

# **Analysis of S-Metolachlor, Metolachlor Ethanesulfonic Acid, Metolachlor Oxanilic Acid, Deschloro Metolachlor, and Hydroxy Metolachlor in Groundwater**

## **1. Scope:**

This Section Method provides stepwise procedures for the analysis of S-metolachlor, metolachlor ethanesulfonic acid (ESA), metolachlor oxanilic acid (OXA), deschloro metolachlor, and hydroxy metolachlor in groundwater. It is followed by all authorized Environmental Analysis Section personnel.

## **2. Principle:**

A 50 mL aliquot of groundwater is passed through an Oasis HLB solid phase extraction (SPE) cartridge (0.2 g). The cartridge is rinsed with water and the analytes are eluted with methanol. The methanol is evaporated at ~45 °C with a gentle stream of nitrogen to approximately 0.4 mL. The volume of extract is adjusted to 0.5 mL with methanol, then 0.5 mL of water is added making the final extract volume 1.0 mL. The sample extract is then analyzed by liquid chromatography tandem mass spectrometry (LC/MS/MS).

## **3. Safety:**

- 3.1 Read the Safety Data Sheet for all materials before use.
- 3.2 All general laboratory safety rules for sample preparation and analysis shall be followed.
- 3.2 Methanol is a flammable and toxic solvent. It should be handled with care in a ventilated area.
- 3.4 Special storage, use, handling and disposal procedures are necessary to ensure safety when using compressed gases.

## **4. Interferences:**

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

## 5. Apparatus and Equipment:

- 5.1 Balance (Mettler PC 4400 or equivalent)
- 5.2 Visiprep Solid Phase Extraction Vacuum Manifold (Supelco, Cat# 913-0445)
- 5.3 Visiprep Large Volume Sampler (Supelco, Cat# 57275)
- 5.4 Graduated conical test tubes, 15 mL, calibrated for 1 mL
- 5.5 Nitrogen Evaporator (Organomation, Model 112)
- 5.6 Vortex mixer (Fisher Scientific, Model Vortex-Genie 2)
- 5.7 Liquid Chromatography system with autosampler and column oven (Shimadzu)

## 6. Reagents and Supplies:

- 6.1 S-Metolachlor CAS# 87392-12-9
- 6.2 Metolachlor ESA CAS# 171118-09-5
- 6.3 Metolachlor OXA CAS# 152019-73-3
- 6.4 Deschloro Metolachlor CAS# 126605-22-9
- 6.5 Hydroxy Metolachlor CAS# 51218-45-2
- 6.6 Methanol, nanograde or equivalent pesticide grade
- 6.7 Water, MS grade, Burdick & Jackson or equivalent
- 6.8 Formic acid, HPLC grade
- 6.9 Ammonium formate 1.0 M
- 6.10 Disposable Pasteur pipettes, and other laboratory ware as needed
- 6.11 Solid Phase Extraction Cartridge (Waters, Oasis HLB 0.2 g 6cc)
- 6.12 Recommended UPLC analytical column:

6.12.1 Waters Acquity BEH C18 1.7  $\mu\text{m}$ , 2.1 x 100 mm column or equivalent

6.13 Aqueous Solution: For 500 mL, mix  $470 \pm 2$  mL water,  $25 \pm 0.5$  mL methanol,  $4.50 \pm 0.25$  mL 1 M ammonium formate and  $0.5 \pm 0.05$  mL formic acid.

6.14 Organic Solution: For 500 mL, mix  $450 \pm 2$  mL methanol and  $45 \pm 0.5$  mL water with  $4.50 \pm 0.25$  mL 1 M ammonium formate and  $0.5 \pm 0.05$  mL formic acid.

## 7. Standards Preparation:

7.1 Stock mixes of 0.1 mg/mL are obtained from an ISO 17034 accredited commercial supplier (such as Restek).

7.2 The stock mixes are diluted to 10  $\mu\text{g/mL}$  with methanol. The combination standard at 10  $\mu\text{g/mL}$  is serially diluted with methanol to produce the following concentrations: 0.00125, 0.0025, 0.005, 0.01, 0.025, 0.05, 0.10, 0.25, 0.5 and 1.0  $\mu\text{g/mL}$  in 1:1 water/methanol 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.

