Determination of 44 pesticides in Well Water by Liquid Chromatography Coupled to Linear Ion Trap Quadrupole and Gas Chromatography Coupled to Triple Quadrupole Mass Spectrometer

1. Scope:

This section method (SM) provides stepwise procedure for 44 pesticides analysis in well water. It is followed by all authorized EA personnel.

2. Principle:

The pesticides are extracted from the well water sample with methylene chloride. The extract is passed through sodium sulfate to remove residual water. The anhydrous extract is evaporated to 2 mL on a nitrogen evaporator. One mL is removed for analysis by GC coupled to a triple quad mass spectrometer and the remaining 1 mL is solvent exchanged to methanol. Then 1 mL of LCMS water is added to the extract to bring final volume to 2 mL. The extract is then analyzed by Liquid Chromatography coupled to a Linear Ion Trap Quadrupole LC/MS/MS.

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

4. Interferences:

The background well water had ~0.05ppb of diazinon in it. This amount of diazinon in each blank sample was subtracted from the spike samples in each set.

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-vibrating mixer
5.5 HPLC coupled to a linear ion trap quadrupole mass spectrometer.
5.6 GC coupled to triple quadrupole mass spectrometer.

6. Reagents and Supplies:
LCMS standards

6.1	Atrazine	CAS# 1912-24-9
6.2	Azinphos-methyl	CAS# 86-50-0
6.3	Azoxystrobin	CAS# 131860-33-8
6.4	Bensulide	CAS# 741-58-2
6.5	Bromacil	CAS# 314-40-9
6.6	Carbaryl	CAS# 63-25-2
6.7	Carbofuran	CAS# 1563-66-2
6.8	Diazinon	CAS# 333-41-5
6.9	Dimethenamide	CAS# 87674-68-8
6.10	Dimethoate	CAS# 60-51-5
6.11	Diuron	CAS# 330-54-1
6.12	Ethofumesate	CAS# 26225-79-6
6.13	Fenamiphos	CAS# 22224-92-6
6.14	Fludioxonil	CAS# 131341-86-1
6.15	Imidacloprid	CAS# 138261-41-3
6.16	Linuron	CAS# 330-55-2
6.17	Mefenoxam	CAS# 70630-17-0
6.18	Methiocarb	CAS# 2032-65-7
6.19	Metolachlor	CAS# 51218-45-2
6.20	Metribuzin	CAS# 21087-64-9
6.21	Napropamide	CAS# 15299-99-7
6.22	Norflurazon	CAS# 27314-13-2
6.23	Oryzalin	CAS# 19044-88-3
6.24	Prometon	CAS# 1610-18-0
6.25	Simazine	CAS# 122-34-9
6.26	Tebuthiuron	CAS# 34014-18-1
6.27	Thiamethoxam	CAS# 153719-23-4
6.28	Thiobencarb	CAS# 28249-77-6
6.29	Uniconizole	CAS# 83657-17-4

GCMS standards

6.30	Alachlor	CAS# 15972-60-8
6.31	Clomazone	CAS# 81777-89-1
6.32	Dichloran	CAS# 99-30-9
6.33	Dichlorbenil	CAS# 1194-65-6
6.34	Disulfoton	CAS# 298-04-4
6.35	Ethoprophos	CAS# 13194-48-4
6.36	Ethyl Parathion	CAS# 56-38-2
6.37	Fonofos	CAS# 944-22-9
6.38	Malathion	CAS# 121-75-5
6.39	Methyl Parathion	CAS# 298-00-0
6.40	Phorate	CAS# 298-02-2
6.41	Piperonyl Butoxide	CAS# 51-03-6
6.42	Prometryn	CAS# 7287-19-6
6.43	Propanil	CAS# 709-98-8
6.44	Triallate	CAS# 2303-17-5

6.47 Methylene Chloride, nanograde or equivalent pesticide grade
6.48 Water, MS grade, Burdick & Jackson or equivalent
6.49 Methanol, MS grade, Burdick & Jackson or equivalent
6.50 Formic Acid, HPLC grade
6.51 Ammonium formate, reagent grade or equivalent
6.52 Separatory funnel, 1 L
6.53 Boiling flask, 500 mL
6.54 Sodium Sulfate, ACS grade
6.55 Funnels, long stem, 60°, 100 mm I.D.
6.56 Graduated conical tubes with glass stopper, 15 mL
6.57 Glass wool, Pyrex® fiber glass slivers 8 microns
6.58 Disposable Pasteur pipettes, and other laboratory ware as needed
6.59 Recommended UPLC analytical column:
Waters Acquity BEH C18 1.7 µm, 2.1 x 100 mm column or equivalent
6:60 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.
6.61 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.
6.62 Recommended GC analytical column
Restek Rxi-5Sil MS 30m X 0.025mmID, 0/025µm df

7. Standards Preparation:

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

LCMS standards
The standards were diluted to10 µg/mL with methanol. A combination standard of 10 µg/mL was prepared from the individual mg/mL standards in methanol. The combination standard was also used to dilute to the following concentrations: 0.0025, 0.005, 0.01, 0.025, 0.05, 0.1, 0.25, 0.5 and 1µg/mL in methanol.
These standards were then diluted in half with water to make the following concentrations: 0.00125, 0.0025, 0.005, 0.0125, 0. 025, 0.05, 0.125, 0.025, 0.05 ug/mL for instrument calibration. Some pesticides had data points excluded from the lowest or highest standards due to weak or strong ionization, respectively.

