STANDARD OPERATING PROCEDURE
TITLE: Determination of Selected Rice Herbicides in Water Samples by Solid Phase Extraction (SPE) and LC/MSMS

REVISION HISTORY		
Revision #	**Summary of Changes**	**Date**
0	Initial release.	10/08/13

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STANDARD OPERATING PROCEDURE

TITLE: Determination of Selected Rice Herbicides in Ground Water by (SPE) and LC/MSMS

1.0 Scope

1.1 This method may be used to determine selected rice herbicides in groundwater and surface waters.

1.2 This method may not be appropriate for aqueous samples with high levels of suspended solids greater than 1%. Consult the client to clarify if total or dissolved analyte values are of interest.

1.3 Use of this method is restricted to use by, or under supervision of appropriately experienced and trained personnel. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.4 The reporting limit is 0.05 ug/L for all compounds except orthosulfamuron (screened at 0.10 ug/L).

2.0 Principle

2.1 Five hundred milliliters of a room-temperature sample is poured though a pre-conditioned solid-phase extraction cartridge under vacuum.

2.2 Target analytes are eluted from the solid-phase cartridge using acetonitrile/methanol.

2.3 An aliquot of the eluate is filtered thru a 0.45µm filter.

2.4 Internal standard is added to the filtered aliquot.

2.5 The extract is analyzed by LC/MSMS in positive or negative mode to acquire the data unique for each target analyte.

3.0 Safety

3.1 The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely determined. However, each chemical compound and sample should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets should be made available to all personnel involved in this procedure. It is the responsibility of the analyst to read the MSDS as part of the training process.

3.2 Wear gloves, lab coats, safety glasses while processing samples. All processes must be performed in an operating hood.

3.3 Wear a face shield while performing any operations involving vacuum.

3.4 Dispose of waste solvents and spiking solutions according to WPCL-EH-049 “Disposal of Hazardous Wastes.”

3.5 The following chemicals have the potential to be highly toxic or hazardous. For details, read the MSDS associated with each chemical.

- 3.5.1 Methanol (MeOH).
- 3.5.2 Sulfuric acid.
- 3.5.3 Trifluoroacetic acid (TFA)
- 3.5.4 Acetonitrile (ACN).

4.0 Comments.

4.1 Solvents, reagents, glassware, and other sample processing hardware may add artifacts and/or interferences to sample analysis. Method blanks must be analyzed to demonstrate that all of these materials are free from interferences under the conditions of the analysis.

4.2 Bonded-phase silica (e.g., C-18) will hydrolyze on prolonged exposure to aqueous samples with pH levels of less than 2 or greater than 9. Hydrolysis will increase at the extremes of this pH range and with longer contact times. Hydrolysis may reduce extraction efficiency or cause baseline irregularities. Styrene divinylbenzene (SDB) extraction disks should be considered when hydrolysis is a problem.

4.3 Phthalates may interfere with some semi-volatile compound classes. Use only glass in this procedure. Phthalates are used as release agents when molding rigid plastic (e.g., PVC) and as plasticizers for flexible tubing. A method blank should be analyzed, demonstrating that there is no phthalate contamination of the sodium sulfate or other reagents listed in this method.

4.4 Sample particulates may clog the solid-phase media and result in extremely slow sample extractions. Use of an appropriate filter will help shorten extraction times without loss of method performance if clogging is a problem. Even when a filter aid is employed, this method may not be appropriate for aqueous samples with high levels of suspended solids (>1%), as the extraction efficiency may not be sufficient, given the small volumes of solvents employed and the short contact time.

5.0 Apparatus and Equipment

5.1 Glass bottles, 500 mL, clear, Wheaton, P/N 219439 or equivalent.
5.2 Ribbed bottle caps, 33-430, PTFE Liner, Wheaton, P/N 240480 or equivalent.
5.3 Filtering flasks, 1000mL, Kimble Chase, P/N 27070-1000 or equivalent.
5.4 Porcelain Buchner funnel with fixed perforated plate, 100mm plate diam, 320 mL capacity, Coorstek, P/N 60243 or equivalent.
5.5 Glass vacuum manifold block, Restek, P/N 26077.
5.6 Vacuum/pressure pump, 115 V, 60 Hz, Pall Corporation, P/N 13157.
5.7 Tygon® tubing, thick wall.
5.8 Side-arm Erlenmeyer flask for waste, 4 liter, P/N 27060-4000 or equivalent.
5.9 Whatman filter papers, 9.0 cm:
5.10 Whatman #5, P/N 1005-090 for clean samples.
5.11 Whatman #2, P/N 1002-090 for dirty samples.
5.12 Whatman #4, P/N 1004-090 for dirty samples.
5.13 Graduated cylinders, 250 mL, VWR International, P/N 89000-272 or equivalent.
5.14 Graduated cylinders, 500 mL, VWR International, P/N 89000-274 or equivalent.
5.15 Oasis HLB cartridges, 6cc x 200 mg, Waters Corporation, P/N WAT106202.
5.16 Disposable Extraction Column Reservoir (SPE Syringes) 75 mL, J.T. Baker, P/N 7120-03.
5.17 PYREX culture tubes with rubber-lined cap, 16mm x 100 mm, Corning, P/N CORN9825-16 or equivalent.
5.18 PYREX culture tubes with rubber-lined cap, 13mm x 100 mm, Corning, P/N CORN9825-13 or equivalent.
5.19 3 mL syringe, BD P/N 309585.

