Determination of 67 pesticides in Surface Water by Triple Quadrupole Mass Spectrometry (LC-MS/MS)

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1. Scope:

This section method (SM) provides a stepwise procedure for 67 pesticides analysis in surface water. The objective of this standard operating procedure is to quantify the concentration of a target list of pesticides in surface water. This solid phase extraction method has been developed and validated using prime HLB cartridge followed by LC-MS/MS analysis.

2. Principle:

The pesticides are extracted from the surface water sample with solid phase extraction technique. After preconditioning the SPE cartridge and sample loading, the samples were eluted and collected with ethyl acetate and hexane/acetone in one glass tube and methanol in another one. The collected extracts were evaporated to 0.5 mL under the stream of nitrogen and the combined extracts were analyzed by LC-MS/MS.

3. Safety:

3.1 Read the Safety Data Sheet (SDS) for all materials before use.

3.2 Pesticides are hazardous substances and may have acute and/or chronic toxic effects. Avoid all contact with and inhalation of the materials containing pesticides. Wear a lab coat as well as safety glasses and chemical resistant gloves when handling the samples.

3.3 All general laboratory safety rules for sample preparation and analysis shall be followed.

3.4 All flammable solvents should be handled with care and used in a fume hood.

3.5 Special storage, use, handling and disposal procedures are necessary to ensure the safety for using compressed gases.

4. Interferences:

There were no matrix interferences for the compounds at the time of method development using clean background surface water.

5. Apparatus and Equipment:

5.1 A Shimadzu LC system comprising of system controller, pumps, degasser, autosampler and column oven coupled to an AB Sciex 6500 QTRAP mass spectrometer with Turbo V-Source, ESI probe, Varian vacuum pump, and Windows 7 Analyst 1.6.2 PC workstation

5.2 Supelco vacuum manifold

5.3 Nitrogen Evaporator (Meyer N-EVAP Organomation Model #112 or equivalent)

5.4 Vortex-vibrating mixer

5.5 Micropipettes, adjustable, recommended sizes as follows: 10µL, 1000µL, and 10mL

6. Reagents and Supplies:

Item	Reagent/Supply	CAS#
6.1	Abamectin	CAS# 71751-41-2
6.2	Acetamiprid	CAS# 135410-20-7
6.3	Atrazine	CAS# 1912-24-9
6.4	Azoxystrobin	CAS# 131860-33-8
6.5	Bensulide	CAS# 741-58-2
6.6	Boscalid	CAS# 188425-85-6
6.7	Bromacil	CAS# 314-40-9
6.8	Carbaryl	CAS# 63-25-2
6.9	Chlorantraniliprole	CAS# 500008-45-7
6.10	Chlorpyrifos	CAS# 2921-88-2
6.11	Clorsulfuron	CAS# 64902-72-3
6.12	Clothianidin	CAS# 210880-92-5
6.13	Cyantraniliprole	CAS# 736994-63-1
6.14	Cyprodinil	CAS# 121552-61-2
6.15	Desulfinyl Fipronil	CAS# 205650-65-3
6.16	Desulfinyl Fipronil Amide	CAS# 205650-69-7
6.17	Diazinon	CAS# 333-41-5
6.18	3,4-dichloroaniline	CAS# 95-76-1
6.19	Dichlorvos (DDVP)	CAS# 62-73-7
6.20	Diflubenzuron	CAS# 35367-38-5
6.21	Dimethoate	CAS# 60-51-5
6.22	Dinotefuran	CAS# 165252-70-0
6.23	Dithiopyr	CAS# 97886-45-8
6.24	Diuron	CAS# 330-54-1
6.25	Ethoprophos	CAS# 13194-48-4
6.26	Etofenprox	CAS# 80844-07-1
6.27	Fenamidone	CAS# 161326-34-7
6.28	Fenhexamid	CAS# 126833-17-8
6.29	Fipronil	CAS# 120068-37-3
6.30	Fipronil Amide	CAS# 205650-69-7
6.31	Fipronil Sulfide	CAS# 120067-83-6
6.32	Fipronil Sulfone	CAS# 120068-36-2
6.33	Fludioxonil	CAS# 131341-86-1
6.34	Flupyradifurone	CAS# 951659-40-8
6.35	Hexazinone	CAS# 51235-04-2
6.36	Imidacloprid	CAS# 138261-41-3
6.37	Indoxacarb	CAS# 173584-44-6
6.38	Isoxaben	CAS# 82558-50-7
6.39	Kresoxim-methyl	CAS# 143390-89-0
6.40	Linuron	CAS# 330-55-2
6.41	Malathion	CAS# 121-75-5
6.42	Mefenoxam	CAS# 70630-17-0
6.43	Methidathion	CAS# 950-37-8
6.44	Methomyl	CAS# 16752-77-5
6.45	Methoxyfenozide	CAS# 161050-58-4
6.46	S-Metolachlor	CAS# 87392-12-9
6.47	Metribuzin	CAS# 21087-64-9

Item	Reagent/Supply	CAS#
6.48	Norflurazon	CAS# 27314-13-2
6.49	Oryzalin	CAS# 19044-88-3
6.50	Oxadiazon	CAS# 19666-30-9
6.51	Prometon	CAS# 1610-18-0
6.52	Prometryn	CAS# 7287-19-6
6.53	Propanil	CAS# 709-98-8
6.54	Propargite	CAS# 2312-35-8
6.55	Propiconazole	CAS# 60207-90-1
6.56	Pyraclostrobin	CAS# 175013-18-0
6.57	Pyriproxyfen	CAS# 95737-68-1
6.58	Quinoxyfen	CAS# 124495-18-7
6.59	Simazine	CAS# 122-34-9
6.60	Sulfoxaflor	CAS# 946578-00-3
6.61	Tebuconazole	CAS# 102534-96-3
6.62	Tebufenozide	CAS# 112410-23-8
6.63	Tebuthiuron	CAS# 34014-18-1
6.64	Thiacloprid	CAS# 111988-49-9
6.65	Thiamethoxam	CAS# 153719-23
6.66	Thiobencarb	CAS# 28249-77-6
6.67	Trifloxystrobin	CAS# 141517-21-7
6.68	Atrazine-d5 (surrogate)	CAS# 163165-75-1
6.69	Imidacloprid-d4(surrogate)	CAS# 1015855-75-0
6.70	Waters Oasis Prime HLB 6cc-500mg, Extraction Cartridge	
6.71	Water, HPLC grade or higher purity	
6.72	Methanol, HPLC grade or higher purity	
6.73	Ethyl Acetate, HPLC grade or higher purity	
6.74	Acetone, HPLC grade or higher purity	
6.75	n-Hexane, High resolution grade	
6.76	Formic Acid, HPLC grade	
6.77	Ammonium formate, reagent grade or equivalent	
6.78	Graduated conical tubes with glass stopper, 15 mL	
6.79	Centrifuge tube, pp, cylindrical, 110 mL	
6.80	Varian bond Elut reservoir, 75 mL	
6.81	Bond Elut SPE cartridge adapter	
6.82	Disposable Pasteur pipettes, and another laboratory ware as needed	
6.83	Recommended UPLC analytical column: Waters Acquity BEH C18 1.7 µm, 2.1 x 100 mm column or equivalent	

7. Standards Preparation:

7.1 Individual stock standards of 1.0 mg/mL were obtained from the CDFA/CAC Standards Repository.

7.2 The standards were diluted to 10 µg/mL with acetonitrile. A combination standard of 10 µg/mL was prepared from the individual mg/mL standards in acetonitrile. The combination standard was also used to dilute to the following concentrations: 0.00125, 0.0025, 0.005, 0.0125, 0.025, 0.05, 0.125, 0.25, 0.5 and 1µg/mL in acetonitrile. These standards were then diluted in half with water right before use to make the following concentrations: 0.000625, 0.00125, 0.0025, 0.005, 0.0125, 0.025, 0.05, 0.125, µg/mL for instrument calibration. Please see the standard preparation sheet.

7.3 Keep all standards in the designated freezer for storage.

7.4 The expiration date of each standard is six months from the preparation date. The standards prepared with water were prepared fresh with each analysis.

8. Mobile Phase Preparation:

8.1 Aqueous Solution: For 500 mL, mix 470 ± 2mL water, 25 ± 0.5 mL methanol, 4.50 ± 0.25 mL 1 M ammonium formate and 0.5 ± 0.05 mL formic acid.

8.2 Organic Solution: For 500mL, mix 450 ± 2mL methanol and 45 ± 0.5 mL water with 4.50 ± 0.25 mL 1 M ammonium formate and 0.5 ± 0.05 mL formic acid.

9. Sample Preservation and Storage:

Store all samples waiting for extraction in a separate refrigerator (4 ± 3 °C). Based on 28 days storage study, holding time for the surface water samples is 7 days from sampling.

10. Test Sample Preparation:

10.1 Background Preparation

The Department of Pesticide Regulations (DPR) provides the clean background surface water for matrix blank and spikes.

10.2 Preparation of blank and spike

10.2.1 Reagent blank: Deliver Mix of 1:1 ACN:H_2O (v:v) into a glass vial and analyze it in a sample batch.

10.2.2 Matrix Blank: Deliver 100 mL of background surface water into a 110 mL centrifuge tube. Then, follow the same extraction procedure.

10.2.3 Matrix spike: Deliver 100 mL of background surface water into a 110 mL centrifuge tube and spike 0.05 ppb, shake it. Then, follow the same extraction procedure.

10.3 Test Sample Extraction

10.3.1 Remove samples from the refrigerator and allow them to reach ambient temperature.

10.3.2 Deliver 100 mL of background surface water into a 110 mL centrifuge tube.

10.3.3 Attach SPE cartridges to vacuum manifold.

10.3.4 Precondition the SPE cartridge with 5mL Ethyl Acetate, 5 mL Hexane, 5 mL Acetone, 5 mL Methanol and 5 mL Water sequentially in a slow dropwise fashion (2-3 mL/min).

10.3.5 Attach Bond Elut adapters on top of SPE cartridge and connect the reservoir to the SPE and load 100 mL of samples into the reservoir.

10.3.6 After loading sample, rinse the cartridge with 5 mL HPLC grade water and dry it under vacuum condition for 60 minutes.

10.3.7 Elute the cartridge with 5 mL Ethyl Acetate followed by 6 mL of 3:1 Hexane:Acetone (v:v) in a calibrated glass tube and separately 5 mL Methanol in another glass tube.

10.3.8 Rinse the 110 mL centrifuge tube with each elution solvents before adding to cartridge to maximize the analyte recoveries.

10.3.9 Evaporate the sample extracts to 0.5 mL in a water bath at 40 ± 2 °C under a gentle stream of nitrogen. Combine these two extracts to the 1 mL final volume in an auto sampler vial. Submit extract for LC-MS/MS analysis.

11. Instrument Calibration:

11.1 The calibration standard curve consists of a minimum of five levels. The lowest level must be at or below the corresponding reporting limit. The current working standard levels range from 0.000625 to 0.125ng/µL.

11.2 Calibration is obtained using a quadratic regression with the correlation coefficient (r) equal to or greater than 0.995, with all levels weighted 1/x.

12. Sequence Arrangement:

The LC-MS needs to be conditioned with standard or a sample extract 2 to 3 runs before running the following recommended sequence: A set of calibration standards (eight levels), a reagent blank, a matrix blank, a reagent blank, a matrix spike, a set of up to 12 test samples, two reagent blanks and three continuing calibration verifications.

13. Instrument condition:

13.1 LC Separation Conditions

A Shimadzu LC30 liquid chromatograph is equipped with Waters Acquity BEH C18 1.7 µm, 2.1 x 100 mm column. Samples are eluted using a gradient system at a flow rate of 0.4 mL/min throughout the 18 min run-time at 50° C with injection volume of 3 µL. See Table 1.