GCMS standards
The standards were diluted to10 µg/mL with acetone. A combination standard of 10 µg/mL was prepared from the individual mg/mL standards in acetone. The combination standard was also used to dilute to the following concentrations: 0.025, 0.05, 0.1, 0.25, 0.5µg/mL in acetone.

7.2 Keep all standards in the designated refrigerator for storage.

7.3 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. 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

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

9.2 Preparation of blank and spike

Matrix blank: Weigh out 1000 g of background water and follow the test sample extraction procedure.

Matrix spike: Weigh out 1000 g of background water. Spike a client requested amount of pesticide into the background water, mix well and let it stand for one minute. Follow the test sample extraction procedure.

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.

9.3.3 Shake with 100 ± 5 mL of methylene chloride for 1 minute. 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 inch 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.

9.3.9 Evaporate the sample extract to 2 mL in a water bath at 40 ± 2 °C under a gentle stream of nitrogen. Then transfer 1mL to an auto sampler vial for

GCMS analysis. The remaining mL is solvent exchange to methanol and brought to a final volume of 1.0 mL with methanol. Add 1.0 mL of water to the extract and mix well, final volume 2mL. Transfer the final extract into an auto sampler vial. Submit extract for LC-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. The current working standard levels range from 0.00125 to 0.5ng/µL for the LCMS. Some data points for the lowest and highest standards were excluded for a few pesticides due to weak or strong ionization, respectively. The current working standard levels range from 0.025 to 0.5ng/µL for GCMS.

10.2 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.

11. Analysis**:**

11.1 Injection Scheme

The LC-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, a matrix blank, a matrix spike, a set of up to 12 test samples, then a set of standards, etc.

11.2 Linear Ion Trap Quadrupole LC/MS/MS Mass Spectrometer

11.2.1 LC Instrument: Shimadzu LC30
Column: Waters Acquity BEH C18 1.7 µm, 2.1 x 100 mm column
Column Temperature: 40 °C
Mobile Phase: Gradient
Solvent 1: Aqueous Solution
Solvent 2: Organic Solution
Gradient:

Time(min)	Flow rate (mL/min)	Solvent 1	Solvent 2
0.50	0.4	95.0	5.0
2.00	0.4	40.0	60.0
8.50	0.4	5.0	95.0
12.00	0.4	5.0	95.0
12.10	0.4	95.0	5.0

Injection Volume: 3.0 µL

11.2.2 Mass Spectrometer and Operating Parameters

Model:	ABSciex QTRAP 6500
Ion ProbeType:	Electrospray Ionization (ESI)
Ion Mode:	Positive
Curtain Gas:	20.00
Ion Spray Voltage:	5500.0
Temp:	500.0
Ion Source Gas 1	50.0
Ion Source Gas 2	50.0
Collision Gas:	Medium
Electron Multiplier:	1700.0
Scheduled MRM:	yes
MRM Detection Window:	30 sec.
Target Scan Time:	0.50 sec.

Compound	RT	Percuror Ion	Product Ion	Declustering Potential	Collision Energy	Entrance Potential	Exit Potential
Atrazine	5.02	216	**174**	41	23	10	18
		216	96.0	41	31	10	10
Azinphos- methyl	5.13	132	**105**	20	25	10	8
		164	132	20	15	10	12
Azoxystrobin	5.59	404	**372**	50	19	10	12
		404	329	50	41	10	10
Bensulide	7.07	420	**240**	1	31	10	5
		397	218	1	21	10	5

