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Original article (Orijinal araştırma)

Investigation of insecticide residues in potato grown in Türkiye by LC-MS/MS and GC-MS and health risk assessment[1]

LC-MS/MS ve GC-MS ile Türkiye menşeli patateslerde insektisit kalıntılarının araştırılması ve sağlık risk değerlendirmesi

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Abstract

Insecticide, acaricide, nematicide and metabolite residues were assayed in 104 potato samples collected from local markets in Tokat, Türkiye in 2022 and the potential health risk for consumers assessed. Analytical method verification was performed for 135 pesticide active substances in potato matrices by liquid chromatography-tandem mass spectrometry and gas chromatography-mass spectrometry. Matrix-matched calibration curves were constructed and good linearity was obtained with a coefficient of determination between 0.990 and 0.999. Average recoveries varied from 73.2 to 119.6%. Repeatability and intra-laboratory reproducibility conditions of the method expressed as %RSD were less than 20%. These figures were within the SANTE/11312/2021 recovery limits (70-120%) and the values specified for the repeatability (RSD ≤ 20%). The limits of quantification were lower than the maximum residue limits set by the European Union for the potato. No pesticide residues were found at detectable limits in 93 samples. Two samples contained residues below the maximum residue limit (MRL), while nine samples contained residues above the MRLs. Clothianidin and thiamethoxam residues detected in one sample, while acetamiprid were detected in nine samples. The health risk assessment study indicated that potato consumption was safe for consumers.

Keywords: Acute risk, chronic risk, matrix effect, method verification, pesticide residue

Öz

Bu çalışmada, 2022 yılında Tokat'ta yerel pazarlarda satılan pateteslerde insektisit, akarisit, nematisit ve metabolit kalıntıları taranmış ve bu kalıntıların tüketiciler açısından potansiyel sağlık riskleri değerlendirilmiştir. Sıvı kromatografi-tandem kütle spektrometrisi ve gaz kromatografi-kütle spektrometrisi ile 135 pestisit etken madde kalıntısını belirlemek için metot doğrulaması yapılmıştır. Matris uyumlu kalibrasyon eğrileri oluşturulmuş ve 0.990 ile 0.999 arasında değişen korelasyon katsayısı ile uygun bir doğrusallık elde edilmiştir. Ortalama geri kazanımlar %73.2 ile %119.6 arasında, %RSD olarak ifade edilen yöntemin tekrarlanabilirlik koşulları ve laboratuvar içi tekrar üretilebilirlik koşulları %20'den daha düşük bulunmuştur. Bu rakamlar, SANTE/11312/2021 dokümanındaki geri kazanım limitleri (%70-120) ve tekrarlanabilirlik için belirtilen değerlere (RSD ≤ %20) uygundur. Miktar tayin limitleri, Avrupa Birliği tarafından patates için belirlenen maksimum kalıntı limitlerinden daha düşük seviyelerde bulunmuştur. 93 örnekte tespit edilebilir limitlerde pestisit kalıntısına rastlanmamıştır. İki numunede MRL değerleri altında, 9 numunede ise MRL değerleri üzerinde pestisit kalıntısı tespit edilmiştir. Bu örneklerden birinde hem clothianidin hem de thiamethoxam, dokuzunda ise acetamiprid tespit edilmiştir. Sağlık risk değerlendirmesi ise patates tüketiminin tüketiciler için güvenli olduğunu göstermiştir.

Anahtar sözcükler: Akut risk, kronik risk, matriks etkisi, metot doğrulaması, pestisit kalıntısı

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Introduction

Potato (*Solanum tuberosum* L.) is the most important crops after cereals for human nutrition. Potato is widely produced due to its adaptability to various climatic conditions and being economical, and it is consumed in many countries of the world due to high nutritional value. Potato is low in protein and high in starch, and is widely used in food and industry. Potato ranks fourth as a food in the world and it is the fifth food product in Türkiye after wheat, tomato, barley and corn (FAO, 2022; TUIK, 2022).

Potato is among the main food sources of many countries. Its consumption is also increasing rapidly in developing countries (FAO, 2008). However, in potato production, there are many biotic and abiotic factors that cause losses in potato crops. Pests are the most important ones. Insects are responsible for 16% of crop losses in potato and can cause 30-70% losses in tuber yield and quality (Weber, 2013). Key pests of potato in Türkiye are *Leptinotarsa decemlineata* (Say, 1824) (Coleoptera: Chrysomelidae), *Phthorimaea operculella* (Zeller, 1873) (Lepidoptera: Gelechiidae), *Globodera rostochiensis* (Wollenweber 1923), *Globodera pallida* (Stone, 1973) (Tylenchida: Heteroderidae) and *Meloidogyne* spp. (Tylenchida: Meloidogynidae) (TAGEM, 2017). In order to prevent the damage of these pests, insecticides, acaricides and nematicides are applied intensively from planting to the harvest.

Pesticides may remain in the harvested products and pose a health risk to consumers due to inappropriate agricultural practices, Therefore, pesticide residues are limited by various organizations with maximum residue limits (MRLs) and these approaches aim to prevent this health risk (EU-MRL, 2022; TGK-MRL, 2022). The MRLs of pesticides to be applied to foods in European Union countries are given in the European Parliament and Council Regulation No. 396/2005 (EC, 2005). In Türkiye, Turkish Food Codex Regulation on Maximum Residue Limits of Pesticides was prepared by taking the EU regulation into account within the scope of harmonizing with the European Union legislation (Anonymous, 2022).

MRL for insecticide, acaricide and nematicide residues in potato within range of 0.001-0.8 mg kg^{-1} depending on the active ingredients. The higher limits can be set in some cases (EU-MRL, 2022; TGK-MRL, 2022). Highly sensitive and accurate analytical methods are required to analyze these trace concentrations (Narenderan & Meyyanathan, 2019). Today, liquid chromatography-tandem mass spectrometry (LC-MS/MS) and gas chromatography-tandem mass spectrometry are more preferred because they provide improved sensitivity and selectivity for analyzing large numbers of pesticides with a single injection (Saha et al., 2015; Balkan, 2021). These techniques have been used for the determination of various pesticide residues in potato (Thompson et al., 2011; Lee et al., 2017; Narenderan & Meyyanathan, 2019; Reis et al., 2020).

Currently, dispersive solid phase extraction (d-SPE) is the most widely used method for cleansing in most multi-residue methods. In the d-SPE, a step of the QuEChERS (quick, easy, cheap, effective, rugged and safe) method, solid phases such as C_{18}, primary secondary amine, graphitized carbon black and zirconia-coated silica are added directly to facilitate the cleansing process. The use of the QuEChERS method has increased over the last decade due to its suitability for multiple residue analysis in various matrices (Narenderan & Meyyanathan, 2019). It is the most widely used method for detecting pesticide residues in potato (Lee et al., 2017; Reis et al., 2020; Sivaperumal et al., 2022).

In this study aimed to develop methods with high sensitivity, accuracy and precision to meet the SANTE/11312/2021 guidelines for determination of insecticide, acaricide and nematicide residues in potato by QuEChERS method using LC-MS/MS and GC-MS. The verified method was used to determine 135 pesticide residues with the QuEChERS method in potato. In addition, the health risk associated with the presence of pesticide residues in potatoes was evaluated.

Materials and Method

Chemicals and reagents

Pesticide reference standards were supplied by Dr. Ehrenstorfer GmbH (Augsburg, Germany) supplied (Tables S1 and S2). Methanol and acetonitrile gradient grade for liquid chromatography (≥99.9% purity), and acetic acid (>99% purity) were supplied by Merck (Darmstadt, Germany). The QuEChERS products were supplied by Restek (Bellefonte, PA, USA).

Preparation of standard solution

One hundred and thirty pesticide active substances were assayed, 23 (and/or their metabolites) by GC-MS analyses and 112 by LC-MS/MS analyses, for method verification and residue detection. A separate stock solution (1 mg mL^{-1}) in methanol for each pesticide was prepared and stored at -20°C. The concentrations of the matrix-matched standards were 5, 10, 25, 50, 100 and 150 µg L^{-1} of each analyte.

Sample collection and storage

Potato samples originating from Adana, Afyon, Malatya, Niğde, Nevşehir Sivas and Tokat were purchased from the supermarkets in Tokat, Türkiye in May and June 2022. Potato (at least 10 units) samples each of 1 kg were collected in sterile polythene bags for pesticide residue analysis (EC, 2002). Samples were labeled and immediately transported to the laboratory in the icebox and immediately processed within 12 h for extraction and cleansing. Blank potato samples were obtained from the tissue culture laboratory, which is known to be pesticide free, for recovery experiment and matrix-matched calibration.

Sample preparation, extraction and cleansing

Extraction and cleansing procedures in QuEChERS AOAC Method 2007.01 were performed according to (AOAC, 2007). The steps for QuEChERS process were shown in Figure 1. Potatoes were analyzed in triplicate by LC-MS/MS and gas chromatography mass spectrometry (GC-MS).

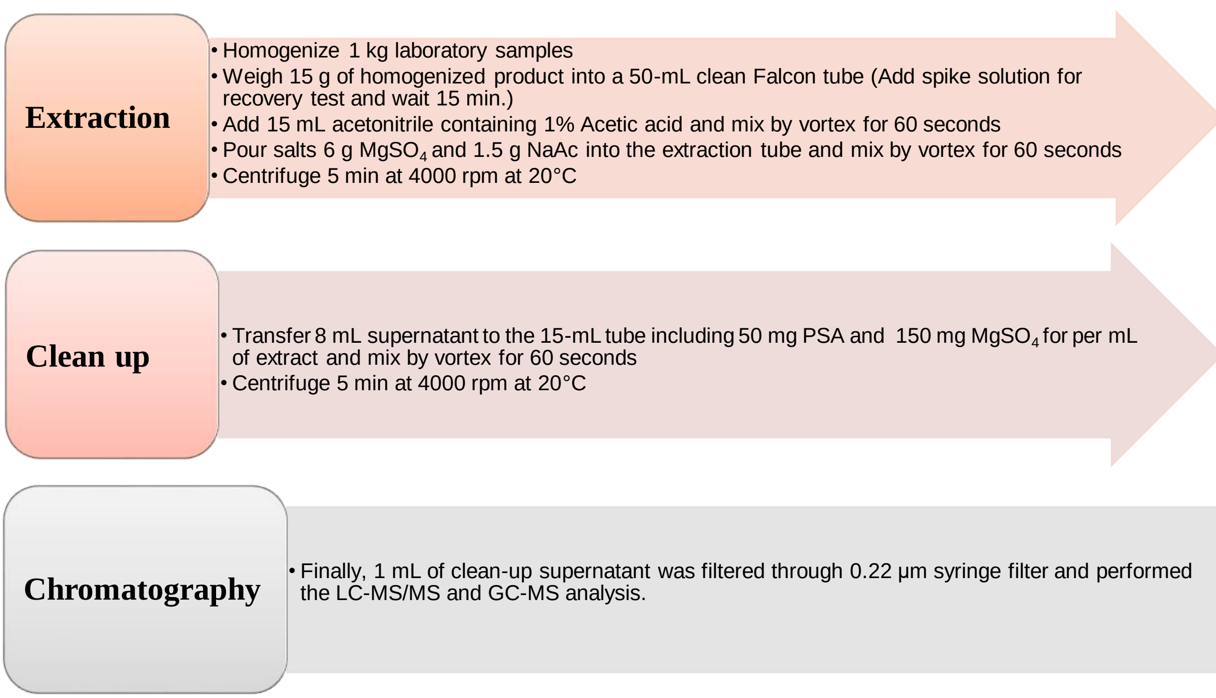

Figure 1. Analytical steps of the QuEChERS-AOAC Official Method 2007.01.

