Using a QuEChERS Approach for the Determination of Pesticide Residues in Soil

UCT Part Numbers

ECQUEU750CT-MP
4g MgSO4, 1g NaCl,
0.5g Na2HCitr.1.5H2O, and
1g Na3Citr.2H2O

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ECQUSF24CT
150 mg MgSO4, 50 mg PSA, and
50 mg C18

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SLC-1800ID21-3UM
Selectra® C18 HPLC column
100 × 2.1 mm, 3 µm

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SLC-18GDC20-3UM
Selectra® C18 guard cartridge
10 × 2.1 mm, 3 µm

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SLGRDHLDR
Guard cartridge holder

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Summary:

The use of pesticides in agriculture and households is widespread. To ensure food safety and prevent the unnecessary exposure of consumers to pesticides it is important to test for these residues in surveillance plans. While the greatest source of pesticide exposure comes from residues that remain in final food products, they can also be found in environmental samples such as water and soil. As a consequence, any pesticides that are present in soil can potentially be incorporated into growing crops. Contaminated soil also represents a serious environmental problem as the pesticides can be transported to other environmental systems such as ground water and air.

Due to the wide range of pesticides used in agriculture, the development of fast multi-residue methods that simultaneously determine a wide range of pesticides is essential. One of the most widely used multi-residue methodologies is the QuEChERS approach. This offers many advantages including speed, cost, ease of use, good performance characteristics and wide applicability range (matrices and analytes).

Soil is a complex matrix consisting of organic and inorganic material. It possesses many active sites (polar, non-polar and ionic) that are capable of retaining pesticides and other residues. Compared to other matrices commonly encountered in pesticide residue analysis (e.g. fruits and vegetable), soil samples are more difficult to extract and require longer extraction times due to the stronger interactions that may occur between the soil and the pesticides.

The aim of this study was to evaluate the effectiveness of the QuEChERS extraction and cleanup approach for the analysis of pesticides in soil. 21 pesticides, comprising various chemical properties, were used for the study. LC-MS/MS was used for detection and quantitation.

QuEChERS Procedure:

Sample Extraction:

1. Weigh 10g soil sample (≥70% H_2O content) into a 50mL centrifuge tube. Alternatively, weigh 3g air-dried soil sample into a 50mL tube and add 7mL H_2O, vortex briefly, and allow to hydrate for 30 min.
2. Add 10 mL of acetonitrile to each sample.
3. Shake (manually or mechanically) or vortex samples for 5 min to extract pesticides. (In this study a Spex SamplePrep Geno/Grinder 2010 operated at 1500 rpm was used).
4. Add the contents of an **ECQUEU750CT-MP** Mylar pouch (citrate buffered salts) to each centrifuge tube.
5. Immediately shake samples for at least 2 min.
6. Centrifuge for 5 min at ≥3000 rcf.

dSPE Clean-up:

1. Transfer 1 ml of supernatant to a SpinFiltr® (**ECQUSF24CT**).
2. Vortex the sample for 30 seconds.
3. Centrifuge the sample at ≥ 5000 rcf for 2 minutes.
4. Transfer the purified and filtered sample extract into an autosampler vial for analysis.

NOTE: It is possible for certain compounds to be covalently bound to the soil. These bound residues can only be removed using an acid or base hydrolysis step prior to extraction. However, if a hydrolysis step is employed, this may have a detrimental effect on pH sensitive analytes.

