Determination of 62 Pesticides in Groundwater by Liquid Chromatography Tandem Mass Spectrometry and Gas Chromatography Tandem Mass Spectrometry

1. Scope:

This Section Method (SM) provides stepwise procedures for the analysis of 62 pesticides in groundwater. It is followed by all authorized personnel from the Nucleus Team and Environmental Analysis Unit.

2. Principle:

The pesticides are extracted from the groundwater sample with methylene chloride. The extract is passed through sodium sulfate to remove residual water. The anhydrous extract is evaporated using a nitrogen evaporator and adjusted to a final volume of 2 mL. An aliquot of 1 mL is removed for analysis by gas chromatography tandem mass spectrometry (GC/MS/MS) and the remaining 1 mL is evaporated to dryness, reconstituted with 1 mL of methanol (MeOH) and then diluted with 1 mL of MS grade water (H_2O). This extract is then analyzed by liquid chromatography tandem mass spectrometry (LC/MS/MS).

The original extracted sample is acidified with hydrochloric acid (HCl) and re-extracted with methylene chloride. The extract is passed through sodium sulfate to remove residual H_2O. The anhydrous extract is evaporated to dryness using a nitrogen evaporator, reconstituted with 1 mL of MeOH and then diluted with 1 mL of LC/MS H_2O. This extract is then analyzed by LC/MS/MS for the pesticide, Bentazon.

3. Safety:

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

3.2 Methylene chloride is a regulated and controlled carcinogenic hazardous substance. It must be stored and handled in accordance with California Code of Regulations, Title 8, Subchapter 7, Group 16, Article 110, Section 5202.

3.3 Hydrochloric acid

3.4 All solvents should be handled with care in a ventilated area.

4. Interferences:

3,4-Dichloroaniline has a large peak that interferes with the peak of interest. The peak of interest for 3,4-Dichloroanaline is the small shouldering peak to the right of the larger interfering peak.

5. Apparatus and Equipment:

5.1 Rotary evaporator (Buchi/Brinkman or equivalent)

5.2 Nitrogen evaporator (Meyer N-EVAP Organomation Model #112 or equivalent)

5.3 Balance (Mettler PC 4400 or equivalent)

5.4 Vortex mixer

5.5 High performance liquid chromatography (HPLC) coupled to a tandem quadrupole mass spectrometer

5.6 GC coupled to triple quadrupole mass spectrometer (MS)

6. Reagents and Supplies:

6.1 Methylene chloride, nanograde or equivalent pesticide grade

6.2 Water, MS grade, Burdick & Jackson or equivalent

6.3 MeOH, MS grade, Burdick & Jackson or equivalent

6.4 Formic acid, HPLC grade

6.5 Ammonium formate, reagent grade or equivalent

6.6 Separatory funnel, 2 L

6.7 Boiling flask, 500 mL

6.8 Sodium sulfate, ACS grade or equivalent

6.9 Funnels, long stem, 60°, 100 mm I.D.

6.10 Graduated conical tubes with glass stopper, 15 mL

6.11 Glass wool, Pyrex® fiber glass slivers 8 microns

6.12 Disposable Pasteur pipettes, and other laboratory ware as needed

6.13 Recommended HPLC analytical column:

- Ace Excel 2 C18-AR, 2.0 µm, 2.1 x 100 mm column or equivalent

6.14 LC/MS/MS Aqueous Solution

- For 500 mL, mix 470 ± 2mL H_2O, 25 ± 0.5 mL MeOH, 4.75 ± 0.25 mL 1 M ammonium formate and 0.5 ± 0.05 mL formic acid.

6.15 LC/MS/MS Organic Solution

- For 500 mL, mix 450 ± 2 mL MeOH and 45 ± 0.5 mL H_2O with 4.50 ± 0.25 mL 1 M ammonium formate and 0.5 ± 0.05 mL formic acid.

6.16 Recommended GC Analytical Column

- Restek Rxi-5Sil MS 30m X 0.025 mm ID, 0/025 µm df

7. Standards Preparation:

7.1 LC/MS/MS Standards

7.1.1	Atrazine	CAS# 1912-24-9
7.1.2	Azinphos-methyl	CAS# 86-50-0
7.1.3	Azoxystrobin	CAS# 131860-33-8
7.1.4	Bensulide	CAS# 741-58-2
7.1.5	Bromacil	CAS# 314-40-9
7.1.6	Carbaryl	CAS# 63-25-2
7.1.7	Carbofuran	CAS# 1563-66-2
7.1.8	Diazinon	CAS# 333-41-5
7.1.9	Dimethenamide	CAS# 87674-68-8
7.1.10	Dimethoate	CAS# 60-51-5
7.1.11	Diuron	CAS# 330-54-1
7.1.12	Ethofumesate	CAS# 26225-79-6
7.1.13	Fenamiphos	CAS# 22224-92-6
7.1.14	Fludioxonil NH4	CAS# 131341-86-1
7.1.15	Imidacloprid	CAS# 138261-41-3
7.1.16	Linuron	CAS# 330-55-2
7.1.17	Mefenoxam	CAS# 70630-17-0
7.1.18	Methiocarb	CAS# 2032-65-7
7.1.19	Metolachlor	CAS# 51218-45-2
7.1.20	Metribuzin	CAS# 21087-64-9
7.1.21	Napropamide	CAS# 15299-99-7
7.1.22	Norflurazon	CAS# 27314-13-2
7.1.23	Oryzalin	CAS# 19044-88-3
7.1.24	Prometon	CAS# 1610-18-0
7.1.25	Simazine	CAS# 122-34-9

7.1.26	Tebuthiuron	CAS# 34014-18-1
7.1.27	Thiamethoxam	CAS# 153719-23-4
7.1.28	Thiobencarb	CAS# 28249-77-6
7.1.29	Uniconizole-p	CAS# 83657-22-1
7.1.30	Methoxyfenozide	CAS# 161050-58-4
7.1.31	Methomyl	CAS# 16752-77-5
7.1.32	Chlorantraniliprole	CAS# 500008-45-7
7.1.33	Isoxaben	CAS# 82558-50-7
7.1.34	Propiconazole	CAS# 60207-90-1
7.1.35	Pyraclostrobin	CAS# 175013-18-0
7.1.36	Cyprodinil	CAS#121552-61-2
7.1.37	Flutriafol	CAS# 76674-21-0
7.1.38	Alachlor	CAS# 15972-60-8
7.1.39	Bentazon	CAS# 25057-89-0
7.1.40	3,4-Dichloroaniline	CAS# 95-76-1
7.1.41	3,5-Dichloroaniline	CAS# 626-43-7
7.1.42	2-amino-N-isopropyl benzamide (AIBA)	CAS#30391-89-0
7.1.43	Flupyradifurone	CAS# 951659-40-8
7.1.44	Myclobutanil	CAS# 88671-89-0
7.1.45	Atrazine-d5 (Surrogate)	CAS# 163165-75-1
7.1.46	Imidacloprid-d4 (Surrogate)	CAS# 1015855-75-0

7.2 LC/MS/MS Stock mixes at 0.1 and 1.0 mg/mL are obtained from a commercial supplier (such as Restek).

7.3 The stock mixes at 0.1 and 1.0 mg/mL are diluted to 10 µg/mL with MeOH.

7.4 A combination of standards at 10 µg/mL are prepared from the individual 0.1 and 1.0 mg/mL standards in MeOH. The combination standard at 10 µg/mL is serially diluted with MeOH to produce the following concentrations: 0.0025, 0.005, 0.01, 0.025, 0.05, 0.1, 0.25, 0.5 and 1 µg/mL.

7.5 The above standards are diluted with an equal volume of H_2O to make the following concentrations: 0.00125, 0.0025, 0.005, 0.0125, 0.025, 0.05, and 0.125 µg/mL. These standards are analyzed by LC/MS/MS to produce the

calibration curve. Some pesticides had data points excluded from the lowest or highest standards due to weak or strong response.

7.6 GC/MS/MS Standards

7.6.0	Clomazone	CAS # 81777-89-1
7.6.1	Dichlobenil	CAS # 1194-65-6
7.6.2	Dichloran	CAS # 99-30-9
7.6.3	Disulfoton	CAS # 298-04-4
7.6.4	Ethoprophos	CAS # 13194-48-4
7.6.5	Fonofos	CAS # 944-22-9
7.6.6	Malathion	CAS # 121-75-5
7.6.7	Parathion Ethyl	CAS # 56-38-2
7.6.8	Parathion Methyl	CAS # 298-00-0
7.6.9	Phorate	CAS # 298-02-2
7.6.10	Piperonyl Butoxide	CAS # 51-03-6
7.6.11	Prometryn	CAS # 7287-19-6
7.6.12	Propanil	CAS # 709-98-8
7.6.13	Triallate	CAS # 2303-17-5
7.6.14	Benfluralin	CAS# 1861-40-1
7.6.15	S-ethyl dispropylthiocarbamate (EPTC)	CAS# 759-94-4

7.7 GC/MS/MS Stock mixes of 0.1 mg/mL are obtained from a commercial supplier (such as Restek).

7.8 The stock mixes at 0.1 mg/mL are diluted to 10 µg/mL with acetone.

7.9 Two combinations of standards at 10 µg/mL are prepared from the individual 0.1 mg/mL standards in acetone and methylene chloride. The combination standard in methylene chloride at 10 µg/mL is serially diluted with methylene chloride to produce the following concentrations: 0.0025, 0.005, 0.01, 0.025, 0.05, 0.1, 0.25, 0.5 and 1.0 µg/mL. These standards are analyzed by GC/MS/MS to produce the calibration curve. Some pesticides had data points excluded from the lowest or highest standards due to weak or strong response.

7.10 A QC spike solution is prepared with all compounds at 1.0 µg/mL in Acetone.

7.11 Keep all standards in the designated refrigerator for storage.

7.12 The expiration date of each mixed working standard is from 6 to 24 months from the preparation date or same as the stock standard, if sooner. The standards prepared with water are prepared fresh with each analysis.

7.13 A portion of the new standard is vialed and set aside in the refrigerator. This will be used when doing the intermediate check and the check for a new set of standards. The intermediate check is performed before the standard is 6 months old and documented along with comparison for that set of standards. There should be <20% difference between the response of the new standard of the intermediate check standard and the response of the vialed standard.

8. Sample Preservation and Storage:

Store all samples waiting for extraction in a separate refrigerator (4 ± 3 °C).

9. Test Sample Preparation:

9.1 Background Preparation

9.1.1 The Department of Pesticide Regulation provides the background water for matrix blank and spikes.

9.2 Preparation of Matrix Blank and Matrix Spike Samples

9.2.1 Matrix Blank: Weigh out 1000 g of background water and follow the test sample extraction procedure in 9.3.

9.2.2 Matrix Spike: Weigh out 1000 g of background water. Spike a client requested amount of pesticide (typically 0.2 µg/L) into the background water, mix well and let it stand for one minute. Follow the test sample extraction procedure in 9.3.

9.3 Test Sample Extraction

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

9.3.2 Record the weight of water samples to 0.1 g by subtracting the weight of the sample container before and after water has been transferred into a separatory funnel. Sample amount is ~1 L.

