UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF PESTICIDE PROGRAMS
ENVIRONMENTAL CHEMISTRY LABORATORY
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September 20, 2006

MEMORANDUM

SUBJECT: Triazines - ECM0225W1-W11

FROM: Joseph Ferrario, Branch Chief
BEAD/Environmental Chemistry Laboratory

TO: Cara Dzubow ECM Gatekeeper
EISB 7507P

The EFED/Environmental Fate and Effects Division has requested an Environmental Chemistry Method Review on Atrazine, Simazine, Ametryn, Prometryn, Metolachlor and their degradates in water using the method submitted by Syngenta Crop Protection in accordance with the registration of the above metioned analytes and there degradates, MRID No.468395-02. The method and independent laboratory validation data was reviewed and the conclusions included in the attached Environmental Chemistry Method Review Report.

The following report includes an overview of the method and the method completeness, statements of adherence to EPA regulations, a presentation of results and a discussion of problems found in the registrant method and those discovered by the independent laboratory. A statement of method acceptability is also included.

If you have any questions concerning this report, please contact Elizabeth Flynt at (228) 688-2410 or me at (228) 688-3212.

Attachments
cc: Dr. Christian Byrne, QA Officer
BEAD/Environmental Chemistry Laboratory

Elizabeth C. Flynt
BEAD/ECL

2052972

Triazines in water/ECM0225W1-W11/Sygenta Crop Protection, Inc./100

ENVIRONMENTAL CHEMISTRY METHOD REVIEW REPORT

9/8/2006

Data Requirement: PMRA Data Code: NA
EPA DP Barcode: D331517
OECD Data Point: NA
EPA Guideline: ECM Method Review

Test material:
Common name: Triazines
Chemical name: Atrazine, Simazine, G-30033, G-28279, G-28273, Ametryn, Prometryn, GS-11355, GS-26831, Metolachlor
IUPAC: See Appendix A

Primary Evaluator: Elizabeth Flynt **Date:** 9/12/06
Elizabeth Flynt, Chemist

Peer Reviewer: Charles Kennedy **Date:** 9/12/06
Charles Kennedy, Chemist

QA Officer: Christian Byrne **Date:** 09/13/06
Dr. Christian Byrne, QA Officer

ANALYTICAL METHOD: 468395-02, Rolando Perez, Jerry Allen, Sung-Ben Huang, Thomas Mayer, Steven Perez, Robert Yokley, November 11, 2005, "*Analytical Method T010097-04 for the Determination of Atrazine, Simazine, G-30033, G-28279, G-28273, Ametryn, Prometryn, GS-11354, GS-11355, GS-26831, and Metolachlor in Water Using Direct Injection LC-ESI/MS/MS Including Validation Data.*" The unpublished study was conducted by ADPEN Laboratories, Inc. of Jacksonville, FL and sponsored by Syngenta Crop Protection, Inc. at 410 Swing Road Greensboro, NC. Pages 1 -119. The study is Syngenta # T010097-04.

EXECUTIVE SUMMARY

The method is applicable for the quantitative determination of residues of Atrazine, Simazine, G-30033, G-28279, G-28273, Ametryn, Prometryn, GS-11355, GS-26831, GS 11354, and Metolachlor in Water Using Direct Injection LC-ESI/MS/MS Including Validation Data. The method was created by Syngenta Crop Protection, Inc. of Greensboro, NC in accordance with EPA's Good Laboratory Practice Standards, Title 40 Code of Federal Regulations Part 160. After a thorough review the ECB finds this method and its validation data acceptable.

Method Summary: Water samples are diluted 1:5 with 5/95 (v/v) methanol/water and injected into a liquid chromatograph with detection by tandem mass spectrometery.

METHOD ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS

There is a minor discrepancy in the registrant method in the description of the sample dilution procedure in the Principle part of the registrant method on page 14. It reads, "Typically, 200 µl of water sample is mixed with 800 µl of 5/95 (v/v) methanol/H_2O in an HPLC vial"; however, on page 68, Figure 2. Flow Diagram of Method, the methanol to water ratio is "10/90 (v/v) methanol/H_2O". There is inconsistency between the ratios.