Instrumentation and optimization for LC-MS/MS and GC-MS

The analyses were performed on Shimadzu UHPLC Nexera X2, and LCMS-8050 triple quadrupole mass spectrometer with an electrospray ionization, and GC-MS QP2010 ultra model (Shimadzu) with mass spectrometry system coupled with an electron ionization. The final LC-MS/MS and GC-MS conditions are given in Table 1. Multiple reaction monitoring was used for optimization in LC-MS/MS and selected reaction monitoring for GC-MS. Optimization parameters in LC-MS/MS and GC-MS were given in Table S1 and S2, respectively.

Table 1. Analysis conditions for LC-MS/MS and GC-MS

LC Conditions (Nexera X2)		MS Conditions (LCMS-8050)	
Column	Inertsil (ODS-3), C_{18} column (2.1 mm x 150 mm, 3 µm)	Ionization mode	ESI (+/ -)
Oven temp.	40°C	Desolvation line temp.	250°C
Solvent A	10 mmol L^{-1} ammonium acetate/distilled water	Interface temp.	300°C
Solvent B	Methanol	Block heater temp.	400°C
Gradient	5% B (0 min) - 60% B (3 min) - 70% B (4 min) - 80% B (6 min) - 95% B (7 - 8.50 min) - 5% B (8.51-15 min)	Nebulizer gas flow	2.9 L/min.
Flow rate	0.4 mL min^{-1}	Drying gas flow	10.0 L min^{-1}.
Injection vol.	10 µL	Heating gas flow	15.0 L min^{-1}.
Rinse solution	R0 50% methanol/water	Dwell time	1-33 ms
GC conditions (GC 2010 Plus)		**MS conditions (GC-QP2010 Ultra)**	
Column	Rxi-5Sil MS column (30 m, 0.25 mm id, 0.25 µm	Ionization mode	EI
Injection temp.	250°C	Interface temp.	270°C
Gradient	90°C (1 min) - (20°C/min) - 150°C - (9°C/min) - 200°C - (12°C/min) - 300°C (5 min)	Ion source temp.	200°C
Carrier gas	Helyum	Solvent cut time	2.5 min
Linear velocity	48.1 cm s^{-1}	Data sampling time	6.3-20 min
Purge flow	3.0 mL min^{-1}	Acquisition Mode	SIM
Injection vol.	1 µL	Event time	0.3 ms

ESI, electrospray ionization; EI, electron ionization.

Method verification

For recovery, 15 g blank potato samples were spiked with the mixed pesticide solutions corresponding 0.01, 0.05 and 0.1 mg kg^{-1} levels for the five replicates. The experiment was repeated in five consecutive weeks by two analysts. Analytical methods were verified in accordance with the internationally accepted guidelines (EURACHEM, 2014; SANTE, 2021). Verified parameters were limit of detection (LOD), limit of quantification (LOQ), sensitivity/linearity, recovery, precision (repeatability; RSD_r and within-laboratory reproducibility; RSD_{wR}), measurement uncertainty, and matrix effect (ME). These parameters were described in detail by Balkan & Yılmaz, (2022).

Pesticide residues in potatoes

One hundred and thirty pesticide active substances in the 104 potato samples were analyzed in LC-MS/MS and GC-MS. The active ingredients detected in these samples were confirmed by the retention time and ion ratio defined as identification criteria according to the SANTE guidelines.

Risk assessment

Health risk assessments include estimated calculations of which extent to the health of those who consume pesticide-containing foods. Health risks for both acute and chronic exposure were assessed. Dietary exposure assessments are based on food consumption data in the relevant countries and data on the pesticide residues detected in the foods.

In assessing the acute and chronic risk of pesticide residues, estimated dietary exposure (based on body weight; BW) was compared to toxicological values known as acute reference dose (ARfD, mg kg BW^{-1} d^{-1})

and acceptable daily intake (ADI, mg kg BW^{-1} d^{-1}). The acute/short-term consumer health risk (aHI) was calculated based on the estimated short-term intake (ESTI, mg kg^{-1} d^{-1}) and the acute reference dose (ARfD). The chronic/long-term consumer health risk (chronic hazard index, cHI) was calculated based on the estimated daily intake (EDI, mg kg^{-1} d^{-1}) and the acceptable daily intake (ADI) (EFSA, 2015). The relevant formulas were given below Liu et al., 2016);

$$\text{ESTI} = \text{high residue level} \times \text{food consumption} / \text{body weight} \quad (1)$$

$$\text{aHI} = \text{ESTI} / \text{ARfD} \times 100 \quad (2)$$

$$\text{EDI} = \text{mean residue level} \times \text{food consumption} / \text{body weight} \quad (3)$$

$$\text{cHI} = \text{EDI} / \text{ADI} \times 100 \quad (4)$$

The average body weight of an adult was considered 73.5 kg (TUIK, 2019; Balkan & Kara, 2022). Daily consumption of potato for the general population in Türkiye were used as 0.14 kg^{-1} d^{-1} respectively (TUIK, 2022). When HI is greater than one, it indicates that pesticide residue could pose health risk to consumers (Akoto et al., 2015; Soydan et al., 2021).

Result and Discussion

Method verification

The results obtained from method verification studies of the detected insecticides were given in Table 2. The verification data of 135 pesticides active substances are given in Table S3. Linearity was obtained for every pesticide and showed good correlation coefficient (R^2) range between 0.990 and 0.999. For the determination of LOD and LOQ, potato blank samples were fortified with a pesticide mixture at the level of 10 µg kg^{-1} and 10 replicate analyses were performed. These values were smaller than the MRLs (except carbofuran, MRL: 1 µg kg^{-1}) for potatoes set by the EU. The recovery rate of 70-120%, and repeatability RSD_r and intra-laboratory reproducibility RSD_{wR} ≤ 20% for pesticides were acceptable. The expanded measurement uncertainties were between 18.6 and 43.2% for all pesticides. These results indicate that QuEChERS is a rapid and accurate method to analyze pesticide residues in potatoes.

MEs are classified into three types: minimal signal suppression or enhancement effects (ME range -20 to 20%), moderate effects (range, 50 to -20% or 20 to 50%) and strong matrix effects (<50% or >50%) (Szarka et al., 2022). In the LC-MS/MS analyses, minimal ME (Carbosulfan, diazinon, dicrotophos, fenthion, flubendiamide, monocrotophos, novaluron and triflumuron), moderate ME (32 pesticides) and strong ME (72 pesticides) was observed in the potato. In the GC-MS analyses, a strong matrix effect was detected in potato. Signal enhancement is generally more common in GG analyzes (Szarka et al., 2022). Signal enhancement was observed in most pesticides (Table 2).

Various degrees of ME were detected in all samples in both GG-MS and LC-MS/MS. In order to eliminate this effect, matrix-match standard solutions or other recommended approaches should be used. The use of matrix-matched calibration curves provides more precise and accurate analysis results guideline.

Table 2. Method verification parameters of detected pesticides in potato samples

Pesticide	LOD	LOQ	R^2	Repeatability (n=10)						Reproducibility (n=10)						U' %	ME %
	(µg kg^{-1})			10 µg kg^{-1}		50 µg kg^{-1}		100 µg kg^{-1}		10 µg kg^{-1}		50 µg kg^{-1}		100 µg kg^{-1}			
				Rec. %	RSD %	Rec. %	RSD %	Rec. %	RSD %	Rec. %	RSD %	Rec. %	RSD %	Rec. %	RSD %		
Acetamiprid	1.9	6.3	0.993	115	9.6	118	4.7	114	5.8	106	8.7	116	13.2	106	5.0	32.8	-28.8
Clothianidine	1.2	4.1	0.995	108	6.3	106	13.6	112	4.5	111	7.9	107	6.6	114	8.5	27.9	-78.2
Thiamethoxam	1.9	6.4	0.994	117	10.2	119	9.7	115	10.3	116	11.6	117	11.3	117	3.6	39.7	-70.4

Rec: Recovery; LOD, limit of detection; LOQ, limit of quantification; U', measurement uncertainty; ME, matrix effect.

Residue analyses in potatoes

One hundred and four potato samples were analyzed. Pesticide residues were determined equal or lower than the LODs in 93 (89%) of 104 samples. Acetamiprid was detected in nine samples, and clothianidin and thiamethoxam in two samples. Acetamiprid and thiamethoxam are currently registered for potato (PPPDA, 2022). Clothianidin has been banned in Türkiye since 31 July 2019 (Polat & Tiryaki, 2022). The results were evaluated according to European Union maximum residue limits (EU-MRL).

The LOQ value (6.3 µg kg^{-1}) determined for acetamiprid was found to be lower than the EU-MRL value (10 µg kg^{-1}). The acetamiprid residues were 60.9, 64.9, 68.7, 71.1, 78.7, 82.2, 85.0, 98.8 and 98.9 µg kg^{-1}. These values were greater than the EU-MRL. One of these samples was from Nevşehir, two from Niğde and six from Adana. The common detection of acetamiprid active in food samples indicates that farmers prefer this pesticide or they are attempting to control similar pests.

The LOQs (6.4 and 4.1 µg kg^{-1}) for thiamethoxam and clothianidin were found be lower than the EU-MRL (70 and 30 µg kg^{-1}), respectively. Clothianidin (23.2 µg kg^{-1}) was detected in one sample from Malatya, and clothianidin (21.6 µg kg^{-1}) and thiamethoxam (46.6 µg kg^{-1}) in one sample from from Niğde. The residues of clothianidin and thiamethoxam were both lower than the EU-MRL. Clothianidin detected with thiamethoxam is thought to be a metabolite of thiamethoxam. However, the detection of clothianidin in the other sample indicates that some farmers have used banned pesticides.

Bakırcı et al. (2014) reported that 4.5% of 66 potato samples contained pesticide residues above MRLs in Aegean region (Türkiye). In the present study, the pesticide residues above MRL were 8.5%. Česnik et al. (2006) detected pesticide residues above EU-MRL in 23% of 150 potato samples from Slovene. Danek et al. (2021) detected residues above EU-MRL in 8 of 15 potato samples from markets in Poland. Česnik et al. (2010) detected residues below LOQ in all 52 potato samples from Slovene. Srivastava et al., (2011) did not detect any pesticide residues in the potatoes from Lucknow City, India. Szpyrka et al. (2015) analyzed 102 unprocessed potato samples from southeastern Poland detecting pesticides under EU-MRL in only two samples. Poulsen et al. (2017) detected pesticides below EU-MRL in only 1% of a total of 669 potato samples from Denmark, France and the UK. Thompson et al. (2011) analyzed 228 fresh potatoes from 34 farmer markets in Alberta, Canada detecting pesticide residues below the Canadian maximum residue limits set for potatoes in 32 samples.

