Determination of 47 pesticides in Surface Water by Liquid Chromatography Coupled to Linear Ion Trap Quadrupole

1. Scope:

This section method (SM) provides stepwise procedure for 47 pesticides analysis in surface water. It is followed by all authorized EA personnel.

2. Principle:

The pesticides are extracted from the surface water sample with methylene chloride. The extract is passed through sodium sulfate to remove residual water. The anhydrous extract is evaporated to 1 mL on a nitrogen evaporator, then solvent exchange to acetonitrile. Before being analyzed by Liquid Chromatography coupled to a Linear Ion Trap Quadrupole LC/MS/MS water is added to the extract to bring the final volume to 2 mL.

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:

There were no matrix interferences for the compounds at the time of method development.

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.

6. Reagents and Supplies:

6.1	Abamectin	CAS# 7151-41-2
6.2	Atrazine	CAS# 1912-24-9
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	Chlorantraniliprole	CAS# 500008-45-7
6.8	Chlorpyrifos	CAS# 2921-88-2
6.9	Cyprodinil	CAS# 121552-61-2
6.10	Diazinon	CAS# 333-41-5
6.11	Diflubenzuron	CAS# 35367-38-5
6.12	Dimethoate	CAS# 60-51-5
6.13	Diuron	CAS# 330-54-1
6.14	Ethoprop	CAS# 13194-48-4
6.15	Etofenprox	CAS# 80844-07-1
6.16	Hexazinone	CAS# 51235-04-2
6.17	Imidacloprid	CAS# 138261-41-3
6.18	Indoxacarb	CAS# 173584-44-6
6.19	Isoxaben	CAS# 82558-50-7
6.20	Kresoxim-methyl	CAS# 143390-89-0
6.21	Malathion	CAS# 121-75-5
6.22	Methidathion	CAS# 950-37-8
6.23	Methomyl	CAS# 16752-77-5
6.24	Methoxyfenozide	CAS# 161050-58-4
6.25	Metribuzin	CAS# 21087-64-9
6.26	Norflurazon	CAS# 27314-13-2
6.27	Oryzalin	CAS# 19044-88-3
6.28	Oxadiazon	CAS# 19666-30-9
6.29	Prometon	CAS# 1610-18-0
6.30	Prometryn	CAS# 7287-19-6
6.31	Propanil	CAS# 709-98-8
6.32	Propargite	CAS# 2312-35-8
6.33	Propiconazole	CAS# 60207-90-1
6.34	Pyraclostrobin	CAS# 175013-18-0
6.35	Pyriproxyfen	CAS# 95737-68-1

6.36	Quinoxyfen	CAS# 124495-18-7
6.37	Simazine	CAS# 175217-20-6
6.38	S-Metolachlor	CAS# 34014-18-1
6.39	Tebufenozide	CAS# 11240-23-8
6.40	Thiobencarb	CAS# 28249-77-6
6.41	Trifloxystrobin	CAS# 41517-21-7
6.42	Fipronil	CAS# 120068-37-3
6.43	Fipronil Amide	CAS# 205650-69-7
6.44	Fipronil Sulfide	CAS# 120067-83-6
6.45	Fipronil Sulfone	CAS# 120068-36-2
6.46	Desulfinyl Fipronil	CAS# 205650-65-3
6.47	Desulfinyl Fipronil Amide	CAS# 205650-69-7
6.48	Atrazine-d5 (surrogate)	CAS#
6.49	Imidacloprid-d4(surrogate)	CAS#

6.50 Methylene Chloride, nanograde or equivalent pesticide grade
6.51 Water, MS grade, Burdick & Jackson or equivalent
6.52 Methanol, MS grade, Burdick & Jackson or equivalent
6.53 Formic Acid, HPLC grade
6.54 Ammonium formate, reagent grade or equivalent
6.55 Separatory funnel, 1 L
6.56 Boiling flask, 500 mL
6.57 Sodium Sulfate, ACS grade
6.58 Funnels, long stem, 60°, 100 mm I.D.
6.59 Graduated conical tubes with glass stopper, 15 mL
6.60 Glass wool, Pyrex® fiber glass slivers 8 microns
6.61 Disposable Pasteur pipettes, and other laboratory ware as needed
6.62 Recommended UPLC analytical column:
Waters Acquity BEH C18 1.7 µm, 2.1 x 100 mm column or equivalent
6:63 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.
6.64 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.

7. Standards Preparation:

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

7.2 The standards were diluted to 10 µg/mL with acetonitrile. A combination standard of 10 µg/mL was prepared from the individual mg/mL standards in acetonitrile. The combination standard was also used to dilute to the following concentrations: 0.00125, 0.0025, 0.005, 0.0125, 0.025, 0.05, 0.125, 0.25, 0.5 and 1µg/mL in acetonitrile. These standards were then diluted in half with water right before use to make the following concentrations: 0.000625, 0.00125, 0.0025, 0.005, 0.0125, 0. 025, 0.05, 0.125, ug/mL for instrument calibration.

7.3 Keep all standards in the designated freezer for storage.

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

8. 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 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 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 to ~ 1 mL in a water bath at 40 ± 2 °C under a gentle stream of nitrogen. Then solvent exchange with acetonitrile and bring to final volume of 1 mL. 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 0.000625 to 0.125ng/µL.

