5495.3413.5879	Chlorpyrifos	103.27	6.84	90.66	17.15	88.23	9.12	132.38	6.94
Fenthion101.275.9481.3910.7178.8611.99208.3422.31Isocarbophos80.7712.69133.322.6762.8715.32Bromophos-methyl104.084.2983.9513.2658.836.8059.5024.83Phenthoate89.418.5877.0513.1171.238.61107.9820.86Procymidone111.254.90113.6912.2183.149.15109.5727.33trans-Chlordane111.694.42101.4815.2471.313.9640.0611.11α-Endosulfan114.148.2291.3315.1976.458.4245.8929.23p,p'-DDE111.327.1873.5317.1570.921.6367.978.88Dieldrin121.143.9486.7419.8562.771.8389.993.04Endrin101.157.9087.9019.9863.923.9463.0928.57β-Endosulfan88.3616.8775.9319.9376.7617.9976.3117.14 $\rho,p'$ -DD104.435.94100.375.8656.545.9029.6534.14 $\rho,p'$ -DDT111.773.5495.3413.5879.7018.4868.3316.36Carbophenothion97.136.9587.886.6885.3223.1969.2113.15 $p,p'-DDT115.784.2554.9817.84$	Aldrin	113.24	5.08	71.91	18.41	66.08	7.57	40.49	16.14
Isocarbophos80.7712.69133.322.6762.8715.32 $ -$ Bromophos-methyl104.084.2983.9513.2658.836.8059.5024.83Phenthoate89.418.5877.0513.1171.238.61107.9820.86Procymidone111.254.90113.6912.2183.149.15109.5727.33trans-Chlordane111.694.42101.4815.2471.313.9640.0611.11 $\alpha$ -Endosulfan114.148.2291.3315.1976.458.4245.8929.23 $p,p'$ -DDE111.327.1873.5317.1570.921.6367.978.88Dieldrin121.143.9486.7419.8562.771.8389.993.04Endrin101.157.9087.9019.9863.923.9463.0928.57 $\beta$ -Endosulfan88.3616.8775.9319.9376.7617.9976.3117.14 $\rho,p'$ -DDD104.435.9410.375.8656.545.9029.6534.14Oxadixyl101.645.8682.5919.1564.5822.59 $o,p'$ -DDT111.773.5495.3413.5879.7018.4868.3316.36Carbophenothion97.136.9587.886.6885.3223.1969.2113.15 $p,p'$ -DDT115.784.2554.9817	Fenthion	101.27	5.94	81.39	10.71	78.86	11.99	208.34	22.31
Bromophos-methyl104.084.2983.9513.2658.836.8059.5024.83Phenthoate89.418.5877.0513.1171.238.61107.9820.86Procymidone111.254.90113.6912.2183.149.15109.5727.33trans-Chlordane111.694.42101.4815.2471.313.9640.0611.11 $\alpha$ -Endosulfan114.148.2291.3315.1976.458.4245.8929.23 $p,p'$ -DDE111.327.1873.5317.1570.921.6367.978.86Dieldrin121.143.9486.7419.8562.771.8389.993.04Endrin101.157.9087.9019.9863.923.9463.0928.57 $\beta$ -Endosulfan88.3616.8775.9319.9376.7617.9976.3117.14 $p,p'$ -DDD104.435.94100.375.8656.545.9029.6534.14Oxadixyl101.645.8682.5919.1564.5822.59 $o,p'$ -DDT111.773.5495.3413.5879.7018.4868.3316.36Carbophenothion97.136.9587.886.6885.3223.1969.2113.15 $p,p'$ -DDT115.784.2554.9817.8456.085.6163.5925.12Fenpropathrin105.225.7398.2620.07<	Isocarbophos	80.77	12.69	133.32	2.67	62.87	15.32	_	-
Phenthoate89.418.5877.0513.1171.238.61107.9820.86Procymidone111.254.90113.6912.2183.149.15109.5727.33trans-Chlordane111.694.42101.4815.2471.313.9640.0611.11 $\alpha$ -Endosulfan114.148.2291.3315.1976.458.4245.8929.23 $p,p'$ -DDE111.327.1873.5317.1570.921.6367.978.88Dieldrin121.143.9486.7419.8562.771.8389.993.04Endrin101.157.9087.9019.9863.923.9463.0928.57 $\beta$ -Endosulfan88.3616.8775.9319.9376.7617.9976.3117.14 $p,p'$ -DDD104.435.94100.375.8656.545.9029.6534.14Oxadixyl101.645.8682.5919.1564.5822.59 $o,p'$ -DDT111.773.5495.3413.5879.7018.4868.3316.36Carbophenothion97.136.9587.886.6885.3223.1969.2113.15 $p,p'$ -DDT115.784.2554.9817.8456.085.6163.5925.12Fenpropathrin105.225.7398.2620.0769.3710.88Tetradifon112.973.7910.3411.5360.54<	Bromophos-methyl	104.08	4.29	83.95	13.26	58.83	6.80	59.50	24.83