Risk assessment

The pesticide risk assessments of pesticides have attracted consumer interest in recent years, in Türkiye (Çatak & Tiryaki, 2020; Soydan et al., 2021; Balkan & Kara, 2022). Health risk analysis was conducted for three pesticides (Table 3). For acute and chronic risk assessment, the highest exposure value was obtained for acetamiprid.

Table 3. Health risk estimation of insecticides residues in potatoes in Türkiye

Insecticide	ADI* (mg kg BW^{-1} d^{-1})	ARfD* (mg kg BW^{-1} d^{-1})	ESTI (mg kg^{-1} d^{-1})	aHI (%)	EDI (mg kg^{-1} d^{-1})	cHI (%)
Acetamiprid	0.025	0.025	1.89E-04	0.755	1.51E-04	0.602
Clothianidin	0.026	0.500	4.58E-05	0.046	4.35E-05	0.045
Thiamethoxam	0.097	0.100	8.89E-05	0.018	8.89E-05	0.342

* ADI and ARfD values are from the IUPAC Pesticides Properties DataBase (IUPAC, 2022).

Earlier studies did not find any health risk for potato related to acetamiprid, clothianidin and thiamethoxam residues. Likewise, health risk assessment studies on other pesticides in potatoes in China (Wang et al., 2020; Yang et al., 2020; Sun et al., 2021) found no consumer health risk in both the short and long term.

Conclusion

This study verified the value of QuEChERS analysis for insecticide, acaricide and nematicide residue detection in potato using by LC-MS/MS and GC-MS systems. This method had acceptable specificity, linearity ($R^2 > 0.99$), LOD/LOQ, precision (RSD < 20%) and trueness values (70-120%) for 135 pesticide active substances in a potato matrix. This method appears to be applicable for routine analysis of pesticide residues in substrates with high water content. One hundred and four potato samples were examined using the method. Although pesticide residues higher than the LOQ were detected in 11% of potato samples, none of them exceeded the MRL values. The results supported the necessity of continuous pesticide residue monitoring in the food supply chain.

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Supplementary Tables

Table S1. Optimization of LC-MS/MS parameters of 112 insecticides, acaricides, nematicides and metabolites in the MRM mode

Analyte	Type of pesticide	Chemical group	Molecular formula	Ion mode	Retention time (min)	Precursor ion (m/z)	Product ions (m/z)	Dwell time (m sec)	Q1 Pre Bias (V)	CE (V)	Q3 Pre Bias (V)
Abamectin	Insecticide, Acaricide	Micro-organism	$C_{95}H_{142}O_{28}$	Positive	8.590	885.90	158.0	3.0	-26.0	-31.0	-30.0
						885.90	82.0	3.0	-26.0	-55.0	-16.0
						885.90	128.0	3.0	-26.0	-44.0	-24.0
Acephate	Insecticide	Organophosphate	$C_4H_{10}NO_3PS$	Positive	2.835	183.90	95.00	20.0	-19.0	-22.0	-17.0
						183.90	143.00	20.0	-19.0	-9.0	-27.0
Acetamiprid	Insecticide	Neonicotinoid	$C_{10}H_{11}ClN_4$	Positive	4.878	223.30	126.10	10.0	-17.0	-20.0	-22.0
						223.30	90.10	10.0	-16.0	-33.0	-16.0
						223.30	56.10	10.0	-16.0	-15.0	-23.0
Acrinathrin	Insecticide, Acaricide, Nematicide	Pyrethroid	$C_{26}H_{21}F_6NO_5$	Positive	8.760	559.10	208.10	5.0	-28.0	-15.0	-21.0
						559.10	181.05	5.0	-28.0	-32.0	-18.0
Aldicarb-sulfone	Insecticide, Nematicide, Metabolite	Oxime carbamate	$C_7H_{14}N_2O_4S$	Positive	3.566	240.10	86.10	13.0	-16.0	-21.0	-15.0
						240.10	148.00	13.0	-16.0	-13.0	-27.0
Aldicarb-sulfoxide	Metabolite	Oxime carbamate	$C_7H_{14}N_2O_3S$	Positive	3.415	207.10	132.00	15.0	-14.0	-8.0	-25.0
						207.10	89.00	15.0	-14.0	-13.0	-16.0
Amitraz	Insecticide, Acaricide	Amidine	$C_{19}H_{23}N_3$	Positive	4.142	294.00	163.25	10.0	-14.0	-14.0	-30.0
						294.00	122.15	10.0	-14.0	-28.0	-22.0
Benfuracarb	Insecticide	Carbamate	$C_{20}H_{30}N_2O_5S$	Positive	8.401	411.00	190.00	5.0	-29.0	-11.0	-19.0
						411.00	102.10	5.0	-28.0	-29.0	-19.0
Buprofezin	Insecticide, Acaricide	Unclassified	$C_{16}H_{23}N_3OS$	Positive	8.507	306.10	57.05	5.0	-23.0	-23.0	-22.0
						305.90	201.10	5.0	-30.0	-11.0	-21.0
Cadusafos	Insecticide	Organophosphate	$C_{10}H_{23}O_2PS_2$	Positive	8.130	270.80	131.00	3.0	-13.0	-17.0	-24.0
						270.80	97.00	3.0	-13.0	-26.0	-18.0
Carbaryl	Insecticide	Carbamate	$C_{12}H_{11}NO_2$	Positive	5.891	202.05	145.00	7.0	-13.0	-9.0	-26.0
						202.05	127.05	7.0	-13.0	-27.0	-23.0
Carbofuran	Insecticide, Nematicide, Acaricide, Metabolite	Carbamate	$C_{12}H_{15}NO_3$	Positive	5.791	222.00	165.10	7.0	-15.0	-12.0	-17.0
						222.00	123.05	7.0	-15.0	-21.0	-23.0
Carbofuran-OH	Insecticide	Carbamate. N-methyl	$C_{12}H_{15}NO_4$	Positive	4.694	255.00	163.15	5.0	-28.0	-19.0	-16.0
						255.00	220.05	5.0	-28.0	-11.0	-24.0
Carbosulfan	Insecticide, Nematicide	Carbamate	$C_{20}H_{32}N_2O_3S$	Positive	9.115	381.20	118.05	6.0	-27.0	-20.0	-21.0
						381.20	160.25	6.0	-26.0	-14.0	-30.0
Chlorantraniliprole	Insecticide	Anthranilic diamide	$C_{18}H_{14}BrCl_2N_5O_2$	Positive	6.549	483.90	452.90	4.0	-14.0	-19.0	-22.0
						483.90	285.90	4.0	-14.0	-17.0	-30.0
Chlorfenvinphos	Insecticide, Acaricide	Organophosphate	$C_{12}H_{14}Cl_3O_4P$	Positive	7.733	358.80	99.00	5.0	-17.0	-29.0	-17.0
						358.80	155.00	5.0	-17.0	-12.0	-28.0
Chlorfluazuron	Insecticide	Benzoylurea	$C_{20}H_9Cl_3F_5N_3O_3$	Positive	8.792	539.80	382.90	2.0	-38.0	-23.0	-26.0
						539.80	158.00	2.0	-38.0	-20.0	-28.0

Table S1. Cont.

Analyte	Type of pesticide	Chemical group	Molecular formula	Ion mode	Retention time (min)	Precursor ion (m/z)	Product ions (m/z)	Dwell time (m sec)	Q1 Pre Bias (V)	CE (V)	Q3 Pre Bias (V)
Chlorpyrifos	Insecticide	Organophosphate	$C_9H_{11}Cl_3NO_3PS$	Positive	8.764	349.90	97.00	5.0	-18.0	-32.0	-16.0
						349.90	197.95	5.0	-18.0	-19.0	-20.0
Clothianidine	Insecticide, Metabolite	Neonicotinoid	$C_6H_8ClN_5O_2S$	Positive	4.640	249.80	169.00	9.0	-27.0	-12.0	-17.0
						249.80	131.90	9.0	-27.0	-15.0	-23.0
Cyantraniliprole	Insecticide	Diamide	$C_{19}H_{14}BrClN_6O_2$	Positive	5.796	473.10	442.00	7.0	-17.0	-19.0	-30.0
						472.90	116.20	7.0	-13.0	-53.0	-19.0
Cyhalothrin	Insecticide, Acaricide	Pyrethroid	$C_{23}H_{19}ClF_3NO_3$	Positive	8.754	467.20	450.10	5.0	-17.0	-10.0	-30.0
						467.20	225.00	5.0	-13.0	-16.0	-23.0
Cypermethrin	Insecticide, Acaricide	Pyrethroid	$C_{22}H_{19}Cl_2NO_3$	Positive	8.847	433.20	190.95	5.0	-16.0	-15.0	-19.0
						435.20	192.85	5.0	-16.0	-15.0	-19.0
Deltamethrin	Insecticide, Metabolite	Pyrethroid	$C_{22}H_{19}Br_2NO_3$	Positive	8.875	523.00	174,20	100,0	-20,0	-31,0	-17,0
						523.00	281,10	100,0	-15,0	-15,0	-28,0
Demeton-s-methyl	Insecticide, Acaricide	Organophosphate	$C_6H_{15}O_3PS_2$	Positive	5.727	230.90	60.90	7.0	-11.0	-31.0	-22.0
						230.90	89.20	7.0	-11.0	-10.0	-15.0
Demeton-s-methyl-sulfone	Insecticide, Acaricide, Metabolite	Organophosphate	$C_6H_{15}O_5PS_2$	Positive	3.989	263.00	169.05	6.0	-30.0	-6.0	-17.0
						263.00	109.05	6.0	-30.0	-18.0	-21.0
Diafenthiuran	Insecticide, Acaricide,	Unclassified	$C_{23}H_{32}N_2OS$	Positive	8.714	385.00	278.10	3.0	-30.0	-32.0	-30.0
						385.00	186.10	3.0	-30.0	-37.0	-19.0
Diazinon	Insecticide, Acaricide	Organophosphate	$C_{12}H_{21}N_2O_3PS$	Positive	7.949	305.10	169.10	3.0	-16.0	-12.0	-17.0
						305.10	153.00	3.0	-16.0	-16.0	-29.0
Dichlorfos	Insecticide, Acaricide, Metabolite	Organophosphate	$C_4H_7Cl_2O_4P$	Positive	5.679	221.00	109.05	7.0	-15.0	-16.0	-19.0
						221.00	127.05	7.0	-15.0	-17.0	-23.0
Dicrotophos	Insecticide, Acaricide	Organophosphate	$C_8H_{16}NO_5P$	Positive	4.383	237.90	72.00	6.0	-12.0	-26.0	-30.0
						237.90	127.00	6.0	-12.0	-16.0	-22.0
Diflubenzuran	Insecticide	Benzoylurea	$C_{14}H_9ClF_2N_2O_2$	Positive	7.499	311.00	141.00	5.0	-21.0	-31.0	-27.0
						311.00	158.00	5.0	-21.0	-14.0	-30.0
Dimethoate	Insecticide, Acaricide, Metabolite	Organophosphate	$C_5H_{12}NO_3PS_2$	Positive	4.790	230.00	198.95	9.0	-15.0	-8.0	-20.0
						230.00	125.05	9.0	-15.0	-20.0	-22.0
Dioxacarb	Insecticide	Carbamate	$C_{11}H_{13}NO_4$	Positive	4.754	224.10	123.00	5.0	-25.0	-16.0	-22.0
						224.10	167.00	5.0	-25.0	-9.0	-11.0
Emamectin	Insecticide	Benzocid acid	$C_{49}H_{75}NO_{13}$	Positive	8.557	886.40	158.20	3.0	-26.0	-31.0	-30.0
						886.40	82.05	3.0	-26.0	-55.0	-16.0
Emamectin benzoat	Insecticide	Benzocid acid	$C_{56} H_{81} NO_{15}$	Positive	8.474	886.50	158.20	100.0	-30.0	-36.0	-15.0
						886.40	82.30	100.0	-30.0	-48.0	-30.0
						886.30	126.40	100.0	-26.0	-48.0	-27.0
EPN	Insecticide, Acaricide	Organophosphate	$C_{14}H_{14}NO_4PS$	Positive	8.358	324.00	157.00	5.0	-16.0	-24.0	-28.0
						324.00	296.00	5.0	-23.0	-13.0	-20.0
Ethiofencarb	Insecticide	Carbamate. N-methyl	$C_{11}H_{15}NO_2S$	Positive	5.947	226.10	107.15	7.0	-15.0	-15.0	-19.0
						226.10	164.10	7.0	-16.0	-8.0	-30.0

Table S1. Cont.