9.3.3 Shake with 100 ± 5 mL of methylene chloride for 2 minutes. Vent frequently to relieve pressure.

9.3.4 After phases have separated, drain the lower methylene chloride layer through 25 ± 4 g of anhydrous sodium sulfate and glass wool into a 500 mL boiling flask.

9.3.5 Repeat steps 9.3.3 & 9.3.4 two more times using 80 ± 5 mL of methylene chloride and shake for 1 minute each time. Combine the extracts in the same boiling flask.

9.3.6 After draining the final extraction, rinse the sodium sulfate with 25 ± 5 mL of methylene chloride.

9.3.7 Evaporate the sample extract to 2 - 4 mL on a rotary evaporator using a water bath at 35 ± 2 °C and 15 – 20 inches of Hg vacuum. Transfer the extract to a calibrated 15 mL graduated test tube.

9.3.8 Rinse flask 3 more times with 2 - 4 mL of methylene chloride and transfer each rinse to the same test tube. The test tube final volume should be 13-15 mL.

9.3.9 Evaporate the sample extract in the calibrated 15 mL graduated test tube to ~1.5 mL in a water bath at 40 ± 2 °C under a gentle stream of nitrogen. Then bring the final volume to 2 mL and transfer 1 mL of the extract to two auto sampler vials with inserts for GC/MS/MS analysis.

9.3.10 The remaining 1 mL of extract is evaporated to dryness in a water bath at 40 ± 2 °C under a gentle stream of nitrogen. Reconstitute the dried extract with 1 mL of MeOH (MS grade). Add 1.0 mL of H_20 (MS grade) to the extract and mix well, for a final volume of 2 mL. Transfer the final extract into two separate auto sampler vials. Submit extract vials for LC/MS/MS analysis.

For the analyte, Bentazon continue with the following procedure below. If Bentazon is not requested, the extraction process is completed.

9.3.11 Place the used glass funnel with sodium sulfate in a clean 500 mL boiling flask. To the original sample in the separatory funnel, add 4 mL of concentrated hydrochloric acid (~12 M). Using pH paper, verify the pH of the sample is less than 2. If the pH is not below 2, add another 1 mL of concentrated hydrochloric acid. Continue adding concentrated hydrochloric acid until the pH of the sample is ≤ 2, then document the additional hydrochloric acid volume on the extraction sheet.

9.3.12 Shake with 80 ± 5 mL of methylene chloride for 1 minute. Vent frequently to relieve pressure.

9.3.13 After phases have separated, drain the lower methylene chloride layer through 25 ± 4 g of anhydrous sodium sulfate and glass wool into a clean 500 mL boiling flask.

9.3.14 Repeat steps 9.3.12 & 9.3.13 two more times using 80 ± 5 mL of methylene chloride and shake for 1 minute each time. Combine the extracts in the same boiling flask.

9.3.15 After draining the final extraction, rinse the sodium sulfate with 25 ± 5 mL of methylene chloride.

9.3.16 Evaporate the sample extract to 2 - 4 mL on a rotary evaporator using a water bath at 35 ± 2 °C and 15 – 20 inches Hg vacuum. Rinse flask 3 more times with 2 - 4 mL of methylene chloride and transfer each rinse to the same test tube. The test tube final volume should be 13-15 mL.

9.3.17 Evaporate the sample extract to dryness in a water bath at 40 ± 2 °C under a gentle stream of nitrogen. Reconstitute the dried extract with 1 mL of MeOH (MS grade). Add 1.0 mL of H_2O (MS grade) to the extract and mix well, for a final volume of 2 mL. Transfer the final extract into

two new auto sampler vials. Submit extract vials for LC/MS/MS analysis.

10. Instrument Calibration:

10.1 The calibration standard curve consists of a minimum of five levels. The lowest level must be at or below the corresponding reporting limit.

10.2 The current working standard levels range from 0.00125 to 0.125 µg/µL for the LC/MS/MS.

10.3 The current working standard levels range from 0.025 to 0.5 ng/µL for GC/MS/MS.

10.4 Some pesticides had data points excluded from the lowest or highest standards due to weak or strong response.

10.5 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.

11. Instrumental Analysis:

11.1 LC/MS/MS Injection Scheme

11.1.1 The LC/MS/MS needs to be conditioned with standard or a sample extract 2 to 5 runs before running the following sequence:

- A set of calibration standards
- Matrix blank
- Matrix spike
- A set of up to 12 test samples
- A set of standards, etc.

11.2 LC/MS/MS Conditions

11.2.1 Column: Ace Excel 2 C18-AR, 2.0 µm, 2.1 x 100 mm column

11.2.2 Column Temperature: 40 °C

11.2.3 Mobile Phase A: Aqueous Solution

11.2.4 Mobile Phase B: Organic Solution

11.2.5 Gradient: See Table 1

Table 1 – LC/MS/MS Mobile Phase Gradient Flow Rate

Flow Rate			
Time (min)	**Flow Rate (mL/min)**	**Mobile Phase A**	**Mobile Phase B**
Initial	0.4	95.0	5.0
1.0	0.4	95.0	5.0
12.0	0.4	5.0	95.0
15.0	0.4	5.0	95.0
16.0	0.4	95.0	5.0

11.2.6 Injection Volume: Typically, 3.0 µL, but can vary due to instrument sensitivity.

11.2.7 Recommended Mass Spectrometer and Operating Parameters:

11.2.7.1 Model: ABSciex 6500+ Triple Quad

11.2.7.2 Ionization: Electrospray Ionization (ESI)

11.2.7.3 Polarity: Positive and Negative

11.2.7.4 Curtain Gas: 30

11.2.7.5 Ion Spray Voltage: 4500 / -4500

11.2.7.6 Source Temp: 350 °C

11.2.7.7 Ion Source Gas 1: 50

11.2.7.8 Ion Source Gas 2: 50

11.2.7.9 Collision Gas: Medium

11.2.7.10 Electron Multiplier: 2600 V for positive / 2700 V for negative

11.2.7.11 Scheduled MRM: Yes

11.2.7.12 MRM Detection Window: 60 sec.

11.2.7.13 Target Scan Time: 1.0 sec.

Table 2 – LC/MS/MS Instrument Conditions

Compound	RT	Precursor Ion [1]	Product Ion [1]	De-Clustering Potential	Collision Energy	Entrance Potential	Exit Potential
Atrazine	10.1	**216.0**	**173.9**	41	23	10	18
		216.0	96.0	41	31	10	10
Azinphos-methyl	12.0	**317.9**	**131.9**	16	19	10	12
		317.9	77.0	16	45	10	10
Azoxystrobin	12.1	**404.0**	**372.0**	50	19	10	12
		404.0	329.0	50	41	10	10
Bensulide	12.9	**398.0**	**313.8**	36	15	10	10
		398.0	157.9	36	31	10	14
Bromacil	9.20	**262.9**	**206.9**	26	19	10	18
		262.9	190.0	26	39	10	16
Carbaryl	9.80	**202.2**	**145.0**	25	13	10	10
		202.2	127.0	25	38	10	16
Carbofuran	9.40	**222.0**	**123.1**	41	29	10	0
		222.0	165.1	41	17	10	46
Diazinon	13.0	**305.0**	**169.1**	20	28	10	9
		305.0	153.0	20	26	10	5
Dimethenamide	11.6	**276.0**	**244.0**	36	19	10	10
		276.0	168.0	36	33	10	10
Dimethoate	7.20	**229.9**	**199.0**	16	13	10	18
		229.9	124.8	16	27	10	16
Diuron	10.6	**234.9**	**72.0**	46	21	10	10
		234.9	46.1	46	35	10	6
Ethofumesate	11.7	**287.0**	**121.0**	1	20	10	10
		287.0	161.0	1	20	10	10
Fenamiphos	12.4	**304.0**	**217.0**	61	31	10	18
		304.0	202.0	61	45	10	16
Fludioxonil NH4	11.6	**266.0**	**229.0**	15	15	10	18
		266.0	158.0	15	47	10	10
Imidacloprid	7.30	**256.0**	**208.9**	30	21	10	26
		256.0	175.1	30	25	10	16
Linuron	11.4	**249.0**	**159.9**	26	23	10	16
		249.0	182.0	26	21	10	20

Compound	RT	Precursor Ion [1]	Product Ion [1]	De-Clustering Potential	Collision Energy	Entrance Potential	Exit Potential
Mefenoxam	10.7	**280.0**	**220.1**	36	19	10	18
		280.0	192.2	36	25	10	16
Methiocarb	11.6	**226.0**	**169.0**	36	15	10	16
		226.0	121.0	36	25	10	12
Metolachlor	12.4	**284.0**	**252.0**	35	19	10	24
		284.0	176.2	35	35	10	16
Metribuzin	9.20	**215.1**	**187.0**	36	25	10	12
		215.1	84.0	36	31	10	10
Napropamide	12.5	**272.0**	**129.0**	34	23	10	14
		272.0	171.1	34	25	10	14
Norflurazon	11.1	**303.9**	**284.0**	106	31	10	26
		303.9	144.9	106	57	10	16
Oryzalin	12.6	**347.0**	**305.0**	31	19	10	10
		347.0	287.9	31	25	10	26
Prometon	10.0	**226.1**	**142.0**	56	31	10	16
		226.1	184.1	56	25	10	16
Simazine	9.00	**202.0**	**124.0**	61	25	10	6
		202.0	67.9	61	43	10	8
Tebuthiuron	9.40	**229.0**	**172.1**	41	23	10	16
		229.0	116.0	41	35	10	14
Thiamethoxam	6.20	**291.9**	**211.0**	16	19	10	20
		291.9	180.9	16	31	10	20
Thiobencarb	13.5	**258.0**	**124.9**	26	25	10	14
		258.0	89.0	26	63	10	14
Uniconazole-p	12.3	**292.0**	**70.0**	180	47	10	13
		294.0	70.0	180	47	10	13
Methoxyfenozide	11.8	**368.9**	**148.9**	35	22	10	16
		368.9	312.9	35	11	10	28
Methomyl	4.80	**162.9**	**87.8**	20	11	10	10
		162.9	105.8	20	12	10	12
Chlorantraniliprole	11.4	**483.9**	**285.7**	30	16	10	21
		483.9	452.9	30	22	10	13
Isoxaben	12.0	**332.8**	**165.0**	50	23	10	12
		332.8	106.8	50	74	10	13

Compound	RT	Precursor Ion [1]	Product Ion [1]	De-Clustering Potential	Collision Energy	Entrance Potential	Exit Potential
Propiconazole	13.3	**341.8**	**158.9**	70	34	10	13
		341.8	204.9	70	24	10	16
Pyraclostrobin	13.8	**387.9**	**194.0**	50	16	10	16
		387.9	163.0	50	31	10	16
Cyprodinil	12.7	**226.0**	**92.8**	85	39	10	8
		226.0	107.9	85	33	10	6
Flutriafol	10.6	**301.8**	**69.9**	45	20	10	10
		301.8	122.8	45	35	10	11
Alachlor	12.5	**270.0**	**238.1**	40	13	10	17
		270.0	147.0	40	39	10	12
Bentazon	8.40	**238.9**	**132.0**	-40	-34	-10	-14
		238.9	175.0	-40	-26	-10	-18
3,5-Dichloroaniline	9.82	**161.0**	**131.0**	160	38	10	15
		161.0	76.8	160	50	10	20
3,4-Dichloroaniline	10.4	**161.9**	**127.0**	140	30	10	12
		161.9	109.0	140	40	10	12
AIBA	6.06	**178.9**	**120.0**	35	19	10	14
		178.9	91.9	35	37	10	10
Flupyradifurone	6.97	**289.9**	**125.9**	46	25	10	14
		289.9	127.0	46	35	10	18
Myclobutanil	11.1	**289.9**	**70.0**	16	21	10	8
		289.9	125	16	37	10	14
Atrazine-d5	9.16	**220.9**	**179.0**	61	25	10	24
(Surrogate)		220.9	101.0	61	31	10	16
Imidacloprid-d4	6.42	**259.9**	**213.0**	170	46	10	9
(Surrogate)		259.9	179.0	170	46	10	9

[1] Quantitation transition is in bold.