Table 1. LC Gradient

Step	Time	Mobile Phase A (%)	Mobile Phase B (%)
0	0.01	98	2
1	0.25	90	10
2	10.00	0	100
3	15.00	0	100
4	15.10	98	2

Step	Time	Mobile Phase A (%)	Mobile Phase B (%)
5	18.00	0	0

13.2 Mass Conditions

To achieve a mass spectrum, a Triple Quad 6500 ABSciex mass spectrometer with an ESI interface is used. See the Table 2 for mass parameters in positive and negative modes. The mass spectrometer operates in positive and negative scheduled MRM (Multiple Reaction Monitoring) modes described in Tables 3 and 4, by monitoring 2 transitions for each compound. Quantitation ion is bold.

Table 2. Mass Spectrometer Operating Parameters

Ion Mode	Positive	Negative
Curtain Gas	20	20
Ion Spray Voltage	4500	-4500
Temperature	250	250
Ion Source Gas 1	50	50
Ion Source Gas 2	50	50
Collision Gas	8 (Medium)	8 (Medium)
Electron Multiplier	1500	1500
MRM Detection Window (sec)	30	60
Target Scan Time (sec)	0.2	0.4

Table 3. MRM Parameters for Pesticides Detection in Positive Mode

Compound	RT	Precursor Ion	Product Ion	Declustering Potential	Collision Energy	Entrance Potential	Exit Potential
Abamectrin	11.77	890.5 890.5	**305.0** 567.4	50 50	30 19	10 10	27 9
Acetamiprid	3.19	223.0 223.0	**125.9** 89.9	56 56	25 43	10 10	18 14
Atrazine	6.00	216.0 216.0	**174.0** 103.9	61 61	25 37	10 10	24 12
Azoxystrobin	7.10	404.0 404.0	**371.9** 344.0	41 41	19 33	10 10	18 16

Compound	RT	Precursor Ion	Product Ion	Declustering Potential	Collision Energy	Entrance Potential	Exit Potential
Bensulide	8.57	397.9 397.9	**313.8** 157.9	31 31	15 31	10 10	14 22
Boscalid	7.38	342.9 342.9	**306.9** 270.9	101 101	25 43	10 10	40 34
Bromacil	4.88	260.9 260.9	**204.9** 187.8	26 26	17 37	10 10	26 20
Carbaryl	5.35	202.0 202.0	**145.0** 127.0	31 31	13 37	10 10	18 16
Chlorantraniliprole	6.70	483.9 483.9	**285.8** 452.9	51 51	17 21	10 10	14 20
Chlorsulfuron	5.32	357.9 357.9	**141.0** 167.1	106 106	21 21	10 10	28 50
Chlorpyrifos	10.46	349.8 349.8	**197.9** 96.8	41 41	25 45	10 10	26 16
Chlothianidin	2.86	249.9 249.9	**168.9** 131.9	36 36	15 19	10 10	16 16
Cyprodinil	8.28	226.0 226.0	**93.0** 108.1	81 81	41 35	10 10	12 14
Cyantraniliprole	5.68	473.0 473.0	**284.0** 442.0	76 76	17 29	10 10	13 12
Diazinon	8.89	305.0 305.0	**169.0** 153.0	66 66	29 27	10 10	22 20
Dichlorvos	4.87	220.9 220.9	**108.9** 78.9	86 86	23 34	10 10	14 20
3,4-dichloroaniline	7.00	161.9 161.9	**127.0** 109.0	140 140	30 40	10 10	12 12
Diflubenzuron	8.37	310.7 310.7	**157.9** 140.8	41 41	17 41	10 10	20 18
Dimethoate	3.14	229.9 229.9	**198.9** 124.8	21 21	13 27	10 10	26 16
Dinotefuran	2.03	203.0 203.0	**129.1** 114.0	43 43	14 16	10 10	16 17
Dithiopyr	9.79	402.0 402.0	**354.0** 272.0	116 116	23 37	10 10	16 46

Compound	RT	Precursor Ion	Product Ion	Declustering Potential	Collision Energy	Entrance Potential	Exit Potential
Diuron	6.22	232.9 232.9	**72.0** 46.1	46 46	21 35	10 10	10 6
Ethoprophos	8.10	242.9 242.9	**173.0** 130.7	61 61	19 27	10 10	22 18
Etofenprox	12.06	394.1 394.1	**177.0** 359.0	41 41	19 15	10 10	24 18
Fenamidone	7.30	311.9 311.9	**236.0** 92.0	56 56	19 39	10 10	30 14
Fenhexamid	8.03	301.9 301.9	**97.1** 54.9	21 21	29 59	10 10	12 14
Fludioxonil	7.33	265.9 265.9	**229.0** 158.0	20 20	13 43	10 10	30 22
Flupyradifurone	3.22	289.0 289.0	**126.1** 90.0	105 105	27 58	10 10	15 15
Hexazinone	4.94	253.1 253.1	**171.0** 71.0	41 41	21 39	10 10	22 12
Imidacloprid	2.80	256.0 256.0	**208.9** 175.1	30 30	21 25	10 10	26 16
Indoxacarb	9.70	527.8 527.8	**150.1** 202.9	76 76	27 49	10 10	20 24
Isoxaben	7.55	333.1 333.1	**165.0** 107.0	41 41	23 79	10 10	22 16
Kresoxim-methyl	8.63	331.1 331.1	**314.0** 206.0	24 24	7 13	10 10	14 28
Linuron	6.96	249.0 249.0	**182.0** 160.0	51 51	23 25	10 10	22 26
Malathion	7.49	330.9 330.9	**126.9** 284.9	31 31	17 11	10 10	16 14
Mefenoxam	6.29	280.0 280.0	**220.0** **248.0**	21 21	19 13	10 10	26 12
Methidathion	6.39	319.8 319.8	**302.9** 144.9	6 6	9 17	10 10	14 18
Methomyl	2.05	163.0 163.0	**87.8** 105.9	11 11	13 13	10 10	14 16

Compound	RT	Precursor Ion	Product Ion	Declustering Potential	Collision Energy	Entrance Potential	Exit Potential
Methoxyfenozide	7.62	369.1 369.1	**149.0** 313.1	36 36	21 11	10 10	20 14
Metribuzin	4.81	215.1 215.1	**187.0** 84.0	36 36	25 31	10 10	12 10
Norflurazon	6.39	303.9 303.9	**284.0** 159.9	101 101	31 39	10 10	26 18
Oryzalin	8.22	347.0 347.0	**304.9** 288.0	41 41	19 23	10 10	14 14
Oxadiazon	10.31	344.9 344.9	**302.9** 219.9	91 91	17 27	10 10	14 28
Prometon	5.96	226.1 226.1	**142.0** 184.1	56 56	31 25	10 10	16 16
Prometryn	7.48	242.0 242.0	**157.9** 200.0	45 45	31 25	10 10	20 24
Propanil	6.99	217.9 217.9	**161.9** 126.9	56 56	21 33	10 10	18 16
Propargite	10.82	368.1 368.1	**231.1** 175.0	21 21	13 21	10 10	12 24
Propiconazole	8.93	341.9 341.9	**158.9** 69.0	56 56	31 23	10 10	20 12
Pyraclostrobin	9.08	388.0 388.0	**193.9** 163.0	36 36	17 31	10 10	26 22
Pyriproxyfen	10.34	322.0 322.0	**95.9** 184.9	46 46	19 29	10 10	16 24
Quinoxyfen	10.43	307.8 307.8	**196.8** 161.9	121 121	43 47	10 10	26 28
Simazine	4.88	202.0 202.0	**124.0** 103.9	61 61	25 33	10 10	16 16
S-Metolachlor	8.20	284.0 284.0	**252.0** 176.1	41 41	19 35	10 10	12 22
Sulfoxaflor	3.42	278.1 278.1	**154.1** 154.1	66 66	13 38	10 10	22 18
Tebuconazole	8.79	308.0 308.0	**69.9** 124.9	66 66	57 39	10 10	16 16

Compound	RT	Precursor Ion	Product Ion	Declustering Potential	Collision Energy	Entrance Potential	Exit Potential
Tebufenozide	8.49	353.1 353.1	**133.0** 297.1	26 26	23 11	10 10	18 14
Tebuthiuron	5.05	229.0 229.0	**172.0** 115.8	46 46	23 35	10 10	24 18
Thiacloprid	3.59	252.9 252.9	**125.8** 90.0	76 76	27 51	10 10	20 12
Thiamethoxam	2.15	291.9 291.9	**211.0** 180.9	41 41	19 29	10 10	30 24
Thiobencarb	9.25	258.0 258.0	**124.9** 89.0	41 41	23 65	10 10	16 14
Trifloxystrobin	9.69	409.0 409.0	**186.0** 144.9	41 41	23 57	10 10	24 20
Atrazine-d5(surrogate)	5.94	220.9 220.9	**179.0** 101.0	61 61	25 31	10 10	24 16
Imidacloprid-d4(surrogate)	2.77	259.9 259.9	**213.0** 179.0	170 170	46 46	10 10	9 9

Table 4. MRM Parameters for Pesticides Detection in Negative Mode

Compound	RT	Precursor Ion	Product Ion	Declustering Potential	Collision Energy	Entrance Potential	Exit Potential
Fipronil	8.55	436.8 436.8	**329.8** 331.8	-45 -45	-22 -22	-10 -10	-19 -27
Fipronil Amide	6.62	452.7 452.7	**347.9** 303.9	-25 -25	-20 -32	-10 -10	-19 -17
Fipronil Sulfide	8.75	418.8 418.8	**382.8** 261.5	-20 -20	-18 -38	-10 -10	-23 -15
Fipronil Sulfone	9.01	450.8 450.8	**414.9** 281.8	-40 -40	-22 -36	-10 -10	-25 -15
Desulfinyl Fipronil	8.35	387.0 387.0	**350.9** 281.8	-45 -45	-16 -42	-10 -10	-21 -15
Desulfinyl Fipronil Amide	5.61	405.0 405.0	**369.0** 329.0	-50 -50	-12 -30	-10 -10	-25 -17

14. Quality Control:

14.1 Method Detection Limits (MDL)

Method Detection Limit (MDL) refers to the lowest concentration of the analyte that a method can detect reliably. To determine the MDL, 7 surface water samples are spiked at 0.01ppb and processed through the entire method along with a blank. The standard deviation derived from the spiked sample recoveries was used to calculate the MDL using the following equation:

$$MDL = tS$$

Where t is the Student t test value for the 99% confidence level with n-1 degrees of freedom and S denotes the standard deviation obtained from n replicate analyses. For the n=7 replicates used to determine the MDL, t=3.143. A set MDL of 0.004 ppb was established for this method. Trace will be reported when results fall within this MDL and the Reporting Limit. The results for the standard deviations and MDL are in Appendix 1.

14.2 Reporting Limit (RL)

Reporting limit (RL) refers to a level at which reliable quantitative results may be obtained. The MDL is used as a guide to determine the RL. The RL is chosen in a range 1-5 times the MDL, as per client agreement. The reporting limit for this method is 0.02ppb for all compounds except Fipronil and metabolites which is 0.01 ppb and the RL for Pyriproxyfen is 0.15 ppb and Imidacloprid is 0.01ppb.

14.3 Method Validation

The method validation consisted of five sample sets. Each set included five levels of fortification and a method blank. All spikes and method blanks were processed through the entire analytical method. Spike levels and recoveries for the analytes are shown in Appendix 2.

14.4 Control Charts and Limits

A control chart was generated using the data from the method validation. The upper and lower control limits are set at ± 3 standard deviations of the percent recovery, shown in Appendix 2.

14.5 Acceptance Criteria

14.5.1 Each set of samples will have one matrix blank and one matrix spike spiked matrix samples.

14.5.2 The retention time should be within ± 0.1 minute of that of the standards.

14.5.3 The recovery of the matrix spike shall be within the control limits. See appendix 2.

14.5.4 The relative abundances of structurally significant ions used for confirmation must be within ±30% relative when compared to a standard injection during the same run.