Analyte	Type of pesticide	Chemical group	Molecular formula	Ion mode	Retention time (min)	Precursor ion (m/z)	Product ions (m/z)	Dwell time (m sec)	Q1 Pre Bias (V)	CE (V)	Q3 Pre Bias (V)
Ethion	Insecticide, Acaricide, Metabolite	Organophosphate	$C_9H_{22}O_4P_2S_4$	Positive	8.773	385.00	199.00	5.0	-27.0	-10.0	-20.0
						402.00	199.00	5.0	-14.0	-15.0	-21.0
						210.20	98.10	4.0	-24.0	-22.0	-18.0
Etofenprox	Insecticide	Pyrethroid. non-ester	$C_{25}H_{28}O_3$	Positive	8.385	394.20	107.05	3.0	-20.0	-31.0	-20.0
						394.20	359.05	3.0	-20.0	-8.0	-25.0
Etoxazole	Acaricide	Diphenyl oxazoline	$C_{21}H_{23}F_2NO_2$	Positive	8.774	360.10	141.00	1.0	-27.0	-28.0	-24.0
						360.10	141.10	1.0	-27.0	-28.0	-25.0
Fenamiphos	Nematicide	Organophosphate	$C_{13}H_{22}NO_3PS$	Positive	7.332	304.20	217.00	5.0	-21.0	-23.0	-22.0
						304.20	201.90	5.0	-21.0	-35.0	-20.0
Fenamiphos-sulfone	Metabolite	Unclassified	$C_{13}H_{22}NO_5PS$	Positive	5.660	336.10	266.00	4.0	-10.0	-15.0	-28.0
						336.10	188.00	4.0	-10.0	-28.0	-20.0
Fenamiphos-sulfoxide	Metabolite	Unclassified	$C_{13}H_{22}NO_4PS$	Positive	5.596	320.10	233.00	4.0	-23.0	-21.0	-24.0
						320.10	108.00	4.0	-23.0	-41.0	-20.0
						330.80	139.00	5.0	-23.0	-36.0	-24.0
Fenazaquin	Acaricide, Insecticide	Quinazoline	$C_{20}H_{22}N_2O$	Positive	9.346	307.00	57.10	7.0	-21.0	-23.0	-22.0
						307.00	161.10	7.0	-21.0	-15.0	-29.0
Fenbutatin oxide	Acaricide, Insecticide	Organometal	$C_{60}H_{78}OSn_2$	Positive	8.933	422.50	366.00	5.0	-15.0	-19.0	-25.0
						422.30	135.00	5.0	-15.0	-34.0	-24.0
						302.05	55.05	5.0	-21.0	-40.0	-21.0
Fenoxycarb	Insecticide	Carbamate	$C_{17}H_{19}NO_4$	Positive	7.531	302.10	88.00	5.0	-15.0	-12.0	-16.0
						302.10	116.15	5.0	-15.0	-11.0	-21.0
Fenpropathrin	Insecticide, Acaricide	Pyrethroid	$C_{22}H_{23}NO_3$	Positive	8.767	349.95	125.10	5.0	-24.0	-11.0	-23.0
						349.95	57.00	5.0	-24.0	-45.0	-21.0
Fenfroxymate	Acaricide, Insecticide	Pyrazolium	$C_{24}H_{27}N_3O_4$	Positive	8.928	422.10	366.00	5.0	-15.0	-19.0	-25.0
						422.10	135.10	5.0	-15.0	-34.0	-24.0
Fenthion	Insecticide	Organophosphate	$C_{10}H_{15}O_3PS_2$	Positive	8.074	279.00	168.90	5.0	-19.0	-16.0	-30.0
						279.00	246.90	5.0	-19.0	-12.0	-26.0
Fenthion-sulfone	Insecticide, Metabolite	Unclassified	$C_{10}H_{15}O_5PS_2$	Positive	5.944	311.00	165.10	4.0	-14.0	-17.0	-17.0
						311.00	233.05	4.0	-14.0	-23.0	-24.0
Fenthion-sulfoxide	Insecticide, Metabolite	Organophosphate	$C_{10}H_{15}O_4PS_2$	Positive	5.841	295.00	279.90	4.0	-15.0	-19.0	-30.0
						295.00	109.00	4.0	-15.0	-32.0	-20.0
Fipronil	Insecticide	Phenylpyrazole	$C_{12}H_4Cl_2F_6N_4OS$	Negative	7.256	434.70	330.00	5.0	10.0	15.0	22.0
						434.70	250.00	5.0	10.0	27.0	26.0
Fipronil-sulfone	Insecticide	Unclassified	$C_{12}H_4Cl_2F_6N_4O_2S$	Negative	7.568	451.00	414.90	3.0	17.0	15.0	30.0
						451.00	282.00	3.0	17.0	26.0	30.0
Flubendiamide	Insecticide	Phthalamide; Organofluoride	$C_{23}H_{22}F_7IN_2O_4S$	Negative	7.405	680.90	254.20	5.0	20.0	29.0	16.0
						680.90	272.10	5.0	20.0	18.0	17.0
Flufenoxuron	Insecticide, Acaricide	Benzoylurea	$C_{21}H_{11}ClF_6N_2O_3$	Positive	8.654	488.80	158.00	5.0	-17.0	-20.0	-29.0
						488.80	141.00	5.0	-17.0	-43.0	-25.0
Formetanete hydrochloride	Acaricide, Insecticide	Formamidine	$C_{11}H_{16}ClN_3O_2$	Positive	5.630	222.0	93.10	100.0	-27.0	-35.0	-16.0
						222.0	120.10	100.0	-27.0	-25.0	-22.0
						222.0	165.20	100.0	-26.0	-15.0	-29.0

Table S1. Cont.

Analyte	Type of pesticide	Chemical group	Molecular formula	Ion mode	Retention time (min)	Precursor ion (m/z)	Product ions (m/z)	Dwell time (m sec)	Q1 Pre Bias (V)	CE (V)	Q3 Pre Bias (V)
Fosthiazate	Insecticide, Nematicide	Organophosphate	$C_9H_{18}NO_3PS_2$	Positive	5.973	284.10	104.10	4.0	-15.0	-11.0	-18.0
						284.10	227.85	4.0	-15.0	-6.0	-23.0
Furathiocarb	Insecticide	Carbamate	$C_{18}H_{26}N_2O_5S$	Positive	8.420	383.10	195.00	5.0	-29.0	-17.0	-20.0
						383.10	252.00	5.0	-30.0	-13.0	-26.0
Heptenophos	Insecticide, Acaricide	Organophosphate	$C_9H_{12}ClO_4P$	Positive	6.367	251.00	127.10	4.0	-13.0	-13.0	-23.0
						251.00	89.10	4.0	-13.0	-30.0	-15.0
Hexythiazox	Acaricide, Insecticide	Carboxamide	$C_{17}H_{21}ClN_2O_2S$	Positive	8.661	353.20	168.10	100.0	-24.0	-25.0	-30.0
						353.20	115.20	100.0	-30.0	-53.0	-18.0
						353.20	151.10	100.0	-29.0	-30.0	-15.0
Imidacloprid	Insecticide	Neonicotinoid	$C_9H_{10}ClN_5O_2$	Positive	4.610	255.90	209.10	21.0	-12.0	-14.0	-21.0
						255.90	174.90	21.0	−14.0	−13.0	−20.0
Indoxacarb	Insecticide	Oxadiazine	$C_{22}H_{17}ClF_3N_3O_7$	Positive	8.098	528.10	203.00	3.0	-26.0	-37.0	-21.0
						528.10	150.10	3.0	-26.0	-24.0	-27.0
Lufenuron	Insecticide, Acaricide	Benzoylurea	$C_{17}H_8Cl_2F_8N_2O_3$	Positive	8.553	509.0	175.1	100.0	34.0	37.0	18.0
						509.0	201.8	100.0	24.0	24.0	19.0
						509.0	325.8	100.0	34.0	18.0	15.0
Malaoxon	Metabolite	Organophosphate	$C_{10}H_{19}O_7PS$	Positive	5.645	314.90	127.00	7.0	-15.0	-12.0	-23.0
						314.90	99.00	7.0	-15.0	-22.0	-17.0
Malathion	Insecticide, Acaricide	Organophosphate	$C_{10}H_{19}O_6PS_2$	Positive	6.996	331.30	99.10	100.0	-13.0	-22.0	-17.0
						331.20	125.10	100.0	-28.0	-29.0	-24.0
Mecarbam	Insecticide, Acaricide	Organophosphate	$C_{10}H_{20}NO_5PS_2$	Positive	7.378	329.90	226.90	5.0	-23.0	-8.0	-23.0
						329.90	96.90	5.0	-23.0	-40.0	-17.0
Metaflumizone	Insecticide	Semicarbazon	$C_{24}H_{16}F_6N_4O_2$	Positive	8.372	507.10	178.05	3.0	-24.0	-27.0	-19.0
						507.10	287.00	3.0	-24.0	-25.0	-30.0
Methacrifos	Insecticide, Acaricide	Organophosphate	$C_7H_{13}O_5PS$	Positive	6.614	241.00	125.00	3.0	-16.0	-19.0	-22.0
						241.00	143.20	3.0	-16.0	-19.0	-26.0
Methamidophos	Insecticide, Acaricide, Metabolite	Organophosphate	$C_2H_8NO_2PS$	Positive	2.429	142.20	94.00	33.0	-27.0	-15.0	-17.0
						142.20	125.00	33.0	-15.0	-16.0	-23.0
Methidathion	Insecticide, Acaricide	Organophosphate	$C_6H_{11}N_2O_4PS_3$	Positive	6.532	303.00	144.90	6.0	-21.0	-9.0	-26.0
						303.00	85.00	6.0	-21.0	-21.0	-15.0
Methiocarb	Insecticide	Carbamate. N-methyl	$C_{11}H_{15}NO_2S$	Positive	6.778	225.90	121.10	5.0	-24.0	-17.0	-22.0
						225.90	169.10	5.0	-24.0	-9.0	-17.0
Methiocarb-sulfone	Metabolite	Carbamate. N-methyl	$C_{11}H_{15}NO_4S$	Positive	4.938	275.10	122.05	5.0	-14.0	-18.0	-23.0
						275.10	258.00	5.0	-14.0	-9.0	-27.0
Methiocarb-sulfoxide	Metabolite	Carbamate. N-methyl	$C_{11}H_{15}NO_3S$	Positive	4.689	242.10	185.05	6.0	-25.0	-3.0	-19.0
						242.10	122.10	6.0	-25.0	-23.0	-22.0
Methomyl	Insecticide, Acaricide	Oxime carbamate	$C_5H_{10}N_2O_2S$	Positive	4.054	162.90	88.00	10.0	-17.0	-9.0	-15.0
						162.90	106.00	10.0	-17.0	-10.0	-19.0
Methoxyfenozide	Insecticide	Carbohydrazide Monomethoxybenzene	$C_{22}H_{28}N_2O_3$	Positive	6.970	369.20	149.15	3.0	-19.0	-8.0	-30.0
						369.20	91.15	3.0	-19.0	-47.0	-16.0
Mevinphos	Insecticide, Acaricide	Organophosphate	$C_7H_{13}O_6P$	Positive	4.776	224.90	127.00	9.0	-24.0	-16.0	-23.0
						224.90	193.00	9.0	-25.0	-7.0	-19.0

Table S1. Cont.