Bromacil	4.45	263	**207**	26	19	10	18
		263	190	26	39	10	16
Carbaryl	4.46	202	**145**	66	15	10	14
		202	127	66	39	10	14
Carbofuran	4.45	222	**123**	41	29	10	0
		222	165	41	17	10	46
Diazinon	7.40	306	**170**	46	27	10	14
		306	154	46	27	10	14
Dimethenamide	5.81	276	**244**	36	19	10	10
		276	168	36	33	10	10
Dimethoate	3.71	230	**199**	16	13	10	18
		230	125	16	27	10	16
Diuron	5.21	235	**72**	46	21	10	10
		235	46.1	46	35	10	6
Ethofumesate NH4	5.68	287	**121**	1	20	10	10
		287	161	1	20	10	10
Fenamiphos	6.90	304	**217**	61	31	10	18
		304	202	61	45	10	16
Fludioxonil NH4	6.00	266	**229**	15	15	10	18
		266	158.1	15	47	10	10
Imidacloprid	3.55	256	**209**	30	21	10	26
		256	175	30	25	10	16
Linuron	5.72	249	**160**	26	23	10	16
		249	182	26	21	10	20
Mefenoxam	5.10	280	**220**	36	19	10	18
		280	192	36	25	10	16
Methiocarb	5.82	226	**169**	36	15	10	16
		226	121	36	25	10	12
Metolachlor	6.70	284	**252**	35	19	10	24
		284	176	35	35	10	16
Metribuzin	4.45	215	**187**	36	25	10	12
		215	84	36	31	10	10

Napropamide	6.59	272	**129**	34	23	10	14
		272	171	34	25	10	14
Norflurazon	5.21	304	**284**	106	31	10	26
		304	145	106	57	10	16
Oryzalin	6.75	347	**305**	31	19	10	10
		347	288	31	25	10	26
Prometon	5.10	226	**142**	56	31	10	16
		226	184	56	25	10	16
Simazine	4.40	202	**124**	61	25	10	6
		202	67.9	61	43	10	8
Tebuthiuron	4.53	229	**172**	41	23	10	16
		229	116	41	35	10	14
Thiamethoxam	3.28	292	**211**	16	19	10	20
		292	181	16	31	10	20
Thiobencarb	7.86	258	**125**	26	25	10	14
		258	89.0	26	63	10	14
Uniconazole-p	6.91	292	**70.0**	80	61	10	8
		294	70.0	80	55	10	8

Quantitation ion is in bold.

Quadrupole GC/MS/MS Mass Spectrometer

11.2.1 Bruker Scion GC QQQ
Column: Restek Rxi-5Sil 30 m 0.25mm, 0.25µm
Oven temperature ramp:

Initial 60°C		Hold 1 min.
50°C/min	to 180°C	Hold 0 min.
1°/min	to 195°C	Hold 0 min.
30°C.min	to 300°C	Hold 2 min.

Pesticide	Precursor Ion	Quant Ion / (C.E)	Qualifier Ion / C.E
Propanil	161	99 / (25)	90 / (20) , 126 / (20)
Dichloran	176	148 / (15)	85 / (40)
Fonofos	246	137 / (10)	109 / (20)
Malathion	173	99 / (15)	117 / (15), 127 / (10)
Piperonyl Butoxide	176	131 / (15)	117 / (20), 103 / (25)
Parathion Ethyl	291	109 / (15)	142 / (5)
Prometryn	241	58 / (10)	184 / (15)
Triallate	268	184 / (20)	226 / (15)
Ethoprophos	158	97 / (20)	81 / (20), 114 / (10)
Disulfoton	274	88 / (10)	60 / (15)
Phorate	260	75 / (10)	175 / (20), 231 / (5)
Clomazone	204	107 / (20)	78 / (30)
Alachlor	188	160 / (10)	130 / (40), 132 / (20)
Parathion Methyl	263	109 / (15)	79 / (25)
Dichlorbenil	171	100 / (25)	136 / (20)

C.E.= collision energy

12. Quality Control:

12.1 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 well water samples are spiked at 0.05ppb for LCMS analysis and 0.025ppb for GCMS 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 1.

12.2 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 0.05ppb for all compounds.

12.3 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.

12.4 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 $\pm$ 3 standard deviations of the percent recovery, shown in Appendix 2.

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 $\pm$ 2 percent of that of the standards.

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

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

13. 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.

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

14. Reporting Procedure**:**

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

15. Discussion and References**:**

15.1 Acephate, dinotefuran, oxdemeton-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.
The water sample needs to be acidified in order to extract chlorothalonil so this compound was removed from the screen list. 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.

References:

15.2 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 1

Pesticide Screen, MDL determination , LCMS -- AB Sciex QTRAP

Calculated without matrix match standards

Results (ppb): Ground Water

Spk\Analyte	Atrazine	Azinphos-methyl	Azoxystrobin	Bensulide	Bromacil	Carbaryl
blk	ND	ND	ND	ND	ND	ND
0.05ppb spk 1	0.0442	0.0435	0.0463	0.0432	0.045	0.0463
0.05ppb spk 2	0.0465	0.0464	0.0470	0.0424	0.0460	0.0434
0.05ppb spk 3	0.0439	0.0506	0.0459	0.0387	0.0446	0.0368
0.05ppb spk 4	0.0487	0.0425	0.0495	0.0536	0.0505	0.0633
0.05ppb spk 5	0.0578	0.0490	0.0559	0.0757	0.0545	0.0507
0.05ppb spk 6	0.0519	0.0508	0.0516	0.0567	0.0527	0.0495
0.05ppb spk 7	0.0488	0.0454	0.0496	0.0514	0.0489	0.0490
SD	0.00485	0.00333	0.00353	0.01247	0.00382	0.00809
MDL	0.01524	0.01048	0.01109	0.03918	0.01200	0.02543