14.5.5 The sample shall be diluted if results fall outside the calibration curve.

14.5.6 Use the established calibration from Section 11.1, check the calibration of the instrument throughout and at the end of the injection. A mid-level standard of known concentration as an indicator of continuing calibration check should result within 20% difference of the known value. If not, then the instrument should be recalibrated (all standards reinjected) and all the samples analyzed since the last acceptable calibration should be re-analyzed.

15. Calculations:

Quantitation is based on an external standard (ESTD) calculation using either the peak area or height. The Linear Ion Trap Quadruple LCMS software used a quadratic curve fit, with all levels weighted 1/x. Alternatively, at the chemist's discretion, sample results may be calculated using the response factor for the standard.

$$\text{ppb} = \frac{(\text{sample peak area or ht}) \times (\text{std conc.}) \times (\text{std vol. Injected}) \times (\text{final vol. of sample})(1000\ \mu L/mL)}{(\text{std peak area or ht}) \times (\text{sample vol. injected}) \times (\text{sample wt (g)})}$$

16. Reporting Procedure:

Sample results are reported out according to the client's analytical laboratory specification sheets.

17. Discussion:

17.1 The Department of Pesticide Regulations requested a comparison study of a liquid-liquid extraction and solid phase extraction for 67 pesticides in surface water. Prime HLB cartridge was selected for extraction process and pesticides were determined by LC/MS-MS.

17.2 There is a clogging concern for SPE cartridge once water samples have high TSS concentrations. CAC experiments illustrate that concentration above 500 mg/L will clog SPE cartridge. Therefore, if we receive samples with high TSS, we can discuss with DPR about the alternatives, using filtration before extraction or liquid-liquid extraction for those specific samples.

17.3 All standards were prepared in acetonitrile. Initially, all individual standards were stored in the freezer and combination standards were stored in the refrigerator. After six months several compounds in the combination standards had degraded, some by 50 percent when compared to freshly prepared standards, while the standards in the freezer showed no degradation. Therefore, all standards will be stored in the freezer. Prior to use working standards will be diluted with water for analysis.

17.4 No substantial matrix suppression occurred during the method validation process using the background clean surface water (American river clean surface water) provided by DPR.

17.5 During Method development, method validation and MDL study, the recoveries for Abamectin and Etofenprox were found approximately 70%. Afterwards, recovery results were decreased in storage stability study. It was found that the cartridge plays an important role for efficient extraction and different cartridge sorbent batch number can influence on results. The recoveries for Abamectin and Etofenprox are 30% and 50% respectively and the client has been informed.

17.6 A storage stability study was done with this project. The storage stability study consisted of a 0.5 ppb spike level and 3 replicates over a 28 day period in amber glass bottle. Three bottles containing background surface water were spiked and stored in the refrigerator until analyzed on 0, 2, 4, 7, 10, 14, 21 and 28 days. Along with the storage spikes a blank and a method control spike were also extracted. This storage study showed no degradation for all compounds until 10 day, so holding time for the surface water samples is 7 days from sampling. The results are shown in Appendix 3.

18. References:

18.1 Vanderford, B. J., Snyder, S. A., Analysis of Pharmaceuticals in Water by Isotope Dilution Liquid chromatography/Tandem Mass Spectrometry, *Environ. Sci. Technol.* **2006**, 40, 7312-7320.

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18.3 Carvalho, J. J., Jeronimo, P. C. A., Goncalves, C., Alpendurada, M. F., Evaluation of a Multiresidue Method for Measuring Fourteen Chemical Groups of Pesticides in Water by Use of LC-MS-MS, *Anal. Bioanal. Chem.* **2008**, 392, 955-968.

Appendix 1

MDL Study for 67 compounds in Surface Water

Compound	Spike ppb	Spike 1	Spike 2	Spike 3	Spike 4	Spike 5	spike 6	Spike 7	SD	MDL
Abamectine NH4	**0.01**	0.00738	0.00643	0.00685	0.00684	0.00672	0.00688	0.00688	0.00028	0.00089
Acetamiprid	**0.01**	0.01142	0.01136	0.01130	0.01113	0.01045	0.01144	0.01161	0.00038	0.00119
Atrazine	**0.01**	0.01091	0.01108	0.01040	0.01072	0.01151	0.01097	0.01157	0.00042	0.00131
Azoxystrobin	**0.01**	0.01135	0.01090	0.01158	0.01167	0.01019	0.01122	0.01091	0.00051	0.00159
Bensulide	**0.01**	0.01020	0.00987	0.00984	0.00951	0.00991	0.00977	0.01001	0.00021	0.00067
Boscalid	**0.01**	0.01131	0.00989	0.00997	0.01005	0.00957	0.01008	0.01028	0.00055	0.00173
Bromacil	**0.01**	0.01048	0.01067	0.01095	0.01133	0.01058	0.01096	0.01143	0.00037	0.00115
Carbaryl	**0.01**	0.01040	0.00913	0.01046	0.00988	0.00958	0.01013	0.01056	0.00052	0.00165
Chlorantraniliprole	**0.01**	0.01066	0.01036	0.01067	0.01122	0.01034	0.01135	0.01109	0.00041	0.00129
Chlorsulfuron	**0.01**	0.01024	0.01083	0.01105	0.01062	0.01076	0.01069	0.00989	0.00039	0.00123
Chlorpyrifos	**0.01**	0.00833	0.00802	0.00817	0.00727	0.00731	0.00795	0.00793	0.00041	0.00129
Clothianidin	**0.01**	0.00908	0.01074	0.01004	0.01054	0.00922	0.01058	0.00991	0.00066	0.00208
Cyprodinil	**0.01**	0.01071	0.01033	0.01065	0.01052	0.00989	0.01038	0.01046	0.00027	0.00085
Cyantraniliprole	**0.01**	0.00899	0.00928	0.00961	0.01048	0.01030	0.01037	0.00888	0.00068	0.00214
Diazinon	**0.01**	0.01028	0.01045	0.01010	0.01037	0.00932	0.01061	0.01112	0.00055	0.00172
Dichlorvos	**0.01**	0.00760	0.00732	0.00778	0.00763	0.00768	0.00830	0.00834	0.00038	0.00119
3,4-dichloroaniline	**0.01**	0.01056	0.01102	0.01105	0.01197	0.01097	0.01130	0.01158	0.00046	0.00144
Diflubenzuron	**0.01**	0.01115	0.01142	0.01072	0.01120	0.01051	0.01129	0.01123	0.00033	0.00104
Dimethoate	**0.01**	0.01177	0.01145	0.01161	0.01110	0.01055	0.01166	0.01144	0.00042	0.00132
Dinotefuran	**0.01**	0.01104	0.01106	0.01152	0.01104	0.01052	0.01119	0.01117	0.00030	0.00093
Dithiopyr	**0.01**	0.01062	0.01012	0.01037	0.01024	0.00986	0.01057	0.01061	0.00029	0.00090
Diuron	**0.01**	0.01146	0.01126	0.01116	0.01107	0.01108	0.01132	0.01162	0.00020	0.00064
Ethoprophos	**0.01**	0.01138	0.01076	0.01125	0.01114	0.01036	0.01109	0.01197	0.00050	0.00158
Etofenprox NH4	**0.01**	0.00748	0.00709	0.00727	0.00668	0.00704	0.00699	0.00697	0.00025	0.00079
Fenamidone	**0.01**	0.01037	0.00961	0.01063	0.00909	0.01068	0.01056	0.01095	0.00067	0.00210
Fenhexamid	**0.01**	0.00976	0.00929	0.00963	0.01103	0.00856	0.01061	0.00955	0.00082	0.00258
Fludioxonil NH4	**0.01**	0.01043	0.00956	0.01136	0.01125	0.01124	0.01111	0.01144	0.00068	0.00215
Flupyradifurone	**0.01**	0.01110	0.01094	0.01187	0.01102	0.01100	0.01127	0.01164	0.00036	0.00113
Hexazinone	**0.01**	0.01034	0.01014	0.01008	0.00997	0.00990	0.01040	0.01124	0.00045	0.00143
Imidacloprid	**0.01**	0.01122	0.01015	0.01031	0.01076	0.00880	0.00985	0.01122	0.00085	0.00268
Indoxacarb	**0.01**	0.00941	0.01072	0.01097	0.01092	0.00798	0.00994	0.01011	0.00106	0.00333
Isoxaben	**0.01**	0.01105	0.01122	0.01074	0.01144	0.0105	0.01108	0.01124	0.00032	0.00101
Kresoxim-methyl NH4	**0.01**	0.01080	0.01076	0.00942	0.01002	0.00938	0.00993	0.01118	0.00071	0.00223
Linuron	**0.01**	0.01178	0.01159	0.01117	0.01161	0.01067	0.01109	0.01158	0.00039	0.00123
Malathion	**0.01**	0.01093	0.01059	0.01058	0.01076	0.01093	0.01118	0.01132	0.00028	0.00088

Compound	Spike ppb	Spike 1	Spike 2	Spike 3	Spike 4	Spike 5	spike 6	Spike 7	SD	MDL
Mefenoxam	**0.01**	0.01132	0.01126	0.01139	0.01067	0.01092	0.01090	0.01095	0.00027	0.00084
Methidathion NH4	**0.01**	0.01125	0.01133	0.01084	0.01111	0.01085	0.01140	0.01149	0.00026	0.00081
Methomyl	**0.01**	0.00773	0.00800	0.00812	0.00782	0.00781	0.00764	0.00839	0.00026	0.00081
Methoxyfenozide	**0.01**	0.01149	0.01058	0.01068	0.01038	0.01090	0.01111	0.01078	0.00037	0.00115
Metribuzin	**0.01**	0.01149	0.01087	0.01091	0.01131	0.00957	0.01033	0.01105	0.00065	0.00205
Norflurazon	**0.01**	0.01123	0.01081	0.01115	0.01067	0.01045	0.01090	0.01078	0.00027	0.00085
Oryzalin	**0.01**	0.01065	0.01046	0.01103	0.01084	0.01010	0.00804	0.01056	0.00101	0.00319
Oxadiazon	**0.01**	0.01147	0.01147	0.01089	0.01064	0.01026	0.01110	0.01149	0.00048	0.00150
Prometon	**0.01**	0.01165	0.0113	0.01136	0.01105	0.01075	0.01126	0.01164	0.00032	0.00100
Prometryn	**0.01**	0.01143	0.01055	0.01045	0.01099	0.01019	0.01067	0.01062	0.00040	0.00126
Propanil	**0.01**	0.01060	0.01100	0.00964	0.01101	0.01005	0.01124	0.01088	0.00058	0.00183
propargite NH4	**0.01**	0.00855	0.00847	0.00850	0.00817	0.00790	0.00850	0.00873	0.00028	0.00087
Propiconazole	**0.01**	0.01110	0.01007	0.01043	0.01051	0.01010	0.01072	0.01101	0.00041	0.00128
Pyraclostrobin	**0.01**	0.01086	0.01035	0.01054	0.01013	0.01001	0.01068	0.01066	0.00031	0.00098
Pyriproxyfen	**0.01**	0.00771	0.00733	0.00728	0.00699	0.00693	0.00734	0.00714	0.00026	0.00082
Quinoxyfen	**0.01**	0.00865	0.00810	0.00812	0.00696	0.00731	0.00819	0.00816	0.00058	0.00183
Simazine	**0.01**	0.01124	0.01069	0.01111	0.01089	0.01065	0.01064	0.01097	0.00024	0.00075
S-Metolachlor	**0.01**	0.01133	0.01089	0.01074	0.01143	0.01018	0.01096	0.01101	0.00041	0.00129
Sulfoxaflor	**0.01**	0.01015	0.00900	0.01091	0.00984	0.00970	0.01015	0.01085	0.00067	0.00209
Tebuconazole	**0.01**	0.01085	0.01053	0.01086	0.01033	0.00905	0.01114	0.01133	0.00076	0.00238
Tebufenozide	**0.01**	0.01104	0.01100	0.01100	0.01127	0.01037	0.01113	0.01137	0.00032	0.00101
Tebuthiuron	**0.01**	0.01123	0.01133	0.01128	0.01129	0.01101	0.01127	0.01225	0.00040	0.00125
Thiacloprid	**0.01**	0.01172	0.01130	0.01121	0.01106	0.01015	0.01102	0.01158	0.00051	0.00160
Thiamethoxam	**0.01**	0.00933	0.00982	0.01073	0.01065	0.00961	0.00971	0.00964	0.00054	0.00170
Thiobencarb	**0.01**	0.00993	0.00923	0.00924	0.00956	0.00870	0.00987	0.00942	0.00042	0.00133
Trifloxystrobin	**0.01**	0.01061	0.01072	0.01063	0.01020	0.01014	0.01040	0.01093	0.00029	0.00090
Atrazine-d5	**0.01**	0.01066	0.01047	0.00993	0.00986	0.00950	0.01048	0.01050	0.00043	0.00136
Imidacloprid-d4	**0.01**	0.01062	0.01037	0.00885	0.00888	0.01055	0.01075	0.01128	0.00095	0.00297
Fipronil	**0.01**	0.01024	0.00998	0.01004	0.00994	0.00934	0.01001	0.00991	0.00028	0.00088
Fipronil Amide	**0.01**	0.01084	0.01075	0.00914	0.00947	0.00869	0.01061	0.01049	0.00088	0.00276
Fipronil Sulfide	**0.01**	0.01007	0.00993	0.00878	0.00869	0.00836	0.00879	0.00931	0.00066	0.00206
Fipronil Sulfone	**0.01**	0.01068	0.01030	0.01013	0.01005	0.01001	0.01001	0.01037	0.00025	0.00078
Desulfinyl Fipronil	**0.01**	0.00996	0.01009	0.00995	0.00968	0.00914	0.00962	0.01001	0.00033	0.00104
Desulfinyl Fipronil Amide	**0.01**	0.01023	0.01028	0.01007	0.01001	0.00864	0.00986	0.00995	0.00056	0.00176