Procymidone111.254.90113.6912.2183.149.15109.5727.33trans-Chlordane111.694.42101.4815.2471.313.9640.0611.11 $\alpha$ -Endosulfan114.148.2291.3315.1976.458.4245.8929.23 $p,p'$ -DE111.327.1873.5317.1570.921.6367.978.88Dieldrin121.143.9486.7419.8562.771.8389.993.04Endrin101.157.9087.9019.9863.923.9463.0928.57β-Endosulfan88.3616.8775.9319.9376.7617.9976.3117.14 $p,p'$ -DD104.435.94100.375.8656.545.9029.6534.14Oxadixyl101.645.8682.5919.1564.5822.59 $o,p'$ -DDT111.773.5495.3413.5879.7018.4868.3316.36Carbophenothion97.136.9587.886.6885.3223.1969.2113.15 $p,p'-DDT$ 115.784.2554.9817.8456.085.6163.5925.12Fenpropathrin105.225.7398.2620.0769.3710.88Tetradifon112.973.7910.3411.5360.5412.1081.3113.29 $\lambda$ -Cyhalothrin97.7010.4987.9412.1162.	Phenthoate	89.41	8.58	77.05	13.11	71.23	8.61	107.98	20.86
trans-Chlordane111.694.42101.4815.2471.313.9640.0611.11 $\alpha$ -Endosulfan114.148.2291.3315.1976.458.4245.8929.23 $p,p'$ -DE111.327.1873.5317.1570.921.6367.978.88Dieldrin121.143.9486.7419.8562.771.8389.993.04Endrin101.157.9087.9019.9863.923.9463.0928.57 $\beta$ -Endosulfan88.3616.8775.9319.9376.7617.9976.3117.14 $p,p'$ -DD104.435.94100.375.8656.545.9029.6534.14Oxadixyl101.645.8682.5919.1564.5822.59 $o,p'$ -DDT111.773.5495.3413.5879.7018.4868.3316.36Carbophenothion97.136.9587.886.6885.3223.1969.2113.15p,p'-DDT115.784.2554.9817.8456.085.6163.5925.12Fenpropathrin105.225.7398.2620.0769.3710.88Tetradifon112.973.7910.3411.5360.5412.1081.3113.29 $\lambda$ -Cyhalothrin97.7010.4987.9412.1162.152.6179.4522.83Coumaphos88.3310.3678.6518.53102.71 </td <td>Procymidone</td> <td>111.25</td> <td>4.90</td> <td>113.69</td> <td>12.21</td> <td>83.14</td> <td>9.15</td> <td>109.57</td> <td>27.33</td>	Procymidone	111.25	4.90	113.69	12.21	83.14	9.15	109.57	27.33
$\alpha$ -Endosulfan114.148.2291.3315.1976.458.4245.8929.23 $p,p'$ -DDE111.327.1873.5317.1570.921.6367.978.88Dieldrin121.143.9486.7419.8562.771.8389.993.04Endrin101.157.9087.9019.9863.923.9463.0928.57 $\beta$ -Endosulfan88.3616.8775.9319.9376.7617.9976.3117.14 $p,p'$ -DDD104.435.94100.375.8656.545.9029.6534.14Oxadixyl101.645.8682.5919.1564.5822.59 $o,p'$ -DDT111.773.5495.3413.5879.7018.4868.3316.36Carbophenothion97.136.9587.886.6885.3223.1969.2113.15 $p,p'$ -DDT115.784.2554.9817.8456.085.6163.5925.12Fenpropathrin105.225.7398.2620.0769.3710.88Tetradifon112.973.7910.3411.5360.5412.1081.3113.29 $\lambda$ -Cyhalothrin97.7010.4987.9412.1162.152.6179.4522.83Coumaphos88.3310.3678.6518.53102.713.18Esfenvalerate107.209.03105.6421.51101	trans-Chlordane	111.69	4.42	101.48	15.24	71.31	3.96	40.06	11.11