11.3 GC/MS/MS Conditions

11.3.1 Instrument Model: Agilent 7890GC 7010 Triple Quadrupole MS

11.3.2 Recommended Instrument Parameters:

11.3.2.1 Injector Temperature: 250 °C

11.3.2.2 MSD Transfer Line Heater: 280 °C

11.3.2.3 Oven temperature: 60 °C, hold 1 min., ramp 35 °C/min. to 180 °C, hold 0 min, ramp 8 °C/min to 220°C, hold 0 min, ramp 35 °C/min to 320 °C hold 2 min.

11.3.2.4 Injection volume: 2 µL.

Table 3 – G/MS/MS Instrument Conditions

Compound	Precursor Ion [1]	Product Ion [1]	Collision Energy
Clomazone	204.1	107.2	20
Clomazone	**204.1**	**78.2**	40
Dichlobenil	**170.9**	**136**	15
Dichlobenil	170.9	110	15
Dichlobenil	170.9	100	25
Dichloran	205.9	176	10
Dichloran	205.9	148	25
Dichloran	**205.9**	**124**	30
Dichloran	176	148	15
Disulfoton	**274**	**88**	10
Disulfoton	274	60	25
Ethoprophos	157.9	114	5
Ethoprophos	157.9	97	20
Ethoprophos	**138.9**	**97**	5
Ethoprophos	125.9	65	10
Fonofos	246	137	10
Fonofos	**246**	**109.1**	15
Fonofos	246	81.1	30
Fonofos	109	80.9	5
Malathion	**173**	**127**	5
Malathion	173	117	13
Malathion	173	99	15
Parathion Ethyl	291	142	5
Parathion Ethyl	**291**	**109**	13

Compound	Precursor Ion [1]	Product Ion [1]	Collision Energy
Parathion Ethyl	291	81	12
Parathion Ethyl	139	109	5
Parathion Methyl	263	137	5
Parathion Methyl	**263**	**109**	13
Parathion Methyl	263	79	30
Phorate	260	231	5
Phorate	**260**	**75**	5
Piperonyl Butoxide	176	131	15
Piperonyl Butoxide	176	117	20
Piperonyl Butoxide	**176**	**103**	25
Prometryn	**241.1**	**184.2**	10
Prometryn	241.1	58.2	15
Propanil	161	126	30
Propanil	**161**	**99**	30
Propanil	161	90	30
Triallate	267.9	226.1	15
Triallate	**267.9**	**184.1**	20
Triallate	267.9	125	45
Benfluralin	**292**	**264**	5
Benfluralin	292	206	10
Benfluralin	292	160	15
EPTC	**189**	**128**	5
EPTC	189	43	20
EPTC	132	90	5
EPTC	128	86	5

[1] Quantitation transition is in bold.

12. Quality Control:

12.1 Method Detection Limit

Method Detection Limit (MDL) refers to the lowest concentration of the analyte that a method can detect reliably. To determine the MDL, 7 groundwater samples are spiked at 0.02 ppb for LC/MS/MS and GC/MS/MS analysis 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.

The results for the standard deviations and MDL are in Appendix I and III.

12.2 Reporting Limit

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 0.02 – 0.05 ppb for all compounds. The RL's are listed in Appendix I and III.

12.3 Method Validation

The method validation consists of five sample sets. Each set includes 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 II and IV.

12.4 Control Charts and Limits

A control chart is generated using the data from the method validation. The upper and lower control limits are set at $\pm$ 3 standard deviations of the percent recovery.

12.5 Acceptance Criteria

12.5.1 Each set of samples will have a matrix blank and a spiked matrix sample.

12.5.2 The retention time should be within $\pm$ 0.1 minute of that of the standards.

12.5.3 The recoveries of the matrix spikes shall be within the control limits.

12.5.3.1 When spike recoveries fall outside the control limits, the chemist must investigate the cause. The entire extraction set of samples is re-analyzed. If the spike recoveries fall within the limit, then the results from the re-analyzed samples shall be reported.

12.5.3.2 If the spike recoveries still fall outside the control limits, the client will be notified. The backup samples will be re-extracted for analysis.

12.5.4 If the calibration curve does not meet the acceptance criteria, the samples shall be re-analyzed. If the calibration criteria are met, the sample results will be reported. If the calibration criteria are still not met, a method deviation will be prepared and approved by the supervisor of designee. The client will be notified of the deviation and a copy of the method deviation detailing what was changed and why it was changed will be included with the samples results and the data will be flagged to let the data user know of the deviation.

12.5.5 The sample shall be diluted if results fall above the calibration curve.

12.5.6 Bracketing standard curves should have a percent change less than 20%.

12.5.7 The relative abundance of qualifier ions shall be within ± 30%.

13. Calculations:

Quantitation is based on an external standard (ESTD) calculation using either the peak area or height. The LC/MS/MS quantitation software uses 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.

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

14. Reporting Procedure:

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

15. Discussion:

15.1 Acephate, azoxystrobin acid, 4-hydroxy chlorothalonil, chlorothalonil, dinotefuran, oxydemeton-methyl, and rimsulfuron were requested as part of the screen, but would not extract out of water using the current liquid/liquid extraction method. Aldicarb was also requested but was not very sensitive and had poor reproducibility so it was left out of the screen.

Iprodione is very unstable with recoveries ranging from 0% recovery for the lowest spike level up to 263% recovery on higher spike levels. Iprodione was also removed from the screen list. 3,5-Dichloroaniline has low sensitivity for the qualifying ion and is not within ± 30% relative abundance of the quantifier ion. Upon discussion with the client, 3,5-Dichloroaniline is an exception and does not have to be within ± 30% relative abundance. 3,5-Dichloroaniline can be reported as is.

15.2 A storage stability study was done for all compounds and the results show that all compounds are stable up to 28 days. See Appendix V for data.

16. References:

16.1 Schwarz, Timo; Snow, Timothy A.; Santee, Christopher J.; Mulligan, Christopher C.; Class, Thomas; Wadsley, Michael P.; and Nanita, Sergio C.,

"QuEChERS Multiresidue Method Validation and Mass Spectrometric Assessment for the Novel Anthranilic Diamide Insecticides Chlorantraniliprole and Cyantraniliprole", J. Agric. Food Chem. 2011, 59, 814-821

16.2 "Crop Protection Handbook, 2010", MeisterPro Executive Office 27722 Euclid Ave., Willoughby, OH

Appendix I

MDL Determination (Fortified at 0.02 ppb) by LC/MS/MS

Compound	MDL -1	MDL -2	MDL -3	MDL -4	MDL -5	MDL -6	MDL -7	SD	MDL	RL
Atrazine	0.0189	0.0187	0.0200	0.0197	0.0185	0.0194	0.0176	0.000820	0.00300	0.0200
Azinphos-methyl	0.0168	0.0196	0.0201	0.0199	0.0196	0.0233	0.0187	0.00194	0.00600	0.0500
Azoxystrobin	0.0195	0.0199	0.0199	0.0203	0.0202	0.0215	0.0213	0.000730	0.00200	0.0200
Bensulide	0.0194	0.0170	0.0182	0.0196	0.0188	0.0194	0.0173	0.00106	0.00300	0.0200
Bromacil	0.0173	0.0167	0.0174	0.0188	0.0201	0.0201	0.0189	0.00137	0.00400	0.0200
Carbaryl	0.0205	0.0207	0.0192	0.0219	0.0206	0.0212	0.0198	0.000890	0.00300	0.0200
Carbofuran	0.0210	0.0211	0.0206	0.0208	0.0210	0.0218	0.0203	0.000480	0.00100	0.0200
Diazinon	0.0201	0.0198	0.0191	0.0194	0.0190	0.0202	0.0192	0.000500	0.00200	0.0300
Dimethenamide	0.0183	0.0193	0.0176	0.0192	0.0200	0.0194	0.0179	0.000890	0.00300	0.0200
Dimethoate	0.0188	0.0176	0.0177	0.0203	0.0204	0.0223	0.0193	0.00168	0.00500	0.0200
Diuron	0.0195	0.0202	0.0192	0.0201	0.0198	0.0214	0.0196	0.000710	0.00200	0.0200
Ethofumesate	0.0181	0.0182	0.0174	0.0196	0.0173	0.0208	0.0181	0.00127	0.00400	0.0300
Fenamiphos	0.0204	0.0201	0.0200	0.0198	0.0203	0.0213	0.0193	0.000610	0.00200	0.0300
Fludioxonil	0.0169	0.0182	0.0169	0.0205	0.0172	0.0188	0.0177	0.00131	0.00400	0.0300
Imidacloprid	0.0194	0.0179	0.0181	0.0184	0.0198	0.0197	0.0184	0.000800	0.00300	0.0200
Linuron	0.0206	0.0192	0.0212	0.0212	0.0210	0.0214	0.0214	0.000790	0.00200	0.0200

Compound	MDL -1	MDL -2	MDL -3	MDL -4	MDL -5	MDL -6	MDL -7	SD	MDL	RL
Mefenoxam	0.0203	0.0207	0.0188	0.0203	0.0202	0.0204	0.0197	0.000630	0.00200	0.0200
Methiocarb	0.0198	0.0193	0.0190	0.0201	0.0213	0.0209	0.0190	0.000900	0.00300	0.0200
Metolachlor	0.0189	0.0191	0.0185	0.0193	0.0183	0.0211	0.0180	0.00102	0.00300	0.0200
Metribuzin	0.0176	0.0187	0.0189	0.0185	0.0195	0.0201	0.0190	0.000780	0.00200	0.0200
Napropamide	0.0195	0.0199	0.0198	0.0193	0.0187	0.0199	0.0185	0.000570	0.00200	0.0200
Norflurazon	0.0183	0.0202	0.0187	0.0194	0.0191	0.0202	0.0185	0.000750	0.00200	0.0200
Oryzalin	0.0206	0.0180	0.0185	0.0215	0.0175	0.0186	0.0184	0.00147	0.00500	0.0500
Prometon	0.0201	0.0198	0.0197	0.0200	0.0193	0.0210	0.0182	0.000850	0.00300	0.0200
Simazine	0.0194	0.0190	0.0202	0.0202	0.0211	0.0217	0.0195	0.000970	0.00300	0.0200
Tebuthiuron	0.0205	0.0200	0.0206	0.0217	0.0199	0.0216	0.0215	0.000750	0.00200	0.0200
Thiamethoxam	0.0154	0.0151	0.0155	0.0177	0.0195	0.0196	0.0177	0.00191	0.00600	0.0200
Thiobencarb	0.0180	0.0182	0.0179	0.0189	0.0184	0.0188	0.0173	0.000560	0.00200	0.0200
Uniconizole	0.0185	0.0160	0.0189	0.0195	0.0187	0.0193	0.0166	0.00137	0.00400	0.0500
Methoxyfenozide	0.0213	0.0181	0.0197	0.0198	0.0195	0.0200	0.0182	0.00109	0.00300	0.0300
Methomyl	0.0166	0.0153	0.0154	0.0184	0.0186	0.0193	0.0176	0.00157	0.00500	0.0200
Chlorantraniliprole	0.0192	0.0212	0.0207	0.0211	0.0208	0.0197	0.0211	0.000770	0.00200	0.0200
Isoxaben	0.0197	0.0188	0.0207	0.0208	0.0199	0.0205	0.0193	0.000730	0.00200	0.0200
Propiconazole	0.0163	0.0152	0.0152	0.0157	0.0156	0.0165	0.0154	0.000530	0.00200	0.0200