5.20 Serological pipet, 1 mL with graduations 1/100. Fischer Scientific, P/N 13-678-31F.
5.21 Acrodisc CR 0.45µ PTFE Membrane Syringe filter, 13 mm, P/N 4423.
5.22 Acrodisc CR 0.45µ PTFE Membrane Syringe filter, 25 mm, P/N 4219.
5.23 Sodium Sulfate (Na_2SO_4)-Anhydrous granular grade. Bake in a muffle furnace at 400°C for about 4 hours. Cool, and store in cleaned, glass jars. Rinse with the extraction solvent prior to use.
5.24 Autosampler vials, graduated, screw cap, 12 x 32. Sun SRI, P/N 500779.
5.25 HPLC water acidified to pH <2. Make fresh each day of use.
5.26 Screw caps, green, 100/package. Agilent Technologies, P/N 5182-0724.
5.27 Analytical system:
5.27.1 The analysis is performed on an Agilent 1200 series LC system with a G6410A QQQ Mass Spectrometer (Agilent Technologies, Inc., Santa Clara, California) with electrospray ionization (ESI). The data are acquired using MassHunter Workstation LC/QQQ Acquisition Software and quantified using MassHunter Workstation Quantitative Analysis program.
5.28 Recommended analytical column:
5.28.1 Phenomenex Kinetex XB-C18, 2.6 µm, 2.1*100mm, P/N 00A-4496-AN.

6.0 Reagents and Supplies

6.1 Trifluoroacetic Acid (TFA), Aldrich, 99%, P/N 30-203-1
6.2 Sulfuric Acid, 1:1 (v/v).
6.3 Methanol (MeOH), Burdick and Jackson, P/N BJ230-4
6.4 Acetone, Burdick and Jackson, P/N BJ010-4
6.5 Acetonitrile UV (ACN), Burdick and Jackson, BJ015-4
6.6 ASTM Type II water (Milli-Q water).
6.7 High Purity Water, Burdick and Jackson, BJ365-4.
6.8 ACN/MeOH (50:50 v/v).
6.9 Acidified High purity water (pH<2). Use H_2SO_4 or TFA to acidify.
6.10 Standards

6.10.1	Orthosulfamuron,	CAS# 213464-77-8
6.10.2	Penoxsulam,	CAS# 219714-96-2
6.10.3	Bispyribac sodium	CAS# 125401-92-5
6.10.4	Bensulfuron-methyl	CAS# 83055-99-6
6.10.5	Halosulfuron-methyl	CAS# 100784-20-1.
6.10.6	Clomazone	CAS# 81777-89-1
6.10.7	Propiconazole	CAS# 60207-90-1
6.10.8	Propanil	CAS# 709-98-8
6.10.9	Triclopyr	CAS# 55335-06-3
6.10.10	Molinate	CAS# 2212-67-1
6.10.11	Thiobencarb	CAS# 28249-77-6

7.0 Sample Preservation and Holding Times

7.1 Store samples at <6°C protected from light until extraction.
7.2 Aim to extract samples within 14 days of collection.
7.3 Dispose of samples according to WPCL-EH-049.
7.4 Store extracts at $\leq$ -20°C.

8.0 Standards Preparation

8.1 Weigh 50 mg of individual compound (target analyte and surrogate) with an adequate volume of methanol to prepare an individual stock standard at 5 mg/mL. The expiration date of each neat or stock standard is 12 months from the preparation date. The standard may be used longer if confirmed that concentrations are within 10% of the initial prepared concentrations. The reconfirmed concentration may be used for another 6 months.

8.2 The individual stock standard was diluted to10 µg/mL with methanol for identification purposes.

8.3 The standard stock solution was prepared in methanol (concentration listed in Table 1). Within surrogate solutions, the standard curve with following concentrations: 100, 50, 20, 10, 5, 2, 1 ng/mL were prepared in methanol/acetonitrile (50/50) for LC instrument calibration

8.4 Store all standards at -20°C.

8.5 The expiration date of each working standard is six months from the preparation date.

9.0 Sample Preparation Procedure

9.1 Pre-preparation.

9.1.1 Retrieve samples from storage and allow them to equilibrate to room temperature.

9.1.2 Pre-label vials, test tubes, and cartridges.

9.1.3 Prepare an extraction benchsheet or extraction logbook page to record sample and extraction information.

9.2 Glassware preparation.

9.2.1 All glassware is washed with Alconox and rinsed with methanol followed by rinsing with DI-water three times before use.

9.3 Sample filtration.

9.3.1 Remove large particulate debris by filtering samples. Use a Buchner filter funnel with Whatman No.2 and/or No.5 filter papers as needed and a filter flask. Rinse sample bottles with a small amount of water and filter. Note on the bench sheet if you have filtered the samples.

9.3.2 If samples have high solids and the customer wants total values, allow the sample to settle before measuring the aliquot to be extracted. Extract the solids separately.

