Title: Determination of Atrazine, Bromacil, Cyanazine, Diuron, Hexazinone, Metribuzin, Norflurazon, Prometon, Prometryn, Simazine, Deethyl Atrazine (DEA), Deisopropyl Atrazine (ACET), and Diamino Chlorotraizine (DACT) in Well Water and River Water By Liquid Chromatography- Atmospheric Pressure Chemical Ionization Mass Spectrometry

1. Scope:

This modified section method (SM) is applicable to the analysis of Atrazine, Bromacil, Cyanazine, Diuron, Hexazinone, Metribuzin, Norflurazon, Prometon, Prometryn, Simazine, Deethyl Atrazine (DEA), Deisopropyl Atrazine (ACET), and Diamino Chlorotraizine (DACT) in well water and river water using APCI/LC/MS/MS. Desmethyl Norflurazon Tebuthiuron, Tebuthiuron-104 , Tebuthiuron-106, Tebuthiuron-107 and Tebuthiuron-108 method detection limit and validation data for well water was added later. The reporting limit for all chemicals is 0.05 ppb.

2. Principle:

Two conditioned Water Oasis ® MCX Cartridges connected in tandem are used to retain the analytes from well water and river water samples. The cartridges are placed under vacuum to eliminate any remaining water. The chemicals are eluted with 5% ammonium hydroxide in methanol. The eluant is then filtered, concentrated, reconstituted in 1:3 methanol/water and analyzed by APCI/LC/MS/MS.

3. Safety:

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

4. Interferences:

There were no matrix interferences that caused quantitative problems during method development and validation

5. Apparatus and Equipment:

5.1 Nitrogen Evaporator (Meyer N-EVAP Organomation Model #112 or equivalent)
5.2 Balance (Mettler PC 4400 or equivalent)
5.3 Vortex-vibrating mixer
5.4 Solid phase extraction manifold, Supelco Visiprep TM24 or equivalent

5.5 Solid phase extraction manifold accessories: vacuum source, vacuum chamber, vacuum controller, cartridge fittings (tube adapters) and connectors,sample delivery tubing with stainless steel weight, sample collection tubes and rack.
5.6 Sample filtration apparatus
5.7 Liquid Chromatograph equipped with an ion trap (LCMS)

6. **Reagents and Supplies**:

6.1	Diamino Chlorotriazine (DACT)	CAS#3397-62-4
6.2	Deisopropyl Atrazine (ACET)	CAS#11007-28-9
6.3	Deethyl Atrazine (DEA)	CAS#6190-65-4
6.4	Metribuzin	CAS#21087-64-9
6.5	Bromacil	CAS#314-40-9
6.6	Atrazine	CAS#1912-24-9
6.7	Norflurazon	CAS#27314-13-2
6.8	Cyanazine	CAS#21725-46-2
6.9	Simazine	CAS#122-34-9
6.10	Hexazinone	CAS#51235-04-2
6.11	Diuron	CAS#330-54-1
6.12	Prometon	CAS#1610-18-0
6.13	Prometryn	CAS#7287-19-6
6.14	Propazine (surrogate)	CAS#139-40-2
6.15	Desmethyl-Norflurzon	CAS#23576-24-1
6.16	Tebuthiuron	CAS#34014-18-1
6.17	Tebuthiuron 108	CAS#
6.18	Tebuthiuron 107	CAS#
6.19	Tebuthiuron 106	CAS#
6.20	Tebuthiuron 104	CAS#

6.21 Methanol, MS grade, Burdick & Jackson or equivalent
6.22 Water, MS grade, Burdick & Jackson or equivalent
6.23 Formic acid, HPLC grade
6.24 Ammonium formate 1.0 M
6.25 Ammonium hydroxide, reagent grade or equivalent.
6.26 Elution reagent: 5% ammonium hydroxide in methanol.
6.27 Hydrochloric acid 6 N
6.28 Reconstitution reagent: 1:3 methanol/water
6.29 Mobil phase A: 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.
6.30 Mobil phase B: 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.

6.31 Solid phase extraction cartridges: Waters Oasis® MCX 6 cc (150 mg), 60-micron particle size cartridge.
6.32 Nylon Acrodisc ®, 0.2 micron, Gelman Sciences
6.33 Syringe and plunger for filtration, 10mL
6.34 Graduated test tube, 15 mL (calibrated at 0.5mL with methanol)
6.35 Fiberglass filters, 1um x 47 mm.