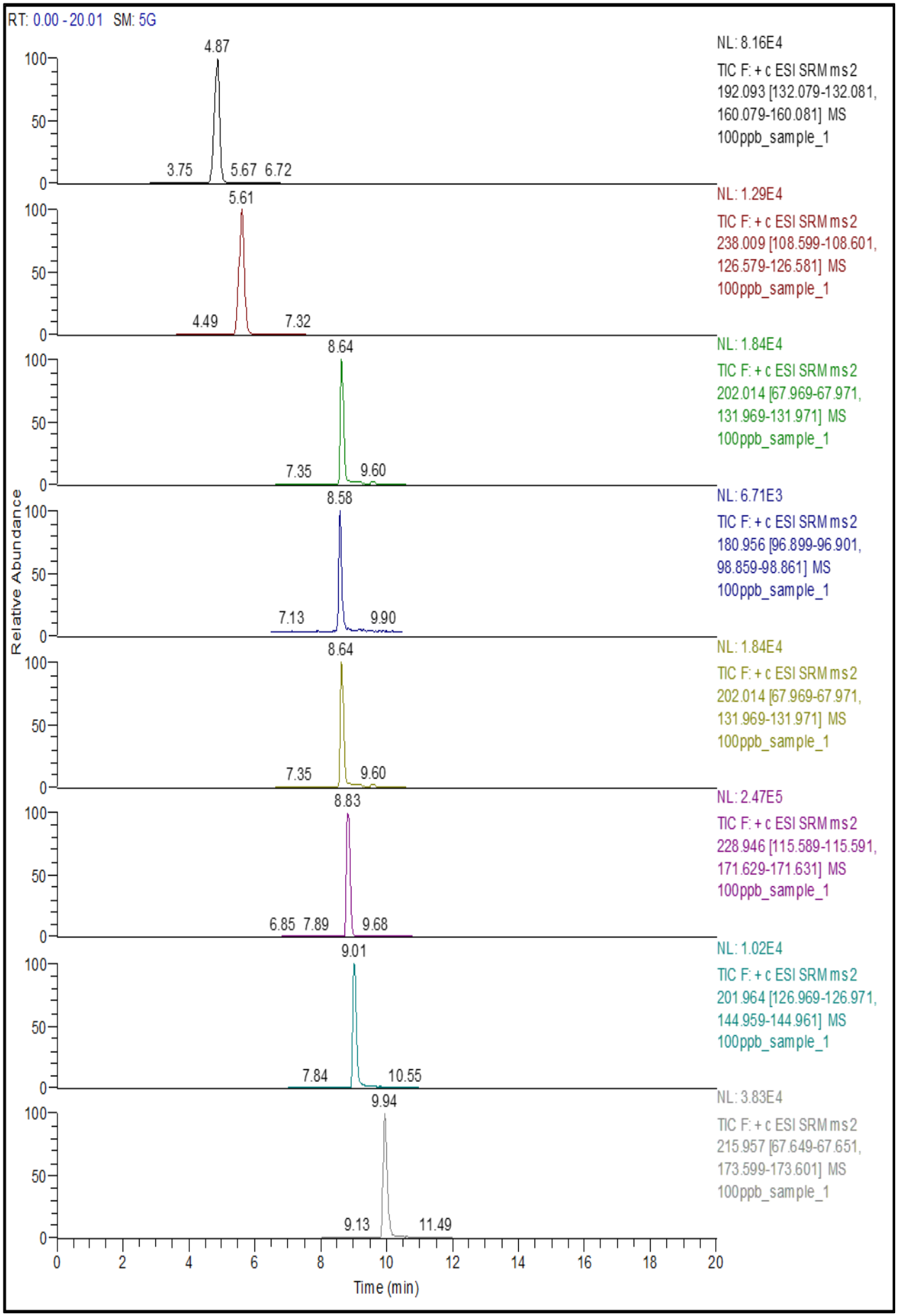
LC-MS/MS Parameters:

HPLC Conditions	
HPLC system	Thermo Scientific™ Dionex™ Ultimate™ 3000
HPLC column	UCT Selectra® C18, 100 × 2.1 mm, 3 µm (p/n: **SLC-18100ID21-3UM**)
Guard column	UCT Selectra® C18, 10 × 2.1 mm, 3 µm (p/n: **SLC-18GDC20-3UM**))
Guard column holder	p/n: SLGRDHLDR
Column temperature	40°C
Flow rate	300 µL/min
Injection volume	3 µL
Autosampler	10°C
Wash solvent	MeOH:ultrapure water (1:1, v/v)
Mobile phase A	0.1% ammonium formate + 0.3% formic acid
Mobile phase B	methanol + 0.1% formic acid
Run time	25 min (including 5 min re-equilibration)