Analyte	Type of pesticide	Chemical group	Molecular formula	Ion mode	Retention time (min)	Precursor ion (m/z)	Product ions (m/z)	Dwell time (m sec)	Q1 Pre Bias (V)	CE (V)	Q3 Pre Bias (V)
Monocrotophos	Insecticide, Acaricide	Organophosphate	$C_7H_{14}NO_5P$	Positive	4.199	223.90	126.90	10.0	-24.0	-14.0	-22.0
						223.90	98.00	10.0	-24.0	-11.0	-17.0
Novaluron	Insecticide	Benzoylurea	$C_{17}H_9ClF_8N_2O_4$	Positive	8.263	493.00	158.00	3.0	-15.0	-18.0	-28.0
						493.00	141.05	3.0	-15.0	-40.0	-27.0
Omethoate	Insecticide, Acaricide, Metabolite	Organophosphate	$C_5H_{12}NO_4PS$	Positive	3.188	213.90	125.00	17.0	-10.0	-21.0	-22.0
						213.90	183.10	17.0	-10.0	-10.0	-19.0
Oxamyl	Insecticide, Acaricide, Nematicide	Oxime carbamate	$C_7H_{13}N_3O_3S$	Positive	3.757	236.95	72.05	12.0	-11.0	-16.0	-29.0
						236.95	90.05	12.0	-11.0	-7.0	-16.0
Oxydemeton-methyl	Insecticide	Organophosphate	$C_6H_{15}O_4PS_2$	Positive	3.886	247.00	109.10	11.0	-18.0	-29.0	-24.0
						247.00	169.00	11.0	-18.0	-14.0	-21.0
Phenthoate	Insecticide, Acaricide	Organophosphate	$C_{12}H_{17}O_4PS_2$	Positive	7.731	321.00	135.15	5.0	-22.0	-19.0	-25.0
						321.00	163.05	5.0	-22.0	-11.0	-30.0
Phorate	Insecticide, Acaricide, Nematicide	Organophosphate	$C_7H_{17}O_2PS_3$	Positive	8.198	261.00	75.00	5.0	-18.0	-10.0	-30.0
						261.00	97.00	5.0	-18.0	-29.0	-17.0
Phosalone	Insecticide, Acaricide	Organophosphate	$C_{12}H_{15}ClNO_4PS_2$	Positive	7.987	367.95	181.95	5.0	-25.0	-15.0	-18.0
						367.95	111.00	5.0	-25.0	-39.0	-19.0
Phosphamidon	Insecticide, Acaricide	Organophosphate	$C_{10}H_{19}ClNO_5P$	Positive	5.385	299.90	174.10	8.0	-21.0	-13.0	-17.0
						299.90	227.00	8.0	-21.0	-13.0	-23.0
Pirimicarb-Desmethyl	Insecticide	Carbamate	$C_{10}H_{16}N_4O_2$	Positive	5.353	225.10	72.10	5.0	-11.0	-21.0	-29.0
						225.10	168.10	5.0	-26.0	-15.0	-30.0
Primicarb	Insecticide	Carbamate	$C_{11}H_{18}N_4O_2$	Positive	6.118	238.90	72.05	7.0	-28.0	-21.0	-29.0
						238.90	182.10	7.0	-30.0	-15.0	-18.0
Primiphos-ethyl	Insecticide, Acaricide	Organophosphate	$C_{13}H_{24}N_3O_3PS$	Positive	8.607	333.90	198.10	5.0	-23.0	-22.0	-20.0
						333.90	182.10	5.0	-23.0	-21.0	-18.0
Primiphos-methyl	Insecticide, Acaricide	Organophosphate	$C_{11}H_{20}N_3O_3PS$	Positive	8.192	305.90	67.10	5.0	-21.0	-44.0	-26.0
						305.90	108.10	5.0	-21.0	-31.0	-19.0
Profenefos	Insecticide	Organophosphate	$C_{11}H_{15}BrClO_3PS$	Positive	8.424	372.95	302.80	5.0	-13.0	-18.0	-20.0
						372.95	344.90	5.0	-13.0	-12.0	-23.0
Promecarb	Insecticide	Carbamate	$C_{12}H_{17}NO_2$	Positive	6.904	208.00	151.10	5.0	-22.0	-9.0	-29.0
						208.00	109.10	5.0	-23.0	-15.0	-20.0
Propargite	Acaricide, Insecticide	Sulphite ester	$C_{19}H_{26}O_4S$	Positive	8.700	368.15	231.10	5.0	-26.0	-10.0	-24.0
						368.15	175.10	5.0	-25.0	-16.0	-18.0
Propoxur	Insecticide, Acaricide	Carbamate	$C_{11}H_{15}NO_3$	Positive	5.569	210.10	111.10	7.0	-14.0	-13.0	-20.0
						210.10	168.00	7.0	-14.0	-8.0	-17.0
Prothiophos	Insecticide	Organophosphate	$C_{11}H_{15}Cl_2O_2PS_2$	Positive	9.185	344.80	240.80	6.0	-24.0	-19.0	-25.0
						344.80	242.80	6.0	-24.0	-19.0	-25.0
Pymetrozine	Insecticide	Pyridine	$C_{10}H_{11}N_5O$	Positive	4.228	217.90	105.00	10.0	-23.0	-20.0	-19.0
						217.90	78.00	10.0	-23.0	-41.0	-30.0
Pyridaben	Insecticide, Acaricide	Pyridazinone	$C_{19}H_{25}ClN_2OS$	Positive	8.946	365.40	309.20	25.0	-14.0	-13.0	-14.0
						365.40	147.30	25.0	-28.0	-23.0	-30.0
						365.40	132.20	25.0	-28.0	-43.0	-23.0

Table S1. Cont.

Analyte	Type of pesticide	Chemical group	Molecular formula	Ion mode	Retention time (min)	Precursor ion (m/z)	Product ions (m/z)	Dwell time (m sec)	Q1 Pre Bias (V)	CE (V)	Q3 Pre Bias (V)
Pyridaphenthion	Insecticide	Organophosphate	$C_{14}H_{17}N_2O_4PS$	Positive	7.047	340.90	189.05	5.0	-24.0	-21.0	-19.0
						340.90	92.10	5.0	-24.0	-39.0	-16.0
Pyriproxyfen	Insecticide	Juvenile hormon mimic	$C_{20}H_{19}NO_3$	Positive	8.770	321.90	78.10	2.0	-30.0	-51.0	-30.0
						321.90	96.00	2.0	-30.0	-14.0	-17.0
Quinalphos	Insecticide, Acaricide	Organophosphate	$C_{12}H_{15}N_2O_3PS$	Positive	7.930	298.90	163.00	5.0	-20.0	-20.0	-30.0
						298.90	147.00	5.0	-20.0	-21.0	-28.0
Spinosyn A	Insecticide	Micro-organism derived	$C_{41}H_{65}NO_{10}$	Positive	8.833	732.50	142.10	100.0	-28.0	-32.0	-24.0
						732.40	98.10	100.0	-24.0	-54.0	-16.0
Spinosyn D	Insecticide	Micro-organism derived	$C_{42}H_{67}NO_{10}$	Positive	9.018	746.30	142.30	100.0	-20.0	-28.0	-25.0
						746.40	98.30	100.0	-24.0	-43.0	-17.0
Spirodiclofen	Acaricide, Insecticide	Tetronic acid	$C_{21}H_{24}Cl_2O_4$	Positive	8.789	411.10	313.05	3.0	-12.0	-14.0	-22.0
						411.10	71.10	3.0	-12.0	-22.0	-27.0
Sulfoxaflor	Insecticide	Sulfoximine	$C_{10}H_{10}F_3N_3OS$	Positive	4.882	278.00	174.00	9.0	-14.0	-11.0	-30.0
						278.20	154.00	9.0	-10.0	-54.0	-25.0
Tebufenozide	Insecticide	Bishydrazide	$C_{22}H_{28}N_2O_2$	Positive	7.478	353.00	133.00	5.0	-17.0	-20.0	-23.0
						353.00	105.10	5.0	-17.0	-43.0	-18.0
Tebufenpyrad	Acaricide, Insecticide	Pyrazole	$C_{18}H_{24}ClN_3O$	Positive	8.439	333.90	171.00	2.0	-16.0	-24.0	-30.0
						333.90	147.10	2.0	-16.0	-25.0	-28.0
Tetramethrin	Insecticide	Pyrethroid	$C_{19}H_{25}NO_4$	Positive	8.486	332.20	164.10	3.0	-10.0	-24.0	-29.0
						332.20	135.10	3.0	-10.0	-18.0	-13.0
Thiacloprid	Insecticide	Neonicotinoid	$C_{10}H_9ClN_4S$	Positive	5.145	507.80	141.10	8.0	-36.0	-24.0	-27.0
						507.80	167.10	8.0	-36.0	-19.0	-17.0
Thiamethoxam	Insecticide	Neonicotinoid	$C_8H_{10}ClN_5O_3S$	Positive	4.138	292.00	211.05	10.0	-20.0	-12.0	-22.0
						292.00	181.00	10.0	-20.0	-22.0	-19.0
Thiodicarb	Insecticide	Oxime carbamate	$C_{10}H_{18}N_4O_4S_3$	Positive	6.167	354.80	88.00	7.0	-17.0	-18.0	-16.0
						354.80	107.95	7.0	-17.0	-15.0	-19.0
Tolfenpyrad	Insecticide	Pyrazolium	$C_{21}H_{22}ClN_3O_2$	Positive	8.544	384.40	197.2	5.0	-11.0	-26.0	-20.0
						384.00	116.00	5.0	-14.0	-21.0	-18.0
Triazophos	Insecticide, Acaricide, Nematicide	Organophosphate	$C_{12}H_{16}N_3O_3PS$	Positive	7.202	314.00	162.00	5.0	-22.0	-19.0	-30.0
						314.00	119.10	5.0	-21.0	-34.0	-22.0
Trichlorfon	Insecticide	Organophosphate	$C_4H_8Cl_3O_4P$	Positive	4.655	256.95	109.00	9.0	-17.0	-17.0	-19.0
						256.95	79.10	9.0	-17.0	-29.0	-14.0
Triflumuron	Insecticide	Benzoylurea	$C_{15}H_{10}ClF_3N_2O_3$	Positive	7.917	359.00	156.05	3.0	-18.0	-17.0	-28.0
						359.00	139.05	3.0	-18.0	-30.0	-26.0