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 3 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
13.0	0.4	5.0	95.0
13.0	0.4	95.0	5.0
17.0	0.4	95.0	5.0

Injection Volume: 3.0 µL

11.2.2 Mass Spectrometer and Operating Parameters

Model:	ABSciex QTRAP 6500
Experiment 1	
Ion ProbeType:	Electrospray Ionization (ESI)
Ion Mode:	Positive
Curtain Gas:	20.00
Ion Spray Voltage:	4500
Temp:	250
Ion Source Gas 1	50.0
Ion Source Gas 2	50.0
Collision Gas:	Medium
Electron Multiplier:	1500

Scheduled MRM: yes
MRM Detection Window: 60 sec.
Target Scan Time: 0.40 sec.

Compound	RT	Precursor Ion	Product Ion	Declustering Potential	Collision Energy	Entrance Potential	Exit Potential
Abamectrin	11.15	890	**305**	61	29	10	14
		890	567	61	17	10	26
Atrazine	4.95	216	**174**	61	25	10	24
		216	104	61	37	10	12
Azoxystrobin	5.51	404	**372**	41	19	10	18
		404	344	41	33	10	16
Bensulide	6.99	398	**314**	31	15	10	14
		398	159	31	31	10	22
Bromacil	4.34	263	**207**	26	17	10	26
		263	190	26	37	10	20
Carbaryl	4.54	202	**145**	31	13	10	18
		202	127	31	37	10	16
Chlorantraniliprole	5.25	484	**286**	51	17	10	14
		484	453	51	21	10	20
Chlorpyrifos	9.30	352	**200**	41	25	10	26
		352	96.8	41	45	10	16
Cyprodinil	6.86	226	**93.0**	81	41	10	12
		226	108	81	35	10	14
Diazinon	7.37	305	**169**	66	29	10	22
		305	153	66	27	10	20
Diflubenzuron	6.83	311	**158**	41	17	10	20
		311	141	41	41	10	18
Dimethoate	3.66	230	**199**	21	13	10	26
		230	125	21	27	10	16
Diuron	5.05	235	**72**	46	21	10	10
		235	46	46	35	10	6

Compound	RT	Percuror Ion	Product Ion	Declustering Potential	Collision Energy	Entrance Potential	Exit Potential
Ethoprop	6.50	243	**173**	61	19	10	22
		243	131	61	27	10	18
Etofenprox	11.6	394	**177**	41	19	10	24
		394	359	41	15	10	18
Hexazinone	4.38	253	**171**	41	21	10	22
		253	71	41	39	10	12
Imidacloprid	3.47	256	**208**	30	21	10	26
		256	175	30	25	10	16
Indoxacarb	8.27	528	**150**	76	27	10	20
		528	203	76	49	10	24
Isoxaben	5.92	333	**165**	41	23	10	22
		333	107	41	79	10	16
Kresoxim-methyl	7.06	331	**314**	24	7	10	14
		331	206	24	13	10	28
Malathion	5.92	331	**127**	31	17	10	16
		331	284	31	11	10	14
Methidathion	5.17	320	**303**	6	9	10	14
		320	145	6	17	10	18
Methomyl	3.11	163	**87.8**	11	13	10	14
		163	106	11	13	10	16
Methoxyfenozide	5.98	369	**149**	36	21	10	20
		369	313	36	11	10	14
Metribuzin	4.33	215	**187**	36	25	10	12
		215	84	36	31	10	10
Norflurazon	5.06	304	**284**	106	31	10	26
		304	145	106	57	10	16
Oryzalin	6.68	347	**305**	41	19	10	14
		347	**198**	41	37	10	26
Oxadiazon	9.08	347	**305**	91	17	10	14
		347	222	91	27	10	28
Prometon	5.10	226	**142**	56	31	10	16
		226	184	56	25	10	16

Compound	RT	Percuror Ion	Product Ion	Declustering Potential	Collision Energy	Entrance Potential	Exit Potential
Prometryn	6.22	242	**158**	1.0	31	10	20
		242	200	1.0	25	10	24
Propanil	5.66	220	**164**	56	21	10	18
		220	127	56	33	10	16
Propargite	9.72	368	**231**	21	13	10	12
		368	175	21	21	10	24
Propiconazole	7.43	344	**161**	56	31	10	20
		344	69	56	23	10	12
Pyraclostrobin	7.58	388	**194**	36	17	10	26
		388	163	36	31	10	22
Pyriproxyfen	9.13	322	**96**	46	19	10	16
		322	185	46	29	10	24
Quinoxyfen	9.26	310	**199**	121	43	10	26
		310	216	121	47	10	28
Simazine	4.35	202	**124**	61	25	10	16
		202	104	61	33	10	16
S-Metolachlor	6.64	284	**252**	41	19	10	12
		284	176	41	35	10	22
Tebufenozide	6.90	353	**133**	26	23	10	18
		353	297	26	11	10	14
Thiobencarb	7.81	258	**125**	41	23	10	16
		258	89	41	65	10	14
Trifloxystrobin	8.27	409	**186**	41	23	10	24
		409	145	41	57	10	20
Atrazine-d5(surrogate)	4.87	221	**179**	61	25	10	24
		221	101	61	31	10	16
Imidacloprid-d4(surrogate)	3.50	260	**213**	56	21	10	26
		260	179	56	23	10	22

Quantitation ion is in bold.