9.3.3 Alternatively if particulate matter is 1% or less and the customer wants total values, then filter the measured aliquot to be extracted. Extract the filter separately.

9.4 Measure 500 mL of water sample or filtered sample using a graduated glass cylinder and transfer to a 500 mL pre-cleaned glass bottle.

9.5 Measure 500 mL of lab deionized water each for:

9.5.1 Method Blank.

9.5.2 Lab control sample

9.5.3 Lab control sample duplicate.

9.6 Add surrogates to all samples.

9.7 Add spikes to LCS/LCSD, MS/MSD samples.

9.7.1 Measure 500 mL of the selected field sample for each MS and MSD.

9.8 Adjust sample pH to 2 with 1:1 H_2SO_4 (few drops).

9.9 Solid phase Extraction.

9.9.1 Assemble the vacuum manifold.
9.9.2 Pre-condition the cartridges with 5 mL of methanol followed by 5 mL of acidified HPLC water using gravimetric flow instead of vacuum suction. **Once wet, do not allow cartridge to run dry between and after conditioning steps!**
9.9.3 Attach a 75 mL reservoir to cartridge and fill with sample. Pour the sample through the cartridge at <20 in Hg. Rinse sample bottle with small amount of water and pass through cartridge. **DO NOT let column go dry during loading sample.**
9.9.3.1 Verify sample IDs to cartridges.
9.9.3.2 Compare label information to sample bottle to chain-of-custody.
9.9.3.3 If cartridge goes dry, start over with a new aliquot of sample. New QC will be required if samples are re-extracted on a different day.
9.9.4 Dry inside of cartridge with a Kimwipe. Shake cartridge to dry tip. Continue drying with vacuum an additional 5-10 minutes.
9.9.5 Elute each cartridge with 2 mL of methanol/acetonitrile (50/50) solution and collect extract into glass culture tubes
9.10 Filter an aliquot, transfer 1 mL of sample to an autosampler vial, add 10 µL of internal standard, vortex for analysis by LC/MSMS.

10.0 Calibration and Standardization/Instrument Set Up.

10.1 The calibration standard curve consists of a minimum of 5 levels. The lowest level is at or below the corresponding reporting limits. See Table 1 for calibration standard curve levels.
10.2 The MassHunter Workstation Quantitative Analysis program is used for quantitation based on an internal standard calculation using peak area ratio. A linear or quadratic curve regression ignoring the origin must have a correlation coefficient (r) greater than or equal to 0.995 with all levels weighted 1/x.

11.0 Analysis

11.1 Condition the instrument with a standard before loading calibration standards and sample.
11.2 Immediately after calibration, analyze a check standard from a source different than the calibration standards (ICV).
11.3 Analyze 10 samples.
11.4 Analyze a mid-level calibration standard (CCV).
11.5 Analyze 10 samples.
11.6 Analyze an ending mid-level calibration standard (CCV).
11.7 The final extracts are analyzed on an Agilent 1200 Agilent 1200 series LC system with a G6410A QQQ Mass Spectrometer with ESI source in both positive and negative ion mode. The data are acquired using MassHunter Workstation LC/QQQ Acquisition Software and quantified using MassHunter Workstation Quantitative Analysis program.

11.8 Chromatographic Conditions

Mobile phase A: Water with 0.1% Formic acid
Mobile phase B: Methanol/Acetonitrile (50/50) with 0.1% Formic acid
Flow rate: 0.3 mL/min
Column temperature: 40°C
Injection volume: 5 µL
Gradient:

Positive mode

Time (min)	B%	Flow rate (ml/min)
0	35	0.3
2	35	0.3
12	85	0.3
15	85	0.3
16	35	0.3

Negative mode

Time (min)	B%	Flow rate (ml/min)
0	45	0.3
2	45	0.3
11	80	0.3
14	80	0.3
15	45	0.3

11.9 MS Condition

Drying gas flow: 11 L/min
Drying gas temperature: 350°C
Nebulizer gas pressure: 40 psi
Capillary voltage: 3500 V
MRM parameters:

Positive mode

Compound	Precursor	Product	Frag (V)	CE (V)	RT (min)
Penoxsulam	484.1	194.9	170	29	8.63
Penoxsulam	484.1	163.9	170	37	8.63
Orthosulfamuron	425.1	199.0	100	9	8.53
Orthosulfamuron	425.1	227.0	100	13	8.53
Clomazone	240.1	125.0	80	16	8.89
Clomazone	240.1	89.1	80	56	8.89
Bensulfuron-methyl	411.1	149.0	110	17	9.54
Bensulfuron-methyl	411.1	182.0	110	17	9.54
Propanil	218.0	127.3	110	28	9.05
Propanil	218.0	162.3	110	12	9.05
Molinate	188.1	126.1	65	8	10.11
Molinate	188.1	55.1	65	24	10.11
Bispyribac-sodium	431.1	274.9	120	9	10.5
Bispyribac-sodium	431.1	118.9	120	49	10.5
Halosulfuron-methyl	435.1	181.9	120	17	11.04
Halosulfuron-methyl	435.1	138.9	120	53	11.04
Propiconazole	342.1	159.0	148	36	12.41
Propiconazole	342.1	69.2	148	20	12.41
Thiobencarb	258.1	125.0	70	20	12.96
Thiobencarb	258.1	89.1	70	56	12.96
Surrogate					
Simazine-d_{10}	212.2	137.1	140	20	3.29
Simazine-d_{10}	212.2	105.0	140	28	3.29
Internal Standard					
Diclofenac-d_4	300.1	218	90	41	10.43
Diclofenac-d_4	300.1	254	90	9	10.43