Spk\Analyte	Carbofuran	Diazinon	Dimethenamide	Dimethoate	Diuron	Ethofumesate
blk						
0.05ppb spk 1	0.0435	0.0397	0.0416	0.0446	0.0470	0.0403
0.05ppb spk 2	0.0455	0.0441	0.0440	0.0455	0.0477	0.0515
0.05ppb spk 3	0.0423	0.0380	0.0410	0.0431	0.0468	0.0411
0.05ppb spk 4	0.0504	0.0456	0.0512	0.0494	0.0494	0.0467
0.05ppb spk 5	0.0561	0.0810	0.0561	0.0569	0.0568	0.0546
0.05ppb spk 6	0.0523	0.0376	0.0555	0.0519	0.0520	0.0404
0.05ppb spk 7	0.0496	0.0376	0.0533	0.0476	0.0494	0.0435
SD	0.00499	0.01567	0.00658	0.00478	0.00354	0.00572
MDL	0.01569	0.04925	0.02068	0.01502	0.01114	0.01799

Spk\Analyte	Fenamiphos	Fludioxonil	Imidacloprid	Linuron	Mefenoxam	Methiocarb
blk						
0.05ppb spk 1	0.0443	0.0421	0.0469	0.0420	0.0436	0.0435
0.05ppb spk 2	0.0447	0.0485	0.0464	0.0440	0.0450	0.0445
0.05ppb spk 3	0.0440	0.0451	0.0463	0.0419	0.0426	0.0416
0.05ppb spk 4	0.0507	0.0431	0.0519	0.0475	0.0523	0.0501
0.05ppb spk 5	0.0598	0.0516	0.0559	0.0536	0.0589	0.0531
0.05ppb spk 6	0.0520	0.0413	0.0516	0.0496	0.0554	0.0521
0.05ppb spk 7	0.0514	0.0467	0.0470	0.0468	0.0524	0.0441
SD	0.00574	0.00371	0.00374	0.00426	0.00633	0.00464
MDL	0.01804	0.01167	0.01176	0.01338	0.01988	0.01457

Spk\Analyte	Metolachlor	Metribuzin	Napropamide	Norflurazon	Oryzalin	Prometon
blk						
0.05ppb spk 1	0.0442	0.0443	0.0464	0.0460	0.0466	0.0491
0.05ppb spk 2	0.0462	0.0478	0.0471	0.0467	0.0464	0.0508
0.05ppb spk 3	0.0438	0.0435	0.0455	0.0452	0.0461	0.0486
0.05ppb spk 4	0.0495	0.0487	0.0497	0.0498	0.0528	0.0522
0.05ppb spk 5	0.0573	0.0539	0.0572	0.0552	0.0568	0.0608
0.05ppb spk 6	0.0549	0.0519	0.0521	0.0520	0.0522	0.0546
0.05ppb spk 7	0.0519	0.0484	0.0597	0.0489	0.0509	0.0520
SD	0.00528	0.00374	0.00553	0.00358	0.00406	0.00415
MDL	0.01658	0.01174	0.01739	0.01124	0.01277	0.01304

Spk\Analyte	Simazine	Tebuthiron	Thiamethoxam	Thiobencarb	Uniconizole
blk					
0.05ppb spk 1	0.0431	0.0463	0.0430	0.0430	0.0467
0.05ppb spk 2	0.0452	0.0478	0.0436	0.0448	0.0481
0.05ppb spk 3	0.0428	0.0453	0.0428	0.0414	0.0475
0.05ppb spk 4	0.0488	0.0507	0.0433	0.0494	0.0512
0.05ppb spk 5	0.0553	0.0580	0.0496	0.0569	0.0584
0.05ppb spk 6	0.0508	0.0540	0.0481	0.0515	0.0532
0.05ppb spk 7	0.0483	0.0507	0.0454	0.0493	0.0504
SD	0.00448	0.00448	0.00272	0.00538	0.00406
MDL	0.01408	0.01408	0.00856	0.01692	0.01276

Pesticide screen , MDL determination Bruker Scion GC/ QQQ

Results (ppb) Ground water

Spk/ Analyte	Propanil	Dichloran	Fonofos	Malathion
Blk	ND	ND	ND	ND
0.05ppb spk 1	0.0554	0.0454	0.0533	0.0588
0.05ppb spk 2	0.0638	0.0617	0.0608	0.0665
0.05ppb spk 3	0.0489	0.0448	0.0513	0.0485
0.05ppb spk 4	0.0442	0.0404	0.0466	0.0464
0.05ppb spk 5	0.0517	0.0509	0.0506	0.0475
0.05ppb spk 6	0.0478	0.0498	0.0505	0.0455
0.05ppb spk 7	0.0446	0.040	0.0451	0.0421
SD	0.0069	0.0075	0.0051	0.0087
MDL (3.14*SD)	0.0217	0.0235	0.0160	0.0272