## 8. Sample Preservation and Storage:

8.1 Check and record sample temperature upon arrival.

8.2 Store all samples in locked designated area in the walk-in refrigerator ( $4 \pm 3$   $^{\circ}\text{C}$ ).

8.3 Return samples to the refrigerator immediately after subsample is taken.

8.4 Sample extracts shall be stored in the refrigerator ( $4 \pm 3$   $^{\circ}\text{C}$ ).

## 9. Test Sample Preparation:

### 9.1 Background Preparation:

The Department of Pesticide Regulation provides the background control groundwater for the blank and matrix spike samples.

#### 9.1.1 Blank

Thoroughly mix background groundwater before weighing out  $50 \pm 0.1$  grams into a beaker. Proceed to step 9.2.2 of section 9.2.

#### 9.1.2 Matrix Spike

Thoroughly mix background groundwater before weighing out  $50 \pm 0.1$  grams into a beaker. Fortify at the level requested by client and mix well to ensure that the pesticides are distributed. Allow the spiked background to sit for approximately 15 minutes before proceeding to step 9.2.2 of section 9.2.

### 9.2 Test Sample Extraction:

9.2.1 Remove sample(s) from the refrigerator and allow them to reach ambient temperature.

9.2.2 Measure  $50 \pm 0.1$  grams of the sample into a beaker.

9.2.3 Set up a 24-channel solid phase extraction (SPE) vacuum manifold.

9.2.4 Connect an Oasis HLB 0.2 g 6cc cartridge to each channel and label with sample I.D.'s. Turn off the unused channels of the manifold. Pre-condition the SPE columns by passing 10 mL of methanol by gravity, followed by 20 mL of water (HPLC grade) by applying vacuum (10-15 in.Hg). Do not allow the column to go dry. After conditioning turn off the vacuum, refill the HLB cartridge with water, then attach SPE adapters and reservoirs to each cartridge.

9.2.5 Transfer each sample to the corresponding SPE reservoir and begin applying vacuum.

9.2.6 As soon as the sample has passed through the cartridge, rinse the beaker with 10 mL of water (HPLC grade), add it to the

reservoir, and continue the extraction until all the rinse has passed through the cartridges. Make sure all the cartridges are properly labeled before disconnecting them.

- 9.2.7 Remove the SPE adapter and reservoir. Apply vacuum (approximately 15 in. Hg) for at least 5 minutes to allow excess water to be removed.
- 9.2.8 Elute the cartridges with 10 mL methanol and collect into a 15 mL graduated conical test tube.
  - 9.2.8.1 Evaporate the eluant in a water bath at  $40 \pm 2$  °C with a gentle stream of nitrogen to approximately 0.4 mL.
  - 9.2.8.2 The volume of extract is adjusted to 0.5 mL with methanol, then 0.5 mL of water is added making the final extract volume 1.0 mL.
- 9.2.9 Transfer the entire content to a Waters total recovery or equivalent autosampler vial.
- 9.2.10 If necessary, dilute the final extract of sample with 1:1 methanol:water to be within the calibration curve range.

## 10. Instrument Calibration:

- 10.1 The calibration standard curve consists of a minimum of three levels. The recommended concentration levels of standards are 0.00125, 0.0025, 0.005, 0.01, 0.025, 0.05 and 0.1 ug/mL.
- 10.2 The calibration standard curve is analyzed before and after each sample set.
- 10.3 Calibration is obtained using a linear or quadratic regression with a correlation coefficient (r) equal to or greater than 0.995.

## 11. Analysis:

### 11.1 Injection Scheme

The instrument may need to be conditioned with a matrix blank or standards prior to analyzing the following suggested sequence:

#### 11.1.1 Standard Curve

11.1.2 Solvent Blank

11.1.3 Matrix Blank

11.1.4 Matrix Spike

11.1.5 Test Samples (maximum of 20)

11.1.6 Standard Curve

11.1.7 Repeat the order for the second injection as needed.

## 11.2 LC/MS/MS System

### 11.2.1 LC/MS/MS Instrument:

11.2.1.1 LC Controller: Shimadzu CBM20A

11.2.1.2 LC Pumps: Shimadzu LC30AD

11.2.1.3 Autosampler: Shimadzu SIL30AC

11.2.1.4 Column Oven: Shimadzu CTO30A

11.2.1.5 Column: Waters Acquity BEH C18 1.7  $\mu\text{m}$ , 2.1 x 100 mm or equivalent.

11.2.1.6 Column Temperature: 40 °C

11.2.1.7 Mobile Phase:

11.2.1.7.1 Solvent 1: Aqueous Solution (94% H<sub>2</sub>O, 5% MeOH, 0.95% Ammonium Formate (1M), 0.1% Formic Acid)

11.2.1.7.2 Solvent 2: Organic Solution (90% MeOH, 9% H<sub>2</sub>O, 0.9% Ammonium Formate (1M), 0.1% Formic Acid)

11.2.1.8 Gradient: See Table 1

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

Time (min)	Flow Rate (mL/min)	Solvent 1	Solvent 2
0.0	0.4	95	5
0.50	0.4	90	10
1.0	0.4	90	10
5.0	0.4	10	90
8.50	0.4	10	90
8.60	0.4	90	10

11.2.1.9 Injection Volume: 3.0  $\mu$ L

11.2.2 Mass Spectrometer and Operating Parameters:

11.2.2.1 Model: ABSciex QTRAP 6500 or 6500+

11.2.2.2 Ionization: Electrospray Ionization (ESI)

11.2.2.3 Polarity: Positive

11.2.2.4 Curtain Gas: 20

11.2.2.5 Ion Spray Voltage: 5500

11.2.2.6 Source Temperature: 500

11.2.2.7 Ion Source Gas 1: 50

11.2.2.8 Ion Source Gas 2: 50

11.2.2.9 Collision Gas: Medium

11.2.2.10 Electron Multiplier: 2300 V

11.2.2.11 Scheduled MRM: No

**Table 2 – LC/MS/MS Instrument Conditions**

<b>Compound</b>	<b>RT</b>	<b>Precursor Ion</b>	<b>Product Ion <sup>1</sup></b>	<b>De-Clustering Potential</b>	<b>Collision Energy</b>	<b>Entrance Potential</b>	<b>Exit Potential</b>
S-Metolachlor	5.99	283.957	<b>251.9</b>	41	19	10	30
		283.957	176.0	41	33	10	22
Metolachlor ESA	4.97	329.943	<b>298.0</b>	71	19	10	10
		329.943	202.1	71	37	10	16
Metolachlor OXA	5.00	279.953	<b>248.0</b>	21	19	10	8
		279.953	90.9	21	65	10	10
Deschloro Metolachlor	5.89	250.100	<b>176.3</b>	40	34	10	10
		250.100	218.1	35	21	10	15
Hydroxy Metolachlor	5.54	266.100	<b>176.2</b>	36	37	10	10
		266.100	234.1	41	29	10	12

<sup>1</sup> Quantitation transition is in bold

## 12. Quality Control:

### 12.1 SPE Cartridge Verification

SPE cartridges are verified per lot number to ensure they meet the manufacturer specifications.

### 12.2 Method Detection Limit (MDL)

Method Detection Limit (MDL) refers to the lowest concentration of each analyte that a method can detect reliably. To determine the MDL, 7 control groundwater samples were spiked at 0.05 ppb 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 metolachlor and its metabolites 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 ( $n - 1$ ,  $1 - \alpha = 0.99$ ) and  $S$  denotes the standard deviation obtained from  $n$  replicate analyses. For the  $n = 7$  replicates used to determine the MDL,  $t = 3.143$ .

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

### 12.3 Reporting Limit

Reporting limit (RL) refers to a level at which reliable quantitative results may be obtained. The MDL is used as a guide to determine the RL. The reporting limits for metolachlor and its metabolites are 0.05 ppb. This reporting limit was chosen after considering matrix effects.

### 12.4 Method Validation Recovery Data

The method validation consisted of 5 sample sets. Each set included five levels of fortification (0.1, 0.25, 0.5, 1.25 and 2.5 ppb) and a method blank. All spikes and method blanks were processed through the entire analytical method.

Recoveries for metolachlor and its metabolites are tabulated in Appendix II.

### 12.5 Control Charts and Limits

Control charts were generated using the data from the method validation. The upper and lower warning and control limits are set at  $\pm 3$  standard deviations of the % recovery and were within 50-150% with the exception of metolachlor OXA, which exhibited marginal performance. The control limits are shown in Appendix II.