Negative mode

Compound	Precursor	Product	Frag (V)	CE (V)	RT (min)
MCPA	199.0	141.3	160	12	4.22
Triclopyr	253.9	195.8	60	4	5.49
Triclopyr	253.9	218.0	60	0	5.49
Surrogate					
2,4,5-T-d4	256.9	196.9	70	8	7.1
Internal Standard					
Diclofenac-d4	300.1	218	90	41	8.81
Diclofenac-d4	300.1	254	90	9	8.81

11.10 Calculation:

$$ppb = \frac{An \times Cs \times Vf}{As \times Vi}$$

Where:
An = The area of the target analyte
As = The area of the internal standard
Cs = The concentration of the internal standard
Vf = Final volume of sample (2 mL)
Vi = Initial volume of sample (500 mL)

12.0 Quality Control

12.1 Method Detection Limits (MDL)

12.1.1 The method detection limit refers to the lowest concentration of analyte that a method can detect reliably. To determine the MDL, 7 ground water samples are spiked and processed through the entire method along with a blank. The standard deviation from the spiked sample recoveries are 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=8 replicates used to determine the MDL, t=2.998.

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

12.2 Reporting Limit (RL)

12.2.1 The reporting limit (RL) refers to the level at which reliable quantitative results may be obtained. The MDL is used as a guide to determine the RL. In general, the RL is chosen in a range 1-5 times the MDL, as per client agreement.

12.3 Method Validation

12.3.1 The method validation consisted of five sample sets. Each set included 5 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

12.4.1 Control charts were generated using 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 from the average percent recovery. See Appendix 2.

12.5 Sample batch: up to 20 samples of similar matrix processed together using the same reagents, equipment, and techniques within a work day.

12.5.1 Every sample batch will include:

12.5.1.1 Method blank.

12.5.1.2 Laboratory control sample (LCS). If insufficient sample is available for an MSD, then an LCS duplicate (LCSD) will be processed with the batch.

12.5.1.3 Matrix spike (MS).

12.5.1.4 Matrix spike duplicate (MSD).

12.5.2 See Table 2 for acceptance criteria and corrective actions.

12.6 Reporting

12.6.1 Report sample results in ug/L.

12.6.2 Report orthosulfamuron concentrations flagged “J” to denote an estimated value.

12.6.3 Report values above the MDL and below the reporting limit as “TR” to denote a trace level concentration.

13.0 Discussion

13.1 A storage stability study was conducted for this project and consisted of analyzing 3 spiked replicates on selected days over a 49 day period. Fifteen liters of background well water were spiked, mixed well, then 500 mL aliquots were removed for analysis at the designated time points. A volume of laboratory deionized water was also stored for the duration of the study to monitor cross-contamination during storage. All samples were stored in a refrigerator at 4°C until pulled for analysis on designated dates. Along with the storage spikes, a blank and method control spike (LCS) were also extracted. This storage study showed no significant degradation for these compounds within 49 days with the exception of Day 35 discussed below. Results for the storage study are shown in Appendix 3.

13.1.1 Orthosulfamuron storage results could not be quantitated due to the observed instability of this standard stored at 4°C in methanol. Comparisons of storage temperature and solvent were made to isolate factors affecting orthosulfamuron. Storage of standards and sample extracts (methanol) at (-20)°C improved the retention of orthosulfamuron but the comparison was conducted after the 49 day storage study was completed. Preliminary

observations indicate that up to 70% of the orthosulfamuron may have been lost within 10 days of extraction when stored at 4°C in methanol. Additional study is recommended to investigate optimal orthosulfamuron storage conditions.

13.1.2 Recoveries for all compounds on Day 35 trend lower than Day 28 and subsequent Days 42 and 49. All instrument quality controls were acceptable. The compounds halosulfuron-methyl and thiobencarb are late eluters and recoveries are noticeably lower than recoveries on previous and subsequent days. The consistency of low bias for this point indicates that an error occurred during the extraction of the sample.

14.0 References

14.1 "Method 3535A, Solid Phase Extraction," Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, U.S. EPA Office of Solid Waste, Update 4.
14.2 "Waters Corporation Applications Notes for Oasis Sep-Pak cartridges.
14.3 WPCL-QA-006, Method Detection Limits and Validation.
14.4 WPCL-EH-049, Disposal of Hazardous Wastes.

15.0 Attachments

15.1 Table 1: Calibration Curve Levels
15.2 Appendix 1: Method Detection Limit
15.3 Appendix 2: Method Validation
15.4 Appendix 3: Storage Stability
15.5 Table 2: Corrective Actions

.