A discrepancy also existed between the registrant method and the ILV. On page 30 of the Morse Labs Project No.: ML05-1270-STN, there are no values for the method validation recoveries for ametryn, prometryn, GS-11354, GS-11355, and GS-26831 in finished water. The omission was stated as "compounds not stable in chlorinated (tap) water". Second and third validation trials for tap water, incorporating differing degassing steps to remove residual chlorine from the tap water, improved the recoveries to 68-106% and 73-111%, overall. It was concluded that "since it was highly unlikely that these compounds, unstable in chlorine-containing water, will survive in treated finished water, there was no need for their specific determination in finished water". However, Syngenta did not indicate any difficulties in the analyses of these compounds and presented data on their recoveries on pages 29-30 of its report. Since there is only a requirement to validate the method in soil and water and the registrant and independent lab validated it in ground and surface water, the lack of ILV validation data in finished water is acceptable but the discrepancy is noted.

Other than the minor discrepancies mentioned above, this is a well documented method successfully validated by the registrant and independently validated by Morse laboratories. Based on the parameters set in the Ecological Effects Test Guidelines, OPPTS 850.7100, Data Reporting for Environmental Chemistry Methods; "Public Draft." (U.S. Environmental Protection Agency. Office of Prevention, Pesticides, and Toxic Substances (7101). U.S. Government Printing Office: Washington, DC, 1996, EPA-712-C-96-348) ECB finds this method acceptable as submitted.

COMPLIANCE

Signed and dated statements that this method was conducted in accordance with the requirements for Good Laboratory Practice Standards, 40 CFR 160 were present in the method. Also present was a statement of non-confidentiality on the basis of the method falling within the scope of FIFRA Section 10 (d)(1)(A), (B), or (C).]

ENVIRONMENTAL CHEMISTRY METHOD REVIEW REPORT

9/8/2006

A. BACKGROUND INFORMATION

Give background information on the active ingredient, its mode of action, and the purpose of the end-use product (one paragraph).

TABLE A.1. Test Compound Nomenclature	
Compound Atrazine	Chemical Structure ***See Appendix A for the information in this section.**
Common name	*
Company experimental name	*
IUPAC name	*
CAS Name	*
CAS #	*

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound	
Parameter	Value
Melting point/range	*** See Appendix A1**
pH	Not provided
Density	Not provided
Water solubility (20 °C)	*
Solvent solubility (mg/ml at 20 °C)	*
Vapour pressure at _ _ °C	Not provided
Dissociation constant (pK_a)	Not provided
Octanol/water partition coefficient	Not provided
UV/visible absorption spectrum	Not provided

MATERIALS AND METHODS

B.1. Principle of Method

Samples are diluted 1 to 5 with methanol:water (5:95, v/v). The diluted samples were, without any cleanup, submitted directly to HPLC analysis. Determination and quantitation of the targeted analytes was conducted using high performance liquid chromatography (HPLC) employing electrospray ionization mass spectrometric (ESI/MS/MS) detection.

TABLE B.1.1.	**Summary Parameters for the Analytical Method Used for the Quantitation of Chemical Residues in Matrices Studied**
Method ID	ECM0225W1-W11
Analyte(s)	Atrazine, Simazine, G-30033, G-28279, Ametryn, Prometryn, GS-11354, GS-11355, GS-26831, G-28273, Metolachlor
Extraction solvent/technique	Dilution in mobile phase
Cleanup strategies	None
Instrument/Detector	LC/MS/MS

C. RESULTS AND DISCUSSION

C.1. Recovery Results Summary

TABLE C.1.1. Recovery Results from Method Validation of [matrices]			
Matrix	Spiking Level (conc. units)	% Recoveries	Relative Standard Deviation
* See Appendix B	*	*	*

C.1.2. Method Characteristics

TABLE C.1.2. Method Characteristics	
Analyte	Atrazine, Simazine, G-30033, G-28279, Ametryn, Prometryn, GS-11354, GS-11355, GS-26831
Limit of Quantitation	0.1 ppb
Limit of Detection (LOD)	0.0005 ng injected
Accuracy/Precision at LOQ	**See Appendix B**
Reliability of the Method/ [ILV]	The ILV validated the method successfully
Linearity	All analytes displayed linearity over the test range
Specificity	

C.2. Independent Laboratory Validation (ILV)

The ILV was conducted in accordance with the *OPPTS 850.7100 Guidelines.*

TABLE C.2.1. Recovery Results Obtained by an Independent Laboratory Validation of the Method for the Determination of Acequinocyl in Soil