### 12.6 Acceptance Criteria

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

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

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

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

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

12.6.4 The sample shall be diluted if results exceed the calibration curve.

12.6.5 The standard curves at the beginning and end of each sample set should not have a percent change greater than 20%. The % change in response is calculated as follows:

$$\% \text{ Change in Response} = \frac{(\text{absolute value of } [\text{response of STD curve before} - \text{response of STD curve after}])}{(\text{response STD curve before})} * 100$$

12.6.6 The R<sup>2</sup> of each calibration curve shall be greater than 0.990.

12.6.7 The relative abundance or ratio of selective ions shall be within ± 30% of the standard.

12.6.8 When the above criteria are met, the analyst may report the average of the two injections.

## 12.7 Storage stability Study

A storage stability study was done with this project. The storage stability study consisted of a 0.5 ppb spike level and 3 replicates over a 28-day period. Three glass bottles containing background groundwater were spiked and stored in the refrigerator until analyzed on day 0, 2, 4, 7, 14, 21 and 28. A matrix blank and a matrix spike (0.15 ppb) were also extracted along with the storage spikes. This storage stability study showed all analytes have storage stability through day 28. The results are shown in Appendix III.

## 13. Calculations:

13.1 Quantitation is based on external standard (ESTD) calculation using either the peak area or height. The LC/MS/MS software uses quadratic curve fit with all levels weighted 1/x. Alternatively, at the analyst's discretion,

concentrations may be calculated using the response factor for the standard whose value is closest to the level in the sample.

- 13.2 Calculate the concentration of the analyte(s) of a sample as follows:

$$\text{ppb} = \frac{(\text{sample peak area or ht})(\text{STD conc})(\text{STD vol. injected})(\text{final vol. of sample})(1000)}{(\text{STD peak area or ht})(\text{sample vol. injected})(\text{sample weight } g)}$$

#### 14. Reporting Procedure:

Sample results are reported accordance with the client's analytical laboratory specification sheets.

#### 15. Discussion:

- 15.1 This method was adapted from the method listed in the references below.

#### 16. References:

- 16.1 Vryzas Z', Tsaboula A, Papadopoulou-Mourkidou E.J. Determination of alachlor, metolachlor, and their acidic metabolites in soils by microwave-assisted extraction (MAE) combined with solid phase extraction (SPE) coupled with GC-MS and HPLC-UV analysis.
- 16.2 Y.H. Long, R.T. Li, X.M. Wu, Degradation of S-metolachlor in soil as affected by environmental factors, Journal of soil science and plant nutrition, version On-line ISSN 0718-9516.
- 16.3 Method of Analysis by the U.S. Geological Survey Organic Geochemistry Research Group-Update and Additions to the Determination of Chloroacetanilide Herbicide Degradation Compounds in Water Using High-Performance Liquid Chromatography/Mass Spectrometry.
- 16.4 E.A. Lee, J.L. Kish, L.R. Zimmerman, and E.M. Thurman, U.S. Department of the Interior, U.S. Geological Survey. Open-File report 01-10.
- 16.5 Determination of Metolachlor (CGA-24705) and CGA-77102, and their Degradates CGA-50212, CGA-354743, CGA-380168, CGA-37735, CGA-67125, and CGA-41638 in Water by High Performance Liquid Chromatography with Mass Spectrometric Detection Including Validation Data.

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16.6 Method Number: AG-682 of Novartis Crop Protection, Inc. Environmental Safety Department, Environmental Residue Studies.

## Appendix I

### Method Detection Limit Data and Reporting Limits

Compound	Blank	Set 1 (ppb)	Set 2 (ppb)	Set 3 (ppb)	Set 4 (ppb)	Set 5 (ppb)	Set 6 (ppb)	Set 7 (ppb)	SD	MDL (ppb)	RL (ppb)
S-Metolachlor	ND	0.0465	0.0455	0.0458	0.0414	0.0464	0.0451	0.0462	0.00178	0.01	0.05
Metolachlor ESA	ND	0.0531	0.0537	0.0534	0.0480	0.0522	0.0534	0.0526	0.00200	0.01	0.05
Metolachlor OXA	ND	0.0493	0.0494	0.0475	0.0427	0.0479	0.0466	0.0485	0.00229	0.01	0.05
Deschloro Metolachlor	ND	0.0452	0.0441	0.0455	0.0404	0.0460	0.0445	0.0451	0.00187	0.01	0.05
Hydroxy Metolachlor	ND	0.0474	0.0466	0.0487	0.0412	0.0489	0.0456	0.0458	0.00261	0.01	0.05