Table 1: Calibration Curve Levels

Compound	Std-100ppb	Std-50ppb	Std-20ppb	Std-10ppb	Std-5ppb	Std-2ppb	Std-1ppb
Penoxsulam	100	50	20	10	5	2	1
Orthosulfamuron	800	400	160	80	40	16	8
Clomazone	20	10	4	2	1	0.4	0.2
Bensulfuron-methyl	100	50	20	10	5	2	1
Propanil	40	20	8	4	2	0.8	0.4
Molinate	100	50	20	10	5	2	1
Bispyribac-sodium	40	20	8	4	2	0.8	0.4
Halosulfuron-methyl	200	100	40	20	10	4	2
Propiconazole	40	20	8	4	2	0.8	0.4
Thiobencarb	5	2.5	1	0.5	0.25	0.1	0.05
Triclopyr	100	50	20	10	5	2	1
Surrogate Spike							
Simazine-d10	50	25	10	5	2.5	1	0.5
2,4,5-T-d4	100	50	20	10	5	2	1

Appendix 1: Method Detection Limit Study

Analyte	Orthosulfamuron	Penoxsulam	Clomazone	Propanil	Bensulfuron-methyl	Molinate	Bispyribac	Halosulfuron-methyl	Propiconazole	Thiobencarb	Triclopyr
CAS#	213464-77-8	219714-96-2	81777-89-1	71-23-8	83055-99-6	2212-67-1	125401-92-5	100784-20-1	60207-90-1	28249-77-6	55335-06-3
Spike, ug/L	0.03200	0.00400	0.00080	0.00200	0.00400	0.00400	0.00160	0.00800	0.00160	0.00080	0.00400
MDL1	0.01612	0.00431	0.00090	0.00186	0.00418	0.00519	0.00154	0.00840	0.00135	0.00079	0.00457
MDL2	0.02467	0.00446	0.00100	0.00157	0.00452	0.00516	0.00155	0.00881	0.00181	0.00107	0.00505
MDL3	0.02530	0.00456	0.00094	0.00151	0.00468	0.00440	0.00154	0.00919	0.00179	0.00085	0.00542
MDL4	0.02443	0.00511	0.00080	0.00177	0.00466	0.00415	0.00156	0.00917	0.00199	0.00098	0.00554
MDL5	0.01670	0.00444	0.00097	0.00157	0.00421	0.00505	0.00159	0.00858	0.00180	0.00072	0.00495
MDL6	0.01693	0.00474	0.00082	0.00159	0.00446	0.00457	0.00168	0.00840	0.00179	0.00112	0.00520
MDL7	0.02036	0.00413	0.00095	0.00154	0.00445	0.00496	0.00173	0.00919	0.00177	0.00069	0.00493
MDL8	0.01808	0.00439	0.00093	0.00148	0.00426	0.00523	0.00148	0.00921	0.00185	0.00067	0.00455
Std. Dev.	0.0039	0.0003	0.0001	0.0001	0.0002	0.0004	0.0001	0.0004	0.0002	0.0002	0.0004
MDL, ug/L	0.0118	0.0009	0.0002	0.0004	0.0006	0.0012	0.0002	0.0011	0.0005	0.0005	0.0011
RL , ug/L	0.1	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05