MS Conditions	
Instrumentation	Thermo Scientific™ TSQ Vantage™ tandem mass spectrometer
Ionization mode	ESI^+
Spray voltage	4500 V
Vaporizer temperature	450°C
Capillary temperature	225°C
Sheath gas pressure	55 arbitrary units
Auxiliary gas pressure	25 arbitrary units
Ion sweep gas	0 arbitrary units
Declustering potential	0 V
Q1 and Q3 peak width	0.2 and 0.7 Da
Collision gas	argon
Collision gas pressure	1.5 mTorr
Acquisition method	EZ method (SRM)
Cycle time	1 sec

MS Parameters and Retention Times						
Analyte	**RT**	**Parent ion**	**Product 1**	**CE 1**	**Product 2**	**CE 2**
Carbendazim	4.9	192.09	132.08	29	160.08	17.00
Dicrotophos	5.6	238.01	108.60	33	126.58	17.00
Thiabendazole	8.6	202.06	131.06	31	175.07	24.00
DIMP	8.6	180.96	96.90	12	98.86	14.00
Simazine	8.6	202.01	67.97	32	131.97	17.00
Tebuthiuron	8.8	228.95	115.59	26	171.63	17.00
Carbaryl	9.0	201.96	126.97	29	144.96	6.00
Atrazine	9.9	215.96	67.65	35	173.60	16.00
DEET	10.1	191.95	90.66	28	118.63	15.00
Pyrimethanil	11.0	199.99	106.97	23	183.00	22.00
Malathion	12.3	331.01	98.57	23	126.86	12.00
Acetochlor	13.3	269.96	148.02	15	223.98	10.00
Cyprodinil	13.6	226.12	77.03	40	93.05	33.00
Tebuconazole	14.2	308.01	69.66	29	124.56	35.00
Diazinon	14.3	304.99	153.04	16	169.02	16.00
TPP	14.4	327.09	77.02	37	152.07	33.00
Zoxamide	14.4	335.92	158.91	36	186.91	19.00
Pyrazophos	14.7	374.10	194.06	20	222.13	20.00
Profenofos	15.7	372.89	127.92	41	302.79	17.00
Chlorpyrifos	16.4	349.70	96.81	29	197.76	20.00
Abamectin	17.6	889.98	304.92	25	751.21	35.00
Bifenthrin	18.2	440.04	165.21	39	180.42	11.00

Figure 1. LC-MS/MS chromatogram of 21 pesticides and internal standard (TPP):