Experiment 2

Ion ProbeType:	Electrospray Ionization (ESI)
Ion Mode:	Negative
Curtain Gas:	20.00
Ion Spray Voltage:	-4500
Temp:	250
Ion Source Gas 1	50.0
Ion Source Gas 2	50.0
Collision Gas:	Medium
Electron Multiplier:	1500
Scheduled MRM:	yes
MRM Detection Window:	60 sec.
Target Scan Time:	0.40 sec.

Compound	RT	Precursor Ion	Product Ion	Declustering Potential	Collision Energy	Entrance Potential	Exit Potential
Fipronil	6.98	437	**330**	-45	-22	-10	-19
		437	332	-45	-22	-10	-27
Fipronil Amide	5.15	453	**348**	-25	-20	-10	-19
		453	304	-25	-32	-10	-17
Fipronil Sulifide	7.19	419	**383**	-20	-18	-10	-23
		419	262	-20	-38	-10	-15
Fipronil Sulfone	7.52	451	**415**	-40	-22	-10	-25
		451	282	-40	-36	-10	-15
Desulfinyl Fipronil	6.76	389	**353**	-30	-18	-10	-21
		389	282	-30	-44	-10	-17
Desulfinyl Fipronil Amide	4.58	407	**371**	-20	-12	-10	-23
		407	369	-20	-14	-10	-25

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 surface water samples are spiked at 0.01ppb and processed through the entire method along with a blank. The standard deviation derived from the spiked sample recoveries was used to calculate the MDL using the following equation:

MDL = tS

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

The results for the standard deviations and MDL are in Appendix 1.

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 0.02ppb for all compounds except Fipronil and metabolites which is 0.01 ppb and Pyriproxyfen which is 0.15 ppb.

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 ± 0.1 minute of that of the standards.

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

12.5.4 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.

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

14. Reporting Procedure**:**

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

15. Discussion and References**:**

15.1 The Department of Pesticide Regulations request a list of pesticides to be analyzed in surface water. These pesticides were determined by LCMS or GCMS. During method development, pesticides determined by LCMS were extracted using liquid/ liquid extraction and solid phase extraction (HLB cartridge). The Liquid/liquid extraction was selected as the extraction method

because more compounds were recovered using this extraction method. There was also some concern about the amount of sediment that might be present in the samples. The samples would have to be filtered before solid phase extraction could be used and the filter analyzed.

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

15.3 No substantial matrix suppression occurred during the method validation process using the background surface water provided by DPR. But matrix suppression was detected in the samples when the surrogate recoveries were low. All samples were diluted 1 to 5 with acetonitrile/water (1:1) to help reduce the matrix suppression. Originally a dilution of 1 to10 was used but it was determined that a dilution of 1 to 5 was sufficient.

15.4 Initially, carbaryl results were inconsistent during validation. It was found later that carbayl in acetonitrile/water solution seems to be more sensitive to the type of glass use in the autosampler vials. Upon changing to certified auto sampler vials the carbaryl results were consistent and validation was easily repeated.

References

16.1 Hsu, J. and Hernandez J. *Determination of Organophosphate Pesticides in Surface Water using Gas Chromatography*, 1997, Environmental Monitoring Method, Center for Analytical Chemistry, CDFA.

16.2 Hladik, Michelle L., Smalling, Kelly L., Kuivila, Kathryn M., “A Multi-residue Method for the Analysis of Pesticides and Pesticides Degradates in Water Using HLB Solid-phase Extraction and Gas Chromatography-Ion Trap Mass Spectrometry”, Bull Environ Contam Toxicol (2008) 80:139-144

16.3 “Crop Protection Handbook, 2010”, MeisterPro Executive Office 27722 Euclid Ave., Willoughby, OH

Appendix 1

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

MDL -Pesticide Screen in Surface Water 0.01ppb spike + 0.01ppb Atrazine d-5 and Imidacloprid d-4 surrogates