Compound	MDL -1	MDL -2	MDL -3	MDL -4	MDL -5	MDL -6	MDL -7	SD	MDL	RL
Pyraclostrobin	0.0184	0.0177	0.0174	0.0185	0.0181	0.0191	0.0177	0.000570	0.00200	0.0200
Cyprodinil	0.0200	0.0206	0.0207	0.0209	0.0197	0.0209	0.0192	0.000670	0.00200	0.0200
Flutriafol	0.0191	0.0194	0.0193	0.0203	0.0187	0.0204	0.0194	0.000630	0.00200	0.0200
Alachlor	0.0193	0.0190	0.0186	0.0192	0.0188	0.0192	0.0183	0.000340	0.00100	0.0300
Bentazon	0.0195	0.0186	0.0165	0.0187	0.0214	0.0215	0.0211	0.00185	0.00600	0.0200
3,4-Dichloroaniline	0.0181	0.0194	0.0200	0.0196	0.0173	0.0198	0.0194	0.00100	0.00300	0.0200
3,5-Dichloroaniline	0.0152	0.0160	0.0204	0.0154	0.0210	0.0169	0.0177	0.00233	0.00700	0.0200
AIBA	0.0126	0.0096	0.0133	0.0151	0.0161	0.0165	0.0143	0.00236	0.00700	0.0200
Flupyradifurone	0.0179	0.0176	0.0183	0.0196	0.0201	0.0212	0.0198	0.00134	0.00400	0.0200
Myclobutanil	0.0205	0.0175	0.0183	0.0202	0.0187	0.0198	0.0200	0.00114	0.00400	0.0200
Atrazine-d5 (Surrogate)	0.0197	0.0205	0.0195	0.0193	0.0194	0.0204	0.0195	0.000510	0.00200	0.0200
Imidacloprid-d4 (Surrogate)	0.0181	0.0183	0.0176	0.0199	0.0187	0.0198	0.0168	0.00114	0.00400	0.0200

Appendix II

Method Validation Data for LC/MS/MS Compounds

Compound	Spike Level						Control Limit (%)	
	MV Run	0.02 ppb	0.04 ppb	0.1 ppb	0.5 ppb	1.0 ppb		
Atrazine	1	85.2	83.5	96.4	100	96.5	**Mean:**	90.3
	2	91.9	83.8	87.9	96.2	93.1	**SD:**	6.14
	3	91.0	86.7	102	84.8	93.7	**RSD:**	6.80
	4	84.1	77.4	92.3	81.5	96.2	**UCL:**	109
	5	87.9	90.0	96.8	87.6	91.1	**LCL:**	71.9
Azinphos-methyl	1	96.3	83.3	95.6	108	95.3	**Mean:**	94.3
	2	95.9	85.6	89.3	86.2	81.0	**SD:**	8.11
	3	96.5	91.4	107	99.5	97.0	**RSD:**	8.60
	4	84.5	90.0	103	92.8	106	**UCL:**	119
	5	86.2	85.5	105	105	91.4	**LCL:**	70.0
Azoxystrobin	1	92.1	88.3	104	98.3	91.5	**Mean:**	94.1
	2	105	88.9	92.0	87.1	110	**SD:**	7.64
	3	96.0	91.4	112	82.7	94.7	**RSD:**	8.12
	4	88.9	90.3	101	85.7	88.9	**UCL:**	117
	5	87.6	93.5	101	95.7	87.1	**LCL:**	71.2
Bensulide	1	76.1	75.2	88.0	90.4	90.1	**Mean:**	85.2
	2	88.2	80.5	83.7	91.9	87.8	**SD:**	7.04
	3	79.1	78.9	92.4	74.1	92.2	**RDS:**	8.26
	4	75.1	74.8	88.5	81.9	92.1	**UCL:**	106
	5	86.8	82.3	99.7	88.8	92.2	LCL:	64.1

Compound	Spike Level						Control Limit (%)	
	MV Run	0.02 ppb	0.04 ppb	0.1 ppb	0.5 ppb	1.0 ppb		
Bromacil	1	87.9	95.0	105	104	96.8	**Mean:**	93.3
	2	96.4	88.1	91.1	95.3	102	**SD:**	6.29
	3	85.8	87.5	97.1	93.5	96.5	**RSD:**	6.74
	4	92.9	88.6	104	90.4	100	**UCL:**	112
	5	83.7	87.3	84.9	88.1	91.5	**LCL:**	74.4
Carbaryl	1	97.9	95.6	104	110	100	**Mean:**	97.6
	2	102	89.3	94.8	97.2	102	**SD:**	5.27
	3	94.3	95.9	109	96.0	96.8	**RSD:**	5.40
	4	92.9	92.9	102	96.8	98.2	**UCL:**	113
	5	90.9	88.6	95.2	99.7	97.6	**LCL:**	81.8
Carbofuran	1	93.2	93.5	103	110	95.5	**Mean:**	95.8
	2	101	85.7	92.3	93.8	96.2	**SD:**	7.37
	3	98.6	97.8	115	101	102	**RSD:**	7.69
	4	85.7	85.1	95.1	90.0	95.4	**UCL:**	118
	5	86.7	88.7	101	98.6	90.7	**LCL:**	73.7
Diazinon	1	91.4	91.6	103	103	97.1	**Mean:**	93.8
	2	98.7	90.4	92.4	94.1	102	**SD:**	6.22
	3	87.4	89.1	104	92.2	94.0	**RSD:**	6.63
	4	85.7	81.0	99.9	92.4	90.8	**UCL:**	112
	5	88.2	87.0	101	100	89.6	**LCL:**	75.1
Dimethenamide	1	91.5	89.4	103	84.4	93.8	**Mean:**	90.1
	2	97.5	84.3	91.3	89.6	105	**SD:**	7.23
	3	92.9	88.3	102	76.8	91.3	**RSD:**	8.02
	4	86.4	79.8	93.3	80.1	90.1	**UCL:**	112
	5	85.2	86.9	97.5	81.4	89.7	**LCL:**	68.4

Compound	Spike Level						Control Limit (%)	
	MV Run	0.02 ppb	0.04 ppb	0.1 ppb	0.5 ppb	1.0 ppb		
Dimethoate	1	94.9	91.6	100	109	96.4	**Mean:**	95.7
	2	99.1	86.1	93.2	101	107	**SD:**	6.67
	3	93.0	96.2	107	96.4	96.8	**RSD:**	6.97
	4	93.3	91.1	103	100	96.3	**UCL:**	116
	5	87.2	84.8	84.6	96.2	89.4	**LCL:**	75.7
Diuron	1	97.6	95.6	107	110	102	**Mean:**	98.7
	2	105	86.0	94.3	101	102	**SD:**	6.08
	3	94.3	94.1	107	99.9	99.0	**RSD:**	6.17
	4	93.4	91.0	107	98.8	102	**UCL:**	117
	5	92.6	89.5	103	100	95.0	**LCL:**	80.5
Ethofumesate	1	84.8	79.4	91.9	91.4	86.5	**Mean:**	87.3
	2	90.4	87.9	86.7	99.7	94.4	**SD:**	6.38
	3	79.4	81.2	97.7	86.2	94.1	**RSD:**	7.30
	4	80.2	73.5	86.4	80.9	94.9	**UCL:**	106
	5	89.5	83.0	92.2	86.4	84.1	**LCL:**	68.2
Fenamiphos	1	85.4	84.4	94.1	87.9	89.0	**Mean:**	85.8
	2	84.6	75.2	81.2	84.2	86.2	**SD:**	6.84
	3	76.7	83.7	86.9	70.9	88.6	**RSD:**	7.98
	4	79.6	85.3	99.4	83.8	93.7	**UCL:**	106
	5	80.0	82.5	100	91.7	89.1	**LCL:**	65.2
Fludioxonil NH4	1	94.1	91.0	104	79.4	90.5	**Mean:**	90.5
	2	89.8	85.9	81.2	93.9	91.2	**SD:**	6.97
	3	90.4	91.0	102	95.0	86.8	**RSD:**	7.70
	4	89.9	96.7	96.4	84.7	96.5	**UCL:**	111
	5	87.1	87.0	101	76.0	81.9	**LCL:**	69.6

Compound	Spike Level						Control Limit (%)	
	MV Run	0.02 ppb	0.04 ppb	0.1 ppb	0.5 ppb	1.0 ppb		
Imidacloprid	1	98.5	97.5	104	117	87.1	**Mean:**	96.6
	2	98.7	85.3	86.6	91.5	107	**SD:**	7.66
	3	93.0	96.8	110	98.8	93.8	**RSD:**	7.93
	4	91.7	93.3	99.8	94.3	94.9	**UCL:**	120
	5	93.4	88.1	94.2	107	92.0	**LCL:**	73.6
Linuron	1	94.8	94.9	104	106	97.2	**Mean:**	97.1
	2	101	86.6	92.8	107	96.6	**SD:**	6.69
	3	96.5	97.8	110	95.3	98.3	**RSD:**	6.88
	4	90.8	82.8	101	106	98.8	**UCL:**	117
	5	89.3	92.9	104	90.9	93.1	**LCL:**	77.1
Mefenoxam	1	96.0	96.7	105	106	101	**Mean:**	98.1
	2	99.6	87.3	99.2	99.4	105	**SD:**	6.96
	3	91.5	93.9	115	92.9	101	**RSD:**	7.10
	4	91.9	89.5	106	103	96.4	**UCL:**	119
	5	87.1	89.1	105	101	93.0	**LCL:**	77.2
Methiocarb	1	93.3	91.2	102	103	90.0	**Mean:**	91.6
	2	97.8	84.9	89.2	87.0	96.0	**SD:**	6.73
	3	91.4	95.4	110	84.9	92.8	**RSD:**	7.34
	4	86.7	84.2	96.0	81.5	91.0	**UCL:**	112
	5	85.2	85.2	94.2	90.6	86.8	**LCL:**	71.4
Metolachlor	1	79.6	77.5	90.0	89.3	86.8	**Mean:**	85.0
	2	86.7	84.1	78.9	80.3	99.7	**SD:**	7.51
	3	78.6	80.1	89.9	74.9	90.4	**RSD:**	8.83
	4	76.9	77.8	95.4	72.4	88.8	**UCL:**	108
	5	90.9	85.3	102	84.5	85.4	**LCL:**	62.5