Table S2. Optimization of GC-MS parameters of 23 insecticides, acaricides, nematicides and metabolites in the SRM mode

Analyte	Type of pesticide	Chemical group	Molecular formula	Retention time (min)	Quantitation ion (m/z)	Confirmation ions (m/z)	
Aldrin	Insecticide	Organochloride	$C_{12}H_8Cl_6$	15.157	66.0	207	137
Alpha HCH	Insecticide	Organochloride	$C_6H_6Cl_6$	10.278	181	264	43
Beta HCH	IMetabolite	Organochloride	$C_6H_6Cl_6$	11.055	181	286	282
Bifenthrin	Insecticide, Acaricide	Pyrethroid	$C_{23}H_{22}ClF_3O_2$	22.384	181	272	307
Bromophos-ethyl	Insecticide	Organophosphate	$C_{10}H_{12}BrCl_2O_3PS$	13.19	359	303	242
Bromophos -methyl	Insecticide, Acaricide	Organophosphate	$C_8H_8BrCl_2O_3PS$	15.844	331	174	187
Delta HCH	Metabolite	Organochloride	$C_6H_6Cl_6$	12.283	181	264	268
Dieldrin	Insecticide, Metabolite	Organochloride	$C_{12}H_8Cl_6O$	18.555	79.0	87	241
Endosulfan sulfate	Metabolite	Unclassified	$C_9H_6Cl_6O_4S$	15.19	274	227	229
Endrin	Insecticide	Organochloride	$C_{12}H_8Cl_6O$	14.41	263	281	345
Ethoprophos	Insecticide, Nematicide	Organophosphate	$C_8H_{19}O_2PS_2$	9.187	158	261	201
Fonofos	Insecticide	Organophosphate	$C_{10}H_{15}OPS_2$	11.660	137	181	219
Heptachlor-exo-epoxide	Metabolite	Unclassified	$C_{10}H_5Cl_7O$	16.491	353	329	125
o,p'-DDD	Metabolite	Organochloride	$C_{14}H_{10}Cl_4$	18.644	237	248	318
o,p'-DDE	Metabolite	Organochloride	$C_{14}H_8Cl_4$	17.401	248	375	97
o,p'-DDT	Insecticide	Organochloride	$C_{14}H_9Cl_5$	19.820	237	159	160
p,p'-DDD	Metabolite	Organochloride	$C_{14}H_{10}Cl_4$	19.746	237	263	67
p,p'-DDE	Metabolite	Organochloride	$C_{14}H_8Cl_4$	18.455	246	329	331
Parathion ethyl	Insecticide	Organophosphate	$C_{10}H_{14}NO_5PS$	12.14	291	109	139
Tefluthrin	Insecticide, Acaricide	Pyrethroid	$C_{17}H_{14}ClF_7O_2$	12.347	177	213	183
Tetrachlorvinphos	Insecticide, Acaricide	Organophosphate	$C_{10}H_9Cl_4O_4P$	17.482	109	375	97
Tetradifon	Insecticide, Acaricide	Bridged diphenyl	$C_{12}H_6Cl_4O_2S$	23.119	159	341	166
Tetrasul	Insecticide, Acaricide, Nematicide	Bridged diphenyl	$C_{12}H_6Cl_4S$	20.176	252	165	235

Table S3. Method verification parameters of 135 pesticides

Pesticide (LC-MS/MS)	Pesticide type*	LOD ($\mu g\ kg^{-1}$)	LOQ ($\mu g\ kg^{-1}$)	R^2	Repeatability (n=10)						Reproducibility (n=10)						U' %	ME %
					10 $\mu g\ kg^{-1}$		50 $\mu g\ kg^{-1}$		100 $\mu g\ kg^{-1}$		10 $\mu g\ kg^{-1}$		50 $\mu g\ kg^{-1}$		100 $\mu g\ kg^{-1}$			
					Recovery %	RSD %	Recovery %	RSD %	Recovery %	RSD %	Recovery %	RSD %	Recovery %	RSD %	Recovery %	RSD %		
Abamectin	IN, AC	2.9	9.5	0.992	101.5	13.0	118.8	9.0	107.2	15.1	104.9	16.3	112.9	11.6	111.7	12.8	37.3	-56.8
Acephate	IN	2.0	6.8	0.995	114.4	11.5	101.6	14.9	100.4	11.9	96.9	17.5	115.7	16.3	87.0	9.0	34.3	-95.0
Acetamiprid	IN	1.9	6.3	0.993	115.1	9.6	118.2	4.7	113.7	5.8	106.1	8.7	115.6	13.2	105.7	5.0	32.8	-28.8
Acrinathrin	IN, AC, NE	2.2	7.4	0.990	92.8	15.6	104.2	15.5	115.6	14.6	97.1	17.5	110.0	16.6	119.5	15.0	41.6	-76.8
Aldicarb-sulfone	IN, NE, MT	1.5	5.0	0.999	115.0	6.8	118.4	5.9	108.5	5.4	117.1	8.3	117.6	11.1	105.3	3.5	33.1	-68.8
Aldicarb-sulfoxide	MT	1.5	5.0	0.994	109.4	14.8	99.6	12.4	115.3	14.6	96.5	15.0	102.1	17.0	94.7	17.2	33.7	-83.4
Amitraz	IN, AC	1.5	4.9	0.991	105.0	9.9	119.0	7.1	105.7	3.5	100.6	12.6	111.2	11.4	97.3	5.7	27.4	-72.0
Benfuracarb	IN,	2.6	8.8	0.991	118.3	11.2	103.6	16.3	95.2	18.5	116.9	9.8	97.4	13.5	81.3	15.2	38.5	-84.9
Buprofezin	IN, AC	2.4	8.0	0.998	114.5	12.1	114.8	7.0	109.5	9.8	113.2	15.7	115.9	9.5	112.9	8.0	36.6	-54.8
Cadusafos	IN	2.7	9.1	0.996	114.9	12.8	117.8	6.9	110.9	9.2	116.1	6.9	117.0	12.3	115.3	9.9	38.0	-63.4
Carbaryl	IN	0.8	2.8	0.998	92.3	7.2	101.5	7.1	86.1	8.5	98.1	14.8	105.6	7.4	104.8	12.2	27.1	-72.3
Carbofuran	IN, AC, NE, MT	1.8	6.0	0.999	117.5	8.2	110.9	3.4	109.0	6.6	118.6	5.8	114.1	6.4	106.8	4.7	30.6	-25.9
Carbofuran-OH	IN	2.1	7.1	0.994	111.6	17.3	113.9	10.4	104.1	6.9	102.2	15.1	106.7	8.8	95.9	17.1	32.1	-75.8
Carbosulfan	IN, NE	1.7	5.8	0.990	116.0	11.9	112.8	5.8	111.4	4.5	117.0	11.7	108.6	4.9	98.2	3.5	31.3	4.1
Chlorantraniliprole	IN	1.3	4.4	0.999	106.9	9.5	110.4	8.5	89.8	12.4	100.6	8.5	94.8	10.3	93.4	15.2	28.7	-26.7
Chlorfenvinphos	IN, AC	2.6	8.8	0.991	110.0	12.2	115.9	10.3	103.1	4.6	104.7	17.8	107.9	13.0	101.5	13.4	32.9	-37.2
Chlorfluazuron	IN	2.8	9.2	0.998	102.7	10.8	109.7	12.1	117.9	11.0	107.4	10.4	116.4	12.6	119.2	12.4	37.1	-78.8
Chlorpyrifos	IN	1.5	4.9	0.991	118.2	6.1	116.7	11.9	115.1	11.1	115.6	11.3	116.3	11.9	115.5	12.7	40.8	-64.3
Clothianidine	IN, MT	1.2	4.1	0.995	108.4	6.3	106.4	13.6	111.9	4.5	111.1	7.9	107.1	6.6	114.2	8.5	27.9	-78.2
Cyantraniliprole	IN	1.6	5.4	0.997	114.2	8.9	117.5	8.4	113.7	5.9	99.9	15.6	116.5	9.7	112.3	7.4	33.8	46.2
Cyhalothrin	IN, AC	2.1	7.1	0.990	91.5	19.3	115.1	18.5	109.6	11.7	91.4	14.2	108.0	15.7	110.0	13.6	38.7	-54.4
Cypermethrin	IN, AC	2.5	8.3	0.994	111.2	14.0	113.3	13.2	117.5	9.1	106.0	8.8	116.1	12.0	112.5	12.1	36.4	-77.4
Deltamethrin	IN, MT	2.6	8.7	0.991	110.0	15.4	116.4	11.5	115.2	9.7	107.9	9.4	118.1	13.7	117.8	7.0	38.7	-81.5
Demeton-s-methyl	IN, AC	2.3	7.6	0.992	100.9	10.9	104.3	12.8	101.9	9.9	102.0	13.5	110.5	8.8	96.5	9.1	23.5	-94.3
Demeton-S-methyl-sulfone	IN, AC, MT	1.9	6.3	0.992	105.1	8.7	111.8	4.0	101.4	8.2	87.2	17.2	93.2	15.6	87.3	15.5	29.9	-59.2
Diafenthiuran	IN, AC	2.4	8.1	0.997	98.6	17.7	104.4	12.0	112.2	6.7	97.1	14.9	106.6	16.4	110.1	14.3	35.6	-99.3
Diazinon	IN, AC,	2.1	7.0	0.998	117.3	4.5	108.6	6.9	101.2	6.9	113.2	13.1	112.3	10.3	103.5	14.8	30.1	10.1
Dichlorvos	IN, AC, MT	1.5	4.9	0.997	111.5	5.6	113.8	10.1	114.0	6.9	111.2	6.6	114.4	5.2	109.3	7.8	29.5	181.1
Dicrotophos	IN, AC	1.2	4.0	0.990	116.7	6.4	115.4	12.4	118.3	6.2	114.4	11.2	115.3	11.6	118.8	4.9	39.2	-15.1
Diflubenzuran	IN	2.6	8.6	0.993	117.4	17.2	114.2	8.7	108.4	6.3	110.8	18.2	118.6	12.5	104.7	8.9	38.1	129.0
Dimethoate	IN, AC, MT	1.5	4.8	0.992	106.5	9.8	117.7	13.7	116.2	6.3	108.8	12.8	116.0	11.0	117.2	4.2	36.2	-56.9
Dioxacarb	IN	2.1	6.9	0.994	105.1	9.9	117.2	5.8	101.7	6.9	103.4	9.3	115.9	3.8	97.4	6.9	25.5	-51.1
Emamectin	IN	2.7	8.9	0.996	100.3	12.4	115.3	8.9	119.2	8.1	100.6	15.8	102.6	19.2	106.0	12.6	35.7	-51.5
Emamectin benzoat	IN	1.8	6.1	0.996	96.8	14.9	108.7	13.0	109.3	15.5	91.4	18.3	114.2	16.6	111.5	13.5	37.8	-58.3
EPN	IN, AC	2.5	8.4	0.991	98.2	9.9	98.7	11.7	118.5	9.9	103.5	19.0	113.8	12.6	117.7	15.6	38.0	169.8
Ethiofencarb	IN	2.5	8.4	0.998	93.2	13.6	97.8	11.9	78.2	10.9	100.4	19.4	95.1	10.0	90.4	14.9	33.7	-55.3
Ethion	IN, AC, MT	3.0	9.9	0.990	114.0	10.0	116.7	5.8	110.7	5.8	108.9	5.5	113.5	8.2	107.5	3.4	29.2	-57.6
Etofenprox	IN	2.8	9.4	0.990	87.1	17.9	113.1	18.2	106.4	11.9	97.8	16.8	103.7	14.3	104.4	10.2	35.9	-85.0
Etoxazole	AC	2.7	8.9	0.995	109.8	6.6	118.1	4.9	116.6	7.8	111.4	6.6	119.4	7.2	116.4	6.6	34.6	-77.3

Table S3. Cont.