Compound Name	Spk 1	Spk 2	Spk 3	Spk 4	Spk 5	Spk 6	Spk 7	SD	MDL
Abamectin	0.00857	0.00905	0.00883	0.00818	0.00898	0.00890	0.00828	0.000345	0.00108
Atrazine	0.00817	0.00858	0.00901	0.00810	0.00893	0.00869	0.00818	0.000377	0.00119
Azoxystrobin	0.00935	0.00970	0.0101	0.00939	0.00991	0.00988	0.00900	0.000383	0.00120
Bensulide	0.00928	0.00984	0.00954	0.00964	0.00971	0.00961	0.00928	0.000210	0.00066
Bromacil	0.00808	0.00839	0.00831	0.00812	0.00790	0.00860	0.00767	0.000311	0.000977
Carbaryl	0.00881	0.00894	0.00959	0.00878	0.00935	0.00919	0.00870	0.000333	0.00105
Chlorantraniliprole	0.00920	0.0105	0.0103	0.00975	0.00968	0.00957	0.00878	0.000580	0.00182
Chlorpyrifos	0.00968	0.00981	0.0104	0.00923	0.00953	0.00946	0.00927	0.000391	0.00123
Cyprodinil	0.00998	0.00941	0.00967	0.00937	0.00949	0.0101	0.00966	0.000286	0.000900
Diazinon	0.00957	0.00973	0.00998	0.00944	0.00983	0.00973	0.00918	0.000267	0.000840
Diflubenzuron	0.00840	0.00829	0.00867	0.00841	0.00873	0.00841	0.00820	0.000192	0.000603
Dimethoate	0.00868	0.00895	0.00913	0.00855	0.00877	0.00882	0.00837	0.000251	0.000788
Diuron	0.00884	0.00895	0.00947	0.00880	0.00946	0.00973	0.00897	0.000368	0.00116
Ethoprop	0.00914	0.00952	0.00989	0.00891	0.00951	0.00923	0.00879	0.000382	0.00120
Etofenprox	0.00919	0.00885	0.00864	0.00781	0.00859	0.00797	0.00762	0.000586	0.00184
Hexazinone	0.00938	0.00967	0.00996	0.00942	0.00964	0.00971	0.00893	0.000328	0.00103
Imidacloprid	0.00745	0.00802	0.00824	0.00780	0.00757	0.00858	0.00747	0.000428	0.00135
Indoxacarb	0.00627	0.00652	0.00628	0.00647	0.00666	0.00646	0.00602	0.000211	0.00066
Isoxaben	0.00912	0.0101	0.00922	0.00916	0.00963	0.0102	0.00924	0.000444	0.00140
Kresoxim-methyl	0.01005	0.0100	0.0101	0.00929	0.00973	0.00914	0.00945	0.000386	0.00121
Malathion	0.00995	0.0104	0.0103	0.00978	0.0101	0.0102	0.00945	0.000328	0.00103
Methidathion	0.00964	0.0105	0.0107	0.00997	0.00989	0.0102	0.00958	0.000429	0.00135
Methomyl	0.00858	0.00879	0.00868	0.00844	0.00871	0.00933	0.00850	0.000295	0.00093
Methoxyfenozide	0.00962	0.00981	0.00995	0.00894	0.00926	0.00984	0.00964	0.000359	0.00113
Metribuzin	0.00808	0.00807	0.00860	0.00791	0.00830	0.00810	0.00875	0.000309	0.000970
Norflurazon	0.00929	0.00952	0.00961	0.00936	0.00954	0.00984	0.00879	0.000330	0.00104
Oryzalin	0.0108	0.0105	0.0101	0.00844	0.00817	0.0107	0.0105	0.001113	0.00350
Oxadiazon	0.00904	0.00919	0.00969	0.00915	0.00923	0.00933	0.00902	0.000227	0.00071
Prometon	0.00934	0.00954	0.00985	0.00941	0.00957	0.00980	0.00910	0.000262	0.000823

Prometryn	0.00953	0.0101	0.0103	0.00936	0.0101	0.00992	0.00932	0.000401	0.001260
Propanil	0.00903	0.00898	0.00975	0.00840	0.00895	0.00903	0.00869	0.000414	0.00130

Compound Name	Spk 1	Spk 2	Spk 3	Spk 4	Spk 5	Spk 6	Spk 7	SD	MDL
Propargite	0.00948	0.00953	0.00967	0.00913	0.00926	0.00934	0.00903	0.000228	0.000717
Propiconazole	0.00847	0.00945	0.00925	0.00969	0.00893	0.00975	0.00902	0.000453	0.00142
Pyraclostrobin	0.00928	0.00921	0.00959	0.00913	0.00930	0.00953	0.00926	0.000170	0.000535
Pyriproxyfen	0.00964	0.0100	0.0104	0.00945	0.00966	0.00995	0.00939	0.000361	0.00114
Quinoxyfen	0.00963	0.00995	0.0101	0.00938	0.00996	0.00985	0.00942	0.000274	0.000861
Simazine	0.00869	0.00874	0.00939	0.00862	0.00897	0.00874	0.00851	0.000291	0.000916
S-Metolachlor	0.0101	0.0103	0.0111	0.00974	0.0102	0.0105	0.00993	0.000427	0.00134
Tebufenozide	0.00931	0.00922	0.00946	0.00901	0.00909	0.00926	0.00883	0.000210	0.000661
Trifloxystrobin 1	0.00859	0.00883	0.00895	0.00866	0.00913	0.00873	0.00839	0.000244	0.000766
Thiobencarb 1	0.00913	0.00935	0.00957	0.00869	0.00916	0.00925	0.00908	0.000269	0.000846
Atrazine-d5 1 *	0.00810	0.00820	0.00844	0.00806	0.00863	0.00844	0.00825	0.000207	0.000652
Imidacloprid-d4 1 *	0.00792	0.00779	0.00823	0.00807	0.00821	0.00783	0.00767	0.000216	0.000678
Fipronil 1	0.0103	0.0106	0.0105	0.0102	0.0110	0.0107	0.0102	0.000275	0.000864
Fipronil Amide 1	0.00990	0.0111	0.0110	0.0105	0.0111	0.0109	0.0101	0.000500	0.00157
Fipronil Sulfide 1	0.0101	0.0100	0.0106	0.0098	0.0098	0.0105	0.0097	0.000354	0.00111
Fipronil Sulfone 1	0.0100	0.0100	0.0102	0.0098	0.0102	0.0102	0.0096	0.000233	0.000732
Desulfinyl Fipronil 1	0.0102	0.0103	0.0108	0.0098	0.0101	0.0103	0.0098	0.000351	0.00110
Desulfinyl Fipronil Amide 1	0.0120	0.0113	0.0129	0.0108	0.0118	0.0118	0.0106	0.000777	0.00244