$p,p'$ -DDE111.327.1873.5317.1570.921.6367.978.88Dieldrin121.143.9486.7419.8562.771.8389.993.04Endrin101.157.9087.9019.9863.923.9463.0928.57 $\beta$ -Endosulfan88.3616.8775.9319.9376.7617.9976.3117.14 $p,p'$ -DDD104.435.94100.375.8656.545.9029.6534.14Oxadixyl101.645.8682.5919.1564.5822.59 $o,p'$ -DDT111.773.5495.3413.5879.7018.4868.3316.36Carbophenothion97.136.9587.886.6885.3223.1969.2113.15 $p,p'$ -DDT115.784.2554.9817.8456.085.6163.5925.12Fenpropathrin105.225.7398.2620.0769.3710.88Tetradifon112.973.7910.3411.5360.5412.1081.3113.29 $\lambda$ -Cyhalothrin97.7010.4987.9412.1162.152.6179.4522.83Coumaphos88.3310.3678.6518.53102.713.18Esfenvalerate107.209.03105.6421.51101.742.27	$\alpha$ -Endosulfan	114.14	8.22	91.33	15.19	76.45	8.42	45.89	29.23
Dieldrin121.143.9486.7419.8562.771.8389.993.04Endrin101.157.9087.9019.9863.923.9463.0928.57 $\beta$ -Endosulfan88.3616.8775.9319.9376.7617.9976.3117.14 $p,p'$ -DDD104.435.94100.375.8656.545.9029.6534.14Oxadixyl101.645.8682.5919.1564.5822.59 $o,p'$ -DDT111.773.5495.3413.5879.7018.4868.3316.36Carbophenothion97.136.9587.886.6885.3223.1969.2113.15 $p,p'$ -DDT115.784.2554.9817.8456.085.6163.5925.12Fenpropathrin105.225.7398.2620.0769.3710.88Tetradifon112.973.7910.3411.5360.5412.1081.3113.29 $\lambda$ -Cyhalothrin97.7010.4987.9412.1162.152.6179.4522.83Coumaphos88.3310.3678.6518.53102.713.18Esfenyalerate107.209.03105.6421.51101.742.27	<i>p,p</i> ′-DDE	111.32	7.18	73.53	17.15	70.92	1.63	67.97	8.88
Endrin101.157.9087.9019.9863.923.9463.0928.57β-Endosulfan88.3616.8775.9319.9376.7617.9976.3117.14 $p,p'$ -DDD104.435.94100.375.8656.545.9029.6534.14Oxadixyl101.645.8682.5919.1564.5822.59 $o,p'$ -DDT111.773.5495.3413.5879.7018.4868.3316.36Carbophenothion97.136.9587.886.6885.3223.1969.2113.15 $p,p'$ -DDT115.784.2554.9817.8456.085.6163.5925.12Fenpropathrin105.225.7398.2620.0769.3710.88Tetradifon112.973.7910.3411.5360.5412.1081.3113.29λ-Cyhalothrin97.7010.4987.9412.1162.152.6179.4522.83Coumaphos88.3310.3678.6518.53102.713.18Esfenvalerate107.209.03105.6421.51101.742.27	Dieldrin	121.14	3.94	86.74	19.85	62.77	1.83	89.99	3.04
$\beta$ -Endosulfan88.3616.8775.9319.9376.7617.9976.3117.14 $p,p'$ -DDD104.435.94100.375.8656.545.9029.6534.14Oxadixyl101.645.8682.5919.1564.5822.59 $o,p'$ -DDT111.773.5495.3413.5879.7018.4868.3316.36Carbophenothion97.136.9587.886.6885.3223.1969.2113.15 $p,p'$ -DDT115.784.2554.9817.8456.085.6163.5925.12Fenpropathrin105.225.7398.2620.0769.3710.88Tetradifon112.973.7910.3411.5360.5412.1081.3113.29 $\lambda$ -Cyhalothrin97.7010.4987.9412.1162.152.6179.4522.83Coumaphos88.3310.3678.6518.53102.713.18Esfenyalerate107.209.03105.6421.51101.742.27	Endrin	101.15	7.90	87.90	19.98	63.92	3.94	63.09	28.57
$p,p'$ -DDD104.435.94100.375.8656.545.9029.6534.14Oxadixyl101.645.8682.5919.1564.5822.59 $o,p'$ -DDT111.773.5495.3413.5879.7018.4868.3316.36Carbophenothion97.136.9587.886.6885.3223.1969.2113.15 $p,p'$ -DDT115.784.2554.9817.8456.085.6163.5925.12Fenpropathrin105.225.7398.2620.0769.3710.88Tetradifon112.973.7910.3411.5360.5412.1081.3113.29 $\lambda$ -Cyhalothrin97.7010.4987.9412.1162.152.6179.4522.83Coumaphos88.3310.3678.6518.53102.713.18Esfenyalerate107.209.03105.6421.51101.742.27	$\beta$ -Endosulfan	88.36	16.87	75.93	19.93	76.76	17.99	76.31	17.14
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	<i>p,p</i> ′ -DDD	104.43	5.94	100.37	5.86	56.54	5.90	29.65	34.14