Pesticide (LC-MS/MS)	Pesticide type*	LOD (µg kg^{-1})	LOQ (µg kg^{-1})	R^2	Repeatability (n=10)						Reproducibility (n=10)						U' %	ME %
					10 µg kg^{-1}		50 µg kg^{-1}		100 µg kg^{-1}		10 µg kg^{-1}		50 µg kg^{-1}		100 µg kg^{-1}			
					Recovery %	RSD %	Recovery %	RSD %	Recovery %	RSD %	Recovery %	RSD %	Recovery %	RSD %	Recovery %	RSD %		
Fenamiphos	NE	2.7	9.1	0.994	99.1	16.5	114.5	11.4	108.8	7.5	101.3	12.7	117.1	10.1	101.6	10.1	31.2	-34.1
Fenamiphos-sulfone	MT	1.4	4.6	0.999	115.5	13.8	115.9	8.0	103.0	7.8	115.7	5.9	116.0	7.8	94.8	9.1	23.3	43.6
Fenamiphos-sulfoxide	MT	2.0	6.5	0.998	108.1	14.5	107.6	9.7	113.7	9.2	107.1	9.1	107.0	13.7	114.6	4.4	38.1	-29.8
Fenazaquin	IN, AC	1.8	5.9	0.992	112.3	5.9	112.5	7.1	107.6	3.4	109.2	16.4	118.6	10.9	109.5	8.4	34.0	87.1
Fenbutatin oxide	IN, AC	2.4	8.0	0.990	118.4	10.0	107.0	9.6	115.9	3.9	109.0	8.6	115.8	17.2	118.4	2.4	37.8	-87.1
Fenoxycarb	IN,	1.8	6.1	0.993	107.2	12.8	118.5	9.1	103.7	4.8	117.0	15.8	110.0	17.6	104.1	4.8	34.3	-36.6
Fenpropathrin	IN, AC	2.5	8.5	0.991	106.7	13.1	113.1	15.0	119.1	3.9	93.0	16.2	115.1	10.5	119.2	8.6	38.7	-65.8
Fenproxymate	IN, AC	2.7	8.9	0.990	109.7	7.1	112.7	12.1	118.2	7.7	94.4	11.9	116.5	13.1	115.8	7.3	36.3	-82.9
Fenthion	IN	2.7	8.9	0.991	118.5	13.2	115.3	14.4	116.2	13.9	99.5	14.4	111.6	11.9	118.8	11.7	41.2	-8.9
Fenthion-sulfone	IN, MT	1.4	4.6	0.999	106.9	9.3	79.1	10.1	90.3	11.2	99.3	16.1	88.8	12.3	85.2	11.3	33.1	-28.4
Fenthion-sulfoxide	IN, MT	1.2	4.0	0.997	103.8	5.5	110.0	8.8	94.3	11.4	100.8	11.2	113.9	10.2	100.1	11.9	26.7	-32.1
Fipronil	IN	1.3	4.4	0.991	106.3	8.6	90.1	12.6	90.8	14.4	109.7	8.0	94.2	10.1	82.3	13.5	30.0	-66.4
Fipronil-sulfone	IN	2.4	7.8	0.992	111.5	7.8	104.7	16.5	87.3	11.1	118.2	11.0	106.3	13.1	89.5	11.8	33.6	-85.2
Flubendiamide	IN	2.8	9.4	0.992	92.6	15.3	112.9	12.7	113.1	11.1	99.6	10.2	109.6	13.0	97.2	19.3	33.2	-16.4
Flufenoxuron	IN, AC	2.5	8.5	0.991	98.5	5.5	109.7	7.0	118.6	7.7	103.7	17.3	112.7	10.7	111.5	6.3	34.8	-52.5
Formetanate hydrochloride	IN, AC	1.2	4.0	0.998	106.4	10.6	108.0	7.5	95.1	3.6	112.8	9.6	109.7	10.9	99.9	5.9	24.7	-41.9
Fosthiazate	IN, NM	1.3	4.5	0.997	87.7	9.7	84.7	14.5	73.5	10.1	92.6	10.3	76.7	9.1	81.9	15.6	42.5	-66.1
Furathiocarb	IN	2.8	9.3	0.996	98.6	9.2	115.9	5.5	111.1	7.5	108.2	11.4	117.9	13.7	112.3	14.7	35.5	-62.9
Heptenophos	IN, AC	0.7	2.5	0.999	97.9	8.5	104.9	7.3	98.6	11.4	103.2	7.8	95.9	9.2	92.1	14.5	23.0	-20.3
Hexythiazox	IN, AC	2.4	8.0	0.991	103.8	15.4	117.7	9.3	115.0	8.9	116.9	18.7	112.5	11.0	119.6	8.3	41.4	-61.6
Imidacloprid	IN	0.9	2.9	0.994	108.7	11.5	116.6	6.3	102.5	6.8	97.8	12.7	115.6	10.1	100.5	5.3	28.2	-55.6
Indoxacarb	IN	2.3	7.7	0.995	115.7	10.3	114.1	13.0	111.2	7.9	109.0	16.2	116.3	13.6	96.3	14.2	37.1	-46.3
Lufenuron	IN, AC	2.7	9.1	0.992	113.3	8.4	114.1	12.0	117.2	6.1	112.8	15.4	112.0	8.7	110.2	10.0	35.7	28.0
Malathion	IN, AC	2.2	7.3	0.996	106.6	7.1	115.4	10.1	109.4	13.8	112.0	14.5	116.1	6.7	100.7	14.0	33.4	-58.4
Malaoxon	MT	2.0	6.8	0.999	112.4	11.2	117.4	8.1	105.4	7.7	110.4	7.9	115.6	4.1	100.0	3.7	28.8	-50.1
Mecarbam	IN, AC	2.6	8.5	0.991	107.2	15.6	119.5	12.8	107.7	15.1	112.8	19.2	118.9	5.2	100.2	18.4	41.1	-69.3
Metaflumizone	IN,	2.3	7.5	0.994	92.8	8.8	112.3	11.6	105.2	10.3	96.9	15.6	101.3	11.7	87.2	11.8	29.9	-22.4
Methacrifos	IN, AC	2.4	8.1	0.999	112.4	10.5	111.8	13.6	109.9	8.4	108.6	7.8	116.5	10.5	113.3	9.9	33.9	58.5
Methamidophos	IN, AC, MT	1.5	4.9	0.992	110.2	10.5	114.6	5.4	102.5	8.9	109.4	5.6	104.8	12.4	92.2	10.0	26.1	-95.7
Methidathion	IN, AC	2.5	8.4	0.996	111.1	14.7	110.8	15.8	85.7	15.4	103.3	17.5	100.7	18.0	86.5	17.7	37.7	-78.7
Methiocarb	IN	2.4	7.9	0.993	117.8	12.0	119.1	11.8	116.4	6.9	109.3	17.4	113.7	8.5	114.4	9.6	40.1	-36.9
Methiocarb-sulfone	MT	1.5	5.1	0.992	101.6	15.8	116.3	5.2	107.4	5.1	97.1	13.9	117.1	8.5	106.5	9.0	30.0	-28.0
Methiocarb-sulfoxide	MT	2.0	6.7	0.998	109.1	11.0	111.2	9.8	107.0	4.9	115.0	6.4	105.9	6.1	105.7	9.3	26.0	-43.1
Methomyl	IN, AC	1.9	6.3	0.994	118.0	9.2	116.2	13.3	108.5	8.4	116.3	10.1	118.2	7.6	110.8	4.8	36.9	-60.1
Methoxyfenozide	IN	2.7	9.0	0.991	108.3	16.1	93.9	16.2	100.8	14.1	96.1	15.8	94.2	18.6	83.1	14.1	36.3	-74.3
Mevinphos	IN, AC	2.4	8.1	0.997	99.6	8.4	112.9	11.1	108.7	9.3	86.6	14.5	107.4	4.5	96.0	9.4	27.8	-58.4
Monocrotophos	IN, AC	1.8	5.9	0.991	117.5	5.3	117.8	5.5	109.0	4.1	118.3	3.8	119.1	7.7	103.8	9.4	33.8	2.3
Novaluron	IN,	2.9	9.7	0.991	116.3	11.2	115.8	9.2	117.5	5.3	115.1	13.7	116.5	16.8	115.9	7.7	41.2	19.2
Omethoate	IN, AC, MT	1.0	3.4	0.993	91.4	15.5	98.4	15.5	83.8	16.9	96.6	16.7	98.3	17.9	96.6	12.2	36.5	-82.9
Oxamyl	IN, AC, NE	1.9	6.2	0.999	112.1	12.6	117.9	10.4	108.7	7.5	109.6	7.8	113.8	7.1	98.1	7.2	30.7	-78.6
Oxydemeton-methyl	IN	1.3	4.5	0.999	115.8	6.4	115.6	9.1	108.9	5.6	114.8	8.8	118.5	7.2	110.9	4.9	32.9	-62.9

Table S3. Cont.