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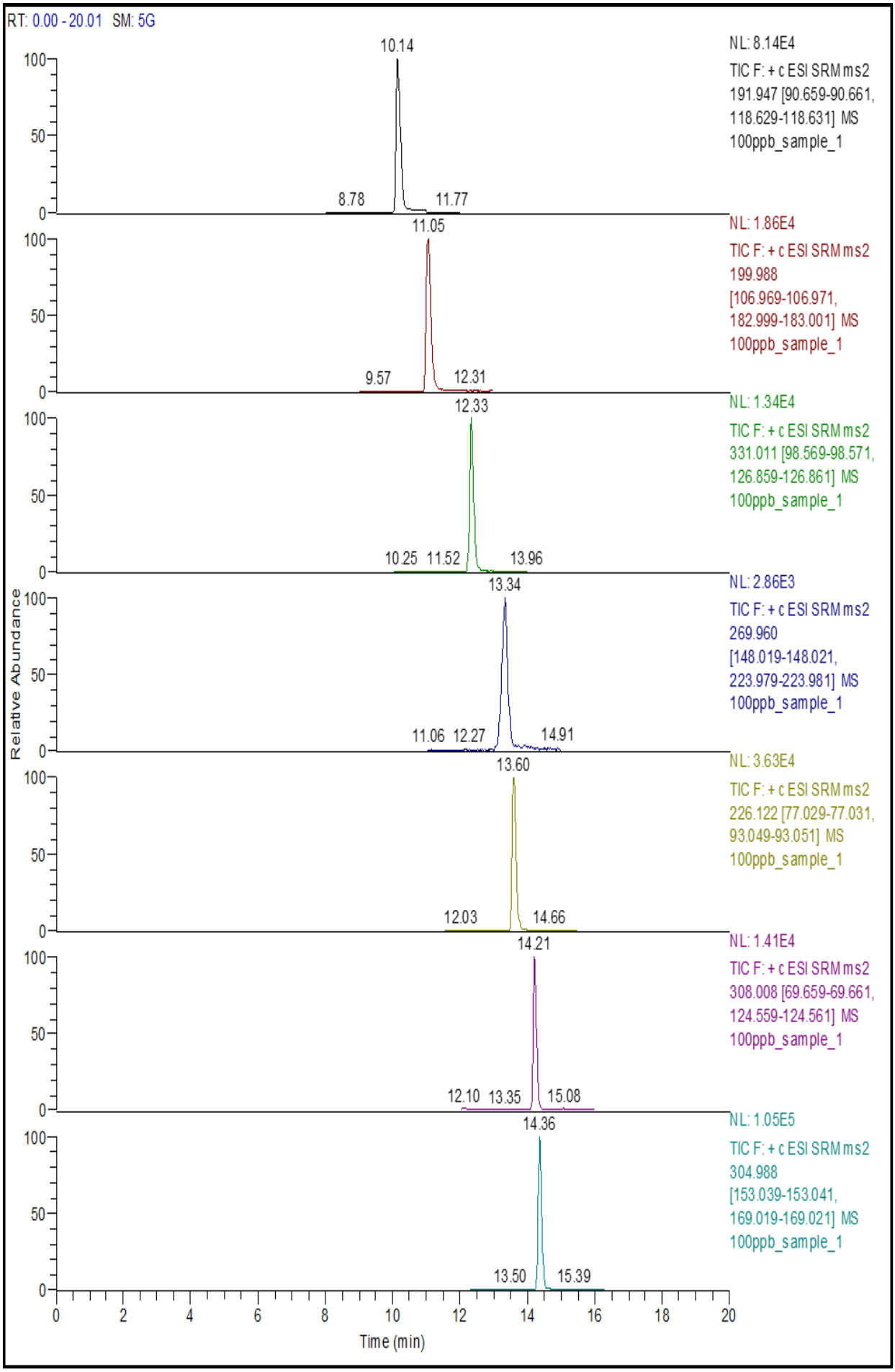
RT: 0.00 - 20.01 SM: 5G
10.14
8.78
11.77
NL: 8.14E4
TIC F: + c ESI SRM ms2 191.947 [90.659-90.661, 118.629-118.631] MS 100ppb_sample_1
11.05
9.57
12.31
NL: 1.86E4
TIC F: + c ESI SRM ms2 199.988 [106.969-106.971, 182.999-183.001] MS 100ppb_sample_1
12.33
10.25
11.52
13.96
NL: 1.34E4
TIC F: + c ESI SRM ms2 331.011 [98.569-98.571, 126.859-126.861] MS 100ppb_sample_1
13.34
11.06
12.27
14.91
NL: 2.86E3
TIC F: + c ESI SRM ms2 269.960 [148.019-148.021, 223.979-223.981] MS 100ppb_sample_1
13.60
12.03
14.66
NL: 3.63E4
TIC F: + c ESI SRM ms2 226.122 [77.029-77.031, 93.049-93.051] MS 100ppb_sample_1
14.21
12.10
13.35
15.08
NL: 1.41E4
TIC F: + c ESI SRM ms2 308.008 [69.659-69.661, 124.559-124.561] MS 100ppb_sample_1
14.36
13.50
15.39
NL: 1.05E5
TIC F: + c ESI SRM ms2 304.988 [153.039-153.041, 169.019-169.021] MS 100ppb_sample_1
Relative Abundance
Time (min)