6.36 LCMS Columns:
Analytical column: Waters SymmetryShieldRP_{18} 5 µm, 3.9 x 150 mm column (part # 186000108) or equivalent
Guard column: Waters SymmetryShieldRP_{18} 5 µm, 3.9 x 20 mm cartridge (Part # 186000107) or equivalent
Guard column holder: Waters Sentry guard holder universal. (Part # wat064610)

7. Standards Preparation:

7.1 A combination stock standard of 0.1 mg/mL for all the triazines except propazine was obtained from the CDFA/CAC Standards Repository. Propazine was received at a concentration of 1 mg/mL and was diluted to 1.0 ug/mL in methanol for spiking as a surrogate. Tebuthiuron and metabolites were received at a concentration of 1 mg/mL and were diluted with the combination triazine standard to 1.0 ug/mL in methanol for spiking.

A combination standard of 10 µg/mL was prepared with 1:3 methanol/water from the combination 0.1mg/mL standard, Tebuthuiron, metabolites and propazine standards. The combination working standard was diluted to the following concentrations: 0.025, 0.05, 0.1, 0.2, 0.5, and 1 µg/mL in 1:3 methanol/water for instrument calibration.

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 or the expiration date of the stock standards which ever comes first.

8. **Sample Preservation and Storage**:

Store all samples waiting for extraction in a separate refrigerator (32-40 °F).

9. **Test Sample Preparation**:

9.1 Background Preparation

The Department of Pesticide Regulation (DPR) provided the surface water and well water for background to be used in method validation and QC.

9.2 Preparation of blank and spike

Matrix blank: Weigh out 500 g of background water and follow the test sample extraction procedure.

Matrix spike: Weigh out 500 g of background water. Spike a client requested amount of herbicides into the background water and let it stand for 1 minute. Follow the test sample extraction procedure.

9.3 Test Sample Extraction

9.3.1 Remove sample from refrigerator and allow them to come to ambient temperature.

9.3.2 Weigh 500 ± 0.5 g of water sample into a 600 mL beaker.

9.3.3 Add 0.1 µg propazine (100 µL of 1 ng/µL spiking solution) as a surrogate to each sample except blank. Note: the volume of methanol in spiking solution added to the sample should be 0.1% or less of the sample volume.

9.3.4 Filter the surface water sample through a 1 µm x 47mm fiberglass filter. Note: no filtration is need for well water sample.

9.3.5 Adjust pH to 2.5 – 3.0 with 3 N HCL.

9.3.6 Two MCX cartridges are connected together in tandem and connected to the vacuum manifold. (Fill the 1st MCX cartridge reservoir with methanol and attach it to the solid phase extraction manifold. Stack the 2nd MCX

cartridge to the 1st MCX cartridge with fitting connector. Add methanol to 2nd reservoir.)

9.3.7 Condition the cartridges with total ~15 mL of methanol at a flow rate ~ 8 mL/minutes followed by ~ 15 mL of D.I. water by applying vacuum.

9.3.8 Turn off the vacuum when the D.I. water has just passed through the cartridges. Refill MCX cartridges with D.I. water. Attach the sample delivery tubes to the 2nd cartridge and place weighted tube ends into water sample.

9.3.9 Allow the sample to pass through the conditioned cartridges by applying vacuum. Adjust the flow rate to ~ 8 mL/minute

9.3.10 After all of the water sample has passed through the cartridges, increase the vacuum to ~ 20 psi for about 2 minutes. Detach the sample delivery tube from MCX cartridge. Shake out any excess water in the cartridge reservoir. Reverse the stacking order of the MCX cartridges on the vacuum manifold.

9.3.11 Place the graduated test tubes into the vacuum manifold.

9.3.12 Elute and collect all chemicals with 15 ± 0.5 mL of 5% ammonium hydroxide in methanol at a flow rate of ~8 mL/minutes.

9.3.13 Concentrate the eluant to ~10 mL in a water bath at 38 ± 2 °C under a gentle stream of nitrogen.

9.3.14 Filter the eluant through a 0.2 µm Acrodisc into a 15 mL graduated test tube, which has been calibrated at 0.5 mL. Rinse the test tube with ~ 2 mL of Methanol and filter the rinsate. Add filtered rinsate to eluant. Rinse the filter and syringe and add to eluant.

9.3.15 Concentrate the eluant to ~0.2 mL in a water bath at 38 ± 2 °C under a gentle stream of nitrogen. Bring to a final volume of 0.5 mL with reconstitution reagent (1:3, water/methanol). Vortex for 30 seconds. Transfer the extract into two autosampler vials with inserts. Analyzed by APCI/LC/MS/MS.