$o,p'$ -DDT111.773.5495.3413.5879.7018.4868.3316.36Carbophenothion97.136.9587.886.6885.3223.1969.2113.15 $p,p'$ -DDT115.784.2554.9817.8456.085.6163.5925.12Fenpropathrin105.225.7398.2620.0769.3710.88Tetradifon112.973.7910.3411.5360.5412.1081.3113.29 $\lambda$ -Cyhalothrin97.7010.4987.9412.1162.152.6179.4522.83Coumaphos88.3310.3678.6518.53102.713.18Esfenyalerate107.209.03105.6421.51101.742.27	Oxadixyl	101.64	5.86	82.59	19.15	64.58	22.59	-	-
Carbophenothion         97.13         6.95         87.88         6.68         85.32         23.19         69.21         13.15           p,p'-DDT         115.78         4.25         54.98         17.84         56.08         5.61         63.59         25.12           Fenpropathrin         105.22         5.73         98.26         20.07         69.37         10.88         -         -           Tetradifon         112.97         3.79         10.34         11.53         60.54         12.10         81.31         13.29           λ-Cyhalothrin         97.70         10.49         87.94         12.11         62.15         2.61         79.45         22.83           Coumaphos         88.33         10.36         78.65         18.53         102.71         3.18         -         -           Esfenyalerate         107.20         9.03         105.64         21.51         101.74         2.27         -         -	<i>o,p</i> ′ -DDT	111.77	3.54	95.34	13.58	79.70	18.48	68.33	16.36
$p,p'$ -DDT115.784.2554.9817.8456.085.6163.5925.12Fenpropathrin105.225.7398.2620.0769.3710.88Tetradifon112.973.7910.3411.5360.5412.1081.3113.29 $\lambda$ -Cyhalothrin97.7010.4987.9412.1162.152.6179.4522.83Coumaphos88.3310.3678.6518.53102.713.18Esfenyalerate107.209.03105.6421.51101.742.27	Carbophenothion	97.13	6.95	87.88	6.68	85.32	23.19	69.21	13.15
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	<i>p,p</i> ′-DDT	115.78	4.25	54.98	17.84	56.08	5.61	63.59	25.12
Tetradifon112.973.7910.3411.5360.5412.1081.3113.29λ-Cyhalothrin97.7010.4987.9412.1162.152.6179.4522.83Coumaphos88.3310.3678.6518.53102.713.18Esfenyalerate107.209.03105.6421.51101.742.27	Fenpropathrin	105.22	5.73	98.26	20.07	69.37	10.88	_	_
λ-Cyhalothrin         97.70         10.49         87.94         12.11         62.15         2.61         79.45         22.83           Coumaphos         88.33         10.36         78.65         18.53         102.71         3.18         -         -           Esfenvalerate         107.20         9.03         105.64         21.51         101.74         2.27         -         -	Tetradifon	112.97	3.79	10.34	11.53	60.54	12.10	81.31	13.29
Coumaphos         88.33         10.36         78.65         18.53         102.71         3.18         -         -           Esfenyalerate         107.20         9.03         105.64         21.51         101.74         2.27         -         -	λ-Cvhalothrin	97.70	10.49	87.94	12.11	62.15	2.61	79.45	22.83
Esfenvalerate 107.20 9.03 105.64 21.51 101.74 2.27	Coumaphos	88.33	10.36	78.65	18.53	102.71	3.18	_	_
	Esfenvalerate	107.20	9.03	105.64	21 51	101.74	2 27	_	_