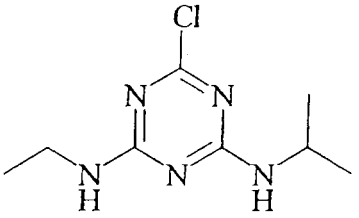
Compound	Spiking Level (ug/L)	Average Recoveries Obtained (%)	Relative Standard Deviation
* See Appendix C	*	*	*

D. CONCLUSION

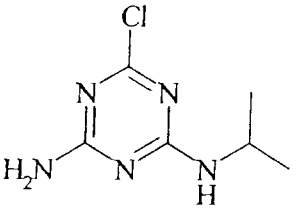
The method presented has been thoroughly studied and validated by both the registrant and the independent laboratories. It was validated in a number of different matrices successfully. ECB considers it acceptable to support the registration studies that it was used for.

Appendix A – Structure and Chemical Names of Triazines

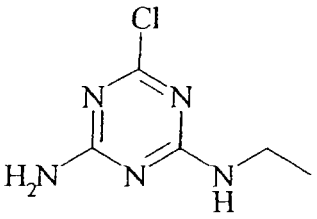
STRUCTURES OF ANALYTES



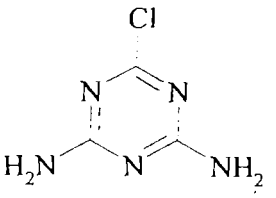
Atrazine
MW 215.7



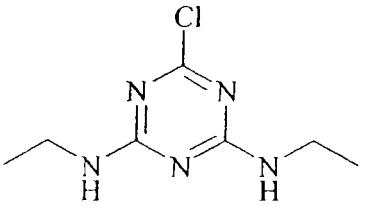
G-30033
MW 187.6



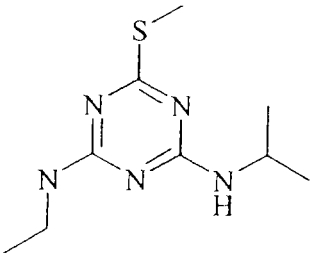
G-28279
MW 173.6



G-28273
MW 145.6

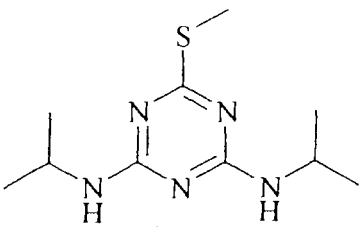


Simazine
MW 201.7

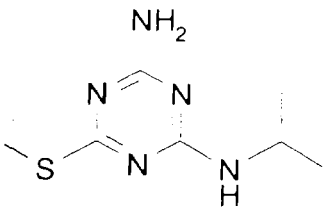


Ametryn
MW 227.3

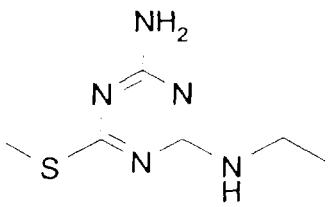
STRUCTURES OF THE ANALYTES (Continued)



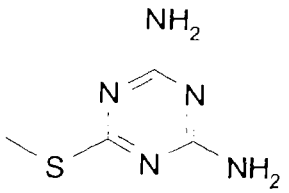
Prometryn
MW 241.4



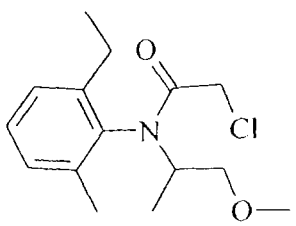
GS-11354
MW 199.1



GS-11355
MW 185.1



GS-26831
MW 157.0



Metolachlor
MW 283.8

Test and Reference Substances

Common Name:	Atrazine (G30027)
Chemical Name:	6-chloro-N^2-ethyl-N^4-isopropyl-1,3,5-triazine-2,4-diamine
CAS No.:	1912-24-9

Common Name:	G-30033
Chemical Name:	1,3,5-Triazine-2,4-diamine, 6-chloro-N-(1-methylethyl)-
CAS No.:	6190-65-4

Common Name:	G-28279
Chemical Name:	1,3,5-Triazine-2,4-diamine, 6-chloro-N-ethyl-
CAS No.:	1007-28-9