10. **Instrument Calibration**:

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

10.2 The LCMS calibration curves were obtained using linear regression.

11. **Analysis:**

11.1 HPLC-MS

11.1.1 HPLC Instrument: Waters model 2695 HPLC and auto-sampler with column heater and remote control through Thermo Finnigan Xcalibur system.
Column: Waters SymmetrySheid RP_{18} 5 µm, 3.9 x 150 mm column
Column Temperature: 40 °C

Mobile Phase: Gradient

Time(min)	Flow rate	Mobile Phase A	Mobile Phase B
0	0.75	85.0	15.0
3.0	0.75	85.0	15.0
4.0	0.75	50.0	50.0
10.0	0.75	50.0	50.0
21.0	0.75	25.0	75.0
22.0	0.75	5.0	95.0
26.0	0.75	85.0	15.0
30.0	0.75	85.0	15.0

Injection Volume: 30 µL

11.1.2 Liquid Chromatograph Mass spectrometer (LC-MS) and Operating Parameters

Model:	Finnigan Model DECA ion trap MS
Ion Source Type:	Atmospheric pressure Ionization (APCI)
Source Polarity:	Positive
APCI Vaporizer Temp:	450 °C
Capillary Temperature:	220 °C
Sheath Gas flow rate:	80 (arb)
Auxiliary Gas flow:	10 (arb)
Mode of operation:	MS/MS

Compound Name	Retention Time (min.)	Molecular Weight	Mass Range	Product Ions
DACT	3.29	145.55	60-200	110
ACET	7.41	173.6	55-200	132,146
Teb-108	7.72	157.23	60-240	158
DEA	8.99	187.63	60-200	146
Teb-106	8.68	200.26	55-220	158, 184
Teb-107	9.19	172.26	50-200	89
Teb-104	9.25	214.28	55-250	172, 215
Hexazinone	10.79	252.32	80-275	171
Tebuthiuron	11.26	228.31	100-250	172
Cyanazine	11.29	240.70	75-275	214,216,241
Metribuzin	11.86	214.29	70-235	186,187
Simazine	12.20	201.66	65-225	124,132,174
Bromacil	12.30	261.1	100-280	205,207
Prometon	13.75	225.3	70-250	142,184
Atrazine	16.10	215.69	70-235	174,176
Norflurazon	17.41	303.7	100-350	284
Desmethyl Norflurazon	16.55	289.65	75-350	248,270,288
Diuron	18.45	233.10	60-250	72
Propazine	19.57	229.7	70-250	188,190
Prometryn	20.66	241.37	75-275	200

Note: The column conditions, temperature, mobile phase, etc. may slightly shift retention time.

11.1.3 Operating parameter

Compound Name	Segment / Scan #	Segment Time	Parent Mass (m/z)	Isolation Width (m/z)	Normalized Collision Energy(%)	Activation Q
DACT	1	5.0	147	5.0	40.0	0.400
ACET	2 / 1	3.1	175	5.0	40.0	0.300
Teb-108	2 / 2		158	3.0	30.0	0.250
DEA	3 / 1	1.50	189	5.0	30.0	0.300
Teb-106	3 / 2		201	3.0	32.0	0.250
Teb-107	3 / 3		172	3.0	35.0	0.250

Teb-104	3 / 4		215	3.0	30.0	0.250
Hexazinone	4 / 1	1.70	253	5.0	37.0	0.300
Cyanazine	4 / 2		242	5.0	37.0	0.300
Compound Name	Segment / Scan #	Segment Time	Parent Mass (m/z)	Isolation Width (m/z)	Normalized Collision Energy(%)	Activation Q
Metribuzin	4 / 3		215	5.0	34.0	0.300
Tebuthiuron	4 / 4		229	3.0	35.0	0.250
Simazine	5 / 1	1.0	203	5.0	40.0	0.300
Bromacil	5 / 2		262	5.0	34.0	0.350
Metribuzin	5 / 3		215	3.0	34.0	0.300
Tebuthiuron	5 / 4		229	3.0	35.0	0.250
Simazine	6 / 1	0.80	203	5.0	40.0	0.300
Bromacil	6 / 2		262	5.0	34.0	0.350
Prometon	6 / 3		226	3.0	38.5	0.300
Prometon	7 / 1	2.20	226	3.0	38.5	0.300
Atrazine	7 / 2		217	5.0	36.0	0.300
Atrazine	8 / 1	1.99	217	5.0	36.0	0.300
Norflurazon	8 / 2		305	5.0	39.0	0.300
Desmethyl Norflurazon	8 / 3		290	4.0	45.0	0.250
Diuron	9 / 1	0.81	235	5.0	35.0	0.240
Norflurazon	9 / 2		305	5.0	39.0	0.300
Diuron	9 / 3		235	5.0	0.0	0.240
Diuron	10 / 1	1.20	235	5.0	35.0	0.240
Diuron	10 / 2		235	5.0	0.0	0.240
Propazine	10 / 3		231	5.0	40.0	0.300
Prometryn	11 / 1	3.20	242	3.0	37.5	0.300
Propazine	11 / 2		231	5.0	40.0	0.300

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/well water samples are spiked at 0.100 µg 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 for each analyte 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 0.05 ppb.