#### Definitions

**MDL** = Method Detection Limit

**ND** = Not detected

**ppb** = Part per billion

**RL** = Reporting limit

**SD** = Standard deviation

## Appendix II

### Method Validation Data and Control Limits

Analyte	Spike Level (ppb)	Day 1 Avg. Spike Recovery (%)	Day 2 Avg. Spike Recovery (%)	Day 3 Avg. Spike Recovery (%)	Day 4 Avg. Spike Recovery (%)	Day 5 Avg. Spike Recovery (%)
S-Metolachlor	0.1	83.6	91.4	90.1	91.5	83.9
S-Metolachlor	0.25	72.0	87.1	91.6	91.3	84.6
S-Metolachlor	0.5	90.2	86.4	87.1	87.9	76.5
S-Metolachlor	1.25	94.6	76.3	81.9	84.2	74.3
S-Metolachlor	2.5	79.6	76.2	87.2	89.7	69.6
Metolachlor ESA	0.1	63.1	98.6	78.5	81.7	79.2
Metolachlor ESA	0.25	72.1	98.0	79.7	82.5	84.1
Metolachlor ESA	0.5	84.7	91.6	78.7	80.9	81.6
Metolachlor ESA	1.25	83.0	98.5	73.6	78.6	75.1
Metolachlor ESA	2.5	78.4	89.8	75.5	76.4	79.4
Metolachlor OXA	0.1	70.5	89.4	61.3	67.5	65.1
Metolachlor OXA	0.25	69.7	91.8	63.2	70.9	69.5
Metolachlor OXA	0.5	79.0	90.6	65.0	82.0	70.0
Metolachlor OXA	1.25	81.4	91.3	67.5	72.5	74.1
Metolachlor OXA	2.5	70.6	80.6	69.1	72.4	65.2
Deschloro Metolachlor	0.1	77.9	82.4	85.1	84.8	78.1
Deschloro Metolachlor	0.25	63.4	81.6	85.1	84.8	85.7
Deschloro Metolachlor	0.5	82.9	75.9	85.9	88.6	70.3
Deschloro Metolachlor	1.25	90.0	73.6	82.0	84.8	76.4
Deschloro Metolachlor	2.5	72.2	73.3	85.8	85.8	79.3

<b>Analyte</b>	<b>Spike Level (ppb)</b>	<b>Day 1 Avg. Spike Recovery (%)</b>	<b>Day 2 Avg. Spike Recovery (%)</b>	<b>Day 3 Avg. Spike Recovery (%)</b>	<b>Day 4 Avg. Spike Recovery (%)</b>	<b>Day 5 Avg. Spike Recovery (%)</b>
Hydroxy Metolachlor	0.1	91.0	96.1	86.0	83.2	85.4
Hydroxy Metolachlor	0.25	85.9	96.3	85.3	83.5	88.8
Hydroxy Metolachlor	0.5	106	89.7	85.1	83.7	82.8
Hydroxy Metolachlor	1.25	107	90.5	82.6	82.8	79.9
Hydroxy Metolachlor	2.5	95.7	83.2	88.2	88.7	84.1

<b>Analyte</b>	<b>Mean Spike Recovery (%)</b>	<b>Standard Deviation</b>	<b>Lower Control Limit</b>	<b>Upper Control Limit</b>
S-Metolachlor	84.35	6.880	63.7	105
Metolachlor ESA	81.73	8.376	56.6	107
Metolachlor OXA	74.01	9.204	46.4	102
Deschloro Metolachlor	80.63	6.439	61.3	100
Hydroxy Metolachlor	88.46	6.990	67.5	109