Spk/ Analyte	Piperonyl Butoxide	Parathion	Prometryn	Triallate	Ethoprophos
Blk	ND	ND	ND	ND	ND
0.05ppb spk 1	0.0609	0.0508	0.0529	0.0488	0.0517
0.05ppb spk 2	0.061	0.0647	0.0691	0.0556	0.0606
0.05ppb spk 3	0.0482	0.0489	0.0551	0.0448	0.0494
0.05ppb spk 4	0.0449	0.0473	0.0492	0.0448	0.0456
0.05ppb spk 5	0.049	0.0498	0.0561	0.0513	0.0501
0.05ppb spk 6	0.0487	0.0547	0.056	0.0497	0.0497
0.05ppb spk 7	0.0426	0.0409	0.0508	0.0417	0.0424
SD	0.0073	0.0073	0.0065	0.0047	0.0057
MDL (3.14*SD)	0.0230	0.0230	0.0204	0.0147	0.0178

Spk/ Analyte	Disulfoton	Phorate	Clomazone	Alachlor	methyl parathion
Blk	ND	ND	ND	ND	ND
0.05ppb spk 1	0.0431	0.0558	0.0481	0.0529	0.0506
0.05ppb spk 2	0.0526	0.0621	0.056	0.0594	0.0614
0.05ppb spk 3	0.035	0.0523	0.0435	0.0476	0.0467
0.05ppb spk 4	0.0351	0.0473	0.0442	0.0448	0.0434
0.05ppb spk 5	0.0389	0.0538	0.0485	0.0498	0.051
0.05ppb spk 6	0.0435	0.0553	0.0502	0.0511	0.0502
0.05ppb spk 7	0.0342	0.0464	0.0394	0.0405	0.0414
SD	0.0066	0.0054	0.0054	0.0060	0.0065
MDL (3.14*SD)	0.0208	0.0168	0.0168	0.0190	0.0205

Spk/ Analyte	Dichlorbenil
Blk	ND
0.05ppb spk 1	0.0479
0.05ppb spk 2	0.0578
0.05ppb spk 3	0.0395
0.05ppb spk 4	0.0384
0.05ppb spk 5	0.0493
0.05ppb spk 6	0.0521
0.05ppb spk 7	0.0389
SD	0.00754
MDL (3.14*SD)	0.0237

Appendix 2

Result: % Recovery

		Spike Level					Control Limits	
Compound	Set#	0.05 ppb	0.1 ppb	0.25 ppb	0.5ppb	1.0 ppb		%
Atrazine	1	91.4	93.0	89.2	89.2	91.6		
	2	93.4	88.5	90.0	92.0	88.9	Mean:	94.1
	3	92.2	90.8	93.2	90.2	90.1	SD:	6.99
	4	110	97.3	118	91.4	94.8	UCL:	115
	5	98.6	96.6	87.2	100	95.1	LCL:	73.2
Azinphos- methyl	1	99.0	100	109	100.6	128		
	2	109	100	90.8	118	74.5	Mean:	101
	3	90.6	94.0	86.4	103	92.4	SD:	16.7
	4	130	92.6	85.2	121	112	UCL:	151
	5	70.4	137	86.8	94.6	111	LCL:	51.4
Azoxystrobin	1	101	99.7	98.8	95.4	113		
	2	99.0	94.3	99.6	97.4	108	Mean:	100
	3	93.4	92.1	92.0	90.4	87.0	SD:	8.57
	4	108	94.9	113	96.2	114	UCL:	126
	5	101	99.3	90.0	104	121	LCL:	74.4
Bensulide	1	89.0	99.5	94.8	86.2	95.6		
	2	97.8	96.8	94.0	123	103	Mean:	101
	3	80.6	75.5	108	98.4	79.2	SD:	26.5
	4	108	106	217	97.4	90.3	UCL:	181
	5	99.0	91.2	81.2	99.6	115	LCL:	21.4
Bromacil	1	98.6	96.8	91.6	92.6	90.7		
	2	97.6	93.3	95.2	90.8	90.1	Mean:	92.3
	3	92.2	85.0	88.8	82.2	90.2	SD:	5.71
	4	104	91.7	102	84.2	84.1	UCL:	109
	5	99.0	98.5	84.4	93.2	91.2	LCL:	75.2