12.3 Method Validation

The method validation consisted of five sample sets. Each set included four 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 triazines are shown in Appendix 2.

12.4 Control Charts and Limits

Control charts were generated using the data from the method validation for each analyte. The upper and lower warning and control limits are set at $\pm$ 2 and 3 standard deviations of the % recovery, respectively, 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 per cent 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 LCMS software used a linear curve fit, with all levels weighted equally. Alternatively, at the chemist's discretion, concentrations may be calculated using the response factor for the standard whose value is < 30% to the level in the sample.

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

14. **Reporting Procedure:**

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

15. **Discussion and References:**

15.1 Propazine is used as a surrogate. Add 0.1 µg of propazine to each sample and processed through the entire analytical method. This allows the extraction steps to be monitored.

15.2 The segment durations in the mass spectrometer settings determine the retention time windows for each analyte. As the HPLC column performance may change over time because of irreversible contamination, phase stripping, etc., it may be necessary to adjust these windows before beginning a sequence for the observed retention times of the analytes. Installation of a new guard column or analytical column may also necessitate adjustments of window times. These retention time windows should be verified before each sequence, and adjusted as necessary.

15.3 The original method "*Determination of Atrazine, Bromacil, Cyanazine, Diuron, Hexazinone, Metribuzin, Norflurazon, Prometon, Prometryn, Simazine, Deethyl Atrazine, (DEA), Deisopropyl Atrazine (ACET), and Diamino Chorotriazine (DACT) in Well Water and River Water By Liquid Chromatography-Atmospheric Pressure Chemical Ionization Mass Spectrometry*" has been updated to reflect what is currently being used. The in house vacuum manifold has been replaced

with a Supelco Visiprep TM24 manifold. The LCQ DECA installed with the Waters SymmetrySheid RP_{18} 5 µm, 3.9 x 150 mm column is the only instrument being used at this time. MDL and method validation data for desmethy norflurazon in well water has been added. Hexazinone mdl and validation data was also updated.

15.4 References:

15.41 SOP # EM 501.4

15.42 SOP # EM 501.5

Appendix 1

The Determination of Method Detection Limit (MDL) and Reporting Limit (RL) in Well Water

Results: Well Water

Spk\Analyte	DACT	ACET	DEA	Bromacil	Cyanazine	Diuron
0.1ppb	0.079	0.083	0.080	0.104	0.086	0.086
0.1ppb spk 2	0.083	0.092	0.088	0.085	0.086	0.108
0.1ppb spk 3	0.079	0.088	0.079	0.095	0.088	0.088
0.1ppb spk 4	0.084	0.091	0.082	0.101	0.087	0.068
0.1ppb spk 5	0.081	0.093	0.088	0.092	0.083	0.081
0.1ppb spk 6	0.081	0.084	0.081	0.095	0.084	0.091
0.1ppb spk 7	0.080	0.086	0.085	0.101	0.084	0.069
SD	0.002	0.0040	0.00372	0.00655	0.00200	0.0137
MDL	0.0063	0.013	0.0110	0.020	0.0063	0.043
RL	0.05	0.05	0.05	0.05	0.05	0.05

Results: Well water

Spk\Analyte	Hexazinone	Metribuzin	Simazine	Prometon	Atrazine	Norflurazon
0.1ppb spk 1	0.082	0.074	0.077	0.077	0.075	0.089
0.1ppb spk 2	0.080	0.086	0.084	0.082	0.087	0.091
0.1ppb spk 3	0.083	0.077	0.073	0.071	0.073	0.090
0.1ppb spk 4	0.086	0.082	0.080	0.076	0.079	0.088
0.1ppb spk 5	0.087	0.083	0.082	0.081	0.082	0.085
0.1ppb spk 6	0.081	0.081	0.083	0.077	0.082	0.088
0.1ppb spk 7	0.083	0.082	0.085	0.081	0.083	0.089
SD	0.0078	0.0040	0.0043	0.0038	0.0048	0.0019
MDL	0.025	0.0125	0.0135	0.012	0.015	0.0063
RL	0.05	0.05	0.05	0.05	0.05	0.05

Appendix 1: Continue

The Determination of Method Detection Limit (MDL) and Reporting Limit (RL) in Well Water