Compound	Spike Level						Control Limit (%)	
	MV Run	0.02 ppb	0.04 ppb	0.1 ppb	0.5 ppb	1.0 ppb		
Metribuzin	1	87.4	90.0	101	108	96.7	**Mean:**	92.8
	2	97.3	86.1	88.8	93.4	98.1	**SD:**	6.21
	3	91.5	90.6	103	95.5	95.3	**RSD:**	6.70
	4	90.8	88.5	97.8	87.2	97.4	**UCL:**	111
	5	87.4	84.2	91.5	90.6	81.3	**LCL:**	74.1
Napropamide	1	91.4	90.3	104	112	106	**Mean:**	96.4
	2	100	82.5	90.8	91.5	107	**SD:**	7.40
	3	94.5	91.7	107	91.9	99.4	**RSD:**	7.68
	4	93.6	87.8	99.9	94.5	93.6	**UCL:**	119
	5	87.8	88.9	104	101.0	97.7	**LCL:**	74.2
Norflurazon	1	88.2	84.9	97.5	88.8	95.8	**Mean:**	90.0
	2	91.6	81.2	82.6	82.6	109	**SD:**	7.61
	3	81.6	81.2	96.3	83.7	98.1	**RSD:**	8.46
	4	86.4	84.0	92.7	85.2	99.1	**UCL:**	113
	5	87.5	83.0	103	89.1	96.3	**LCL:**	67.1
Oryzalin	1	85.6	93.8	100	84.9	87.0	**Mean:**	92.8
	2	90.0	82.8	90.4	114	111	**SD:**	13.3
	3	112	101	116	81.8	76.0	**RSD:**	14.4
	4	72.4	85.9	88.5	110	70.5	**UCL:**	133
	5	90.6	79.2	91.2	111	94.5	**LCL:**	52.8
Prometon	1	96.2	94.1	106	104	95.2	**Mean:**	97.3
	2	104	88.5	93	97.8	110	**SD:**	6.62
	3	94.3	92.3	114	98.6	97.4	**RSD:**	6.81
	4	92.6	88.9	104	96.2	97.0	**UCL:**	117
	5	89.9	90.1	102	92.4	94.5	**LCL:**	77.5

Compound	Spike Level						Control Limit (%)	
	MV Run	0.02 ppb	0.04 ppb	0.1 ppb	0.5 ppb	1.0 ppb		
Simazine	1	93.0	91.5	104	105	97.1	**Mean:**	96.0
	2	99.6	86.6	90.4	91.5	106	**SD:**	6.40
	3	97.3	95.6	110	96.6	98.3	**RSD:**	6.66
	4	89.9	91.9	101	94.0	97.4	**UCL:**	115
	5	88.0	86.2	99.2	102	88.3	**LCL:**	76.8
Tebuthiuron	1	93.1	94.8	103	108	94.8	**Mean:**	96.8
	2	98.7	86.7	94.8	94.4	93.4	**SD:**	6.56
	3	95.2	99.1	113	99.8	97.6	**RSD:**	6.78
	4	88.6	87.9	103	109	97.4	**UCL:**	116
	5	92.5	91.0	98.0	96.2	89.5	**LCL:**	77.1
Thiamethoxam	1	90.9	89.7	96.8	97.5	89.3	**Mean:**	88.0
	2	88.7	79.2	86.5	92.2	94.8	**SD:**	6.07
	3	88.8	86.9	101	88.1	93.7	**RSD:**	6.89
	4	83.6	83.2	89.5	85.1	89.5	**UCL:**	106
	5	78.1	77.8	83.7	87.0	79.1	**LCL:**	69.8
Thiobencarb	1	86.4	79.2	89.3	92.9	92.1	**Mean:**	88.8
	2	87.2	80.5	90.5	97.6	96.5	**SD:**	5.70
	3	85.2	80.7	97.0	80.5	94.2	**RSD:**	6.42
	4	88.2	80.5	90.6	85.4	89.4	**UCL:**	106
	5	83.3	93.6	95.3	91.4	92.4	**LCL:**	71.7
Uniconazole-p	1	94.7	78.3	87.6	87.5	88.1	**Mean:**	89.1
	2	87.4	86.6	82.7	99.2	103	**SD:**	8.18
	3	84.9	85.9	105	87.1	96.6	**RSD:**	9.18
	4	79.4	71.0	85.4	86.1	92.4	**UCL:**	114
	5	87.7	84.8	106	91.4	89.0	**LCL:**	64.6

Compound	Spike Level						Control Limit (%)	
	MV Run	0.02 ppb	0.04 ppb	0.1 ppb	0.5 ppb	1.0 ppb		
Methoxyfenozide	1	75.1	74.1	88.2	89.0	90.5	**Mean:**	84.8
	2	83.2	75.2	76.1	78.3	101	**SD:**	8.86
	3	74.8	76.8	88.8	76.8	93.5	**RSD:**	10.4
	4	74.6	78.0	90.5	83.9	97.9	**UCL:**	111
	5	85.5	83.5	104	86.6	94.2	**LCL:**	58.2
Methomyl	1	89.6	87.7	92.5	104	89.5	**Mean:**	90.6
	2	94.8	82.6	88.0	99.6	99.2	**SD:**	7.38
	3	89.9	90.7	108	92.5	94.9	**RSD:**	**8.15**
	4	84.1	82.6	93.4	89.6	93.0	**UCL:**	113
	5	78.2	78.3	91.3	90.6	79.7	**LCL:**	68.4
Chlorantraniliprole	1	90.1	109	102	97.0	91.7	**Mean:**	96.7
	2	104	83.8	93.2	115	103	**SD:**	7.92
	3	94.2	97.7	107	92.5	99.8	**RSD:**	8.19
	4	93.1	81.9	101	93.8	90.0	**UCL:**	120
	5	87.5	90.0	96.1	99.4	105	**LCL:**	73.0
Isoxaben	1	91.8	89.9	109	113	107	**Mean:**	98.7
	2	97.7	93.0	92.3	103	94.8	**SD:**	8.01
	3	102	89.7	116	109	102	**RSD:**	8.12
	4	91.7	95.2	101	101	93.3	**UCL:**	123
	5	91.3	87.3	107	97.9	90.6	**LCL:**	74.6
Propiconazole	1	82.3	90.8	87.9	87.2	87.9	**Mean:**	84.8
	2	82.1	73.2	85.9	80.5	100	**SD:**	6.71
	3	80.5	82.0	91.7	80.2	92.3	**RSD:**	7.91
	4	76.1	74.4	87.9	88.4	84.0	**UCL:**	105
	5	79.9	73.2	90.3	91.9	89.7	**LCL:**	64.7

Compound	Spike Level						Control Limit (%)	
	MV Run	0.02 ppb	0.04 ppb	0.1 ppb	0.5 ppb	1.0 ppb		
Pyraclostrobin	1	84.2	82.3	93.6	103	91.4	**Mean:**	89.3
	2	89.9	81.9	87.7	91.9	101	**SD:**	6.64
	3	85.8	82.3	98.3	83.6	86.4	**RSD:**	7.43
	4	84.8	81.1	95.4	87.0	89.0	**UCL:**	109
	5	79.7	87.4	99.6	96.7	89.6	**LCL:**	69.4
Cyprodinil	1	97.2	88.7	98.5	106	97.9	**Mean:**	96.3
	2	97.7	88.5	91.6	100	96.6	**SD:**	6.22
	3	90.9	91.2	108	97.9	99.9	**RSD:**	6.46
	4	93.7	88.9	108	96.0	97.3	**UCL:**	115
	5	86.7	86.9	103	102	94.2	**LCL:**	77.6
Flutriafol	1	96.5	85.3	102	108	96.3	**Mean:**	93.9
	2	98.8	85.9	93.0	86.5	97.0	**SD:**	6.74
	3	95.8	90.3	108	90.1	94.8	**RSD:**	7.18
	4	90.0	87.1	94.3	89.5	102	**UCL:**	114
	5	84.9	85.1	96.1	100	91.0	**LCL:**	73.7
Alachlor	1	82.0	79.9	91.7	93.8	90.6	**Mean:**	87.5
	2	92.1	82.7	85.8	88.8	102	**SD:**	6.67
	3	82.7	81.9	94.1	79.9	91.7	**RSD:**	7.63
	4	77.8	76.3	93.0	81.8	91.8	**UCL:**	107
	5	85.8	82.6	99.6	87.9	90.0	**LCL:**	67.4
Bentazon	1	97.0	94.0	96.0	115	99.5	**Mean:**	96.4
	2	89.4	85.8	87.8	101	98.1	**SD:**	9.74
	3	89.4	91.4	103	108	95.8	**RSD:**	10.1
	4	94.2	89.7	107	106	100	**UCL:**	126
	5	66.2	91.5	110	94.6	99.6	**LCL:**	67.2
3,4-Dichloroaniline	1	90.0	90.2	96.0	93.9	94.2	**Mean:**	92.0
	2	104	93.4	86.9	102	101	**SD:**	5.90
	3	86.3	86.2	94.8	85.6	88.5	**RSD:**	6.41
	4	84.3	85.7	99.6	90.7	97.8	**UCL:**	110
	5	89.8	85.0	93.7	95.9	84.3	**LCL:**	74.3
3,5-Dichloroaniline	1	92.3	94.3	108	110	102	**Mean:**	98.3
	2	91.9	93.6	98.9	97.2	110	**SD:**	6.81
	3	101	98.2	109	95.4	93.2	**RSD:**	6.93
	4	92.0	84.3	96.4	92.8	102	**UCL:**	119
	5	88.0	100	103	105	98.7	**LCL:**	77.9

Compound	Spike Level						Control Limit (%)	
	MV Run	0.02 ppb	0.04 ppb	0.1 ppb	0.5 ppb	1.0 ppb		
AIBA	1	67.0	64.9	85.6	99.5	84.3	**Mean:**	82.4
	2	87.1	78.5	82.8	92.7	94.9	**SD:**	10.6
	3	89.2	82.8	102	85.4	91.2	**RSD:**	12.9
	4	66.6	64.6	85.6	76.7	84.3	**UCL:**	114
	5	70.1	69.8	91.0	85.7	77.4	**LCL:**	50.6
Flupyradifurone	1	98.3	97.9	106	98.4	96	**Mean:**	96.6
	2	98.2	90.0	94.9	93.2	106	**SD:**	5.22
	3	96.1	96.4	106	98.4	93.8	**RSD:**	5.41
	4	92.5	92.1	103	96.2	97.9	**UCL:**	112
	5	91.6	93.9	102	88.1	86.8	**LCL:**	80.9
Myclobutanil	1	99.1	102	96.6	93.4	81.3	**Mean:**	90.2
	2	103	77.8	78.4	85.2	94.8	**SD:**	9.31
	3	96.8	90.1	101	76.5	84.1	**RSD:**	10.3
	4	93.2	92.0	102	86.8	89.1	**UCL:**	118
	5	81.0	88.0	107	77.1	78.5	**LCL:**	62.3
Atrazine-d5 (Surrogate)	1	92.0	85.7	98.4	104	89.5	**Mean:**	92.4
	2	98.3	90.7	94.9	98.6	97.7	**SD:**	6.03
	3	89.8	88.3	105	86.6	91.0	**RSD:**	6.53
	4	88.2	83.0	99.6	84.9	94.0	**UCL:**	110
	5	88.1	86.2	96.8	89.7	88.0	**LCL:**	74.3
Imidacloprid-d4 (Surrogate)	1	93.2	95.4	107	119	92.9	**Mean:**	98.3
	2	89.9	88.5	90.5	103	96.3	**SD:**	7.85
	3	93.7	101	107	106	98.2	**RSD:**	7.98
	4	96.2	97.4	102	108	92.4	**UCL:**	122
	5	87.4	95.8	94.8	111	91.4	**LCL:**	74.8