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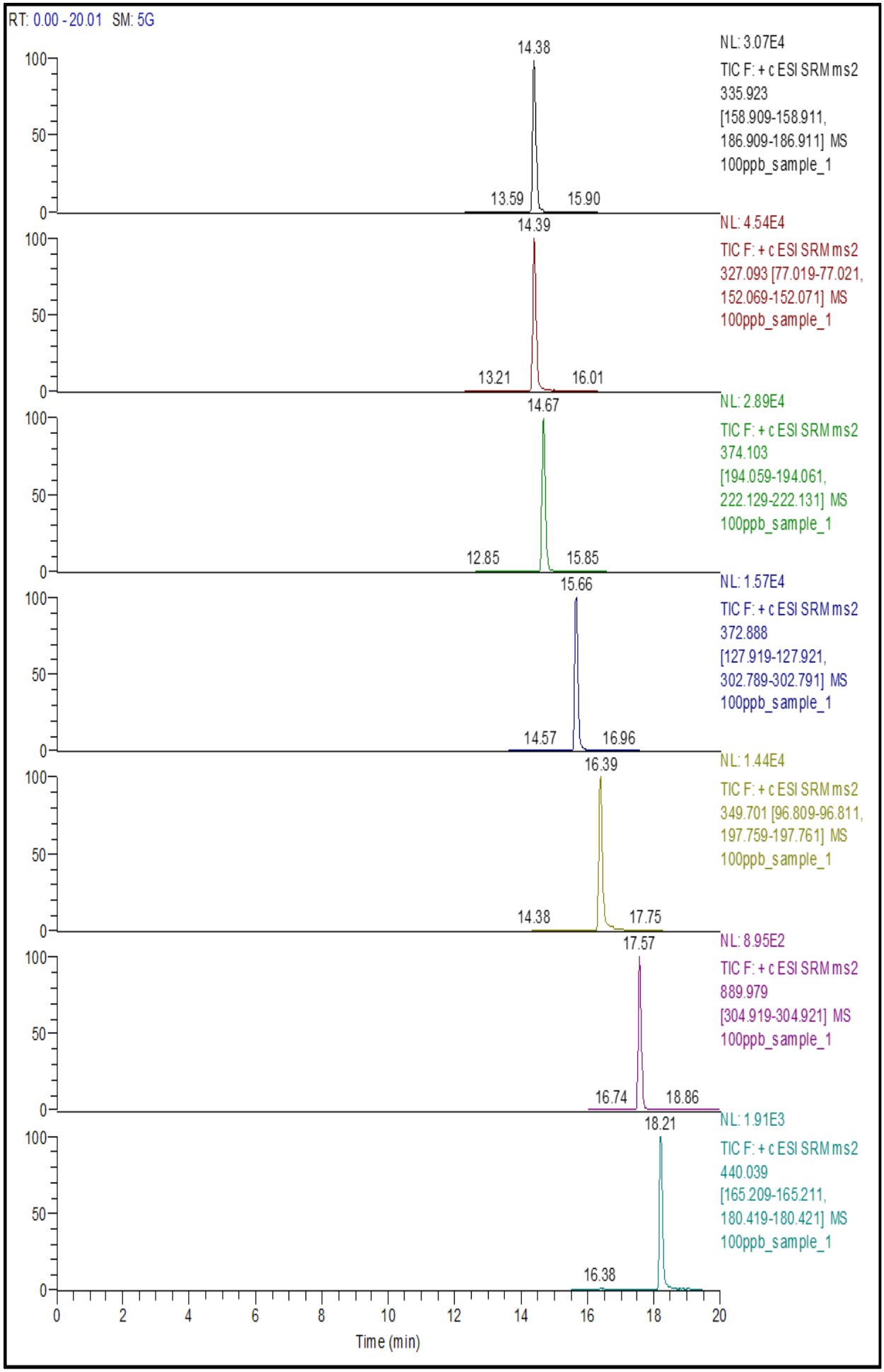
RT: 0.00 - 20.01 SM: 5G
14.38
NL: 3.07E4
TIC F: + c ESI SRM ms2 335.923 [158.909-158.911, 186.909-186.911] MS 100ppb_sample_1
13.59
15.90
14.39
NL: 4.54E4
TIC F: + c ESI SRM ms2 327.093 [77.019-77.021, 152.069-152.071] MS 100ppb_sample_1
13.21
16.01
14.67
NL: 2.89E4
TIC F: + c ESI SRM ms2 374.103 [194.059-194.061, 222.129-222.131] MS 100ppb_sample_1
12.85
15.85
15.66
NL: 1.57E4
TIC F: + c ESI SRM ms2 372.888 [127.919-127.921, 302.789-302.791] MS 100ppb_sample_1
14.57
16.96
16.39
NL: 1.44E4
TIC F: + c ESI SRM ms2 349.701 [96.809-96.811, 197.759-197.761] MS 100ppb_sample_1
14.38
17.75
17.57
NL: 8.95E2
TIC F: + c ESI SRM ms2 889.979 [304.919-304.921] MS 100ppb_sample_1
16.74
18.86
18.21
NL: 1.91E3
TIC F: + c ESI SRM ms2 440.039 [165.209-165.211, 180.419-180.421] MS 100ppb_sample_1
16.38
100
50
0
0
2
4
6
8
10
12
14
16
18
20
Time (min)