* compounds were calculated with a single pt

Appendix 2

LC/MS/MS compounds for Pesticide screen analysis in surface water

Result: % Recovery

		Spike Level					Control Limits	
Compound	Set#	0.01 ppb	0.05 ppb	0.1 ppb	0.5ppb	1.0 ppb		%
Abamectin	1	89.3	87.2	89.2	91.6	91.4		
	2	65.7	64.9	62.9	86.0	89.5	Mean:	77.8
	3	64.7	63.8	60.6	84.4	83.7	SD:	13.3
	4	62.7	72.2	66.1	91.2	96.8	UCL:	118
	5	67.9	61.5	64.1	92.4	95.4	LCL:	38.1
Atrazine	1	81.8	81.2	81.5	99.7	91.7		
	2	70.91	70.2	68.6	88.7	90.5	Mean:	83.2
	3	71.7	62.7	66.9	90.6	85.7	SD:	11.4
	4	80.5	85.2	79.7	99.0	101	UCL:	117
	5	82.3	74.5	75.1	99.4	99.6	LCL:	49.0
Azoxystrobin	1	91.4	90.0	85.7	98.2	90.7		
	2	69.7	71.0	65.7	95.7	97.4	Mean:	84.9
	3	69.2	65.2	62.9	90.4	84.8	SD:	13.9
	4	82.5	90.2	77.0	109	106	UCL:	127
	5	78.5	73.3	71.5	101	106	LCL:	43.1
Bensulide	1	100	93.9	88.1	93.7	92.2		
	2	84.7	83.9	88.5	91.6	89.9	Mean:	90.0
	3	85.4	83.7	79.7	93.2	86.1	SD:	5.7
	4	94.9	93.7	88.2	102	96.5	UCL:	107
	5	87.2	81.7	84.0	95.0	91.3	LCL:	72.9
Bromacil	1	86.6	85.2	81.1	96.0	89.2		
	2	78.2	80.0	79.3	89.5	87.2	Mean:	86.3
	3	82.5	84.9	78.5	87.3	78.9	SD:	6.07
	4	91.3	86.7	83.4	95.6	96.0	UCL:	105
	5	81.3	83.6	83.2	96.9	95.7	LCL:	68.1
Carbaryl	1	116	91.6	105	103	90.3		
	2	110	100	92.3	104	99.3	Mean:	101
	3	110	99.2	106	97.4	114	SD:	7.9
	4	107	103	111	91.6	95.3	UCL:	124
	5	96	97	93	91.0	90.4	LCL:	76.9

		Spike Level					Control Limits	
Compound	Set#	0.01 ppb	0.05ppb	0.1 ppb	0.5ppb	1.0 ppb		%
Chlorantraniliprole	1	102	97.1	92.7	102	99.3		
	2	101	98.4	98.0	101	96.1	Mean:	101
	3	104	96.9	93.9	94.3	91.1	SD:	5.74
	4	107	104	105	106	109	UCL:	119
	5	116	104	106	107	106	LCL:	84.2
Chlorpyrifos	1	95.7	86.3	90.5	99.7	95.8		
	2	88.3	82.5	91.1	89.3	92.9	Mean:	93.4
	3	98.5	91.9	91.8	90.9	88.6	SD:	4.72
	4	97.5	91.7	95.4	97.9	97.4	UCL:	108
	5	95.0	89.5	95.0	101	101	LCL:	79.2
Cyprodinil	1	99.0	92.8	95.5	97.3	93.6		
	2	89.4	86.3	85.8	93.5	96.5	Mean:	92.1
	3	88.7	82.7	81.9	90.8	86.1	SD:	5.57
	4	90.8	96.8	91.6	100	99.5	UCL:	109
	5	90.5	87.1	86.7	101	98.3	LCL:	75.4
Diazinon	1	96.0	92.3	93.4	94.4	90.5		
	2	90.4	83.0	91.0	83.9	87.4	Mean:	92.6
	3	93.7	97.3	89.6	88.9	86.2	SD:	4.36
	4	97.7	99.5	96.5	95.9	95.5	UCL:	106
	5	94.7	94.7	92.5	91.3	97.9	LCL:	79.5
Diflubenzuron	1	89.4	85.9	79.9	96.6	89.5		
	2	79.4	75.3	71.4	92.7	96.5	Mean:	83.9
	3	75.4	72.2	68.9	86.9	81.2	SD:	8.85
	4	81.2	85.4	75.7	92.1	90.9	UCL:	110
	5	78.1	75.6	81.7	98.0	97.9	LCL:	57.4
Dimethoate	1	81.1	82.3	88.5	93.3	88.9		
	2	84.1	84.2	88.8	88.3	92.8	Mean:	89.6
	3	85.4	90.3	85.6	89.0	85.1	SD:	4.67
	4	90.6	91.4	91.8	99.5	98.6	UCL:	104
	5	93.9	92.8	89.7	88.6	95.8	LCL:	75.6
Diuron	1	93.1	91.0	92.8	99.4	92.8		
	2	83.0	86.8	89.7	94.3	92.3	Mean:	91.5
	3	90.4	92.5	86.7	89.4	80.8	SD:	5.02
	4	89.1	92.2	90.0	97.9	98.8	UCL:	107
	5	84.6	88.7	94.3	97.0	101	LCL:	76.5