Result: % Recovery

Compound	Set#	Spike Level 0.05 ppb	0.1 ppb	0.25 ppb	0.5ppb	1.0 ppb	Control Limits	%
Carbaryl	1	113	104	118	128	112		
	2	126	116	111	106	109	Mean:	104
	3	91.4	86.4	96.8	89.8	107	SD:	13.3
	4	101	98.8	136	92.2	105	UCL:	144
	5	98.6	91.8	93.2	88.6	92.0	LCL:	64.6
Carbofuran	1	99.6	99.7	93.2	93.2	96.6		
	2	102	96.6	96.0	94.2	94.8	Mean:	95.2
	3	90.2	87.5	89.6	87.6	87.4	SD:	6.51
	4	107	93.3	115	91.6	92.5	UCL:	115
	5	97.6	96.4	85.2	99.4	94.1	LCL:	75.7
Diazinon	1	87.4	90.2	86.0	88.2	92.7		
	2	93.4	86.2	87.6	92.6	90.2	Mean:	88.8
	3	84.2	87.8	88.8	88.2	88.5	SD:	9.05
	4	93.4	84.0	118	88.4	95.5	UCL:	116
	5	63.8	77.6	77.6	96.2	93.4	LCL:	61.6
Dimethenamide	1	98.6	99.0	89.6	88.8	92.0		
	2	101	93.8	90.8	91.6	88.5	Mean:	94.6
	3	86.4	84.5	85.6	85.2	92.2	SD:	7.88
	4	108	93.7	115	92.0	92.8	UCL:	118
	5	106	105	90.4	102	92.0	LCL:	71.0
Dimethoate	1	99.0	99.0	95.6	94.0	91.7		
	2	100	95.8	95.6	93.8	90.9	Mean:	94.5
	3	89.8	76.8	92.0	88.8	86.4	SD:	7.33
	4	109	96.4	114	92.2	92.5	UCL:	116
	5	96.4	94.9	84.8	100	92.0	LCL:	72.5
Diuron	1	99.2	96.9	93.2	93.2	95.9		
	2	101	92.9	95.2	93.8	95.6	Mean:	95.9
	3	95.4	92.5	96.4	93.2	89.4	SD:	6.34
	4	110	94.4	117	93.0	93.4	UCL:	115
	5	97.6	91.5	84.8	98.8	93.4	LCL:	76.9

		Spike Level					Control Limits	
Compound	Set#	0.05 ppb	0.1 ppb	0.25 ppb	0.5ppb	1.0 ppb		%
Ethofumesate	1	85.0	90.8	98.8	77.8	93.7		
	2	82.0	77.6	108	91.6	115	Mean:	89.4
	3	67.6	87.5	111	88.8	79.0	SD:	14.5
	4	126	70.0	76.8	85.6	88.3	UCL:	133
	5	93.6	94.0	72.8	74.2	99.5	LCL:	45.9
Fenamiphos	1	96.4	98.6	94.4	90.2	96.1		
	2	98.4	93.7	94.8	96.2	93.8	Mean:	95.6
	3	88.0	86.5	87.2	83.6	94.4	SD:	7.37
	4	111	99.5	117	90.0	92.8	UCL:	118
	5	104	101	88.8	97.2	96.1	LCL:	73.5
Fludioxonil	1	87.6	86.0	87.2	92.0	90.2		
	2	87.4	93.2	98.4	98.8	84.4	Mean:	92.4
	3	73.0	76.6	85.2	98.4	69.0	SD:	10.1
	4	108	100	98.8	94.6	88.9	UCL:	123
	5	104	98.2	106	103	102	LCL:	62.2
Imidacloprid	1	97.4	96.9	95.6	97.0	94.0		
	2	97.8	94.7	96.0	97.0	94.8	Mean:	94.3
	3	89.2	74.5	92.8	88.8	83.2	SD:	7.86
	4	109	99.0	115	93.4	89.4	UCL:	118
	5	95.6	96.7	82.8	96.6	89.7	LCL:	70.7
Linuron	1	97.0	95.7	93.2	93.6	94.2		
	2	98.6	92.6	94.8	97.0	92.0	Mean:	94.5
	3	86.8	85.3	91.6	91.2	91.7	SD:	6.150
	4	102	91.3	116	93.2	94.4	UCL:	113
	5	94.6	92.8	85.6	102	95.6	LCL:	76.1
Mefenoxam/Metalaxyl	1	99.6	106	98.0	95.2	90.7		
	2	105	100	96.0	96.4	90.3	Mean:	97.3
	3	89.4	86.4	87.6	86.8	98.6	SD:	7.55
	4	109	99.8	117	92.2	92.1	UCL:	120
	5	106	103	92.0	99	94.7	LCL:	74.6