Results: Well water

Spk\Analyte	Desmethyl Norflurazon	Prometryn	Tebuthiuron	Metabolite 104	Metabolite 106	Metabolite 107	Metabolite 108
0.1ppb spk 1	0.093	0.077	0.093	0.101	0.098	0.085	0.081
0.1ppb spk 2	0.089	0.084	0.090	0.110	0.101	0.093	0.085
0.1ppb spk 3	0.097	0.077	0.095	0.116	0.107	0.093	0.101
0.1ppb spk 4	0.093	0.074	0.100	0.138	0.102	0.102	0.101
0.1ppb spk 5	0.099	0.083	0.088	0.103	0.096	0.094	0.082
0.1ppb spk 6	0.100	0.084	0.089	0.099	0.090	0.092	0.081
0.1ppb spk 7	0.0102	0.084	0.098	0.115	0.100	0.112	0.099
SD	0.005	0.0043	0.0046	0.0134	0.0053	0.0087	0.0098
MDL	0.015	0.0135	0.014	0.042	0.017	0.027	0.031
RL	0.05	0.05	0.05	0.05	0.05	0.05	0.05

The Determination of Method Detection Limit (MDL) and Reporting Limit (RL) in Surface Water

Results: Surface Water

Spk\Analyte	DACT	ACET	DEA	Bromacil	Cyanazine	Diuron
0.1ppb	0.075	0.088	0.082	0.077	0.082	0.077
0.1ppb spk 2	0.077	0.096	0.090	0.102	0.095	0.087
0.1ppb spk 3	0.075	0.086	0.088	0.095	0.088	0.085

0.1ppb spk 4	0.087	0.086	0.083	0.100	0.083	0.097
0.1ppb spk 5	0.087	0.090	0.088	0.099	0.087	0.093
0.1ppb spk 6	0.082	0.107	0.089	0.108	0.087	0.094
0.1ppb spk 7	0.081	0.109	0.089	0.097	0.087	0.088
SD	0.005	0.010	0.003	0.010	0.0040	0.007
MDL	0.016	0.030	0.010	0.031	0.013	0.022
RL	0.05	0.05	0.05	0.05	0.05	0.05

Appendix 1: Continue

The Determination of Method Detection Limit (MDL) and Reporting Limit (RL) in Surface Water

Result Surface Water

Spk\Analyte	Hexazinone	Metribuzin	Simazine	Prometon	Atrazine	Norflurazon
0.1ppb spk 1	0.110	0.076	0.077	0.076	0.075	0.083
0.1ppb spk 2	0.094	0.080	0.085	0.087	0.081	0.093
0.1ppb spk 3	0.102	0.081	0.080	0.083	0.078	0.092
0.1ppb spk 4	0.099	0.085	0.081	0.083	0.082	0.096
0.1ppb spk 5	0.122	0.088	0.089	0.088	0.087	0.101
0.1ppb spk 6	0.122	0.097	0.092	0.087	0.084	0.095
0.1ppb spk 7	0.125	0.097	0.093	0.091	0.088	0.102
SD	0.013	0.008	0.0042	0.005	0.005	0.006
MDL	0.040	0.025	0.013	0.016	0.016	0.019
RL	0.05	0.05	0.05	0.05	0.05	0.05

The Determination of Method Detection Limit (MDL) and Reporting Limit (RL) in Surface Water

Results: Surface Water

Spk\Analyte	Prometryn
0.1ppb spk 1	0.077
0.1ppb spk 2	0.088
0.1ppb spk 3	0.083
0.1ppb spk 4	0.088
0.1ppb spk 5	0.089
0.1ppb spk 6	0.084
0.1ppb spk 7	0.090
SD	0.005
MDL	0.016
RL	0.05

Appendix 2

Method Validation Data in Well Water

Results: **Well Water**

Analyte	Spike ppb	Recovery Set 1	(%) set 2	set 3	set 4	set 5		%
DACT	0.1	97.0	80.5	70.0	82.0	90.0	Mean:	90.9
	0.5	120	88.1	97.6	81.0	84.8	SD:	13.0
	2.0	119.3	88.8	83.4	74.6	87.5	UCL:	130.
	6.0	103.5	105.3	91.7	84.7	88.5	UWL:	117.
							LWL:	64.8
							LCL:	51.7
ACET	0.1	96.0	84.5	84.5	100.0	102.0	Mean:	92.2
	0.5	100.3	83.8	94.8	82.6	80.0	SD:	9.34
	2.0	114.6	86.6	90.0	83.8	98.4	UCL:	120
	6.0	98.6	100.0	99.2	81.7	83.4	UWL:	111
							LWL:	73.6
							LCL:	64.2
DEA	0.1	86.0	75.5	79.0	88.0	87.0	Mean:	86.8
	0.5	92.3	79.8	98.2	79.6	75.0	SD:	7.65
	2.0	96.8	77.8	88.8	85.2	96.6	UCL:	110
	6.0	87.3	94.8	99.5	85.0	84.0	UWL:	102
							LWL:	71.5
							LCL:	63.9
Bromacil	0.1	87.5	93.0	101	94.0	110.0	Mean:	98.3
	0.5	99.5	104.1	106.0	89.2	87.2	SD:	9.39
	2.0	99.2	108.7	97.8	91.0	99.2	UCL:	127
	6.0	88.8	125.4	100.5	93.3	91.3	UWL:	117
							LWL:	79.6
							LCL:	70.2