Appendix 2

Method Validation Study **for 67 compounds in Surface Water**

Compound	Spike Level (ppb)						Control Limit	%
Abamactine NH4	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	70.4	72.0	78.5	69.6	65.4	**Mean**	67.1
	2	61.3	67.3	67.3	74.6	65.2	**SD**	7.0
	3	63.8	66.3	63.0	62.4	53.7	**RSD**	10.2
	4	65.5	77.8	74.1	73.3	52.5	**UCL**	88.1
	5	55.0	71.9	62.7	75.4	68.0	**LCL**	46.1
Acetamiprid	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	102.6	103.8	104.0	107.5	101.6	**Mean**	106.3
	2	109.3	110.0	111.8	117.5	105.4	**SD**	5.5
	3	102.0	110.8	109.5	103.3	98.9	**RSD**	5.1
	4	103.9	114.7	111.5	107.1	113.3	**UCL**	122.7
	5	105.5	106.7	92.5	103.7	101.5	**LCL**	90.0
Atrazine	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	106.2	105.9	114.1	110.2	99.8	**Mean**	109.4
	2	103.4	112.3	116.5	122.1	116.4	**SD**	5.5
	3	104.2	108.5	105.9	110.3	104.2	**RSD**	5.1
	4	100.7	115.8	112.5	110.2	111.5	**UCL**	126.0
	5	108.0	107.7	102.0	114.7	111.3	**LCL**	92.8
Azoxystrobin	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	104.2	103.0	110.3	108.3	97.4	**Mean**	105.7
	2	105.0	111.6	111.8	118.5	111.2	**SD**	6.2
	3	99.2	108.8	103.1	98.6	99.4	**RSD**	5.8
	4	107.1	118.0	109.9	110.6	102.2	**UCL**	124.2
	5	101.4	103.7	93.7	102.3	103.1	**LCL**	87.2
Bensulide	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	102.7	91.8	105.4	102.3	95.7	**Mean**	99.8
	2	88.1	100.3	96.5	111.0	99.4	**SD**	7.7
	3	97.2	102.4	110.4	102.6	96.2	**RSD**	7.8
	4	98.2	113.7	113.1	104.9	87.2	**UCL**	122.9
	5	94.3	95.2	83.9	98.3	104.0	**LCL**	76.6
Boscalid	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	110.7	99.0	111.0	108.5	97.7	**Mean**	109.0
	2	106.2	110.6	114.8	117.4	118.6	**SD**	5.9
	3	109.4	108.5	114.8	107.3	103.3	**RSD**	5.4
	4	105.7	119.6	108.2	106.8	101.7	**UCL**	126.8
	5	111.8	113.0	98.2	109.7	112.1	**LCL**	91.2

Compound		Spike Level (ppb)					Control Limit	%
Bromacil	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	100.8	101.5	93.0	89.6	85.6	**Mean**	91.1
	2	95.1	82.5	84.4	98.3	83.2	**SD**	7.2
	3	96.4	95.4	82.1	99.7	86.1	**RSD**	7.8
	4	80.9	104.7	91.2	95.6	94.6	**UCL**	112.6
	5	83.1	88.7	93.5	80.1	90.3	**LCL**	69.6
Carbaryl	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	105.7	107.7	107.9	93.5	87.9	**Mean**	103.2
	2	99.9	103.5	110.9	103.7	97.7	**SD**	8.3
	3	91.5	107.9	110.2	94.6	96.2	**RSD**	7.9
	4	87.1	110.8	112.1	97.5	106.4	**UCL**	128.1
	5	97.4	112.0	116.6	106.8	113.5	**LCL**	78.2
Chlorantraniliprole	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	102.6	98.5	110.4	106.2	94.3	**Mean**	95.7
	2	102.3	88.5	90.2	100.9	84.8	**SD**	8.4
	3	105.5	102.2	85.6	102.8	87.9	**RSD**	8.7
	4	91.3	113.7	88.9	94.8	88.4	**UCL**	120.9
	5	95.8	88.2	90.3	83.0	94.4	**LCL**	70.4
Chlorsulfuron	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	103.8	110.2	96.8	96.4	89.7	**Mean**	95.2
	2	99.9	88.7	84.8	102.0	88.1	**SD**	8.4
	3	102.4	101.2	86.7	105.6	93.8	**RSD**	8.7
	4	93.0	114.1	92.7	96.0	93.0	**UCL**	120.2
	5	82.2	83.9	94.7	83.6	95.6	**LCL**	70.1
Chlorpyrifos	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	71.8	69.6	73.0	70.9	70.3	**Mean**	78.7
	2	77.7	78.9	84.6	99.9	82.4	**SD**	7.5
	3	77.0	77.3	80.5	78.6	73.5	**RSD**	9.5
	4	77.5	87.1	81.1	75.1	68.9	**UCL**	101.1
	5	86.7	85.2	68.4	86.6	85.4	**LCL**	56.3
Chlothianidin	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	92.9	98.5	99.4	101.3	96.4	**Mean**	91.4
	2	96.5	82.3	84.1	97.8	81.2	**SD**	7.6
	3	89.2	92.4	81.0	99.6	89.7	**RSD**	8.5
	4	88.2	108.3	89.5	97.6	93.4	**UCL**	114.3
	5	82.7	79.8	91.7	80.5	91.1	**LCL**	68.5

Compound		**Spike Level (ppb)**					**Control Limit**	**%**
Cyprodinil	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	110.8	106.3	107.5	108.8	94.9	**Mean**	105.6
	2	107.4	111.4	107.8	108.4	109.3	**SD**	5.7
	3	106.3	101.3	108.9	105.1	102.6	**RSD**	5.4
	4	91.1	111.8	109.9	106.5	102.4	**UCL**	122.5
	5	108.5	103.6	91.4	109.4	107.7	**LCL**	88.6
Cyantraniliprole	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	96.4	98.6	99.3	86.1	78.7	**Mean**	90.3
	2	92.6	79.0	78.1	87.8	74.7	**SD**	9.0
	3	92.0	94.8	79.0	91.1	82.2	**RSD**	9.7
	4	89.1	113.0	84.6	91.8	95.7	**UCL**	117.2
	5	94.5	94.1	98.1	84.1	101.7	**LCL**	63.4
Diazinon	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	89.8	86.9	97.9	96.6	89.3	**Mean**	100.1
	2	96.9	104.4	104.4	108.4	104.2	**SD**	7.2
	3	91.3	97.4	106.3	98.6	95.9	**RSD**	7.3
	4	101.6	112.2	109.9	110.0	99.7	**UCL**	121.7
	5	95.0	103.8	89.7	103.8	107.3	**LCL**	78.4
Dichlorvos	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	71.4	68.0	72.4	72.0	52.1	**Mean**	78.5
	2	82.4	78.8	74.2	84.0	71.3	**SD**	10.1
	3	80.2	76.9	73.2	80.5	61.9	**RSD**	12.7
	4	85.9	98.6	91.7	85.5	84.4	**UCL**	108.9
	5	85.4	88.8	69.3	87.7	86.3	**LCL**	48.1
3,4-dichloroaniline	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	102.1	97.0	107.9	107.4	96.7	**Mean**	106.1
	2	107.5	102.7	100.9	111.9	103.8	**SD**	5.4
	3	106.0	113.1	109.1	108.8	107.5	**RSD**	5.1
	4	105.6	114.7	109.8	116.4	113.6	**UCL**	122.3
	5	97.3	102.8	103.3	103.7	103.2	**LCL**	89.9
Diflubenzuron	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	98.3	96.5	98.1	87.4	84.1	**Mean**	92.1
	2	92.6	82.4	87.0	95.5	84.4	**SD**	6.9
	3	96.3	99.9	81.9	95.7	91.7	**RSD**	7.5
	4	92.1	110.5	89.2	100.2	87.6	**UCL**	112.8
	5	91.0	88.3	86.5	84.9	99.2	**LCL**	71.3

Compound		Spike Level (ppb)					Control Limit	%
Dimethoate	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	104.1	104.5	110.9	112.3	103.6	**Mean**	106.8
	2	102.6	110.5	107.8	114.3	103.9	**SD**	4.0
	3	101.6	108.1	110.5	107.0	104.6	**RSD**	3.8
	4	104.7	111.7	110.6	110.9	110.0	**UCL**	118.9
	5	99.4	99.9	105.9	105.2	106.6	**LCL**	94.8
Dinotefuran	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	99.2	98.1	60.6	102.4	101.7	**Mean**	93.3
	2	99.1	98.1	70.1	103.8	95.7	**SD**	13.3
	3	94.4	98.4	72.1	99.2	77.8	**RSD**	14.8
	4	94.6	110.2	77.7	100.8	110.1	**UCL**	133.2
	5	98.0	103.2	71.7	98.2	97.8	**LCL**	53.4
Dithiopyr	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	90.1	88.3	95.8	94.5	88.4	**Mean**	98.0
	2	90.3	105.9	103.7	110.3	100.6	**SD**	7.7
	3	95.6	96.8	109.9	104.4	95.1	**RSD**	7.9
	4	98.1	113.5	107.9	101.7	88.9	**UCL**	121.2
	5	93.9	95.7	84.1	97.2	99.9	**LCL**	74.9
Diuron	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	99.0	99.6	108.6	108.1	98.9	**Mean**	106.3
	2	96.6	111.9	107.9	116.9	100.5	**SD**	6.3
	3	96.4	107.8	115.6	112.4	109.5	**RSD**	6.0
	4	105.7	115.6	109.0	109.7	114.5	**UCL**	125.2
	5	97.4	102.9	101.5	104.9	106.4	**LCL**	87.3
Ethoprophos	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	101.8	99.1	112.0	109.0	99.8	**Mean**	108.2
	2	112.8	113.6	114.6	117.2	109.7	**SD**	5.2
	3	101.7	106.6	109.0	110.0	105.4	**RSD**	4.9
	4	108.2	115.2	109.5	114.4	114.4	**UCL**	123.9
	5	101.5	104.6	104.6	104.7	105.6	**LCL**	92.5
Etofenprox NH4	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	76.6	71.6	70.9	71.1	67.6	**Mean**	72.3
	2	76.5	72.0	70.0	77.0	68.2	**SD**	6.1
	3	80.0	70.9	69.8	69.4	60.1	**RSD**	8.3
	4	78.8	74.9	79.5	75.6	56.0	**UCL**	90.5
	5	76.3	73.4	63.2	79.1	78.0	**LCL**	54.0