Result: % Recovery

Compound	Set#	Spike Level 0.05 ppb	0.1 ppb	0.25 ppb	0.5ppb	1.0 ppb	Control Limits	%
Methiocarb	1	117	111	120	122	112		
	2	119	111	114	114	112	Mean:	104
	3	85.6	83.5	93.6	91.8	87.8	SD:	12.1
	4	113	101	116	104	103	UCL:	140
	5	87.4	93.8	89.6	100	97.5	LCL:	67.6
Metolachlor	1	100	100	94.4	95.0	132		
	2	102	97.1	94.0	98.8	126	Mean:	101
	3	90.8	89.9	90.0	91.6	111	SD:	11.0
	4	108	95.3	117	92.6	106	UCL:	134
	5	104	99.0	89.6	98.6	97.5	LCL:	68.0
Metribuzin	1	97.6	97.6	91.2	88.2	91.6		
	2	102	94.8	92.8	91.6	90.6	Mean:	93.3
	3	90.6	92.1	92.4	86.2	81.9	SD:	5.88
	4	104	91.4	108	88.2	89.1	UCL:	111
	5	98.8	96.2	86.0	97.6	93.3	LCL:	75.7
Napropamide	1	97.8	97.6	92.0	90.0	91.3		
	2	98.6	93.6	93.2	92.4	89.7	Mean:	96.3
	3	93.4	93.3	95.2	94.6	93.0	SD:	6.53
	4	109	97.6	119	93.6	97.6	UCL:	116
	5	99.0	96.9	87.2	103	99.3	LCL:	76.7
Norflurazon	1	101	101	95.2	94.2	95.4		
	2	102	96.1	96.0	95.0	94.4	Mean:	96.7
	3	91.4	90.5	94.8	94.2	90.8	SD:	5.81
	4	107	94.7	116	94.6	95.8	UCL:	114
	5	98.8	96.2	86.4	101	96.3	LCL:	79.3
Oryzalin	1	101	98.9	99.2	96.0	98.0		
	2	101	98.5	99.2	97.4	96.5	Mean:	96.5
	3	92.4	90.6	92.0	86.8	90.5	SD:	5.65
	4	108	93.9	110	91.2	94.1	UCL:	113
	5	100	96.9	86.0	97.2	95.6	LCL:	79.5

Result: % Recovery

Compound	Set#	Spike Level 0.05 ppb	0.1 ppb	0.25 ppb	0.5ppb	1.0 ppb	Control Limits	%
Prometon	1	102	100	95.2	93.6	97.8		
	2	102	96.8	97.2	96.4	95.0	Mean:	99.1
	3	100	98.8	97.6	91.6	98.1	SD:	6.46
	4	115	101	120	92.8	94.3	UCL:	118
	5	102	101	90.8	99.6	97.3	LCL:	79.7
Simazine	1	94.8	94.9	90.4	87.6	90.0		
	2	96.2	92.7	91.6	91.0	88.4	Mean:	93.2
	3	90.4	87.6	91.6	88.8	86.9	SD:	5.96
	4	105	93.5	114	91.4	92.7	UCL:	111
	5	96.0	95.0	86.8	100	92.5	LCL:	75.3
Tebuthiuron	1	98.2	98.4	95.2	95.6	117		
	2	99.0	94.8	97.2	96.4	110	Mean:	99.7
	3	95.2	91.1	89.6	91.6	79.0	SD:	10.0
	4	110	98.3	113	94.6	124	UCL:	130
	5	102	98.8	88.0	103	113	LCL:	69.7
Thiamethoxam	1	92.2	90.5	93.2	87.0	85.7		
	2	92.6	91.3	79.2	89.4	86.2	Mean:	86.4
	3	86.2	75.1	84.0	81.2	73.3	SD:	6.98
	4	97.8	88.6	102	80.8	75.0	UCL:	107
	5	91.4	88.9	80.8	85.0	82.8	LCL:	65.5
Thiobencarb	1	92.2	94.1	91.2	90.2	92.4		
	2	95.6	95.8	91.6	94.4	91.9	Mean:	94.4
	3	88.4	89.1	90.0	87.6	89.3	SD:	6.47
	4	108	95.1	116	90.6	96.0	UCL:	114
	5	98.4	97.8	87.2	100	96.6	LCL:	75.0
Uniconizole	1	102	103	96.0	95.8	95.7		
	2	101	96.8	97.2	99.0	94.7	Mean:	98.0
	3	94.8	95.1	96.8	92.0	88.1	SD:	6.21
	4	110	98.2	118	93.6	94.4	UCL:	117
	5	102	100	89.6	99.8	96.5	LCL:	79.4