a) The spiking level of the pesticide residues was 50  $\mu g/kg.$ 

b) No pesticide was detected.

Sample	Source	Contents of pesticic	des detected (mg/	'kg) (RSD%, <i>n</i> = 4	(†						
		Monocrotophos	Carbofuran	Quintozene	Lindane	Chlorothalonil	Endrin	Metalaxyl	Fonofos	<i>p,p</i> '-DDT	λ-Cyhalothrin
P. thomsonii	Yuexi, Anhui	0.026 (7)	_a)	I	I	I	I	I	I	<l00< td=""><td>0.200(4)</td></l00<>	0.200(4)
P. thomsonii	Yichang, Hubei	0.029 (9)	I	I	0.035(6)	I	<pre><poo< pre=""></poo<></pre>	I	I	<l00< td=""><td>0.258(4)</td></l00<>	0.258(4)
P. thomsonii	Meishan, Sichuan	I	I	I	I	0.031(6)	I	I	I	<l00< td=""><td>0.035(6)</td></l00<>	0.035(6)
P. thomsonii	Meishan, Sichuan	I	I	I	I	I	I	I	I	I	0.047(8)
P. thomsonii	Yifeng, Jiangxi	I	I	I	I	0.041(7)	I	I	I	I	<l00< td=""></l00<>
P. cablin	Zhanjiang, Guangdong	0.127(6)	0.024(9)	I	I	I	I	0.037(5)	0.012(6)	<l00< td=""><td>I</td></l00<>	I
P. cablin	Zhanjiang, Guangdong	0.056(8)	<l00< td=""><td>I</td><td>0.062(7)</td><td>0.018(8)</td><td>I</td><td>I</td><td>I</td><td><l00< td=""><td>0.043(6)</td></l00<></td></l00<>	I	0.062(7)	0.018(8)	I	I	I	<l00< td=""><td>0.043(6)</td></l00<>	0.043(6)
P. cablin	Zhanjiang, Guangdong	0.107(5)	I	I	I	0.208(5)	I	0.116(4)	I	<l00< td=""><td>I</td></l00<>	I
P. cablin	Nantong, Jiangsu	<100	I	<l00< td=""><td>I</td><td>0.042(7)</td><td>I</td><td>I</td><td><l00< td=""><td>0.011(7)</td><td>I</td></l00<></td></l00<>	I	0.042(7)	I	I	<l00< td=""><td>0.011(7)</td><td>I</td></l00<>	0.011(7)	I
P. cablin	Nantong, Jiangsu	0.077(8)	0.028(9)	I	I	<l00< td=""><td>I</td><td>0.204(3)</td><td><l00< td=""><td>I</td><td>I</td></l00<></td></l00<>	I	0.204(3)	<l00< td=""><td>I</td><td>I</td></l00<>	I	I
H. cordatia	Yaan, Sichuan	I	0.023(8)	I	<l00< td=""><td>I</td><td><l00< td=""><td>I</td><td>I</td><td>0.004(13)</td><td><l00< td=""></l00<></td></l00<></td></l00<>	I	<l00< td=""><td>I</td><td>I</td><td>0.004(13)</td><td><l00< td=""></l00<></td></l00<>	I	I	0.004(13)	<l00< td=""></l00<>
H. cordatia	Yaan, Sichuan	<l00< td=""><td>I</td><td>I</td><td>Ι</td><td>I</td><td>Ι</td><td>0.104(3)</td><td>I</td><td>Ι</td><td>I</td></l00<>	I	I	Ι	I	Ι	0.104(3)	I	Ι	I
H. cordatia	Yaan, Sichuan	0.033(8)	0.017(7)	I	I	I	0.061(4)	I	<l00< td=""><td><l00< td=""><td><pre>~</pre>LOO</td></l00<></td></l00<>	<l00< td=""><td><pre>~</pre>LOO</td></l00<>	<pre>~</pre> LOO
H. cordatia	Yibin, Sichuan	I	I	I	I	I	I	I	I	I	I
H. cordatia	Yibin, Sichuan	I	I	I	I	I	I	I	I	I	I
D. opposita	Jiaozuo, Henan	I	0.086(6)	0.064(4)	Ι	0.023(6)	0.047(6)	0.156(3)	0.015(5)	0.086(7)	0.061(6)
D. opposita	Jiaozuo, Henan	0.017(6)	I	I	Ι	I	I	Ι	I	<l00< td=""><td>I</td></l00<>	I
D. opposita	Qinyang, Henan	<l00< td=""><td>I</td><td>I</td><td>0.007(9)</td><td>0.042(7)</td><td>I</td><td>0.267(4)</td><td>I</td><td><l00< td=""><td>0.037(7)</td></l00<></td></l00<>	I	I	0.007(9)	0.042(7)	I	0.267(4)	I	<l00< td=""><td>0.037(7)</td></l00<>	0.037(7)
D. opposita	Dujiangyan, Sichuan	0.025(5)	I	I	Ι	I	<l00< td=""><td><l00< td=""><td>I</td><td>I</td><td>0.049(6)</td></l00<></td></l00<>	<l00< td=""><td>I</td><td>I</td><td>0.049(6)</td></l00<>	I	I	0.049(6)
D. opposita	Dujiangyan, Sichuan	0.031(5)	I	I	I	0.042(7)	0.109(4)	I	I	I	<l00< td=""></l00<>

Table 3. The contents (mg/kg) of the found pesticide residues in four MFDPHs

a) No pesticide was detected.