Appendix 2: Method Validation

Sample Name	Orthosulfamuron %	Penoxsulam %	Clomazone %	Propanil %	Bensulfuron-methyl %	Molinate %	Bispyribac %	Halosulfuron-methyl %	Propiconazole %	Thiobencarb %	Triclopyr %
2RL	0.020 ug/L	0.01 ug/L	0.01 ug/L	0.01 ug/L	0.01 ug/L	0.01 ug/L	0.01 ug/L	0.01 ug/L	0.01 ug/L	0.01 ug/L	0.01 ug/L
L-114-13_2RL_LCS1	139.03	120.82	114.79	121.94	126.64	117.40	104.58	117.33	126.92	105.07	119.38
L-114-13_2RL_LCS2	128.31	106.49	101.21	110.83	114.27	104.21	91.54	104.34	114.83	91.02	109.11
L-114-13_2RL_LCS3	106.20	98.12	95.99	104.16	106.43	99.44	88.60	102.52	111.30	85.44	102.92
L-114-13_2RL_LCS4	138.62	99.48	99.92	109.14	110.56	107.15	102.86	101.98	120.78	92.71	110.72
L-114-13_2RL_LCS5	61.61	83.40	84.09	91.07	90.90	89.19	73.27	86.56	99.40	71.84	91.51
Average	115	102	99.2	107	110	103	92.2	103	115	89.2	107
StdDev	32.6	13.6	11.0	11.2	13.0	10.3	12.6	10.9	10.4	12.1	10.3
CV(%)	28.4	13.4	11.1	10.4	11.8	10.0	13.7	10.7	9.06	13.5	9.7
5RL	0.05 ug/L	0.025 ug/L	0.025 ug/L	0.025 ug/L	0.025 ug/L	0.025 ug/L	0.025 ug/L	0.025 ug/L	0.025 ug/L	0.025 ug/L	0.025 ug/L
L-114-13_5RL_LCS1	99.07	94.21	98.32	103.44	102.70	103.85	88.66	102.37	115.98	91.32	101.54
L-114-13_5RL_LCS2	102.48	93.22	95.83	101.04	101.84	101.13	89.41	100.62	113.52	88.55	105.85
L-114-13_5RL_LCS3	85.26	82.64	85.14	87.56	88.59	87.71	76.07	87.08	101.69	75.12	93.74
L-114-13_5RL_LCS4	90.46	86.21	91.09	96.22	93.25	97.42	86.11	93.19	104.78	85.58	98.24
L-114-13_5RL_LCS5	116.50	92.85	100.42	107.12	99.61	107.89	94.08	108.48	119.51	98.76	110.19
Average	99	90	94	99	97	100	87	98	111	88	102
StdDev	12.0	5.1	6.1	7.6	6.1	7.7	6.7	8.3	7.6	8.6	6.4
CV(%)	12.2	5.7	6.5	7.6	6.2	7.7	7.7	8.5	6.8	9.8	6.3
10RL	0.10 ug/L	0.05 ug/L	0.05 ug/L	0.05 ug/L	0.05 ug/L	0.05 ug/L	0.05 ug/L	0.05 ug/L	0.05 ug/L	0.05 ug/L	0.05 ug/L
L-114-13_10RL_LCS1	82.84	79.36	83.38	87.47	85.14	87.55	84.58	85.08	97.11	78.84	89.12
L-114-13_10RL_LCS2	90.58	81.77	85.41	93.67	87.71	92.81	86.89	92.89	102.38	85.89	97.73
L-114-13_10RL_LCS3	76.03	69.03	69.58	70.87	72.42	72.86	71.40	71.76	82.84	60.21	73.71
L-114-13_10RL_LCS4	94.43	82.14	87.72	94.97	89.43	97.46	89.92	96.11	105.13	91.80	104.24
L-114-13_10RL_LCS5	90.99	77.92	84.30	90.86	83.42	90.82	85.33	88.52	100.02	84.53	95.99
Average	87	78	82	88	84	88	84	87	97	80	92
StdDev	7.4	5.3	7.2	9.8	6.7	9.3	7.1	9.4	8.7	12.1	11.6
CV(%)	8.6	6.8	8.7	11.2	8.0	10.6	8.5	10.9	8.9	15.1	12.6
20RL	0.20 ug/l	0.10 ug/L	0.10 ug/L	0.10 ug/L	0.10 ug/L	0.10 ug/L	0.10 ug/L	0.10 ug/L	0.10 ug/L	0.10 ug/L	0.10 ug/L
L-114-13_20RL_LCS1_1/10	73.78	62.79	69.24	81.09	69.10	79.93	72.60	81.44	88.67	71.22	89.93
L-114-13_20RL_LCS2_1/10	57.21	68.76	75.90	88.35	75.49	85.34	79.66	81.75	95.67	79.19	92.92
L-114-13_20RL_LCS3_1/10	69.53	68.49	75.20	88.33	73.85	87.61	77.43	82.66	96.94	80.33	93.99
L-114-13_20RL_LCS4_1/10	52.88	69.89	77.76	93.92	77.38	91.39	80.97	86.89	101.32	83.29	101.44
L-114-13_20RL_LCS5_1/10	51.09	77.20	86.64	102.11	85.10	100.87	91.63	96.17	110.11	90.90	108.83
Average	61	69	77	91	76	89	80	86	99	81	97
StdDev	10.2	5.1	6.3	7.8	5.9	7.8	7.0	6.2	7.9	7.1	7.7
CV(%)	16.7	7.4	8.2	8.6	7.7	8.8	8.7	7.2	8.0	8.8	7.9
100RL	1.00 ugL	0.50 ug/L	0.50 ug/L	0.50 ug/L	0.50 ug/L	0.50 ug/L	0.50 ug/L	0.50 ug/L	0.50 ug/L	0.50 ug/L	0.50 ug/L
L-114-13_100RL_LCS1_1/20	107.61	86.92	100.20	110.94	97.51	110.58	101.95	108.53	123.28	103.90	117.49
L-114-13_100RL_LCS2_1/20	92.42	79.22	87.97	98.31	85.10	99.87	89.66	94.23	109.73	88.24	101.25
L-114-13_100RL_LCS3_1/20	86.02	79.89	91.62	102.05	88.96	101.05	94.59	99.56	114.65	93.58	103.73
L-114-13_100RL_LCS4_1/20	75.55	79.97	89.71	95.97	88.15	98.50	90.77	94.50	111.04	83.83	98.64
L-114-13_100RL_LCS5_1/20	86.67	78.01	89.08	99.93	84.22	99.46	88.91	96.65	109.28	91.27	105.96
Total Average	90.21	83.95	88.82	97.25	91.11	96.46	87.26	94.45	107.08	86.10	100.73
Total SD	23.92	13.13	10.71	10.79	13.83	10.02	8.96	10.33	10.71	10.10	9.79
UCL	162.0	123.3	120.9	129.6	132.6	126.5	114.1	125.4	139.2	116.4	130.1
UWL	138.1	110.2	110.2	118.8	118.8	116.5	105.2	115.1	128.5	106.3	120.3
LWL	42.36	57.70	67.40	75.68	63.45	76.43	69.34	73.79	85.66	65.90	81.15
LCL	18.44	44.58	56.69	64.90	49.61	66.41	60.38	63.46	74.95	55.81	71.37