		Spike Level					Control Limits	
Compound	Set#	0.01 ppb	0.05ppb	0.1 ppb	0.5ppb	1.0 ppb		%
Ethoprop	1	88.1	89.2	92.0	85.3	89.1		
	2	84.7	79.9	85.4	84.3	85.1	Mean:	87.7
	3	91.8	88.0	89.6	86.7	81.4	SD:	3.56
	4	86.2	95.8	88.3	91.6	88.6	UCL:	98.4
	5	89.7	86.36	84.3	90.04	91.51	LCL:	77.0
Etofenprox	1	97.5	84.6	78.4	89.9	87.4		
	2	84.7	81.6	80.3	87.4	89	Mean:	87.8
	3	87.7	83.3	79.1	86.3	81.5	SD:	5.97
	4	90.9	92.2	86.3	97.9	95.0	UCL:	106
	5	90.0	87.4	81.9	97.8	97.1	LCL:	69.9
Hexazinone	1	98.2	91.4	94.4	101	92.9		
	2	85.3	88.2	93.5	91.8	93.1	Mean:	93.5
	3	92.3	94.8	86.5	91.4	83.4	SD:	4.54
	4	93.6	91.4	91.1	99.9	100	UCL:	107
	5	95.0	96.8	96.2	96.5	99.4	LCL:	79.9
Imidacloprid	1	80.0	73.7	80.9	95.1	90.5		
	2	90.4	84.8	81.1	91.1	92.1	Mean:	86.0
	3	97.2	89.8	82.8	89.8	82.8	SD:	7.46
	4	75.4	77.4	77.8	93.2	93.5	UCL:	108
	5	76.9	80.3	81.2	96.7	97.0	LCL:	63.7
Indoxacarb	1	63.7	61.9	59.3	87.3	86.6		
	2	58.6	58.8	60.9	79.1	86.9	Mean:	75.9
	3	69.4	64.6	63.7	79.8	80.2	SD:	12.1
	4	71.3	75.3	76.9	90.7	100	UCL:	112
	5	78.7	80.4	85.2	86.9	92.4	LCL:	39.7
Isoxaben	1	96.5	95.0	95.9	100.1	97.7		
	2	93.5	90.0	91.6	89.9	95.5	Mean:	96.3
	3	95.6	100	90.4	92.6	86.2	SD:	4.59
	4	98.5	94.2	102	99.3	104	UCL:	110
	5	99.3	104	94.9	99.3	100	LCL:	82.5
Kresoxim-methyl	1	98.1	97.4	95.3	96.2	95.1		
	2	96.8	94.3	97.4	93.2	90.4	Mean:	98.0
	3	101	104	104	93.7	90.4	SD:	4.36
	4	110	101	99.9	99.8	101	UCL:	111
	5	99.7	98.9	101	96.4	96.6	LCL:	85.0

		Spike Level					Control Limits	
Compound	Set#	0.01 ppb	0.05 ppb	0.1 ppb	0.5ppb	1.0 ppb		%
Malathion	1	97.6	93.5	96.3	103.2	92.3		
	2	92.0	90.6	93.4	92.9	90.5	Mean:	96.0
	3	95.5	101	95.3	92.4	88.9	SD:	3.97
	4	98.5	96.9	99.3	103	96.0	UCL:	108
	5	96.3	101	99.6	94.1	99.5	LCL:	84.1
Methidation	1	99.3	97.4	96.7	98.3	93.3		
	2	92.5	94.7	99.4	93.5	94.5	Mean:	96.9
	3	98.5	99.6	92.8	92.6	86.6	SD:	3.54
	4	101	98.6	99.4	99.4	101	UCL:	108
	5	97.6	97.6	96.6	101	100	LCL:	86.3
Methomyl	1	85.4	87.5	91.9	91.8	85.0		
	2	80.7	79.5	85.7	84.2	84.3	Mean:	85.8
	3	86.3	91.8	86.8	84.5	80.3	SD:	3.93
	4	80.7	84.7	82.2	91.6	89.4	UCL:	97.7
	5	83.2	82.5	85.4	88.6	92.2	LCL:	74.0
Methoxyfenozide	1	99.4	96.5	99.9	99.7	92.3		
	2	92.6	95.2	95.5	94.6	92.6	Mean:	97.5
	3	98.8	99.5	94.9	94.7	87.4	SD:	4.07
	4	106	102	97.3	97.7	100	UCL:	110
	5	99.2	104	98.2	101	97.3	LCL:	85.3
Metribuzin	1	89.4	83.1	81.1	92.8	87.6		
	2	79.4	84.6	81.6	90.4	88.5	Mean:	87.9
	3	87.3	84.7	80.1	88.3	83.2	SD:	5.91
	4	85.3	88.1	84.6	100	99.0	UCL:	106
	5	90.5	86.8	85.1	100	96.2	LCL:	70.2
Norflurazon	1	97.3	97.3	96.2	103	94.8		
	2	94.6	92.0	94.4	92.8	95.6	Mean:	96.0
	3	98.4	97.4	89.7	92.8	88.9	SD:	3.57
	4	97.4	96.8	93.4	99.1	93.2	UCL:	107
	5	100	93.9	98.8	101	102	LCL:	85.3
Oryzalin	1	107	87.9	90.0	90.6	100		
	2	97.1	86.3	98.3	91.9	97.1	Mean:	98.0
	3	97.8	94.8	95.8	91.9	94.5	SD:	7.65
	4	86.4	91.5	109	102	110	UCL:	121
	5	104	113	104	103	104	LCL:	75.1