Appendix III

MDL Determination (Fortified at 0.02 ppb) by GC/MS/MS

Compound	Blank	MDL-1	MDL-2	MDL-3	MDL-4	MDL-5	MDL-6	MDL-7	SD	MDL	RL
Clomazone	ND	0.0202	0.0228	0.0217	0.0203	0.0216	0.0191	0.0171	0.00190	0.00600	0.0500
Dichlobenil	ND	0.0194	0.0212	0.0200	0.0194	0.0204	0.0175	0.0163	0.00172	0.00500	0.0300
Dichloran	ND	0.0172	0.0206	0.0197	0.0189	0.0200	0.0186	0.0158	0.00169	0.00500	0.0500
Disulfoton	ND	0.0166	0.0196	0.0153	0.0169	0.0207	0.0174	0.0170	0.00186	0.00600	0.0500
Ethoprophos	ND	0.0158	0.0180	0.0178	0.0172	0.0180	0.0162	0.0145	0.00133	0.00400	0.0300
Fonofos	ND	0.0203	0.0226	0.0215	0.0205	0.0218	0.0192	0.0172	0.00182	0.00600	0.0300
Malathion	ND	0.0233	0.0260	0.0218	0.0227	0.0201	0.0219	0.0214	0.00186	0.00600	0.0300
Parathion Ethyl	ND	0.0155	0.0167	0.0142	0.0147	0.0147	0.0141	0.0191	0.00179	0.00600	0.0300
Parathion Methyl	ND	0.0187	0.0210	0.0185	0.0184	0.0195	0.0176	0.0174	0.00122	0.00400	0.0300
Phorate	ND	0.0176	0.0195	0.0188	0.0187	0.0194	0.0173	0.0155	0.00141	0.00400	0.0300
Piperonyl Butoxide	ND	0.0204	0.0227	0.0222	0.0202	0.0238	0.0215	0.0204	0.00140	0.00400	0.0300
Prometryn	ND	0.0236	0.0242	0.0209	0.0208	0.0241	0.0202	0.0203	0.00185	0.00600	0.0300
Propanil	ND	0.0208	0.0241	0.0220	0.0201	0.0209	0.0202	0.0183	0.00178	0.00600	0.0500
Triallate	ND	0.0210	0.0228	0.0218	0.0208	0.0220	0.0195	0.0177	0.00172	0.00500	0.0300
Benfluralin	ND	0.0156	0.0177	0.0176	0.0171	0.0185	0.0166	0.0153	0.00116	0.00400	0.0500
EPTC	ND	0.0128	0.0129	0.0134	0.0138	0.0140	0.0121	0.0111	0.00102	0.00300	0.0500

Appendix IV

Method Validation Data for GC/MS/MS Compounds

Compound	Spike Level						Control Limit (%)	
	MV Run	0.025 ppb	0.05 ppb	0.1 ppb	0.5 ppb	2.0 ppb		
Clomazone	1	90.5	89.3	89.0	106	103	**Mean:**	87.7
	2	83.0	100	92.8	107	95.4	**SD:**	13.1
	3	68.0	72.5	71.2	73.6	85.0	**RSD:**	14.9
	4	95.5	89.3	93.5	109	106	**UCL:**	127
	5	74.5	76.5	71.3	78.2	72.4	**LCL:**	48.5
Dichlobenil	1	104	91.0	90.3	105	110	**Mean:**	90.0
	2	85.0	103	95.8	102	98.6	**SD:**	15.0
	3	72.5	76.0	74.0	73.8	83.2	**RSD:**	16.7
	4	110	94.5	90.1	114	111	**UCL:**	135
	5	78.5	82.8	66.7	69.4	68.2	**LCL:**	45.0
Dichloran	1	90.5	87.8	91.6	109	116	**Mean:**	88.8
	2	75.5	95.0	88.4	106	98.3	**SD:**	13.8
	3	68.0	73.8	72.3	77.0	93.7	**RSD:**	15.5
	4	94.0	88.5	93.5	107	111	**UCL:**	130
	5	71.5	78.0	74.0	83.8	76.6	**LCL:**	47.5
Disulfoton	1	88.5	85.8	86.9	104	101	**Mean:**	85.8
	2	81.0	99.5	93.2	106	95.5	**SD:**	13.2
	3	67.0	69.5	70.9	73.4	84.8	**RSD:**	15.4
	4	90.5	83.8	91.2	108	105	**UCL:**	125
	5	71.0	73.3	68.8	76.2	71.4	**LCL:**	46.2

Compound	Spike Level						Control Limit (%)	
	MV Run	0.025 ppb	0.05 ppb	0.1 ppb	0.5 ppb	2.0 ppb		
Ethoprophos	1	92.5	88.0	90.7	107	106	**Mean:**	89.9
	2	85.0	101	95.5	113	98.6	**SD:**	14.2
	3	69.5	73.8	72.5	74.2	85.4	**RSD:**	15.8
	4	107	95.3	97.9	112	107	**UCL:**	133
	5	75.5	77.0	71.5	78.6	74.1	**LCL:**	47.3
Fonofos	1	93.5	88.8	90.7	106	104	**Mean:**	87.9
	2	81.5	99.8	93.9	106	96.2	**SD:**	13.5
	3	67.0	72.0	70.7	73.8	84.8	**RSD:**	15.3
	4	95.5	89.0	94.7	111	107	**UCL:**	128
	5	74.0	76.3	71.7	77.4	73.0	**LCL:**	47.5
Malathion	1	93.5	93.0	94.3	99.2	105	**Mean:**	92.0
	2	87.0	107	97.1	105	103	**SD:**	14.0
	3	67.0	72.5	71.8	72.8	82.4	**RSD:**	15.2
	4	95.0	95.0	102	119	120	**UCL:**	134
	5	81.5	87.3	81.4	87.6	81.2	**LCL:**	50.1
Parathion Ethyl	1	49.4	82.5	88.2	104	107	**Mean:**	83.4
	2	53.5	103	95.2	116	102	**SD:**	23.0
	3	64.5	70.3	69.7	42.2	89.1	**RSD:**	27.6
	4	99.0	92.8	97.5	117	113	**UCL:**	152
	5	45.0	76.3	59.2	88.2	59.9	**LCL:**	14.5
Parathion Methyl	1	74.0	80.5	83.6	115	110	**Mean:**	84.4
	2	71.5	97.0	88.1	121	90.1	**SD:**	18.8
	3	66.5	66.5	68.6	57.4	93.6	**RSD:**	22.2
	4	100	85.5	93.4	110	105	**UCL:**	141
	5	61.5	68.3	60.2	83.0	60.7	**LCL:**	28.1

Compound	Spike Level						Control Limit (%)	
	MV Run	0.025 ppb	0.05 ppb	0.1 ppb	0.5 ppb	2.0 ppb		
Phorate	1	92.5	89.3	91.1	108	104	**Mean:**	86.2
	2	79.0	95.8	90.7	104	92.7	**SD:**	13.6
	3	65.0	70.0	68.8	71.8	83.3	**RSD:**	15.8
	4	93.0	88.8	94.1	108	102	**UCL:**	127
	5	70.0	74.8	69.7	76.6	71.4	**LCL:**	45.4
Piperonyl Butoxide	1	117	123	115	133	116	**Mean:**	107
	2	91.0	118	105	134	110	**SD:**	22.0
	3	79.5	87.0	81.9	76.6	107	**RSD:**	20.6
	4	143	126	123	140	132	**UCL:**	173
	5	76.5	88.0	76.0	101	79.0	**LCL:**	41.1
Prometryn	1	89.5	88.0	90.4	123	114	**Mean:**	91.3
	2	88.5	104	99.3	130	94.8	**SD:**	19.0
	3	64.5	65.5	71.6	65.0	97.2	**RSD:**	20.8
	4	114	89.5	96.8	116	108	**UCL:**	148
	5	70.5	74.5	73.5	81.6	72.9	**LCL:**	34.2
Propanil	1	84.0	93.5	91.4	114	111	**Mean:**	92.1
	2	81.5	105	97.9	116	99.9	**SD:**	16.0
	3	74.0	77.3	73.2	70.8	91.0	**RSD:**	17.4
	4	107	95.3	102	118	114	**UCL:**	140
	5	75.0	79.5	70.0	92.6	68.9	**LCL:**	44.0
Triallate	1	94.0	88.5	89.7	105	102	**Mean:**	87.9
	2	84.0	103	95.5	105	94.6	**SD:**	12.7
	3	68.5	74.3	72.3	73.4	83.7	**RSD:**	14.5
	4	96.0	89.0	93.8	109	103	**UCL:**	126
	5	74.5	77.8	71.3	77.4	72.0	**LCL:**	49.7
Benfluralin	1	91.0	89.5	93.1	113	106	**Mean:**	88.0
	2	82.0	100	94.6	109	94.7	**SD:**	13.6
	3	68.0	74.5	71.4	72.2	88.9	**RSD:**	15.4
	4	93.0	89.8	93.6	106	101	**UCL:**	129
	5	71.0	75.8	70.8	78.8	72.4	**LCL:**	47.3
EPTC	1	81.0	77.0	88.5	106	103	**Mean:**	83.8
	2	78.0	95.3	91.3	100	93.8	**SD:**	13.8
	3	60.5	68.0	75.0	76.6	84.2	**RSD:**	16.5
	4	83.5	85.5	97.1	108	97.0	**UCL:**	125
	5	59.5	72.3	73.3	71.2	69.6	**LCL:**	42.3

Appendix V

Storage Stability Data for LC/MS/MS Compounds

Compound	% Recovery							
	Sample	**Day 0**	**Day 2**	**Day 4**	**Day 8**	**Day 14**	**Day 21**	**Day 28**
Atrazine	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	85.3	95.8	85.3	84.3	96.7	88.9	104
	Rep 1	86.3	90.6	104	94.6	101	109	106
	Rep 2	83.6	102	98.6	89.6	115	99.0	108
	Rep 3	87.2	91.9	95.0	95.9	93.3	108	125
Azinphos-methyl	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	103	85.2	123	77.4	114	105	103
	Rep 1	115	109	103	88.6	100	106	124
	Rep 2	103	102	94.0	95.5	112	103	101
	Rep 3	101	78.1	99.4	92.9	115	101	114
Azoxystrobin	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	85.7	102	95.3	91.7	102	87.5	105
	Rep 1	94.7	88.6	107	93.7	99.1	100	108
	Rep 2	89.4	97.1	104	96.4	105	88.5	98.0
	Rep 3	83.5	90.9	96.4	99.2	98.3	91.8	107
Bensulide	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	82.0	86.9	82.6	83.1	98.9	86.3	105
	Rep 1	94.3	80.1	94.3	95.2	101	110	102
	Rep 2	93.6	97.2	92.2	92.2	96.3	104	88.6
	Rep 3	92.0	88.3	90.4	102	95.0	100	99.6
Bromacil	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	87.9	85.0	85.2	92.9	93.1	84.7	103
	Rep 1	89.7	98.5	116	106	96.6	114	112
	Rep 2	91.7	104	105	102	109	107	101
	Rep 3	94.9	92.7	93.2	100	97.4	117	115
Carbaryl	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	93.0	99.6	97.2	97.8	105	92.1	111
	Rep 1	103	99.5	107	101	94.1	89.7	82.0
	Rep 2	106	104	103	96.0	96.9	84.4	80.5
	Rep 3	100	95.5	92.1	98.0	97.6	83.2	87.9