## Appendix III

### Storage Stability Study

Analyte	Sample Type	Day 0 Spike Rec. (%)	Day 2 Spike Rec. (%)	Day 4 Spike Rec. (%)	Day 7 Spike Rec. (%)	Day 14 Spike Rec. (%)	Day 21 Spike Rec. (%)	Day 28 Spike Rec. (%)
S-Metolachlor	Blank	ND	ND	ND	ND	ND	ND	ND
S-Metolachlor	Spike	69.2	83.4	85.1	75.5	86.1	87.6	87.4
S-Metolachlor	Spike 1	78.7	86.2	72.9	79.3	74.6	87.2	81.3
S-Metolachlor	Spike 2	69.9	77.7	92.8	84.5	77.8	86.5	78.0
S-Metolachlor	Spike 3	83.6	82.5	85.5	76.1	87.0	82.3	77.5
Metolachlor ESA	Blank	ND	ND	ND	ND	ND	ND	ND
Metolachlor ESA	Spike	76.8	87.0	75.1	71.2	92.5	97.8	86.3
Metolachlor ESA	Spike 1	68.3	86.7	73.4	67.6	94.4	97.8	84.3
Metolachlor ESA	Spike 2	73.2	80.0	85.7	75.0	95.5	101	79.8
Metolachlor ESA	Spike 3	82.7	83.5	74.1	70.8	92.8	95.1	81.2
Metolachlor OXA	Blank	ND	ND	ND	ND	ND	ND	ND
Metolachlor OXA	Spike	64.4	82.4	62.9	61.4	79.8	83.8	73.9
Metolachlor OXA	Spike 1	65.5	88.8	80.3	75.9	83.5	89.7	73.7
Metolachlor OXA	Spike 2	64.4	85.0	85.9	82.0	87.3	87.9	71.2
Metolachlor OXA	Spike 3	68.6	83.3	78.9	78.0	90.0	83.9	74.1
Deschloro Metolachlor	Blank	ND	ND	ND	ND	ND	ND	ND
Deschloro Metolachlor	Spike	70.3	81.9	84.6	76.0	85.5	85.5	77.8
Deschloro Metolachlor	Spike 1	78.7	84.2	78.7	76.5	79.0	86.3	75.4
Deschloro Metolachlor	Spike 2	72.6	81.4	90.1	82.7	82.3	86.5	73.5
Deschloro Metolachlor	Spike 3	82.9	81.9	85.8	72.3	86.7	84.0	72.8



Analyte	Sample Type	Day 0 Spike Rec. (%)	Day 2 Spike Rec. (%)	Day 4 Spike Rec. (%)	Day 7 Spike Rec. (%)	Day 14 Spike Rec. (%)	Day 21 Spike Rec. (%)	Day 28 Spike Rec. (%)
Hydroxy Metolachlor	Blank	ND	ND	ND	ND	ND	ND	ND
Hydroxy Metolachlor	Spike	74.5	84.5	84.1	73.1	86.2	87.0	83.3
Hydroxy Metolachlor	Spike 1	77.7	85.6	81.3	72.9	87.4	90.7	81.9
Hydroxy Metolachlor	Spike 2	77.0	83.2	90.7	80.0	84.8	89.5	82.2
Hydroxy Metolachlor	Spike 3	86.1	83.2	85.4	73.2	88.3	84.7	80.1

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**Revision Log:**

<b>Date</b>	<b>What was revised? Why?</b>
2/4/2021	Re-validated the method using Waters HLB cartridges
	9.2.3 Switched from Sep-Pak Vac 6cc 1-gram cartridges to Waters HLB cartridges for ease of use and higher recoveries.
	9.2.7 Volume of extract adjusted to 0.5 mL with methanol and 0.5 mL of water is added for a final volume of 1 mL (MeOH/H <sub>2</sub> O 1:1) to match the solvent of the standards and diluent.
6/30/2022	Reformatted the entire document in accordance with web accessibility requirements
	Made editorial revisions throughout the document for improved readability
	Corrected grammatical errors
	7.1 The procedures for standards preparation were revised to reflect the current practice of obtaining stock mixes from ISO 17034 accredited suppliers.
	12.1 Added SPE cartridge verification
	12.6.3 Added procedures to follow when spike recoveries fall outside the control limits
1/5/2023	Updated the method to include detection of deschloro metolachlor, and hydroxy metolachlor. Sections that were updated include: Section 1 (Scope), Section 6 (Reagents and Supplies), Section 11 (Analysis), Appendix I (Method Detection Limit Data and Reporting Limits), Appendix II (Method Validation Data and Control Limits) and Appendix III (Storage Stability Study)
	Made editorial revisions throughout the document for clarification and improved readability
	Section 3 Added safety procedures
	Section 9 Procedures for sample preparation and sample extraction were revised to reflect current procedures
	Section 11 Added formula for Mobile Phase Solvent 1 and 2. Updated LC/MS/MS instrument conditions (Table 2)

	Section 12 Updated the MDL spike concentration (12.2) and method validation spike concentration (12.4). Updated the equation for calculating the % change in response (12.6.5).
	Section 15 Updated to include a discussion on the storage stability study
4/25/2023	Test sample has been identified as "Groundwater" from the earlier "Well water", per Ground water program's advice.