		Spike Level					Control Limits	
Compound	Set#	0.01 ppb	0.05 ppb	0.1 ppb	0.5ppb	1.0 ppb		%
Oxadiazon	1	90.6	87.2	85.5	96.7	90.8		
	2	75.4	79.3	80.0	84.1	91.0	Mean:	87.1
	3	86.8	88.5	82.2	86.3	83.7	SD:	5.97
	4	93.8	85.9	86.5	90.3	96.8	UCL:	105
	5	75.3	88.3	86.2	89.0	98.3	LCL:	69.2
Prometon	1	96.2	94.0	96.3	100	95.8		
	2	78.8	85	87.2	90.4	90.8	Mean:	90.7
	3	86.8	91.5	84.9	90.1	86.0	SD:	5.77
	4	88.4	92.2	89.1	96.8	99.4	UCL:	108
	5	84.5	83.6	83.3	97.1	97.9	LCL:	73.4
Prometryn	1	101	95.3	97.5	99.0	95.3		
	2	92.1	93.3	95.1	92.1	93.8	Mean:	95.5
	3	93.2	95.8	91.2	91.0	86.6	SD:	3.53
	4	103	95.9	96.3	101	98.2	UCL:	106
	5	95.9	95.3	96.4	95.9	98.2	LCL:	84.9
Propanil 1	1	93.6	92.8	93.3	101	88.7		
	2	86.7	84.3	87.3	90.6	92.8	Mean:	92.1
	3	88.5	89.5	86.0	87.4	85.2	SD:	5.28
	4	89.1	98.1	92.8	99.7	102	UCL:	108
	5	89.3	92.4	91.5	98.2	102	LCL:	76.2
Propargite	1	96.8	92.6	89.2	97.1	95.2		
	2	91.7	89.8	88.6	88.3	90.6	Mean:	93.4
	3	94.4	94.9	89.4	88.0	85.5	SD:	3.94
	4	102	94.4	95.1	94.4	95.5	UCL:	105
	5	98.9	94.2	95.4	97.2	96.9	LCL:	81.6
Propiconazole	1	93.9	93.6	89.9	92.1	92.5		
	2	83.9	82.8	86.8	89.6	91.7	Mean:	93.2
	3	104	93.4	86.4	92.2	84.9	SD:	5.46
	4	93.7	95.8	96.0	97.3	101	UCL:	110
	5	99.5	93.7	96.9	98.5	99.0	LCL:	76.8
Pyraclostrobin	1	94.0	89.2	90.1	94.1	93.6		
	2	85.9	84.6	85.3	91.5	92.5	Mean:	90.9
	3	89.3	88.0	81.6	92.1	85.0	SD:	4.46
	4	93.1	93.4	91.2	100	95.3	UCL:	104
	5	91.5	89.6	86.8	98.3	96.1	LCL:	77.5