Results: **Well Water**

Analyte	Spike ppb	Recovery (%) Set 1	set 2	set 3	set 4	set 5		%
Cyanazine	0.1	82.0	79.0	82.0	87.0	86.0	Mean:	86.0
	0.5	89.5	85.0	90.6	77.2	77.2	SD:	4.73
	2.0	89.9	83.7	86.8	83.0	93.0	UCL:	100
	6.0	89.0	90.0	92.5	87.5	88.2	UWL:	95.4
							LWL:	76.5
							LCL:	71.8
Diuron	0.1	83.5	79.0	80.0	85.0	84.0	Mean:	88.3
	0.5	81.7	75.5	100.8	83.0	89.6	SD:	9.59
	2.0	78.1	72.3	99.4	93.8	103.8	UCL:	117
	6.0	90.3	89.5	97.7	96.2	103.7	UWL:	108
							LWL:	69.2
							LCL:	59.6
Hexazinone	0.1	73.0	71.0	64.0	74.0	74.0	Mean:	95.0
	0.5	84.6	74.3	81.2	67.4	69.4	SD:	5.49
	2.0	91.2	79.2	83.6	76.4	81.6	UCL:	111
	6.0	94.2	86.4	88.3	82.5	80.2	UWL:	106
							LWL:	84.0
							LCL:	78.5
Metribuzin	0.1	79.0	72.5	82.0	89.5	82.0	Mean:	81.1
	0.5	77.3	69.3	95.4	79.2	71.6	SD:	7.25
	2.0	83.9	72.4	79.8	80.0	89.8	UCL:	103
	6.0	79.7	86.8	94.5	76.7	81.3	UWL:	95.6
							LWL:	66.6
							LCL:	59.4

Results: **Well Water**

Analyte	Spike ppb	Recovery Set 1	(%) set 2	set 3	set 4	set 5		%
Simazlne	0.1	85.5	70.5	74.0	86.0	84.0	Mean:	82.9
	0.5	94.3	73.3	91.4	74.4	72.0	SD:	9.21
	2.0	100.6	72.8	82.2	76.2	90.4	UCL:	110
	6.0	89.0	91.8	95.5	75.3	77.8	UWL:	101
							LWL:	64.4
							LCL:	55.2
Prometon	0.1	75.0	72.5	63.0	73.0	76.0	Mean:	80.6
	0.5	85.8	75.3	88.6	71.2	69.8	SD:	8.90
	2.0	95.6	79.4	82.2	79.0	90.2	UCL:	107
	6.0	84.6	91.7	95.8	80.7	82.0	UWL:	98.4
							LWL:	62.8
							LCL:	53.9
Atrazine	0.1	77.0	71.5	74.0	86.0	78.0	Mean:	79.5
	0.5	80.6	70.3	90.2	76.2	69.4	SD:	7.12
	2.0	84.9	71.0	79.8	79.0	88.4	UCL:	101
	6.0	76.3	86.7	95.5	77.3	78.0	UWL:	93.8
							LWL:	65.3
							LCL:	58.1
Norflurazon	0.1	89.0	78.0	82.0	91.0	88.0	Mean:	90.3
	0.5	97.5	78.9	99.8	80.0	84.6	SD:	7.01
	2.0	99.0	87.2	96.8	87.0	96.0	UCL:	111
	6.0	96.8	94.5	98.2	90.8	91.2	UWL:	104
							LWL:	76.3
							LCL:	69.3