Compound	Spike Level (ppb)						Control Limit	%
Fenamidone	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	94.2	97.0	108.8	102.7	93.7	**Mean**	104.5
	2	100.8	112.4	109.6	115.6	110.1	**SD**	5.7
	3	100.2	103.0	107.0	102.4	101.1	**RSD**	5.4
	4	104.2	113.2	109.6	109.5	101.7	**UCL**	121.5
	5	105.9	102.4	99.7	105.4	103.5	**LCL**	87.6
Fenhexamid	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	104.4	89.0	89.8	85.9	85.9	**Mean**	87.9
	2	92.1	80.4	79.1	90.4	83.9	**SD**	7.3
	3	85.1	91.7	78.0	98.6	88.0	**RSD**	8.3
	4	83.6	105.2	84.9	93.9	86.8	**UCL**	109.8
	5	82.2	79.2	86.0	79.4	93.9	**LCL**	66.0
Fludioxonil NH4	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	85.6	93.4	98.0	99.8	94.3	**Mean**	101.2
	2	89.0	108.6	101.0	114.7	104.7	**SD**	7.8
	3	86.3	105.1	108.6	99.7	100.8	**RSD**	7.8
	4	94.9	111.4	111.3	104.9	107.3	**UCL**	124.7
	5	93.6	107.1	103.0	104.6	103.0	**LCL**	77.8
Flupyradifurone	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	106.8	104.6	110.7	112.5	101.6	**Mean**	110.1
	2	107.0	115.7	111.7	114.9	114.6	**SD**	4.0
	3	106.1	113.2	113.6	112.2	108.7	**RSD**	3.6
	4	106.5	113.9	108.6	112.8	111.6	**UCL**	121.9
	5	106.1	109.9	102.8	114.0	111.3	**LCL**	98.2
Hexazinone	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	87.5	91.7	99.3	99.9	92.7	**Mean**	101.3
	2	98.1	95.8	99.1	108.6	97.8	**SD**	6.8
	3	93.5	98.9	104.3	94.8	98.4	**RSD**	6.7
	4	107.2	110.0	108.8	102.9	111.4	**UCL**	121.6
	5	106.2	111.0	99.7	110.8	105.0	**LCL**	81.1
Imidacloprid	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	105.3	98.1	102.8	106.4	101.6	**Mean**	103.5
	2	102.5	102.7	104.5	116.0	97.5	**SD**	6.0
	3	98.9	106.6	108.2	107.1	102.0	**RSD**	5.9
	4	95.7	113.6	106.2	105.5	113.4	**UCL**	121.5
	5	99.8	105.0	88.1	101.4	98.4	**LCL**	85.5

Compound	Spike Level (ppb)						Control Limit	%
Indoxacarb	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	87.2	83.3	99.4	92.1	81.7	**Mean**	88.0
	2	91.0	94.9	91.7	102.4	84.5	**SD**	8.3
	3	80.4	91.9	96.6	94.5	87.2	**RSD**	9.4
	4	89.4	95.5	95.0	90.3	69.4	**UCL**	112.9
	5	77.2	86.8	70.4	79.2	87.8	**LCL**	63.1
Isoxaben	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	103.5	106.2	113.9	112.2	100.1	**Mean**	109.7
	2	104.7	112.7	111.2	116.1	112.6	**SD**	4.9
	3	106.1	110.7	112.7	114.0	107.5	**RSD**	4.5
	4	105.5	113.0	106.4	112.9	103.6	**UCL**	124.4
	5	112.1	113.8	100.4	116.4	115.4	**LCL**	95.1
Kresoxim-methyl NH4	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	81.4	100.1	102.4	105.1	91.5	**Mean**	96.5
	2	81.4	98.0	101.9	108.8	106.9	**SD**	9.1
	3	77.2	94.8	104.0	104.0	92.6	**RSD**	9.6
	4	82.3	105.4	104.1	102.9	91.5	**UCL**	123.7
	5	89.4	98.8	87.4	101.4	99.1	**LCL**	69.3
Linuron	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	103.1	100.3	109.1	107.0	92.7	**Mean**	108.1
	2	104.5	113.5	111.9	114.9	112.9	**SD**	5.6
	3	106.4	108.1	113.1	109.5	105.4	**RSD**	5.2
	4	104.2	114.2	104.1	110.5	112.6	**UCL**	124.8
	5	107.4	111.1	99.2	115.4	112.3	**LCL**	91.5
Malathion	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	97.7	96.7	105.6	103.6	93.7	**Mean**	105.2
	2	99.9	111.3	109.5	109.6	108.3	**SD**	5.7
	3	96.6	102.5	110.3	102.6	103.0	**RSD**	5.4
	4	103.2	111.1	109.4	109.0	105.2	**UCL**	122.2
	5	104.4	110.7	99.0	114.8	111.9	**LCL**	88.2
Mefenoxam	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	104.6	103.3	109.7	107.3	99.0	**Mean**	109.3
	2	105.5	113.8	111.9	116.0	114.2	**SD**	4.3
	3	105.3	110.4	113.2	107.6	107.0	**RSD**	4.0
	4	108.5	111.9	110.6	114.5	107.5	**UCL**	122.2
	5	110.6	110.0	102.4	111.7	115.2	**LCL**	96.3

Compound		Spike Level (ppb)					Control Limit	%
Methidathion NH4	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	98.8	101.5	111.1	105.4	92.4	**Mean**	106.1
	2	99.0	109.7	109.4	114.3	110.3	**SD**	6.2
	3	98.6	103.9	112.6	107.9	105.2	**RSD**	5.9
	4	99.9	116.4	108.0	110.8	106.9	**UCL**	124.7
	5	100.2	110.1	97.9	109.5	113.9	**LCL**	87.6
Methomyl	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	81.2	86.2	58.6	83.0	82.3	**Mean**	78.2
	2	71.1	73.8	73.7	84.7	73.4	**SD**	6.7
	3	79.6	76.5	83.4	79.9	73.6	**RSD**	8.7
	4	75.0	86.1	83.3	75.4	83.1	**UCL**	98.3
	5	73.3	83.4	67.1	85.0	82.8	**LCL**	58.1
Methoxyfenozide	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	108.7	113.1	103.9	110.4	104.2	**Mean**	109.9
	2	113.8	110.2	107.6	117.8	110.8	**SD**	4.2
	3	114.2	114.0	112.2	107.9	104.4	**RSD**	3.8
	4	107.0	113.3	109.8	104.8	110.8	**UCL**	122.7
	5	110.1	115.7	103.1	104.7	116.1	**LCL**	97.2
Metribuzin	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	103.2	102.9	107.6	108.8	98.6	**Mean**	107.5
	2	101.3	111.9	111.6	118.3	113.5	**SD**	5.5
	3	99.9	106.5	111.0	108.5	106.1	**RSD**	5.2
	4	99.8	113.8	113.8	109.9	110.9	**UCL**	124.1
	5	101.6	108.9	98.0	111.8	110.2	**LCL**	91.0
Norflurazon	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	104.1	100.3	112.7	107.0	98.0	**Mean**	106.9
	2	101.6	108.6	112.7	115.7	108.0	**SD**	4.5
	3	106.0	108.4	106.6	104.8	101.8	**RSD**	4.3
	4	103.9	112	107.7	110.6	111.3	**UCL**	120.5
	5	103.6	107.4	100.0	110.5	110.2	**LCL**	93.4
Oryzalin	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	105.0	98.8	101.4	104.2	93.7	**Mean**	104.0
	2	108.0	82.3	97.6	111.3	98.7	**SD**	7.9
	3	112.5	107.6	97.7	108.0	100.8	**RSD**	7.6
	4	109.6	114.6	114.3	106.8	100.7	**UCL**	127.7
	5	108.7	110.0	103.3	90.1	113.3	**LCL**	80.2

Compound	Spike Level (ppb)						Control Limit	%
Oxadiazon	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	95.4	89.4	92.9	91.9	85.9	**Mean**	95.8
	2	93.3	103.3	101.7	109.6	101.4	**SD**	6.7
	3	99.0	101.2	107.2	100.0	91.3	**RSD**	6.9
	4	91.7	101.8	98.0	91.2	82.9	**UCL**	115.9
	5	93.2	95.3	84.9	92.7	98.6	**LCL**	75.7
Prometon	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	110.8	108.0	111.8	110.2	103.4	**Mean**	111.9
	2	111.4	109.2	110.7	117.0	110.3	**SD**	3.8
	3	110.4	111.9	112.3	110.9	108.1	**RSD**	3.4
	4	106.8	117.9	114.6	117.7	117.8	**UCL**	123.4
	5	114.8	117.5	109.3	108.9	115.2	**LCL**	100.4
Prometryn	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	92.9	94.2	106.6	101.7	97.0	**Mean**	102.1
	2	91.8	107.6	105.7	112.0	111.0	**SD**	7.1
	3	89.5	97.0	105.5	97.0	98.3	**RSD**	7.1
	4	94.0	113.7	113.1	109.7	104.8	**UCL**	123.5
	5	99.4	104.5	95.3	104.3	106.1	**LCL**	80.7
Propanil	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	107.1	108.9	112.0	109.6	98.9	**Mean**	108.4
	2	105.1	106.6	108.1	116.0	104.2	**SD**	4.4
	3	103.7	110.2	111.4	112.7	106.8	**RSD**	4.0
	4	101.3	114.7	111.8	114.9	106.7	**UCL**	121.5
	5	104.1	107.8	104.1	111.5	111.6	**LCL**	95.3
Propargite NH4	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	73.4	71.2	76.3	76.2	71.5	**Mean**	75.9
	2	75.1	80.3	80.3	86.4	73.0	**SD**	6.6
	3	80.4	80.0	81.9	77.3	71.0	**RSD**	8.6
	4	82.5	88.7	81.0	81.8	64.1	**UCL**	95.7
	5	70.5	71.6	60.6	69.8	73.3	**LCL**	56.2
Propiconazole	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	98.2	94.9	106.7	101.0	91.1	**Mean**	102.8
	2	98.5	103.4	105.4	113.8	108.0	**SD**	6.1
	3	100.8	110.5	112.1	110.3	101.7	**RSD**	6.0
	4	96.3	107.0	98.2	98.6	96.5	**UCL**	121.2
	5	96.2	108.0	97.7	109.6	104.4	**LCL**	84.3