Appendix 3: Storage Stability

Day	Simazine-d10	Penoxsulam	Clomazone	Propanil	nsulfuron-met	Molinate	Bispyribac	Halosulfuron-methyl	Propiconazole	Thiobencarb	MCPA	Triclopyr	2,4,5-T-d4
0	91.7	82.5	93.2	80.6	100	72.7	87.0	96.4	81.6	74.4	76.7	80.0	86.4
	109	97.1	111	97.6	120	88.7	107	114	97.9	96.2	96.5	103	110
	112	99.9	113	100	124	90.8	110	118	101	98.6	98.0	105	115
Average	104.2	93.2	105.7	92.8	114.7	84.1	101.1	109.3	93.4	89.7	90.4	96.2	103.8
StdDev	10.8	9.4	10.9	10.7	12.8	9.9	12.3	11.3	10.3	13.3	11.9	14.1	15.3
CV%	10.4	10.0	10.3	11.5	11.2	11.8	12.2	10.3	11.0	14.9	13.2	14.7	14.7
2	93.1	86.3	98.5	84.7	106	76.7	92.7	98.3	86.1	81.5	82.0	86.4	86.9
	99.4	92.7	107	91.8	113	85.3	102	108	95.5	91.2	93.1	95.9	97.9
	90.0	87.0	101	84.0	109	79.3	92.8	99.1	89.6	90.9	87.1	89.9	92.0
Average	94.2	88.7	102.0	86.8	109.6	80.4	95.9	101.9	90.4	87.9	87.4	90.7	92.3
StdDev	4.8	3.5	4.3	4.3	3.4	4.4	5.5	5.6	4.8	5.5	5.6	4.8	5.5
CV%	5.1	3.9	4.2	4.9	3.1	5.4	5.7	5.5	5.3	6.3	6.4	5.3	6.0
5	110	97.0	115	101	121	94.4	111	115	100	108	99.5	107	114
	105	92.4	109	98.0	115	87.6	103	108	93.4	93.7	93.5	97.2	102
	108	94.3	110	101	121	88.6	107	112	98.5	106	96.4	102	108
Average	107.4	94.5	111.6	100.3	119.2	90.2	107.0	111.5	97.3	102.5	96.5	102.0	107.7
StdDev	2.8	2.3	3.2	2.0	3.5	3.7	3.7	3.7	3.5	7.7	3.0	5.0	5.9
CV%	2.6	2.5	2.9	2.0	2.9	4.1	3.4	3.3	3.6	7.5	3.1	4.9	5.5
7	103	84.5	95.3	85.4	105	77.9	91.6	95.4	86.4	82.8	88.8	89.6	101
	107	88.0	102	90.4	108	82.8	92.0	99.2	89.1	92.4	89.1	92.2	102
	96.2	83.7	97.4	86.4	103	77.2	90.4	94.5	86.6	87.7	87.1	89.5	93.8
Average	102.3	85.4	98.2	87.4	105.5	79.3	91.3	96.4	87.4	87.6	88.3	90.5	99.2
StdDev	5.7	2.3	3.3	2.6	2.8	3.1	0.8	2.5	1.5	4.8	1.1	1.6	4.7
CV%	5.5	2.7	3.4	3.0	2.6	3.9	0.9	2.6	1.7	5.5	1.2	1.7	4.7
15	112	89.4	104	89.3	113	83.1	101	103	94.5	82.9	94.2	96.6	114
	104	88.7	106	89.1	115	82.0	100	105	95.1	82.0	97.6	101	109
	103	87.3	101	88.6	110	80.2	99.4	100	91.1	81.7	91.7	94.2	105
Average	106.2	88.5	103.9	89.0	112.8	81.8	100.3	102.4	93.6	82.2	94.5	97.3	109.4
StdDev	4.9	1.1	2.4	0.4	3.0	1.5	0.9	2.1	2.2	0.6	3.0	3.5	4.5
CV%	4.6	1.2	2.3	0.4	2.7	1.8	0.9	2.1	2.3	0.8	3.1	3.6	4.1
21	115	90.2	103	83.2	112	94.8	94.5	94.9	93.5	83.4	93.3	93.6	106
	99.5	84.2	95.3	77.0	101	87.1	87.6	86.5	86.7	76.7	88.6	85.0	91.6
	106	90.1	103	81.1	111	88.2	94.1	92.3	91.2	77.7	92.7	90.2	96.0
Average	106.7	88.2	100.4	80.4	107.8	90.0	92.1	91.2	90.4	79.3	91.5	89.6	98.0
StdDev	7.6	3.4	4.4	3.2	6.0	4.2	3.9	4.3	3.5	3.6	2.6	4.3	7.6
CV%	7.1	3.9	4.4	3.9	5.6	4.6	4.2	4.8	3.8	4.6	2.8	4.8	7.7
28	91.2	91.2	93.0	89.1	114	86.1	95.5	86.2	97.2	89.9	101	98.0	102
	101	105	104	98.0	127	96.2	106	95.4	108	95.9	111	104	108
	90.3	96.0	96.1	92.0	121	90.9	97.8	90.5	101	93.4	107	103	105
Average	94.3	97.3	97.9	93.0	120.4	91.1	99.8	90.7	102.0	93.1	106.5	101.8	105.0
StdDev	6.2	6.8	5.9	4.5	6.5	5.1	5.6	4.6	5.3	3.0	4.7	3.3	2.9
CV%	6.6	7.0	6.0	4.9	5.4	5.6	5.7	5.0	5.2	3.2	4.5	3.3	2.8
35*	82.3	89.3	86.7	82.8	103	92.5	87.6	61.3	90.0	28.7	96.2	90.2	82.3
	80.2	88.0	86.4	80.6	102	90.4	87.2	59.8	87.8	26.2	99.4	93.3	83.7
	81.0	83.4	82.7	77.9	96.6	90.2	84.0	57.4	84.8	29.7	97.5	90.8	86.8
Average	81.1	86.9	85.3	80.4	100.6	91.0	86.3	59.5	87.5	28.2	97.7	91.4	84.3
StdDev	1.1	3.1	2.2	2.4	3.4	1.2	2.0	2.0	2.6	1.8	1.6	1.6	2.3
CV%	1.3	3.6	2.6	3.0	3.4	1.4	2.3	3.3	3.0	6.4	1.7	1.8	2.7
42	92.6	92.5	91.5	84.6	119	81.4	97.5	91.6	95.6	88.4	109	101	106
	95.9	92.4	91.9	85.9	119	81.4	98.5	91.5	96.5	89.8	116	105	112
	93.9	93.2	93.0	84.9	122	83.3	98.4	91.0	98.3	91.8	110	101	105
Average	94.1	92.7	92.1	85.1	120.1	82.0	98.1	91.4	96.8	90.0	111.8	102.5	107.8
StdDev	1.6	0.4	0.7	0.7	1.5	1.1	0.5	0.3	1.4	1.7	3.3	2.3	4.0
CV%	1.7	0.5	0.8	0.8	1.2	1.3	0.6	0.4	1.4	1.9	3.0	2.3	3.7
49	95.2	107	94.1	83.1	126	87.4	89.7	74.3	89.1	90.8	84.5	97.7	109
	91.7	107	92.4	82.2	126	86.5	84.7	70.8	87.2	88.8	79.5	95.0	104
	87.5	105	91.7	82.3	126	86.2	85.3	71.0	87.4	87.7	80.1	92.8	97.0
Average	91.4	106.3	92.7	82.5	126.0	86.7	86.5	72.1	87.9	89.1	81.4	95.2	103.3
StdDev	3.9	1.1	1.2	0.5	0.2	0.6	2.7	2.0	1.1	1.6	2.7	2.5	6.1
CV%	4.2	1.0	1.3	0.6	0.1	0.7	3.2	2.7	1.2	1.8	3.3	2.6	5.9