GC/MS/MS compounds for 2014 Pesticide screen analysis

Result: % Recovery **Method Validation** **Blank: ND**

Compound	Set No.	0.025 ppb Spk	0.05 ppb Spk	0.10 ppb Spk	0.25ppb Spk	0.50 ppb Spk	Control Limits	
Propanil	1	97	120	87	97	131		
	2	113	95	83	95	101	**Mean:**	**103.7**
	3	85	86	98	98	96	**SD**	**15.176**
	4	124	126	121	130	126	**UCL**	**149.208**
	5	95	102	96	95	95	**LCL**	**58.1521**
Dichloran	1	108	113	83	101	125		
	2	96	97	77	94	99	**Mean:**	**99.76**
	3	83	71	94	97	95	**SD**	**16.159**
	4	116	131	120	127	120	**UCL**	**148.236**
	5	86	89	89	91	92	**LCL**	**51.2836**
Fonofos	1	105	121	85	101	111		
	2	109	99	89	90	84	**Mean:**	**97.56**
	3	73	64	85	92	98	**SD**	**16.386**
	4	124	122	116	121	115	**UCL**	**146.719**
	5	91	92	82	84	86	**LCL**	**48.4015**
Malathion	1	119	117	94	101	116		
	2	109	100	87	93	87	**Mean:**	**107**
	3	91	84	98	103	102	**SD**	**18.667**
	4	150	142	137	136	125	**UCL**	**162.721**
	5	96	91	94	102	94	**LCL**	**50.7188**
Piperonyl	1	114	155	97	105	135		
Butoxide	2	106	93	79	86	80	**Mean:**	**109.12**
	3	96	77	95	100	111	**SD**	**25.613**
	4	148	143	139	154	151	**UCL**	**185.959**
	5	95	89	87	96	97	**LCL**	**32.2809**

Parathion Ethyl	1	113	123	98	107	122		
	2	111	102	91	102	94	**Mean:**	**103**
	3	78	71	91	94	97	**SD**	**15.964**
	4	123	128	125	127	119	**UCL**	**150.891**
	5	94	88	89	96	92	**LCL**	**55.1095**
Prometryn	1	120	125	97	111	111		
	2	108	91	90	83	81	**Mean:**	**101.12**
	3	84	71	91	90	95	**SD**	**18.274**
	4	136	133	124	126	117	**UCL**	**155.942**
	5	88	89	86	89	92	**LCL**	**46.2977**
Triallate	1	99	108	82	99	103		
	2	105	95	82	86	79	**Mean:**	**96.9565**
	3	75	72	83	91	93	**SD**	**17.473**
	4	140	108	123	125	111	**UCL**	**149.376**
	5	108	80	83			**LCL**	**44.5366**
Ethoprophos	1	108	111	90	99	108		
	2	107	94	90	94	89	**Mean:**	**98.12**
	3	84	67	85	87	91	**SD**	**15.398**
	4	123	126	120	124	117	**UCL**	**144.315**
	5	93	87	83	87	89	**LCL**	**51.9249**
Disulfoton	1	86	106	77	92	100		
	2	78	75	60	66	74	**Mean:**	**89.4**
	3	75	60	92	93	88	**SD**	**18.244**
	4	112	115	118	126	115	**UCL**	**144.131**
	5	97	85	74	82	89	**LCL**	**34.6688**
Phorate	1	114	115	96	103	105		
	2	113	94	89	90	85	**Mean:**	**101.32**
	3	97	75	89	94	90	**SD**	**13.284**
	4	116	123	120	125	113	**UCL**	**141.173**
	5	107	103	98	91	88	**LCL**	**61.4666**
Clomazone	1	103	107	85	101	109		
	2	99	90	79	82	81	**Mean:**	**99.4**

	3	89	74	91	91	97	**SD**	**18.991**
	4	139	136	127	135	126	**UCL**	**156.374**
	5	93	87	86	88	90	**LCL**	**42.4263**
Alachor	1	103	105	88	100	111		
	2	109	93	85	85	83	**Mean:**	**97.4**
	3	78	68	89	90	98	**SD**	**14.172**
	4	119	119	114	122	116	**UCL**	**139.915**
	5	101	92	90	88	89	**LCL**	**54.8853**
Parathion Methyl	1	104	108	85	105	128		
	2	103	94	86	92	92	**Mean:**	**102.2**
	3	91	75	97	97	92	**SD**	**15.785**
	4	125	121	125	134	120	**UCL**	**149.555**
	5	115	87	98	92	89	**LCL**	**54.845**
Dichlobenil	1	96	100	74	101	108		
	2	93	75	76	73	82	**Mean:**	**91.6**
	3	84	62	76	82	87	**SD**	**18.978**
	4	123	126	113	132	120	**UCL**	**148.534**
	5	85	82	80	76	84	**LCL**	**34.6658**

Written By:

_____ _____
Jean Hsu Date
Staff Environmental Scientist

Written By:

_____ _____
Jane White Date
Staff Environmental Scientist

Approved By:

_____ _____
Stephen Siegel Date
Sr. Environmental Scientist

Approved By:

_____ _____
Elaine Wong Date
Environmental Program Manager I

Revision Log:

Date	What was revised? Why?