Compound	Spike Level (ppb)						Control Limit	%
Pyraclostrobin	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	102.0	93.3	104.3	102.7	92.8	**Mean**	101.5
	2	103.3	113.7	109.8	111.9	108.9	**SD**	7.1
	3	105.9	104.0	105.3	109.9	104.8	**RSD**	7.0
	4	98.5	105.5	99.5	99.4	88.8	**UCL**	122.7
	5	92.4	96.7	87.0	96.3	100.7	**LCL**	80.3
Pyriproxyfen	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	74.5	69.1	71.7	71.8	67.7	**Mean**	71.3
	2	69.0	72.8	73.8	79.0	70.0	**SD**	4.6
	3	73.0	68.3	72.4	69.5	61.3	**RSD**	6.5
	4	71.5	72.4	72.3	69.5	63.9	**UCL**	85.2
	5	72.1	77.5	62.3	78.7	79.0	**LCL**	57.4
Quinoxyfen	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	75.8	69.3	71.4	73.2	71.2	**Mean**	72.1
	2	71.4	70.5	71.5	76.0	70.8	**SD**	4.1
	3	72.8	71.0	74.9	73.4	65.4	**RSD**	5.7
	4	74.1	79.9	75.9	69.9	63.7	**UCL**	84.5
	5	68.9	76.7	62.6	76.8	75.6	**LCL**	59.7
Simazine	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	105.3	103.6	110.2	110.2	100.2	**Mean**	109.7
	2	108.7	114.6	111.8	117.6	112.1	**SD**	4.5
	3	104.0	109.2	112.5	108.8	105.7	**RSD**	4.1
	4	106.3	111.8	114.6	113.5	112.0	**UCL**	123.2
	5	113.9	113.0	100.6	112.8	109.3	**LCL**	96.2
S-Metolachlor	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	103.8	102.2	111.3	108.3	96.2	**Mean**	108.7
	2	105.4	114.5	112.8	114.5	112.8	**SD**	5.1
	3	103.5	107.1	109.0	108.5	102.0	**RSD**	4.7
	4	109.9	111.9	115.0	110.3	104.9	**UCL**	124.1
	5	113.6	115.5	101.2	109.2	113.6	**LCL**	93.2
Sulfoxaflor	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	104.3	100.2	104.4	105.9	93.6	**Mean**	105.4
	2	113.7	114.7	114.4	115.5	99.9	**SD**	6.1
	3	104.0	98.8	109.1	103.0	100.7	**RSD**	5.8
	4	103.9	115.0	107.1	101.8	103.8	**UCL**	123.8
	5	100.6	108.4	95.6	111.1	106.7	**LCL**	87.1

Compound	Spike Level (ppb)						Control Limit	%
Tebuconazole	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	92.3	94.2	99.8	102.7	93.8	**Mean**	104.0
	2	103.8	112.3	108.7	109.5	109.5	**SD**	6.4
	3	106.7	110.6	113.7	108.0	101.5	**RSD**	6.1
	4	96.9	102.5	103.1	99.0	99.4	**UCL**	123.1
	5	105.8	112.2	95.2	109.6	108.3	**LCL**	84.9
Tebufenozide	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	108.4	105.7	110.9	112.3	98.6	**Mean**	108.6
	2	107.0	105.3	114.4	117.2	106.7	**SD**	5.0
	3	103.0	113.2	110.3	107.0	104.8	**RSD**	4.6
	4	109.6	113.5	112.4	103.2	103.9	**UCL**	123.5
	5	107.0	107.7	101.0	114.0	117.9	**LCL**	93.7
Tebuthiuron	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	105.0	104.9	106.4	111.5	102.3	**Mean**	108.9
	2	107.4	114.6	111.3	111.8	111.1	**SD**	4.6
	3	99.5	108.7	111.4	108.6	101.0	**RSD**	4.2
	4	105.4	110.8	112.1	114.9	106.9	**UCL**	122.6
	5	111.2	115.9	103.2	115.0	112.4	**LCL**	95.2
Thiacloprid	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	103.2	104.2	107.3	111.8	101.7	**Mean**	109.2
	2	108.8	115.0	116.5	117.2	117.5	**SD**	4.8
	3	104.7	111.8	108.3	111.9	109.1	**RSD**	4.5
	4	103.5	107.8	108.2	105.2	105.0	**UCL**	123.7
	5	108.1	113.8	102.9	115.5	111.7	**LCL**	94.7
Thiamethoxam	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	82.8	85.9	87.3	83.8	83.4	**Mean**	87.7
	2	93.4	82.3	82.4	92.2	79.3	**SD**	6.5
	3	87.1	82.3	81.0	83.7	82.9	**RSD**	7.3
	4	91.1	107.3	96.1	91.0	99.3	**UCL**	107.1
	5	86.0	88.4	92.1	83.7	87.4	**LCL**	68.3
Thiobencarb	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	82.1	80.1	90.4	86.5	82.4	**Mean**	93.2
	2	93.4	97.5	100.5	109.0	99.7	**SD**	7.0
	3	90.7	92.6	100.8	95.2	91.8	**RSD**	7.6
	4	89.3	98.2	99.4	91.8	87.0	**UCL**	114.3
	5	92.7	95.3	83.9	98.2	100.6	**LCL**	72.1

Compound	Spike Level (ppb)						Control Limit	%
Trifloxystrobin	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	95.1	95.1	104.0	102.0	93.0	**Mean**	100.3
	2	97.8	105.1	105.1	112.5	102.2	**SD**	5.7
	3	104.2	104.4	103.2	105.5	100.3	**RSD**	5.7
	4	101.2	105.1	96.8	97.7	88.5	**UCL**	117.5
	5	96.3	97.8	87.8	101.0	105.7	**LCL**	83.1
Atrazine-d5 (Surrogate)	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	106.6	101.8	110.5	111.2	97.9	**Mean**	107.5
	2	103.9	113.5	111.4	112.8	109.7	**SD**	5.3
	3	103.0	108.5	113.4	109.8	107.3	**RSD**	5.0
	4	94.0	112.8	104.7	112.0	102.4	**UCL**	123.5
	5	108.3	110.1	99.6	113.4	109.8	**LCL**	91.6
Imidacloprid-d4 (Surrogate)	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	96.6	114.0	115.5	106.1	97.6	**Mean**	102.8
	2	102.5	102.1	111.7	112.8	97.0	**SD**	10.9
	3	79.9	87.3	72.1	97.5	96.7	**RSD**	10.8
	4	101.3	101.9	105.5	112.7	111.1	**UCL**	135.5
	5	114.3	106.4	104.7	111.1	112.7	**LCL**	70.2
Fipronil	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	88.8	91.0	100.6	95.9	81.1	**Mean**	102.0
	2	102.7	107.4	107.5	109.0	103.2	**SD**	8.1
	3	103.4	110.0	107.2	96.7	90.4	**RSD**	7.8
	4	105.5	114.4	112.1	104.7	99.9	**UCL**	126.4
	5	95.1	107.7	99.5	108.6	108.0	**LCL**	77.7
Fipronil Amide	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	108.0	102.9	109.4	104.8	93.2	**Mean**	108.2
	2	106.0	108.2	114.8	112.8	106.1	**SD**	5.9
	3	102.6	108.0	119.9	112.7	108.5	**RSD**	5.5
	4	104.0	113.7	100.3	102.5	111.1	**UCL**	126.0
	5	111.9	112.3	102.3	115.1	115.0	**LCL**	90.5
Fipronil Sulfide	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	93.8	92.1	102.4	99.6	83.2	**Mean**	101.7
	2	100.2	112.2	102.2	110.2	102.9	**SD**	7.3
	3	94.3	101.9	107.0	100.7	91.6	**RSD**	7.2
	4	105.1	110.2	108.6	106.8	95.7	**UCL**	123.7
	5	103.4	105.9	92.6	107.9	111	**LCL**	79.6

Compound	Spike Level (ppb)						Control Limit	%
Fipronil Sulfone	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	98.7	99.9	108	107.5	91.4	**Mean**	106.7
	2	105.8	111.9	104.3	114.2	112.3	**SD**	6.1
	3	101.3	108.8	110.9	104.1	107.7	**RSD**	5.8
	4	109.7	107.5	105.7	109.8	100.6	**UCL**	125.0
	5	110.1	110	96.4	112.3	118.8	**LCL**	88.4
Desulfinyl Fipronil	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	97.2	99.5	108.1	106.1	91.4	**Mean**	107.6
	2	104.8	112.6	111.2	112.8	111.3	**SD**	5.8
	3	101.1	109.1	115.9	109.7	107.2	**RSD**	5.4
	4	106.8	110.6	110.0	109.3	106.4	**UCL**	125.0
	5	110.9	112.5	100.4	114.5	110.3	**LCL**	90.2
Desulfinyl Fipronil Amide	**Set #**	**0.02**	**0.05**	**0.1**	**0.2**	**0.5**		
	1	100.8	96.6	105.4	104.1	92.6	**Mean**	107.5
	2	104.1	117.6	113.7	111.6	113.8	**SD**	6.3
	3	101.8	113.2	114.3	105.9	105.9	**RSD**	5.8
	4	102.1	113.5	111.2	106.6	105.0	**UCL**	126.4
	5	113.2	115.7	101.6	108.7	108.8	**LCL**	88.6

Appendix 3

Storage Stability Study for 67 compounds in Surface Water

Compound	Recovery (%)								
Abamactine NH4	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	30.1	29.6	30.8	29.7	35.7	33.8	29.8	32.8
	Spk 1	24.1	25.4	31.1	30.6	42.7	39.6	33.2	36.5
	Spk 2	33.5	26.1	29.0	38.0	38.5	38.2	28.8	31.7
	Spk 3	27.0	25.2	33.0	36.6	33.7	39.3	32.8	36.0
Acetamiprid	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	103.8	104.4	100.1	103.7	105.4	104.3	111.8	114.3
	Spk 1	102.2	101.8	102.1	100.1	100.6	101.1	105.1	100.6
	Spk 2	106.6	103.3	104.5	103.0	103.7	98.4	101.7	105.6
	Spk 3	102.1	104.0	104.7	104.1	102.6	100.1	100.9	101.9
Atrazine	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	107.8	110.3	101.4	100.8	110.5	107.3	104.4	106.9
	Spk 1	100.8	110.6	110.0	102.6	104.0	103.5	101.4	103.7
	Spk 2	115.7	106.2	111.8	105.2	102.2	103.4	97.3	99.2
	Spk 3	113.9	108.6	106.2	110.4	96.9	100.7	98.7	96.1
Azoxystrobin	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	95.1	99.9	90.8	91.8	94.5	90.6	91.0	91.8
	Spk 1	94.0	96.8	97.9	92.3	91.7	86.6	93.3	84.5
	Spk 2	103.3	99.9	101.2	99.4	84.5	88.5	87.0	87.6
	Spk 3	107.8	95.4	99.3	97.5	80.6	83.4	86.2	88.3
Bensulide	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	90.2	96.3	82.2	80.3	90.9	81.0	90.9	94.5
	Spk 1	87.3	87.8	94.5	92.2	88.5	75.1	87.4	88.4
	Spk 2	103.5	90.9	94.4	97.1	79.7	72.2	79.1	82.4
	Spk 3	84.6	86.7	87.9	95.3	81.5	76.1	82.4	79.8
Boscalid	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	101.8	114.4	101.1	100.3	115.5	99.5	103.6	104.6
	Spk 1	101.0	114.5	100.1	96.9	94.0	96.0	101.7	95.2
	Spk 2	116.6	109.6	110.4	111.8	98.1	92.0	99.1	100.0

Compound	Recovery (%)								
	Spk 3	108.9	111.5	99.7	110.6	91.8	94.5	93.8	95.1
Bromacil	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	92.6	99.2	98.6	96.3	93.0	88.3	96.4	97.8
	Spk 1	81.1	92.8	100.8	102.0	89.7	90.3	86.5	82.7
	Spk 2	100.4	96.2	94.2	97.8	96.9	95.4	77.4	78.0
	Spk 3	99.9	94.6	100.7	100.8	92.4	88.3	74.8	71.9
Carbaryl	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	94.4	107.2	98.9	96.2	108.8	92.5	100.6	102.7
	Spk 1	92.5	108.0	110.3	102.3	80.9	71.1	71.9	64.0
	Spk 2	107.6	105.7	108.1	92.9	80.4	70.9	62.8	59.0
	Spk 3	103.0	108.7	100.5	96.2	71.7	71.1	62.4	57.5
Chlorantraniliprole	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	99.4	108.8	107.6	107.1	106.9	99.3	105.8	107.5
	Spk 1	91.7	99.6	107.4	106.3	107.5	106.2	108.4	106.6
	Spk 2	104.3	108.2	101.0	108.7	109.8	106.8	105.7	98.0
	Spk 3	106.5	97.7	105.9	104.4	105.3	106.2	97.3	98.5
Chlorsulfuron	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	90.3	98.6	85.2	81.1	88.6	82.5	84.5	85.3
	Spk 1	79.9	75.9	89.2	86.3	71.3	72.1	72.8	68.1
	Spk 2	94.3	87.7	88.8	85.8	67.2	70.6	74.0	69.8
	Spk 3	98.5	100.1	83.1	82.0	67.4	70.5	76.5	71.7
Chlorpyrifos	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	78.3	85.1	75.9	73.6	77.7	77.8	82.6	83.5
	Spk 1	73.2	81.1	75.4	73.7	76.2	74.4	77.7	72.4
	Spk 2	87.9	78.0	74.2	84.2	76.6	75.5	74.8	69.6
	Spk 3	79.7	80.1	72.0	80.9	70.5	72.4	64.6	64.5
Chlothianidin	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	91.8	99.0	94.8	93.4	99.3	90.9	94.3	95.6
	Spk 1	80.7	85.1	98.5	95.6	91.4	90.4	96.0	88.3
	Spk 2	94.7	96.4	88.6	96.0	95.0	95.8	84.8	84.9