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column. When forward elution program is over, backflush program can be activated. The pressure of inlet immediately fell to 1 psi, the pressure of three-way splitter rose up to 60 psi, and the column temperature was changed to 280°C. The flow rate of analytical column was about 6 mL/min. On the high temperature and high flow rate condition, high boiling compounds can be removed from the split of injection inlet. Supporting Information Fig. S6 showed that a 5 min backflush cleaned column as well as a 20 min bake-out and the residues on liner were significantly reduced too.

## 3.5 Validation of method

All calibration curves for the 52 target compounds were linear in a relatively wide concentration in the ranges of 2-400 µg/kg (Supporting Information Table S5). The correlation coefficient values ( $r^2 > 0.996$ ) indicated good correlations between the investigated compounds concentrations and their ratios of the peak areas of each standard to IS within the tested ranges. The LOD and LOQ were in the range of 0.2–5  $\mu$ g/kg and 1–10 g/kg, respectively (Supporting Information Table S5). Method precision was also evaluated by determining reproducibility, and the intra- and inter-day precisions (RSD) of the 52 analytes were less than 2.61% and 3.11%, respectively. The repeatability presented as RSD (n = 5) was between 3.26 and 11.54%. Recovery experiments with spiked blank samples were performed at three concentrations. Supporting Information Table S6 shows the recoveries of the 52 investigated pesticides were 62-127% and RSD < 19%.

#### 3.6 Real sample analysis

The developed SLPE and fast GC-MS/MS method in this work was applied to simultaneously determine 52 pesticides in 20 samples including *P. thomsonii*, *P. cablin*, *H. cordata*, and *D. opposite*. Ten pesticides were identified in the MFDPHs. Retention time and monitor ions of the ten pesticide residues detected in MFDPHs were consistent with matrix-matched standards. Table 3 showed the contents of detectable pesticides including monocrotophos, carbofuran, quintozene, lindane, chlorothalonil, endrin, metalaxyl, fonofos, *p,p'*-DDT, and  $\lambda$ -cyhalothrin.

Unfortunately, four forbidden pesticides including monocrotophos, endrin, lindane, and p,p'-DDT were found in the tested MFDPHs. Monocrotophos is extremely dangerous organophosphate insecticide, which has acute toxicity to human body. Endrin, lindane, and p,p'-DDT are persistent organic pollutants. Therefore, these pesticides have been banned in many countries. In European Pharmacopoeia (EP), the maximum residue limits (MRLs) of monocrotophos, endrin, lindane, and p,p'-DDT are 0.1, 0.05, 0.6, and 1 mg/kg, respectively [35]. Table 3 shows that the contents of monocrotophos in one batch of sample and endrin in two batches of samples exceeded MRL. Although the contents of lindane

and p,p'-DDT are lower than the MRL of EP, the detection rates of them are very high.

Furthermore, carbofuran and fonofos are classified as restricted use pesticides by United States Environmental Protection Agency (EPA) [www.epa.gov]. They are found in multibatches MFDPHs and the contents are in the range of 0.012– 0.086 mg/kg. Quintozene, chlorothalonil, and metalaxyl are classified as a general use pesticide by EPA and they are used as fungicide to control a wide range of fungi species in vegetables, crops, and soil.  $\lambda$ -Cyhalothrin is a pyrethroid insecticide. Table 3 shows that the contents of  $\lambda$ -cyhalothrin are lower than MRL (1 mg/kg) of EP.

## 4 Concluding remarks

In this study, an optimized SPLE and fast GC-MS/MS method was developed. The method was applied for the determination of 52 pesticide residues in MFDPHs. Results showed that the optimized SPLE can simplify sample preparation and obtain high recoveries for most pesticide residues. The column backflush was used to decrease analysis time and extend the life of GC-MS/MS system. Therefore, SPLE and fast GC-MS/MS method is a good method for the determination of multiple pesticide residues in MFDPHs.

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The authors have declared no conflict of interest.

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