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Results:

Accuracy and Precision Data				
(n=6)	Mean (%)	RSD (%)	Mean (%)	RSD (%)
Analyte	20 ng/g		100 ng/g	
Abamectin	74.9	11.17	71.8	6.28
Acetochlor	93.9	7.32	97.5	3.19
Atrazine	95.3	5.16	98.1	1.30
Bifenthrin	94.9	12.90	90.9	10.32
Carbaryl	95.2	7.13	93.9	3.53
Carbendazim	69.6	8.55	81.6	5.06
Chlorpyrifos	89.5	6.36	93.1	3.96
Cyprodinil	93.2	9.12	94.1	1.78
DEET	107.3	6.75	101.1	0.67
Diazinon	94.4	7.53	98.2	1.36
Dicrotophos	91.0	6.61	99.1	3.35
DIMP	82.5	6.74	88.1	1.47
Malathion	52.3	9.29	78.1	1.78
Profenofos	79.5	8.76	88.6	2.75
Pyrazophos	80.5	8.01	93.9	2.63
Pyrimethanil	90.2	4.88	92.2	2.36
Simazine	92.4	7.74	98.9	2.77
Tebuconazole	88.5	6.69	93.1	3.08
Tebuthiuron	100.7	7.39	101.1	2.14
Thiabendazole	52.8	5.61	63.1	6.80
Zoxamide	92.4	7.92	99.4	2.11
Note: TPP was used as an internal standard. Matrix-matched calibration curves were used for quantification.				

Results/Discussion:

The vast majority of pesticides included in the study could be efficiently extracted from soil using the QuEChERS approach. Neutral pesticides, in particular, could be readily extracted using acetonitrile in combination with the citrate buffered QuEChERS salts. Thiabendazole on the other hand gave low, though reproducible, recovery throughout the study. Thiabendazole is a basic compound that is positively charged at low pH and is capable of being retained on the soil through ionic interactions, particularly by humic/fulvic acids. In addition, it is a planar pesticide and could potentially be retained by strong hydrophobic interactions on the soil (e.g. similar to analyte retention on graphitized carbon black (GCB)).

In the dispersive-SPE cleanup step, using a combination of PSA/C18 yields cleaner extracts than using PSA alone and should be used whenever possible. Linearity in detector response was observed over the concentration ranges investigated with correlation coefficients (R2 values) greater than 0.99 for all 21 analytes. As outlined in the Accuracy and Precision Data table, the majority of results were found be within an acceptable recovery range of 70-110 % and have RSD values <10 %, demonstrating that the method meets acceptable performance criteria.

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