Results: **Well Water**

Analyte	Spike ppb	Recovery Set 1	(%) set 2	set 3	set 4	set 5		%
Desmethyl Norflurazon	0.1	101.2	111	99.0	88.0	107	Mean:	100
	0.5	96.2	105.8	110	85.8	98.8	SD:	6.80
	2.0	103.3	97.9	103.6	89.5	103	UCL:	121
	5.0	101.4	99.2	106.8	97.4	97.3	UWL:	114
							LWL:	86.5
							LCL:	79.7
Propazine	0.1	84.3	79.0	85.0	95.5	87.0	Mean:	83.4
	0.5	83.3	75.5	100.0	83.0	80.0	SD:	7.02
	2.0	83.8	72.3	79.5	78.5	88.0	UCL:	104
	6.0	78.3	89.5	91.5	75.5	78.0	UWL:	97.4
							LWL:	69.3
							LCL:	62.3
Prometryn	0.1	82.5	74.0	73.0	87.0	85.0	Mean:	83.0
	0.5	86.3	74.6	91.2	76.6	70.4	SD:	7.13
	2.0	93.1	75.5	85.0	80.4	90.0	UCL:	104
	6.0	86.8	91.0	93.8	82.8	81.0	UWL:	97.3
							LWL:	68.7
							LCL:	61.6

Validation of Tebuthiuron and its metabolites were added at a later date

Results: **Well Water**

Analyte	Spike ppb	Recovery Set 1	(%) set 2	set 3	set 4		%
Tebuthiuron	0.1	97.0	90.0	91.0	89.0	Mean:	96.6
	0.5	103	98.6	89.6	89.8	SD:	11.1
	2.0	108	89.0	107	82.5	UCL:	130
	6.0	96.2	129	95.7	90.5	UWL:	119
						LWL:	74.4
						LCL:	63.3

Validation of Tebuthiuron and it's metabolites in well water was added at a later date

Results: **Well Water**

Analyte	Spike ppb	Recovery Set 1	(%) set 2	set 3	set 4		%
Tebuthiuron 104	0.1	134	120	86.0	115	Mean:	98.1
	0.5	94.8	102	95.0	91.8	SD:	13.9
	2.0	104	91.5	94.0	86.5	UCL:	140
	6.0	88.5	93.3	83.5	89.2	UWL:	126
						LWL:	70.2
						LCL:	56.3

Analyte	Spike ppb	Recovery Set 1	(%) set 2	set 3	set 4		%
Tebuthiuron 106	0.1	96.0	101	106	87.0	Mean:	94.6
	0.5	102	95.2	84.0	92.4	SD:	8.06
	2.0	104	97.0	101	69.5	UCL:	119
	6.0	88.0	89.3	84.7	88.5	UWL:	111
						LWL:	78.4
						LCL:	70.4

Analyte	Spike ppb	Recovery Set 1	(%) set 2	set 3	set 4		%
Tebuthiuron 107	0.1	99.0	86.0	118	87.0	Mean:	91.9
	0.5	108	84.4	91.8	92.4	SD:	11.4
	2.0	99.5	83.5	102	69.5	UCL:	126
	6.0	91.6	84.5	84.5	88.5	UWL:	115
						LWL:	69.0
						LCL:	57.6

Analyte	Spike ppb	Recovery Set 1	(%) set 2	set 3	set 4		%
Tebuthiuron 108	0.1	81.0	80.0	73.0	72.0	Mean:	84.1
	0.5	96.6	83.4	81.4	89.6	SD:	8.91
	2.0	107	81.0	93.0	81.0	UCL:	111
	6.0	87.8	78.5	78.7	82.2	UWL:	102
						LWL:	66.3
						LCL:	57.4

Method Validation Data in Surface Water

Results: **Surface Water**

Analyte	Spike ppb	Recovery Set 1	(%) set 2	set 3	set 4	set 5		%
DACT	0.1	84.0	80.0	80.8	96.8	82.0	Mean:	84.5
	0.5	87.6	87.4	81.0	97.8	84.8	SD:	5.37
	2.0	83.0	83.4	77.0	90.0	80.3	UCL:	101
	6.0	85.3	82.7	79.0	82.0	84.7	UWL:	95.2
							LWL:	73.7
							LCL:	68.4
ACET	0.1	107.0	110.0	110.0	147.0	97.0	Mean:	103
	0.5	93.8	104.0	95.0	97.4	81.6	SD:	12.3
	2.0	95.6	106.0	95.4	104.0	103.0	CL:	140
	6.0	102.0	105.0	99.8	103.0	101.0	UWL:	127
							LWL:	78.3
							LCL:	66.0
DEA	0.1	93.0	87.0	88.0	83.0	81.0	Mean:	93.7
	0.5	104.0	98.6	90.2	95.0	86.4	SD:	7.3
	2.0	95.4	100.0	88.4	99.6	86.2	UCL:	116
	6.0	103.0	107.0	94.2	95.3	98.8	UWL:	108
							LWL:	79.2
							LCL:	71.9
Bromacil	0.1	101.0	89.0	101.0	91.0	89.0	Mean:	97.5
	0.5	107.0	110.0	88.2	101.0	92.4	SD:	7.1
	2.0	84.0	106.0	98.0	100.0	96.6	UCL:	119
	6.0	102.0	106.0	94.0	96.7	96.8	UWL:	112
							LWL:	83.3
							LCL:	76.3