Compound	% Recovery							
	Sample	**Day 0**	**Day 2**	**Day 4**	**Day 8**	**Day 14**	**Day 21**	**Day 28**
Carbofuran	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	91.3	105	99.8	94.6	102	86.7	100
	Rep 1	97.5	97.6	106	94.0	100	103	99.0
	Rep 2	88.7	112	96.6	94.1	106	93.6	95.0
	Rep 3	95.2	102	97.9	94.9	97.6	105	95.2
Diazinon	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	92.2	93.0	97.8	97.4	103	93.2	101
	Rep 1	94.8	103	99.3	107	97.3	107	104
	Rep 2	94.6	109	104	106	106	98.2	98.6
	Rep 3	100	99.4	92.8	113	96.6	105	103
Dimethenamide	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	85.6	91.9	88.0	89.6	98.1	94.1	98.5
	Rep 1	83.8	90.1	96.6	88.6	97.3	107	105
	Rep 2	86.0	101	87.2	88.7	111	89.8	102
	Rep 3	87.8	90.9	85.9	93.6	99.4	100	112
Dimethoate	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	91.8	89.4	94.4	95.3	105	90.0	108
	Rep 1	92.6	93.4	104	108	97.4	111	116
	Rep 2	95.9	109	112	112	103	103	115
	Rep 3	97.0	94.3	106	107	101	107	123
Diuron	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	93.3	98.9	101	94.4	107	89.9	108
	Rep 1	99.5	97.1	116	102	104	113	114
	Rep 2	97.5	109	114	101	110	103	109
	Rep 3	99.0	97.2	104	103	104	111	111
Ethofumesate	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	81.2	82.3	85.7	83.8	99.2	80.2	97.2
	Rep 1	79.8	90.5	95.4	86.5	94.4	98.8	96.6
	Rep 2	85.7	94.1	86.6	86.8	104	88.8	95.2
	Rep 3	81.1	79.9	87.2	91.4	96.2	106	94.3
Fenamiphos	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	81.3	85.6	89.6	88.0	110	82.8	106
	Rep 1	85.0	102	106	97.6	90.7	104	112
	Rep 2	93.0	110	99.1	92.4	92.9	92.0	106
	Rep 3	87.1	104	94.2	97.4	86.2	95.7	122

Compound	% Recovery							
	Sample	**Day 0**	**Day 2**	**Day 4**	**Day 8**	**Day 14**	**Day 21**	**Day 28**
Fludioxonil NH4	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	88.3	77.9	85.7	87.8	116	92.8	107
	Rep 1	89.6	97.0	106	94.3	90.6	95.0	103
	Rep 2	91.8	106	108	93.8	97.3	88.9	97.7
	Rep 3	112	108	103	94.5	95.8	87.2	130
Imidacloprid	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	91.5	88.4	95.9	101	111	87.6	109
	Rep 1	93.1	96.3	95.9	103	96.8	115	119
	Rep 2	97.6	100	105	107	107	112	107
	Rep 3	96.5	91.4	97.8	106	105	112	123
Linuron	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	92.4	99.1	95.0	97.7	103	91.8	122
	Rep 1	101	98.6	110	107	104	115	112
	Rep 2	98.6	116	106	103	118	96.0	115
	Rep 3	99.8	96.2	99.1	108	99.3	108	113
Mefenoxam	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	94.1	95.1	105	101	115	89.8	106
	Rep 1	92.8	104	103	113	94.8	109	115
	Rep 2	97.1	110	101	115	104	102	113
	Rep 3	95.4	105	92.6	119	98.5	103	120
Methiocarb	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	90.3	92.2	95.0	95.5	99.6	84.8	104
	Rep 1	92.5	87.1	99.0	96.7	88.0	78.0	75.1
	Rep 2	98.4	101	91.6	97.7	91.5	74.6	74.4
	Rep 3	98.2	91.3	83.5	90.4	83.2	76.8	77.4
Metolachlor	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	85.1	97.5	86.8	88.9	99.1	90.0	95.0
	Rep 1	90.1	87.6	101	96.1	90.6	103	100
	Rep 2	89.4	93.9	95.8	90.1	99.3	94.1	113
	Rep 3	92.6	82.3	91.2	97.5	87.4	94.9	109
Metribuzin	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	83.2	85.4	85.4	83.3	80.3	77.1	99.5
	Rep 1	93.2	96.2	98.5	97.8	96.4	92.4	105
	Rep 2	91.7	113	97.0	96.9	110	82.6	99.0
	Rep 3	90.6	98.9	83.5	102	92.2	87.3	102

Compound	% Recovery							
	Sample	**Day 0**	**Day 2**	**Day 4**	**Day 8**	**Day 14**	**Day 21**	**Day 28**
Napropamide	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	93.5	99.6	94.0	97.3	99.6	90.5	107
	Rep 1	100	97.7	113	110	98.9	110	116
	Rep 2	98.5	106	110	104	106	97.4	114
	Rep 3	96.2	99.0	103	110	104	106	124
Norflurazon	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	90.1	103	93.2	92.9	103	91.3	109
	Rep 1	94.5	93.9	110	105	96.8	113	108
	Rep 2	94.9	102	110	103	108	106	98.9
	Rep 3	97.2	97.1	97.9	106	95.2	107	110
Oryzalin	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	112	70.7	117	114	116	79.7	121
	Rep 1	98.1	113	163	91.3	113	111	141
	Rep 2	81.5	115	134	114	125	117	93.1
	Rep 3	111	111	185	96.9	100	93.3	130
Prometon	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	88.4	100	93.6	94.9	109	91.6	109
	Rep 1	93.0	96.1	115	99.3	103	104	110
	Rep 2	95.2	108	110	101	109	102	104
	Rep 3	96.5	95.4	98.6	101	96.8	103	113
Simazine	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	93.1	100	98.0	91.2	97.8	87.2	108
	Rep 1	94.2	93.8	118	109	102	110	110
	Rep 2	98.5	108	107	104	116	101	111
	Rep 3	95.7	96.6	102	104	105	110	111
Tebuthiuron	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	87.3	103	96.3	84.7	102	100	108
	Rep 1	96.6	91.1	109	105	102	96.4	114
	Rep 2	94.9	99.3	102	102	120	93.4	118
	Rep 3	101	92.6	91.3	104	98.2	97.6	116
Thiamethoxam	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	81.9	85.5	84.3	81.1	95.1	74.3	94.3
	Rep 1	82.4	85.9	99.9	89.6	86.9	104	101
	Rep 2	84.7	97.0	93.8	90.3	95.8	92.3	97.7
	Rep 3	82.0	84.1	89.4	90.9	89.4	105	99.1

Compound	% Recovery							
	Sample	**Day 0**	**Day 2**	**Day 4**	**Day 8**	**Day 14**	**Day 21**	**Day 28**
Thiobencarb	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	84.5	91.1	85.1	87.2	95.5	88.9	105
	Rep 1	89.9	96.8	91.7	87.7	87.9	107	93.3
	Rep 2	86.6	103	95.5	91.4	95.8	97.8	98.6
	Rep 3	87.2	92.5	86.0	94.9	86.9	99.2	101
Uniconazole-p	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	82.7	88.8	79.5	79.2	88.2	80.3	97.2
	Rep 1	85.0	92.0	106	108	97.1	113	106
	Rep 2	84.4	94.3	97.8	101	110	92.5	103
	Rep 3	85.2	85.9	87.8	116	111	104	110
Methoxyfenozide	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	85.9	111	86.8	77.2	103	83.6	106
	Rep 1	92.4	106	98.4	112	94.4	104	98.9
	Rep 2	80.9	113	96.7	81.2	102	108	102
	Rep 3	75.6	104	92.5	104	101	105	120
Methomyl	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	80.3	85.4	90.3	84.7	93.4	77.0	97.4
	Rep 1	86.0	87.3	102	96.1	89.2	105	101
	Rep 2	87.7	97.3	99.6	99.7	101	99.2	99.8
	Rep 3	89.3	84.4	92.7	96.9	96.9	107	107
Chlorantraniliprole	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	82.0	98.8	90.3	91.8	116	88.4	95.4
	Rep 1	91.8	97.4	114	101	97.4	111	97.6
	Rep 2	104	111	111	100	116	93.4	98.5
	Rep 3	93.7	104	108	102	101	102	98.3
Isoxaben	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	87.8	96.8	109	95.5	98.2	89.1	109
	Rep 1	101	101	106	101	101	111	109
	Rep 2	98.7	104	103	104	121	102	98.9
	Rep 3	101	98.7	101	104	112	107	109
Propiconazole	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	75.1	80.3	79.0	77.7	80.2	73.0	85.5
	Rep 1	75.5	90.3	90.1	75.4	91.6	87.4	95.0
	Rep 2	77.3	95.3	91.2	88.1	92.7	81.6	92.0
	Rep 3	75.1	82.6	80.9	87.6	78.7	88.0	94.8

Compound	% Recovery							
	Sample	**Day 0**	**Day 2**	**Day 4**	**Day 8**	**Day 14**	**Day 21**	**Day 28**
Pyraclostrobin	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	84.4	90.9	87.1	88.3	95.3	84.8	103
	Rep 1	91.0	97.5	103	99.9	97.6	99.7	103
	Rep 2	91.4	102	104	95.6	108	92.8	96.5
	Rep 3	90.8	94.2	91.1	100	93.1	99.9	106
Cyprodinil	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	90.2	93.7	101	100	104	90.0	105
	Rep 1	96.9	101	106	110	101	105	110
	Rep 2	102	113	101	103	113	95.3	103
	Rep 3	102	99.8	96.8	115	105	105	112
Flutiafol	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	90.5	104	95.9	87.8	92.0	81.2	97.2
	Rep 1	92.9	88.5	119	107	93.9	99.8	107
	Rep 2	96.0	98.0	104	100	106	96.2	96.4
	Rep 3	94.0	90.7	101	104	99.1	96.8	98.3
Alachlor	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	83.7	89.3	90.1	88.0	98.8	87.8	100
	Rep 1	88.0	94.2	110	95.6	97.2	108	101
	Rep 2	89.3	105	101	94.5	106	101	97.0
	Rep 3	92.4	94.4	97.6	97.3	96.8	105	105
Bentazon	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	87.0	83.7	97.2	80.1	94.5	96.1	99.8
	Rep 1	93.6	105	93.4	111	117	85.9	88.3
	Rep 2	95.5	109	88.9	98.6	113	86.8	86.0
	Rep 3	100	106	92.6	106	120	88.9	87.0
3,4-Dichloroaniline	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	96.0	93.7	88.6	86.6	102	98.2	99.0
	Rep 1	96.8	111	100	101	104	113	99.6
	Rep 2	93.4	109	105	95.5	102	96.9	87.8
	Rep 3	93.6	101	93.7	105	98.5	98.8	101
3,5-Dichloroaniline	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	99.9	97.2	103	99.9	108	96.7	102
	Rep 1	103	101	113	111	99.4	104	113
	Rep 2	103	107	103	110	112	97.7	111
	Rep 3	108	102	97.2	112	103	97.7	130