Compound	Recovery (%)								
	Spk 3	99.3	95.0	96.5	99.2	95.8	86.1	82.0	80.2
Cyprodinil	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	95.5	105.3	91.9	92.7	104.9	103.1	99.0	101.1
	Spk 1	95.2	102.0	102.8	94.9	93.6	96.8	96.3	90.9
	Spk 2	106.6	95.9	104.9	101.4	95.8	94.3	91.9	93.3
	Spk 3	100.8	100.5	96.1	100.5	89.1	91.8	93.6	95.1
Cyantraniliprole	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	91.1	109.8	100.3	104.2	105.9	91.6	99.9	100.3
	Spk 1	82.9	86.3	101.4	97.0	79.4	82.2	80.5	73.1
	Spk 2	94.8	101.5	96.8	105.7	87.7	84.2	82.3	77.5
	Spk 3	98.3	102	101.1	107.7	85.1	77.8	81.4	78.0
Diazinon	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	99.0	103.6	92.2	90.1	104.3	100.8	100.3	101.9
	Spk 1	97.7	99.7	104.7	99.7	98.6	96.1	94.7	100.1
	Spk 2	105.2	101.3	98.6	101.7	96.2	96.2	98.6	95.2
	Spk 3	102.6	102.4	100.4	105.8	91.1	91.9	94.0	96.8
Dichlorvos	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	85.9	94.1	94.1	93.1	91.7	78.4	73.3	71.1
	Spk 1	75.7	89.7	87.6	88.9	78.1	76.0	69.5	62.4
	Spk 2	86.0	87.2	94.4	92.6	75.6	75.2	61.8	55.9
	Spk 3	84.0	90.4	88.3	91.7	70.1	72.1	60.5	53.7
3,4-dicloroaniline	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	108.3	110.4	101.4	99.5	105.8	100.2	107.9	109.5
	Spk 1	100.5	107.9	106.2	111.3	98.4	95.4	96.6	90.1
	Spk 2	102.7	105.8	106.8	102.5	94.0	95.0	93.9	94.8
	Spk 3	109.1	103.1	102.1	102.8	93.4	94.3	97.7	90.6
Diflubenzuron	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	95.1	95.7	92.7	92.4	92.0	94.6	95.2	97.2
	Spk 1	92.1	94.8	101.1	95.2	89.0	86.6	87.2	82.1
	Spk 2	101.5	95.9	95.9	101.3	94.5	91.7	79.7	80.4

Compound		Recovery (%)							
	Spk 3	99.6	97.6	99.2	95.4	86.9	82.1	79.7	73.4
Dimethoate	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	107.0	110.4	105.3	104.2	106.6	100.3	103.9	105.2
	Spk 1	102.4	104.0	106.7	108.2	95.3	90.9	100.8	99.2
	Spk 2	107.1	106.8	105.6	102.9	95.8	88.9	98.2	92.0
	Spk 3	104.5	107.7	103.6	105.6	92.4	92.9	91.2	95.5
Dinotefuran	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	99.0	103.0	95.3	92.3	85.5	86.2	96.6	97.6
	Spk 1	99.0	103.1	104.0	97.8	77.6	76.8	79.7	80.0
	Spk 2	105.9	102.4	102.9	102.8	77.5	78.8	77.7	72.3
	Spk 3	105.6	106.3	100.5	105.5	75.8	74.9	74.1	69.8
Dithiopyr	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	87.5	98.0	81.4	82.0	87.5	84.7	88.2	87.5
	Spk 1	81.3	91.6	90.3	87.1	82.2	85.1	83.7	80.2
	Spk 2	95.9	94.5	88.0	99.7	87.1	85.5	81.2	81.5
	Spk 3	89.5	90.9	86.5	99.1	87.7	83.8	83.1	81.1
Diuron	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	103.4	107.9	101.7	99.4	113.4	104.6	108.4	111.3
	Spk 1	101.1	106.3	106.4	104.6	104.0	99.1	98.6	94.4
	Spk 2	114.2	104.0	110.5	101.9	102.1	99.0	95.0	96.6
	Spk 3	109.6	101.5	99.8	103.4	99.8	100.2	98.5	96.2
Ethoprophos	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	103.2	112.2	100.5	99.2	110.4	101.3	100.5	101.6
	Spk 1	95.9	108.5	105.1	109.5	101.9	101.9	102.8	97.3
	Spk 2	111.3	108.2	110.4	104.7	103.5	101.8	98.6	99.7
	Spk 3	107.0	108.4	104.1	109.7	97.6	100.2	99.7	94.5
Etofenprox NH4	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	54.2	56.7	57.8	54.9	51.2	57.2	52.7	51.8
	Spk 1	55.6	55.1	47.7	45.1	21.2	2.3	ND	ND
	Spk 2	49.4	47.5	42.2	50.8	12.7	1.5	ND	ND

Compound		Recovery (%)							
	Spk 3	51.1	55.1	49.7	46.7	7.8	1.1	ND	ND
Fenamidone	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	102.0	110.9	105.6	102.8	106.4	97.7	105.8	106.7
	Spk 1	94.3	107.5	108.3	103.7	96.5	88.2	93.2	83.2
	Spk 2	110.1	105.7	111.0	99.6	97.8	87.8	87.3	84.1
	Spk 3	104.7	105.9	103.6	102.0	91.5	91.1	87.2	80.2
Fenhexamid	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	93.5	99.6	92.4	92.4	92.1	89.1	94.3	95.9
	Spk 1	80.5	92.5	92.9	95.9	74.5	75.6	77.7	74.6
	Spk 2	97.7	93.5	88.1	92.6	83.4	80.8	79.5	75.2
	Spk 3	97.4	84.4	97.8	100.2	84.3	73.6	79.6	75.1
Fludioxonil NH4	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	99.5	102.3	100.2	101.5	104.5	102.4	104.1	105.5
	Spk 1	98.7	102.2	103.6	101.8	100.6	98.5	101.0	96.4
	Spk 2	109.3	100.9	111.7	101.6	99.3	98.1	97.1	98.2
	Spk 3	105.1	103.1	100.8	106.4	94.3	96.4	97.4	98.5
Flupyradifurone	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	111.7	111.5	107.2	107.2	113.1	103.0	104.2	106.3
	Spk 1	104.7	111.0	111.9	107.6	102.9	98.5	99.5	95.5
	Spk 2	111.6	106.6	113.7	103.4	103.9	103.1	96.5	98.0
	Spk 3	111.5	111.5	109.6	111.6	103.8	101.4	96.3	97.8
Hexazinone	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	98.9	98.4	101.6	101.2	104.1	104.2	104.2	105.3
	Spk 1	100.8	100.4	101.4	104.6	105.0	95.9	96.6	100.0
	Spk 2	108.5	103.6	104.0	98.2	101.9	95.9	93.9	94.6
	Spk 3	103.7	99.6	99.0	102.4	100.1	96.7	93.1	96.1
Imidacloprid	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	102.3	107.0	102.7	100.9	106.7	107.1	102.3	108.7
	Spk 1	102.1	104.0	105.4	103.3	102.0	100.0	100.3	103.0
	Spk 2	112.8	103.5	106.7	105.3	102.3	101.3	93.8	96.1

Compound		Recovery (%)							
	Spk 3	105.4	102.6	104.2	104.6	99.9	101.5	93.9	94.2
Indoxacarb	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	84.6	86.5	77.9	79.1	73.4	75.4	74.7	75.2
	Spk 1	73.3	74.5	79.5	77.3	57.0	42.1	44.0	37.1
	Spk 2	86.4	74.4	74.2	75.5	54.6	44.0	35.7	34.6
	Spk 3	73.7	75.7	79.6	70.8	48.4	40.7	40.2	36.7
Isoxaben	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	107.7	112.3	104.1	107.6	112.0	108.3	106.1	108.2
	Spk 1	104.5	108.0	109.6	105.3	104.2	102.1	99.8	94.9
	Spk 2	111.2	107.4	111.4	104.0	102.9	101.2	99.1	100.9
	Spk 3	113.8	107.6	104.0	106.7	95.7	98.0	94.9	96.4
Kresoxim-methyl NH4	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	96.2	104.3	96.2	98.9	104.1	102.7	100.3	111.4
	Spk 1	100.8	100.2	103.0	99.7	86.4	83.5	77.6	72.2
	Spk 2	103.9	95.1	104.7	95.2	85.2	81.8	75.6	68.0
	Spk 3	104.9	99.8	96.9	95.3	83.0	83.1	75.9	69.8
Linuron	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	107.3	108.5	102.6	99.4	105.9	105.8	102.8	109.2
	Spk 1	101.2	109.9	108.6	103.8	103.9	103.6	102.3	99.5
	Spk 2	106.4	107.2	106.1	111.8	100.3	99.4	98.5	98.5
	Spk 3	106.3	110.1	106.2	112.2	97.2	98.3	100.1	94.2
Malathion	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	103.5	107.4	102.1	101.6	107.0	103.8	106.9	104.2
	Spk 1	101.2	105.7	106.3	101.4	81.3	77.9	74.6	69.9
	Spk 2	113.7	104.9	108.9	94.6	82.3	73.3	69.7	63.0
	Spk 3	110.5	104.6	101.6	97.6	73.7	76.0	67.8	63.2
Mefenoxam	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	111.6	113.6	104.6	102.3	114.2	104.5	113.6	107.4
	Spk 1	107.3	111.5	111.5	106.2	106.8	99.5	104.5	99.8
	Spk 2	114.5	108.8	112.9	109.6	105.6	105.0	98.4	93.3

Compound		Recovery (%)							
	Spk 3	111.4	106.4	106.8	106.2	101.7	99.3	100.1	95.8
Methidathion NH4	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	106.4	106.3	101.0	103.5	108.3	103.6	105.2	107.6
	Spk 1	102.2	104.1	105.2	103.2	99.6	98.0	95.5	91.9
	Spk 2	111.7	108.2	108.1	105.7	100.7	99.2	93.7	95.2
	Spk 3	107.5	109.6	106.6	104.4	98.9	99.7	93.0	94.4
Methomyl	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	74.4	82.8	74.2	87.1	87.7	77.1	76.3	76.6
	Spk 1	72.5	81.8	83.6	79.3	77.1	71.3	69.2	71.9
	Spk 2	80.0	76.5	83.9	78.6	80.5	74.5	66.3	66.8
	Spk 3	76.9	75.5	76.2	75.2	77.7	76.6	62.1	67.9
Methoxyfenozide	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	110.1	110.2	106.5	105.4	113.0	112.7	112.4	115.6
	Spk 1	105.8	110.9	111.5	108.3	102.6	106.1	105.4	102.4
	Spk 2	109.4	109.5	108.5	107.4	101.6	102.3	102.3	104.6
	Spk 3	113.3	110.2	108.9	110.4	99.7	103.3	101.2	103.3
Metribuzin	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	100.7	109.5	101.5	103.7	108.0	98.0	106.8	100.4
	Spk 1	94.7	108.6	107.2	105.5	97.5	93.7	99.2	101.5
	Spk 2	109.2	105.5	109.3	104.1	94.8	91.7	93.1	96.9
	Spk 3	100.7	107.9	105.2	105.4	93.0	95.0	95.1	94.9
Norflurazon	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	103.6	109.2	103.6	104.2	108.2	103.3	104.8	106.2
	Spk 1	106.3	110.4	108.4	113.3	98.0	98.0	99.5	95.4
	Spk 2	111.8	108.3	108.1	108.5	98.5	101.1	97.0	98.0
	Spk 3	108.6	103.5	104.4	109.9	94.0	98.5	100.2	101.4
Oryzalin	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	106.6	109.1	101.4	100.3	110.5	113.5	106.1	108.6
	Spk 1	104.9	104.1	105.1	102.1	105.8	99.0	104.7	107.1
	Spk 2	110.3	103.3	101.2	99.1	101.0	104.3	97.6	101.1