Results: **Surface Water**

Analyte	Spike ppb	Recovery Set 1	(%) set 2	set 3	set 4	set 5		%
Cyanazine	0.1	102.0	88.0	94.0	83.0	88.0	Mean:	107.
	0.5	95.4	106.0	90.4	95.8	79.8	SD:	18.2
	2.0	115.0	131.0	128.0	128.0	107.0	UCL:	162
	6.0	109.0	136.0	128.0	134.0	107.0	UWL:	144
							LWL:	70.8
							LCL:	52.6
Diuron	0.1	102.0	93.0	72.0	81.0	98.0	Mean:	92.2
	0.5	96.2	110.0	76.0	102.0	86.4	SD:	9.8
	2.0	100.0	90.4	87.2	93.4	85.8	UCL:	122
	6.0	89.5	89.3	95.0	109.0	88.3	UWL:	112
							LWL:	72.5
							LCL:	62.7
Hexazinone	0.1	117.0	105.0	98.0	93.0	87.0	Mean:	94.7
	0.5	104.0	99.8	86.4	97.6	76.8	SD:	8.9
	2.0	96.8	98.4	94.8	86.8	82.2	UCL:	121
	6.0	96.3	99.3	94.2	90.2	90.0	UWL:	112
							LWL:	77.0
							LCL:	68.1
Metribuzin	0.1	93.0	87.0	92.0	75.0	79.8	Mean:	89.2
	0.5	92.2	103.0	80.2	87.6	79.6	SD:	6.78
	2.0	85.2	95.8	95.2	90.4	90.0	UCL:	110
	6.0	90.8	98.2	89.3	90.0	88.9	UWL:	103
							LWL:	75.6
							LCL:	68.8

Results: **Surface Water**

Analyte	Spike ppb	Recovery (%) Set 1	set 2	set 3	set 4	set 5		%
Simazlne	0.1	93.0	85.0	82.0	80.0	75.0	Mean:	87.0
	0.5	93.2	99.2	78.8	89.8	78.8	SD:	6.88
	2.0	86.6	91.2	82.8	91.2	78.8	UCL:	107.6
	6.0	94.4	98.0	85.3	85.8	90.2	UWL:	100.7
							LWL:	73.2
							LCL:	66.3
Prometon	0.1	86.0	80.0	76.0	78.0	79.0	Mean:	86.5
	0.5	92.8	96.2	80.6	89.4	81.6	SD:	6.36
	2.0	86.4	91.4	82.0	89.0	80.4	UCL:	106
	6.0	92.5	96.5	89.5	92.0	91.3	UWL:	99.2
							LWL:	73.8
							LCL:	67.5
Atrazine	0.1	88.0	82.0	78.0	78.0	76.0	Mean:	85.5
	0.5	92.4	97.2	83.4	86.2	72.2	SD:	6.33
	2.0	83.8	92.8	84.6	86.4	84.8	UCL:	104
	6.0	90.0	94.7	88.7	85.3	85.2	UWL:	98.1
							LWL:	72.8
							LCL:	66.5
Norflurazon	0.1	98.0	92.0	88.0	86.0	89.0	Mean:	96.0
	0.5	104.0	106.0	89.6	95.3	90.6	SD:	5.59
	2.0	96.8	101.0	96.0	95.2	101.0	UCL:	113
	6.0	95.8	103.0	96.7	101.0	95.8	UWL:	107
							LWL:	84.9
							LCL:	79.3

Results: **Surface Water**

Analyte	Spike ppb	Recovery Set 1	(%) set 2	set 3	set 4	set 5		%
Propazine	0.1	98.0	90.5	78.5	84.0	79.0	Mean:	89.8
	0.5	110.0	105.0	86.5	97.5	81.5	SD:	8.65
	2.0	90.0	93.0	81.5	86.5	77.5	CL:	116
	6.0	96.5	93.0	89.5	90.0	88.5	UWL:	107
							LWL:	72.5
							LCL:	63.9
Prometryn	0.1	92.0	90.0	95.0	86.0	86.0	Mean:	91.9
	0.5	96.6	102.0	83.2	89.2	80.0	SD:	6.46
	2.0	88.0	98.0	93.0	93.6	83.4	UCL:	111
	6.0	97.3	106.0	93.8	93.2	91.2	UWL:	105
							LWL:	78.9
							LCL:	72.5

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Revision Log:

Date	What was revised? Why?
9/10/07	**Add data for Desmethyl Norflurazon in well water**
1/09/09	**Add data for Tebuthiuron and metabolites in well water**