Compound	% Recovery							
	Sample	**Day 0**	**Day 2**	**Day 4**	**Day 8**	**Day 14**	**Day 21**	**Day 28**
AIBA (2-amino-N-isopropyl benzamide)	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	67.5	65.3	77.8	49.8	102	60.6	80.6
	Rep 1	70.9	78.3	69.0	82.5	104	63.7	82.2
	Rep 2	77.1	96.6	76.0	90.7	102	64.7	76.1
	Rep 3	73.5	85.8	60.2	91.7	98.5	60.4	85.6
Flupyradifurone	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	89.7	87.7	103	89.2	108	94.9	102
	Rep 1	92.8	97.1	98.0	112	94.2	98.2	119
	Rep 2	93.8	111	100	110	101	96.9	106
	Rep 3	92.0	94.3	92.2	118	97.9	97.6	115
Myclobutanil	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	88.0	84.5	88.3	96.4	102	79.4	96.5
	Rep 1	85.2	81.8	90.5	101	91.0	83.8	97.5
	Rep 2	81.8	98.0	93.0	87.6	96.5	81.6	98.8
	Rep 3	90.1	91.0	82.1	101	87.3	82.2	104
Atrazine-d5 (Surrogate)	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	89.9	88.5	93.0	89.4	109	87.8	107
	Rep 1	78.7	95.3	94.1	93.4	94.1	101	110
	Rep 2	81.7	104	96.1	86.9	102	94.1	98.1
	Rep 3	82.7	89.0	85.0	98.6	93.1	97.4	114
Imidacloprid-d4 (Surrogate)	**Blank**	ND	ND	ND	ND	ND	ND	ND
	Spike	90.4	95.6	84.7	86.2	97.5	92.1	106
	Rep 1	92.9	92.6	112	107	104	109	108
	Rep 2	92.1	100	111	106	104	100	107
	Rep 3	93.6	90.0	95.4	108	98.8	101	109

Storage Stability Data for GC/MS/MS Compounds

Compound	% Recovery							
	Sample	Day 0	Day 2	Day 4	Day 8	Day 14	Day 21	Day 28
Clomazone	Blank	ND	ND	ND	ND	ND	ND	ND
	Spike	98.9	70.3	67.0	68.9	109	93.3	118
	Rep 1	79.3	73.2	69.9	69.3	70.1	65.0	113
	Rep 2	98.8	83.6	88.2	92.4	91.9	78.7	104
	Rep 3	109	88.5	69.9	72.4	82.9	67.8	102
Dichlobenil	Blank	ND	ND	ND	ND	ND	ND	ND
	Spike	92.1	68.4	75.0	75.9	101	95.0	117
	Rep 1	78.0	64.1	73.2	70.3	61.3	60.6	110
	Rep 2	86.2	80.6	104	93.3	84.0	78.7	102
	Rep 3	95.3	83.9	68.2	70.6	76.6	66.2	99.1
Dichloran	Blank	ND	ND	ND	ND	ND	ND	ND
	Spike	105	72.6	65.2	63.7	116	92.5	114
	Rep 1	82.4	74.2	71.5	67.8	68.5	67.8	110
	Rep 2	103	83.1	85.5	92.4	91.8	79.3	104
	Rep 3	111	90.4	73.9	72.3	82.7	68.1	102
Disulfoton	Blank	ND	ND	ND	ND	ND	ND	ND
	Spike	96.6	56.3	58.4	67.8	93.9	82.8	89.2
	Rep 1	76.5	70.4	69.8	69.6	68.1	59.9	112
	Rep 2	94.3	72.0	86.9	91.2	88.0	72.2	104
	Rep 3	106	85.6	72.0	73.9	78.8	61.4	99.9
Ethoprophos	Blank	ND	ND	ND	ND	ND	ND	ND
	Spike	94.6	71.5	70.8	75.2	95.2	90.8	111
	Rep 1	77.6	72.5	69.7	73.4	63.3	62.1	112
	Rep 2	90.5	83.1	93.8	91.9	86.0	78.7	102
	Rep 3	99.8	86.9	71.2	75.2	77.1	65.9	104
Fonofos	Blank	ND	ND	ND	ND	ND	ND	ND
	Spike	95.7	66.8	67.4	70.4	110	94.1	118
	Rep 1	77.0	70.5	70.0	69.0	71.0	64.8	115
	Rep 2	101	74.3	91.5	90.8	92.3	79.2	105
	Rep 3	111	87.1	70.1	70.7	84.2	68.5	104

Compound	% Recovery							
	Sample	Day 0	Day 2	Day 4	Day 8	Day 14	Day 21	Day 28
Malathion	Blank	ND	ND	ND	ND	ND	ND	ND
	Spike	104	70.1	60.6	59.3	112	107	134
	Rep 1	79.1	73.7	67.3	63.7	67.3	62.0	96.4
	Rep 2	104	76.6	78.7	76.9	84.7	69.8	88.3
	Rep 3	114	87.8	69.7	69.1	77.8	61.0	83.7
Parathion Ethyl	Blank	ND	ND	ND	ND	ND	ND	ND
	Spike	106	71.8	59.3	59.5	81.3	98.7	87.1
	Rep 1	83.0	75.6	69.3	68.0	57.9	71.6	119
	Rep 2	105	77.3	79.5	83.7	106	82.7	109
	Rep 3	116	88.8	73.8	74.1	84.0	56.0	109
Parathion Methyl	Blank	ND	ND	ND	ND	ND	ND	ND
	Spike	99.1	60.7	55.6	75.7	100	93.1	104
	Rep 1	76.4	70.8	66.7	86.2	66.4	68.4	112
	Rep 2	106	64.9	76.0	83.0	98.2	79.2	104
	Rep 3	113	83.8	80.9	60.4	81.5	63.6	103
Phorate	Blank	ND	ND	ND	ND	ND	ND	ND
	Spike	92.9	69.4	68.5	72.4	99.8	90.5	109
	Rep 1	76.2	69.2	67.2	66.8	59.2	53.4	89.8
	Rep 2	93.0	79.3	89.3	84.9	77.6	65.4	84.1
	Rep 3	106	84.4	66.3	66.5	71.1	55.0	82.1
Piperonyl Butoxide	Blank	ND	ND	ND	ND	ND	ND	ND
	Spike	104	87.6	61.8	53.6	151	108	138
	Rep 1	78.8	85.7	69.0	61.2	73.9	77.5	131
	Rep 2	103	80.2	71.6	90.7	96.3	81.4	119
	Rep 3	111	96.4	73.5	69.3	84.8	68.3	116
Prometryn	Blank	ND	ND	ND	ND	ND	ND	ND
	Spike	101	67.2	59.9	56.5	111	98.1	117
	Rep 1	77.3	72.8	70.9	86.3	68.8	63.5	131
	Rep 2	108	72.4	79.0	82.2	110	80.5	115
	Rep 3	113	89.4	78.7	92.8	91.0	62.2	118
Propanil	Blank	ND	ND	ND	ND	ND	ND	ND
	Spike	101	59.3	57.2	61.9	122	99.4	124
	Rep 1	71.6	69.7	76.7	66.9	71.8	76.1	121
	Rep 2	103	61.1	73.9	97.2	99.8	82.1	109
	Rep 3	117	82.1	89.2	75.4	87.8	70.2	107

Compound	% Recovery							
	Sample	**Day 0**	**Day 2**	**Day 4**	**Day 8**	**Day 14**	**Day 21**	**Day 28**
Triallate	Blank	ND	ND	ND	ND	ND	ND	ND
	Spike	96.6	70.7	67.0	70.3	109	93.7	118
	Rep 1	72.6	68.7	68.4	71.4	71.1	64.7	113
	Rep 2	93.7	82.7	85.7	82.6	90.1	78.4	104
	Rep 3	104	86.1	69.6	73.4	81.7	67.3	102
Benfluralin	Blank	ND	ND	ND	ND	ND	ND	ND
	Spike	95.5	74.2	69.2	76.3	97.0	89.1	98.5
	Rep 1	74.6	73.0	68.2	72.1	64.1	61.5	98.6
	Rep 2	85.6	81.6	94.6	89.5	80.9	76.9	96.1
	Rep 3	98.9	86.9	68.4	72.6	72.5	64.2	96.8
EPTC	Blank	ND	ND	ND	ND	ND	ND	ND
	Spike	71.8	56.6	58.6	55.1	61.9	63.5	68.0
	Rep 1	82.2	68.6	64.4	59.9	63.5	59.3	106
	Rep 2	91.7	86.5	95.4	75.9	85.9	74.4	98.4
	Rep 3	99.3	88.1	57.5	59.0	80.2	64.6	96.3

Approved By:

_____ _____

Bahar Nakhjavan Date

Senior Environmental Scientist, Supervisor

_____ _____

Jacob Oaxaca Date

Senior Environmental Scientist, Supervisor

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Maryam Khosravifard Date

Environmental Program Manager I

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Sarva Balachandra Date

Quality Assurance Officer

Date	What was revised? Why?
2/22/22	Reformatted the entire document in accordance with web accessibility requirements.
	Revised the title of method for consistency with the method outline.
	Made multiple editorial revisions throughout the document for improved readability.
	Updated procedures for standards preparation to reflect current practices.
	Added a title to the table of LC/MS/MS Instrument Conditions.
	Added a title to the table of GC/MS/MS Instrument Conditions.
	Revised Table 3 to include malathion, parathion ethyl, piperonyl butoxide, and prometryn.
	Reorganized the tables in Appendix I-IV to match the order of the compounds listed in Section 6.
3/23/2023	Revised Title to reflect new compounds added to the analysis.
	Changed wording: well water to groundwater and methanol to MeOH.
	Updated Section 4 because of an interference for 3,4-Dichloroaniline.
	Latest revision had both reagents and supplies/ standard preparation together. New revision has them divided into two sections.
	Updated Section 7 to reflect the new compounds and levels added to the analysis. Pesticide spelling correction.
	Updated Section 10 to reflect the current calibration range.
	Updated Table 2 to reflect the LC/MS/MS instrument conditions of the new compounds added to the analysis.
	Updated Table 3 to reflect the GC/MS/MS instrument conditions of the new compounds added to the analysis.
	Updated Section 12.1 to reflect the GC/MS/MS spike level of the compounds for the MDL study.
	Updated Section 15.1 to note that azoxystrobin acid, 4-hydroxy chlorothalonil, and chlorothalonil could not be added to the list of compounds and that 3,5-Dichloroaniline does not meet the criteria for relative abundance of the ion ratios.
	Updated Section 15.2 to include a storage stability discussion.
	Updated Appendix I to show the LC/MS/MS data from the new MDL study.
	Updated Appendix II to show the LC/MS/MS data from the new method validation study.
	Updated Appendix III to show the GC/MS/MS data from the new MDL study.
	Updated Appendix IV to show the GC/MS/MS data from the new method validation study.
	Updated Appendix V to show the LC/MS/MS and GC/MS/MS data from the storage stability study.