Pesticide (LC-MS/MS)	Pesticide type*	LOD (µg kg^{-1})	LOQ (µg kg^{-1})	R^2	Repeatability (n=10)						Reproducibility (n=10)						U' %	ME %
					10 µg kg^{-1}		50 µg kg^{-1}		100 µg kg^{-1}		10 µg kg^{-1}		50 µg kg^{-1}		100 µg kg^{-1}			
					Recovery %	RSD %	Recovery %	RSD %	Recovery %	RSD %	Recovery %	RSD %	Recovery %	RSD %	Recovery %	RSD %		
Phenthoate	IN, AC	2.7	9.0	0.997	117.0	7.8	115.7	15.1	115.3	7.1	109.8	13.7	115.2	10.7	111.5	12.2	38.9	-26.1
Phorate	IN, AC, NE	2.0	6.8	0.996	116.6	11.7	113.5	16.3	117.6	8.7	111.7	14.9	114.1	15.4	115.3	8.7	40.8	-45.2
Phosalone	IN, AC	2.3	7.7	0.992	118.2	6.0	114.2	11.0	112.4	9.9	96.2	16.0	116.3	6.9	116.3	8.2	36.3	-43.8
Phosphamidon	IN, AC	2.0	6.7	0.999	111.3	7.8	116.8	6.7	106.0	4.5	112.7	7.7	115.9	6.7	103.6	7.0	28.5	-46.4
Pirimicarb-Desmethyl	IN	1.7	5.5	0.999	103.4	7.3	105.2	7.9	104.5	10.2	110.6	13.8	107.8	8.5	106.8	11.4	25.1	-36.6
Primicarb	IN	2.3	7.7	0.998	113.3	8.7	117.4	10.1	107.6	8.9	112.6	11.6	116.4	16.1	109.5	13.1	38.0	-91.7
Primiphos -ethyl	IN, AC	2.3	7.5	0.993	105.1	6.6	108.0	8.3	98.0	7.3	107.3	10.1	113.5	11.1	108.1	12.0	26.3	-70.3
Primiphos -methyl	IN, AC	2.4	7.9	0.990	113.6	11.6	116.9	6.2	104.3	6.1	117.4	14.5	115.7	12.4	111.7	7.7	35.9	-47.7
Profenofos	IN	2.6	8.8	0.994	112.6	6.3	117.7	13.1	116.8	5.5	111.3	13.8	109.9	11.4	107.6	6.9	35.4	-29.6
Promecarb	IN	1.5	5.2	0.996	116.5	8.9	113.0	9.5	106.6	6.5	104.8	12.5	117.8	6.2	95.3	12.0	32.4	-46.3
Propargite	IN, AC	2.6	8.5	0.994	118.1	11.5	111.6	13.5	119.1	11.6	114.4	15.1	117.3	12.5	116.3	8.7	43.2	-74.2
Propoxur	IN, AC	1.6	5.2	0.999	118.8	7.9	115.8	11.1	110.3	13.7	114.2	14.0	113.3	8.0	116.6	12.5	39.7	-25.2
Prothiophos	IN	2.7	8.8	0.991	109.9	15.1	104.5	4.9	117.4	7.4	98.3	15.0	108.1	10.0	111.1	16.3	33.5	-37.2
Pymetrozine	IN	1.6	5.4	0.998	118.1	11.8	116.3	12.5	119.4	4.8	115.6	14.1	117.4	13.4	116.3	3.6	41.8	-72.4
Pyridaben	IN, AC	1.6	5.2	0.992	116.3	13.0	106.2	13.1	115.7	6.6	97.3	9.7	118.3	15.0	119.5	8.5	39.0	-82.7
Pyridaphenthion	IN	2.0	6.6	0.991	107.5	15.5	112.0	16.1	106.0	7.5	106.5	17.6	114.4	13.6	109.4	6.8	35.0	-72.1
Pyriproxyfen	IN,	2.9	9.8	0.995	114.4	4.4	118.7	8.7	113.2	10.9	116.4	12.0	118.9	16.3	118.1	10.0	41.5	-62.8
Quinalphos	IN, AC	1.8	5.9	0.992	104.0	13.5	106.1	7.3	104.0	7.4	105.2	8.5	111.0	11.7	104.4	9.6	27.4	-58.7
Spinosyn A	IN	2.5	8.3	0.994	108.4	4.8	106.3	6.3	102.2	8.7	102.9	7.3	95.7	7.5	96.0	7.0	20.2	-83.2
Spinosyn D	IN	3.0	9.9	0.993	104.3	14.1	110.3	12.0	113.4	4.3	102.6	13.7	110.8	8.7	102.6	6.0	30.0	-66.8
Spirodiclofen	IN, AC	2.6	8.7	0.991	114.5	16.4	107.6	7.3	118.1	6.7	93.2	15.4	116.1	12.0	118.6	9.0	38.4	-82.4
Sulfoxaflor	IN	1.7	5.7	0.995	117.6	13.8	110.8	7.8	106.7	13.8	111.3	12.7	116.3	12.4	104.6	12.5	37.6	-71.7
Tebufenozide	IN	2.6	8.7	0.991	96.0	13.6	103.1	9.0	85.8	12.4	106.8	8.5	104.0	11.5	90.6	11.2	26.1	-75.4
Tebufenpyrad	AC, IN	2.8	9.3	0.994	107.3	16.1	116.4	12.8	115.1	9.4	103.3	10.0	109.3	15.7	113.8	7.9	37.0	-49.1
Tetramethrin	IN	2.8	9.5	0.993	95.0	12.3	117.4	7.3	112.2	7.0	108.3	12.8	109.8	8.7	106.6	7.6	30.1	-63.1
Thiacloprid	IN	1.5	5.1	0.993	95.8	7.9	118.2	7.3	108.8	5.3	100.7	9.1	116.0	7.3	107.8	7.5	27.2	-73.4
Thiamethoxam	IN	1.9	6.4	0.994	116.8	10.2	118.6	9.7	114.8	10.3	115.6	11.6	117.0	11.3	116.8	3.6	39.7	-70.4
Thiodicarb	IN	1.8	5.9	0.994	113.2	4.4	111.1	10.9	109.2	5.8	100.8	16.0	93.6	10.9	95.2	8.4	28.5	-91.1
Tolfenpyrad	IN	2.5	8.5	0.990	83.0	12.2	104.3	7.1	90.1	8.0	74.7	7.7	96.9	9.4	82.9	7.0	35.6	-27.2
Triazophos	IN, AC, NE	1.7	5.7	0.996	117.0	13.8	119.3	7.3	113.3	8.3	100.1	12.5	117.8	7.4	110.5	9.3	37.5	-69.6
Trichlorfon	IN	1.3	4.3	0.991	112.7	14.1	118.2	8.8	119.4	4.9	114.3	11.0	116.6	12.9	108.9	6.6	38.0	-22.9
Triflumuron	IN	2.1	7.1	0.995	104.0	11.2	108.9	8.1	100.5	5.2	106.0	12.4	115.9	7.3	96.8	8.0	27.0	3.4
Pesticide (GC-MS)																		
Aldrin	IN	0.6	2.0	0.995	100.6	1.8	84.2	4.8	107.9	9.3	104.8	5.3	109.0	5.2	109.5	3.8	23.5	374.1
Alpha HCH	IN	2.8	9.4	0.991	95.4	7.8	89.0	9.0	109.8	4.3	90.6	16.6	111.9	10.5	104.9	10.5	27.0	-90.9
Beta HCH	MT	2.1	6.9	0.998	101.1	11.9	89.9	7.4	108.6	4.4	78.3	13.7	111.6	3.9	111.8	2.6	29.8	150.3
Bifenthrin	IN, AC	2.6	8.6	0.992	93.5	13.9	105.3	7.5	100.9	11.7	98.1	14.6	103.1	10.7	100.1	9.3	24.8	236.4
Bromophos-ethyl	IN,	1.4	4.8	0.993	75.2	5.7	82.8	9.5	108.8	3.0	76.2	7.0	102.5	5.1	112.0	4.9	35.7	267.6
Bromophos -methyl	IN, AC	1.3	4.5	0.992	113.1	3.9	82.0	6.5	103.4	9.4	113.9	6.0	110.5	5.7	104.6	7.6	28.2	399.4
Delta HCH	MT	0.8	2.6	0.998	96.5	3.3	87.6	6.6	109.7	7.1	97.1	8.1	108.7	6.2	110.1	6.5	24.7	394.2

Table S3. Cont.

Pesticide (LC-MS/MS)	Pesticide type*	LOD (µg kg^{-1})	LOQ (µg kg^{-1})	R^2	Repeatability (n=10)						Reproducibility (n=10)						U' %	ME %
					10 µg kg^{-1}		50 µg kg^{-1}		100 µg kg^{-1}		10 µg kg^{-1}		50 µg kg^{-1}		100 µg kg^{-1}			
					Recovery %	RSD %	Recovery %	RSD %	Recovery %	RSD %	Recovery %	RSD %	Recovery %	RSD %	Recovery %	RSD %		
Dieldrin	IN, MT	0.8	2.5	0.991	109.4	6.0	88.0	8.8	105.1	8.2	103.2	4.9	102.3	7.9	95.9	9.3	22.2	107.7
Endosulfan sulfate	MT	2.1	6.9	0.993	84.0	10.2	93.8	9.9	108.4	7.1	74.1	2.5	104.6	10.6	105.7	10.0	31.7	208.8
Endrin	IN	2.9	9.6	0.993	96.7	5.3	83.3	3.5	97.3	5.3	98.0	7.6	93.4	5.0	98.9	6.0	19.5	99.7
Ethoprophos	IN, NE	2.3	7.5	0.998	92.4	18.3	93.8	12.6	108.6	9.4	73.8	11.8	97.2	11.2	106.8	10.3	33.6	152
Fonofos	IN	1.1	3.7	0.990	89.7	5.9	90.4	3.7	103.6	9.2	93.3	4.7	99.4	10.2	109.1	7.4	24.5	54.4
Heptachlor exo epoxide	MT	1.2	4.1	0.991	116.3	1.9	79.8	9.3	108.8	8.7	115.3	2.2	109.4	6.1	109.1	5.1	30.8	200
o.p DDD	MT	0.5	1.6	0.991	85.6	2.2	79.4	5.4	102.2	3.3	89.2	2.0	100.5	4.1	107.0	3.1	25.1	-62.2
o.p DDE	MT	0.4	1.3	0.991	88.9	2.0	86.8	8.0	87.6	2.6	87.6	2.1	87.6	3.5	94.2	3.1	27.8	61
o.p DDT	IN	2.5	8.3	0.997	109.6	4.6	92.6	5.2	103.1	10.1	97.6	17.2	97.7	4.5	109.2	7.1	24.3	-57.1
p.p DDD	MT	1.9	6.3	0.991	110.2	4.7	108.3	6.4	97.4	7.9	101.3	11.2	99.8	11.6	93.3	10.5	23.4	98.3
p.p DDE	MT	0.3	1.1	0.992	85.7	1.7	84.9	7.0	101.7	3.4	89.3	2.0	100.6	4.1	106.2	3.1	21.6	108.9
Parathion ethyl	IN, AC	0.6	1.9	0.994	86.4	2.4	81.5	3.2	100.3	2.5	88.3	2.7	104.7	2.7	106.8	1.6	23.4	-66.2
Tefluthrin	IN	0.7	2.4	0.992	84.2	3.0	83.7	5.1	106.3	4.0	85.8	2.4	106.9	4.3	111.4	3.4	26.5	253.9
Tetrachlorvinphos	IN, AC	0.7	2.2	0.993	89.2	1.7	86.5	3.1	102.3	2.8	91.5	4.4	103.5	3.0	107.8	2.1	18.6	683.7
Tetradifon	IN, AC	2.1	7.0	0.992	82.4	8.5	96.1	6.1	101.8	11.9	74,0	6.0	94.8	13.1	105.0	6.0	36.1	101.5
Tetrasul	IN, AC, NE	0.9	2.9	0.993	118.0	1.4	87.8	5.0	103.0	3.2	117.7	1.5	98.4	3.7	106.8	3.3	24.8	-25.6

* IN: Insecticide, AC: Acaricide, NE: Nematicide and MT: Metabolite