* See Discussion.

Table 2: Corrective Actions

QC TYPE	CONTROL	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Batch	Unit of sample processing.	Up to 20 samples of similar matrix, same reagents, equipment, techniques.	Batch is comprised of 20 or fewer field samples.	Include additional controls during processing or reextract.
Method blank.	Indicator of contamination that may be introduced by reagents, equipment during processing.	Every batch.	Must be less than reporting limit or project requirements, whichever is more stringent.	Reanalyze blank to confirm result. Evaluate impact on sample results. Re-extract affected samples as needed.
LCS	Accuracy and recovery of target analytes from a clean, lab matrix.	Every batch.	Must be within control limits.	Reanalyze LCS to confirm result. Evaluate impact on sample results. Low recoveries require re-extraction of the batch.
LCS Duplicate	Accuracy and reproducibility of target analyte recovery in a clean lab matrix	Every batch where a MS/MSD is not processed.	Recoveries must be within control limits. RPD must be within control limits.	Reanalyze LCSD to confirm result. Evaluate impact on sample results. Low recoveries require re-extraction of the batch.
MS	Accuracy and recovery of target analytes in a field sample.	Every batch (assumes sufficient sample).	Recoveries should be within control limits.	Reanalyze MS to confirm result. Review against LCS.
MSD	Accuracy and reproducibility of target analytes in a field sample.	Every batch (assumes sufficient sample).	Recoveries should be within control limits. RPD should be within control limits.	Reanalyze MSD to confirm result. Review against LCS/LCSD.
CRM	Accuracy and recovery of target analytes from a well-characterized matrix.	Every batch as directed by project if commercially available.	Recoveries should be within limits as defined by the project.	Reanalyze CRM to confirm result. Compare against LCS recoveries. Consistent failure requires reextraction of the batch.
Surrogates	Accuracy and recovery of chemically similar compounds in field samples.	Every sample.	Should be within limits.	Reanalyze sample to confirm result. Review against LCS.
ICV/CCV	Instrument drift.	After multipoint calibration, prior to sample analysis after every 10 samples, and end of run.	$\pm$ 20% from expected concentration.	If exceeds acceptance criteria, verify that the standard was not mis-injected, then review bracketed sample results. If CCV response is higher than expected, reanalyze samples with positive detections and surrogate failures. Analyze samples back to the last acceptable CCV. Document decisions with reported results. Recalibrate if ICV/CCV fails.
Internal standard	Instrument drift, matrix effects.	Every sample, standard, and QC.	Factor of 2x of the initial calibration average.	Guideline to assist analyst in troubleshooting. Reanalyze if needed.