Compound		Recovery (%)							
	Spk 3	107.0	104.2	101.8	106.5	96.6	99.3	94.0	102.2
Oxadiazon	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	87.4	95.6	88.2	89.2	88.6	90.7	87.7	88.5
	Spk 1	86.0	92.1	93.0	90.9	89.0	89.3	88.3	82.9
	Spk 2	100.3	94.4	96.7	100.0	84.0	88.1	84.2	84.8
	Spk 3	94.6	93.2	87.9	96.6	83.0	85.0	85.5	86.2
Prometon	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	108.7	111.7	105.2	104.4	113.0	113.2	108.4	110.1
	Spk 1	103.2	112.9	111.3	116.2	108.4	103.6	100.9	96.6
	Spk 2	107.5	115.7	114.9	112.2	108.8	107.1	99.4	93.3
	Spk 3	113.0	111.9	109.5	110.2	100.7	106.7	102.4	96.3
Prometryn	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	91.3	104.2	93.1	93.5	96.1	92.6	98.5	99.6
	Spk 1	90.8	101.8	102.8	99.9	91.2	92.0	95.8	94.3
	Spk 2	103.1	98.0	102.7	96.6	88.2	87.2	90.0	92.5
	Spk 3	103.0	98.4	96.3	100.8	85.2	90.2	91.4	95.0
Propanil	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	101.6	110.0	103.2	106.8	105.9	98.5	104.4	105.8
	Spk 1	96.2	107.5	105.9	108.3	93.9	97.2	97.2	93.2
	Spk 2	112.5	106.7	107.3	105.6	90.8	94.8	95.5	96.3
	Spk 3	105.3	109.4	107.9	105.5	91.2	94.4	98.4	91.0
Propargite NH4	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	74.3	77.7	71.3	70.1	70.4	72.6	71.2	71.4
	Spk 1	65.6	75.3	68.3	67.1	78.1	69.7	73.8	68.9
	Spk 2	73.6	68.8	63.0	77.0	77.3	70.7	63.7	63.6
	Spk 3	74.9	74.1	70.2	72.0	67.8	67.7	70.4	69.4
Propiconazole	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	96.4	103.3	96.8	97.8	105.5	96.7	103.0	100.2
	Spk 1	96.7	101.7	101.3	99.8	98.7	97.0	101.8	96.0
	Spk 2	110.8	96.8	103.3	98.0	92.5	94.4	93.9	94.7

Compound		Recovery (%)							
	Spk 3	99.0	99.8	94.2	100.7	91.1	92.1	96.7	97.6
Pyraclostrobin	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	96.4	102.8	90.1	91.6	97.0	95.6	95.8	96.9
	Spk 1	92.1	96.7	93.1	94.6	86.7	86.9	88.0	84.1
	Spk 2	104.0	95.6	97.9	100.0	90.8	87.4	83.5	83.7
	Spk 3	99.5	95.7	92.6	95.2	83.9	82.9	85.6	86.2
Pyriproxyfen	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	72.0	74.7	78.4	73.5	72.9	75.6	70.6	70.8
	Spk 1	70.2	78.2	74.1	69.4	44.7	28.2	1.5	1.7
	Spk 2	77.1	71.2	70.1	77.1	41.3	20.4	1.9	1.8
	Spk 3	73.0	71.8	71.9	71.5	34.5	21.5	5.2	4.5
Quinoxyfen	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	71.7	77.7	75.3	76.2	77.0	75.7	73.9	75.2
	Spk 1	70.2	79.5	73.3	71.8	70.7	71.6	66.7	62.5
	Spk 2	76.5	72.7	71.7	72.6	71.0	72.7	64.4	60.0
	Spk 3	79.5	75.3	71.3	74.6	68.0	70.1	63.3	59.1
Simazine	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	97.0	110.8	104.0	104.3	108.8	104.2	105.9	108.6
	Spk 1	108.5	110.8	108.3	105.2	103.7	96.9	96.2	98.0
	Spk 2	101.7	109.0	110.6	104.3	102.7	98.5	92.2	93.6
	Spk 3	98.8	105.4	102.4	106.6	99.1	96.8	98.5	93.3
S-Metolachlor	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	109.5	113.4	111.9	103.8	104.7	100.5	111.3	106.5
	Spk 1	101.4	108.3	103.6	106.6	100.1	99.3	103.8	100.1
	Spk 2	112.1	110.4	109.8	108.6	100.1	99.8	97.9	99.8
	Spk 3	108.0	109.0	111.2	106.6	98.1	101.8	98.8	100.8
Sulfoxaflor	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	103.0	106.4	100.7	106.7	112.3	103.0	107.1	109.0
	Spk 1	103.3	100.5	100.1	103.0	103.9	103.7	101.6	97.8
	Spk 2	114.9	104.1	106.5	102.4	107.2	105.4	98.1	99.5

Compound		Recovery (%)							
	Spk 3	107.8	102.8	102.1	106.8	102.8	101.8	98.3	99.6
Tebuconazole	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	104.9	107.1	105.2	101.1	99.4	96.9	107.7	106.0
	Spk 1	93.9	106.8	103.2	105.6	91.3	92.2	96.4	91.3
	Spk 2	110.5	100.8	106.4	102.5	87.8	87.8	91.8	93.5
	Spk 3	103.2	100.3	99.9	106.1	86.2	85.5	91.6	93.3
Tebufenozide	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	108.4	109.6	99.8	99.8	113.6	106.5	108.2	109.7
	Spk 1	106.2	111.8	111.7	108.4	99.3	99.2	103.5	104.9
	Spk 2	111.5	109.9	112.7	108.8	107.4	102.6	99.1	100.1
	Spk 3	115.7	110.4	105.4	112.9	99.1	100.7	101.8	103.0
Tebuthiuron	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	100.4	109.5	100.2	102.6	107.8	101.4	111.8	110.7
	Spk 1	95.2	107.8	107.9	109.5	101.7	102.6	103.4	99.1
	Spk 2	110.1	103.5	111.0	103.6	101.9	99.4	95.9	97.1
	Spk 3	107.1	101.9	100.6	102.2	97.7	99.6	96.4	97.7
Thiacloprid	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	108.2	107.2	105.1	105.2	111.3	107.9	110.1	102.2
	Spk 1	104.8	107.7	108.3	109.3	106.0	99.6	99.8	101.5
	Spk 2	111.4	111.9	113.5	105.6	104.8	101.2	100.8	102.5
	Spk 3	113.3	106.9	103.6	108.0	99.0	100.9	96.0	98.2
Thiamethoxam	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	94.6	85.8	97.2	95.3	98.8	88.9	90.4	91.8
	Spk 1	87.4	87.3	96.3	97.6	96.0	91.3	91.8	90.1
	Spk 2	98.5	90.8	97.8	97.6	94.9	92.1	90.3	91.6
	Spk 3	97.9	97.2	96.9	99.5	89.6	92.6	80.2	80.8
Thiobencarb	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	90.9	98.7	91.4	89.6	91.0	88.5	93.5	94.4
	Spk 1	85.7	97.2	97.3	92.0	85.8	84.9	87.2	79.3
	Spk 2	97.1	95.2	99.2	98.6	86.5	83.7	82.8	83.2

Compound	Recovery (%)								
	Spk 3	92.3	95.9	90.2	98.8	85.0	83.6	83.4	80.8
Trifloxystrobin	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	91.6	100.0	86.4	87.5	94.1	94.7	88.9	89.6
	Spk 1	85.3	92.8	93.9	90.2	82.6	78.2	76.4	69.8
	Spk 2	102.2	92.3	92.3	97.9	79.5	79.0	66.2	63.4
	Spk 3	92.7	92.0	90.2	94.3	75.1	75.1	74.2	66.9
Atrazine-d5	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	105.3	111.0	101.5	103.0	107.3	100.4	105.4	107.9
	Spk 1	99.9	110.0	110.2	104.5	93.9	92.8	101.3	95.5
	Spk 2	109.6	103.9	108.6	101.6	92.2	90.4	95.0	96.5
	Spk 3	106.1	107.2	105.6	106.0	89.9	91.6	91.9	93.3
Imidacloprid-d4	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	104.2	105.2	101.7	103.7	106.7	100.3	102.1	103.9
	Spk 1	103.8	102.3	105.8	103.7	102.8	101.5	88.7	84.5
	Spk 2	109.7	100.9	104.0	99.9	103.7	95.5	83.7	84.4
	Spk 3	106.8	99.7	98.9	104.6	99.0	103.5	84.2	84.9
Fipronil	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	96.6	102.2	102.7	101.1	106.2	100.1	100.3	102.3
	Spk 1	87.4	102.9	107.4	105.8	93.6	91.3	97.3	99.1
	Spk 2	104.3	100.4	102.1	103.6	92.2	88.3	88.1	90.7
	Spk 3	93.8	102.2	102.6	105.4	90.5	86.7	90.1	96.2
Fipronil Amide	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	104.8	114.8	108.2	104.0	114.9	108.8	108.1	105.0
	Spk 1	95.0	104.2	106.4	103.3	98.6	96.9	100.6	91.6
	Spk 2	107.7	108.5	107.8	107.3	97.8	97.7	91.2	91.5
	Spk 3	102.6	108.8	100.9	111.0	91.6	92.6	94.3	88.8
Fipronil Sulfide	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	95.2	105.3	99.7	101.5	103.1	98.8	101.9	104.0
	Spk 1	91.4	101.1	101.7	97.4	89.9	91.6	98.0	94.0
	Spk 2	102.3	99.9	104.8	100.8	86.6	85.5	88.2	94.4

Compound		Recovery (%)							
	Spk 3	100.8	101.5	99.2	102.9	84.4	86.2	90.2	94.3
Fipronil Sulfone	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	98.1	113.2	98.0	99.4	103.3	100.1	97.9	98.9
	Spk 1	92.7	108.3	106.8	110.0	95.4	94.8	97.0	92.0
	Spk 2	107.0	107.7	106.5	107.2	93.2	90.1	89.6	90.3
	Spk 3	98.4	105.3	101.4	108.9	88.4	92.0	90.0	95.5
Desulfinyl Fipronil	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	99.7	109.4	105.0	100.6	108.1	102.8	105.8	108.4
	Spk 1	92.8	105.2	104.1	115.6	94.8	93.6	94.8	96.5
	Spk 2	103.9	105.2	106.0	104.9	93.6	94.0	92.5	99.6
	Spk 3	100.3	105.9	101.2	111.5	89.0	92.9	90.3	95.1
Desulfinyl Fipronil Amide	**Spike ppb**	**Day 0**	**Day 2**	**Day 4**	**Day 7**	**Day 10**	**Day 14**	**Day 21**	**Day 28**
	blk								
	QC Spk	103.2	110.6	105.0	107.2	110.9	106.0	105.5	108.2
	Spk 1	96.9	106.0	106.8	105.1	101.6	101.5	96.1	97.9
	Spk 2	107.4	105.7	110.8	104.8	100.7	98.2	95.3	97.0
	Spk 3	103.8	108.1	104.3	105.4	101.0	96.1	96.4	98.3

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Date	What was revised? Why?