		Spike Level					Control Limits	
Compound	Set#	0.01 ppb	0.05 ppb	0.1 ppb	0.5ppb	1.0 ppb		%
Pyriproxyfen	1	96.7	95.0	91.6	99.9	97.8		
	2	86.8	88.2	89.3	84.8	89.5	Mean:	91.9
	3	91.2	92.8	88.9	86.3	84.2	SD:	4.45
	4	96.2	92.3	94.8	92.8	100	UCL:	105
	5	89.0	91.5	89.7	91.4	96.8	LCL:	78.6
Quinoxyfen	1	96.2	94.5	94.5	98.7	95.2		
	2	90.2	91.1	94.2	89.5	93.6	Mean:	94.7
	3	95.3	97.8	91.1	91.9	86.7	SD:	3.30
	4	98.2	94.4	95.1	94.4	95.5	UCL:	105
	5	96.9	96.3	95.6	98.8	102	LCL:	84.8
Simazine	1	91.9	87.3	88.5	95.7	91.3		
	2	82.9	83.6	87.4	89.1	93.8	Mean:	91.3
	3	91.8	89.2	86.1	91.0	83.5	SD:	4.80
	4	91.3	95.8	96.0	97.3	101	UCL:	106
	5	91.0	91.2	90.4	97.7	97.8	LCL:	76.9
S-Metolachlor	1	102	92.3	95.7	95.3	93.5		
	2	95.4	91.1	93.3	90.2	94.4	Mean:	94.2
	3	98.6	94.6	87.4	88.9	84.4	SD:	4.00
	4	99.1	93.4	91.2	100	95.3	UCL:	106
	5	95.0	96.5	94.3	94.9	99.1	LCL:	82.2
Tebufenozide	1	88.9	87.1	86.2	96.5	95.3		
	2	75.9	76.3	72.2	91.5	92.4	Mean:	85.4
	3	76.6	73.5	71.1	89.4	83.6	SD:	9.28
	4	82.1	88.2	80.0	98.1	97.9	UCL:	113
	5	83.3	76.0	74.8	100	98.3	LCL:	57.6
Thiobencarb	1	100	92.4	90.3	96.2	91.0		
	2	93.0	89.0	91.7	88.5	89.5	Mean:	95.4
	3	150	101	96.2	90.7	84.7	SD:	12.0
	4	95.2	93.1	91.2	94.5	93.2	UCL:	131
	5	97.3	93.6	91.5	93.8	97.7	LCL:	59.4
Trifloxystrobin	1	86.3	86.7	84.4	96.4	93.2		
	2	84.0	82.9	80.8	86.9	90.5	Mean:	90.2
	3	88.4	88.5	84.7	89.0	87.5	SD:	4.91
	4	94.7	92.4	92.2	96.1	98.5	UCL:	105
	5	94.8	93.6	93.2	93.4	97.2	LCL:	75.5

Compound	Set#	Spike Level 0.01 ppb	0.05 ppb	0.1 ppb	0.5ppb	1.0 ppb	Control Limits %
Atrazine-d5 (0.05ppb)	1	82.0	78.6	80.2	100	94.0	
	2	67.8	70.6	68.6	96.0	91.8	Mean: 80.1
	3	66.6	67.8	62.6	88.6	87.8	SD: 12.13
	4	70.2	80.2	74.0	95.6	95.0	UCL: 116
	5	71.2	64.8	65.4	89.6	93.6	LCL: 43.7
Imidacloprid-d4 (0.05ppb)	1	85.0	83.6	84.0	110	98.4	
	2	78.0	79.4	77.4	94.6	94.2	Mean: 88.5
	3	90.4	90.6	84.0	97.6	84.0	SD: 9.42
	4	84.0	84.4	80.8	102	102	UCL: 117
	5	79.6	77.0	76.2	98.6	96.8	LCL: 60.2
Fipronil	1	119	98.6	101	102	97.0	
	2	103	97.9	99.8	97.0	93.4	Mean: 101
	3	92.3	102	97.0	95.5	88.5	SD: 6.32
	4	111	107	102	108	107	UCL: 120
	5	98.3	101	105	104	102	LCL: 82.2
Fipronil Amide	1	110	100	101	101	96.0	
	2	98.3	100	94.2	89.5	95.8	Mean: 104
	3	109	104	99.6	99.8	87.3	SD: 8.75
	4	117	119	116	112	114	UCL: 131
	5	116	109	112	105	103	LCL: 78.1
Fipronil Sulfide	1	100	100	96.7	99.7	96.7	
	2	94.5	94.9	94.4	97.2	98.3	Mean: 101
	3	101	104	97.4	95.1	88.6	SD: 5.32
	4	108	108	109	107	108	UCL: 117
	5	101	102	102	106	103	LCL: 84.6
Fipronil Sulfone	1	101	95.4	97.2	99.6	93.4	
	2	91.5	91.9	93.1	92.8	95.9	Mean: 97.8
	3	94.9	95.0	96.5	95.9	87.4	SD: 5.1
	4	99.6	103	106	104	109	UCL: 113
	5	98.1	95.7	99.6	102	104	LCL: 82.4
Desulfinyl Fipronil	1	107	98.7	97.9	97.9	94.5	
	2	99.5	94.8	98.4	95.0	97.9	Mean: 100
	3	99.9	97.5	97.4	95.8	86.6	SD: 5.38
	4	108	107	107	109	107	UCL: 117
	5	102	104	103	101	103	LCL: 84.3

		Spike Level					Control Limits	
Compound	Set#	0.01 ppb	0.05 ppb	0.1 ppb	0.5ppb	1.0 ppb		%
Desulfinyl Fipronil Amide	1	115	112	107	104	97.9		
	2	101	104	108	92.2	95.3	Mean:	106
	3	115	111	106	97.3	92.4	SD:	7.67
	4	116	116	117	104	112	UCL:	129
	5	110	115	106	98.3	105	LCL:	83.3

Written By:

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Jean Hsu Date
Sr. Environmental Scientist (Specialist)

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Jane White Date
Sr. Environmental Scientist (Specialist)

Approved By:

Original Signed by _____ 2/1/2018 _____
Stephen Siegel Date
Sr. Environmental Scientist (Supervisor)

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Maryam Khosravifard Date
Environmental Program Manager I

Revision Log:

Date	What was revised? Why?