Common Name:	G-28273
Chemical Name:	1,3,5-Triazine-2,4-diamine, 6-chloro-N-ethyl-
CAS No.:	1007-28-9

Common Name:	Simazine (G-27692)
Chemical Name:	1,3,5-Triazine-2,4-diamine, 6-chloro-N,N'-diethyl-
CAS No.:	122-34-9

Common Name:	Ametryn (G-34162)
Chemical Name:	1,3,5-Triazine-2,4-diamine, 6-chloro-N,N'-diethyl-
CAS No.:	122-34-9

Common Name:	GS-11354
Chemical Name:	1,3,5-Triazine-2,4-diamine, N,N'-bis(1-methylethyl)-6-(methylthio)-
CAS No.:	7287-19-6

Common Name:	Prometryn (G-34161)
Chemical Name:	1,3,5-Triazine-2,4-diamine, N,N'-bis(1-methylethyl)-6-(methylthio)-
CAS No.:	7287-19-6

Common Name:	GS-11355
Chemical Name:	1,3,5-Triazine-2,4-diamine, N-ethyl-6-(methylthio)-
CAS No.:	4147-58-4

Common Name:	GS-26831
Chemical Name:	N/A
CAS No.:	N/A

Common Name:	Metolachlor
Chemical Name:	Acetamide, 2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)-
CAS No.:	51218-45-2

Appendix A1 – Physicochemical Properties of Triazines

Atrazine

Melting point/range	171-174°
Water solubility	70 ppm at 25°C
Solvent solubility (mg/ml at 20°C)	ether 12,000 ppm; chloroform 52,000 ppm; methanol 18,000 ppm

Prometryn

Melting point/range	118-120°C
Water solubility	48 ppm at 20°C
Solvent solubility (mg/ml at 20°C)	Stable in neutral or slightly acid or alkaline media

Metolachlor

Melting point/range	118-120°C
Water solubility	48 ppm at 20°C
Solvent solubility (mg/ml at 20°C)	Stable in neutral or slightly acid or alkaline media

Simazine

Melting point/range	226-227°C
Water solubility	Practically insoluble in water .
Solvent solubility (mg/ml at 20°C)	Slightly soluble in dioxane

Ametryn

Melting point/range	88-89°C
Water solubility	
Solvent solubility (mg/ml at 20°C)	

Appendix B - Summary of Registrant Data at LOQ

Matrix	Analyte	Spike level (ppb)	Sample size	Mean %	RSD
Surface water	Atrazine	0.10 ppb (LOQ)	5	93.4	10.43
	Simazine	0.10 ppb (LOQ)	5	103	2.04
	G-30033	0.10 ppb (LOQ)	5	100	2.3
	G-28279	0.10 ppb (LOQ)	5	98.9	2.46
	G-28273	0.10 ppb (LOQ)	5	94.1	2.11
	Metolachlor	0.10 ppb (LOQ)	5	85	17.73
	Ametryn	0.10 ppb (LOQ)	5	92	8.72
	Prometryn	0.10 ppb (LOQ)	5	89.3	9.44
	GS-11354	0.10 ppb (LOQ)	5	93.5	10.63
	GS-11355	0.10 ppb (LOQ)	5	98.1	3.25
	GS-26831	0.10 ppb (LOQ)	5	101	2.16

Matrix	Analyte	Spike level (ppb)	Sample size	Mean %	RSD
Ground water	Atrazine	0.10 ppb (LOQ)	5	108	1.68
	Simazine	0.10 ppb (LOQ)	5	102	9.15
	G-30033	0.10 ppb (LOQ)	5	110	1.29
	G-28279	0.10 ppb (LOQ)	5	108	6.55
	G-28273	0.10 ppb (LOQ)	5	99.4	5.26
	Metolachlor	0.10 ppb (LOQ)	5	91.3	5.30
	Ametryn	0.10 ppb (LOQ)	5	89.8	2.61
	Prometryn	0.10 ppb (LOQ)	5	86.1	2.10
	GS-11355	0.10 ppb (LOQ)	5	101	2.56
	GS-26831	0.10 ppb (LOQ)	5	109	2.85
	GS-11354	0.10 ppb (LOQ)	5	105	2.9

Matrix	Analyte	Spike level (ppb)	Sample size	Mean %	RSD
Finish water	Atrazine	0.10 ppb (LOQ)	5	101	2.89
	Simazine	0.10 ppb (LOQ)	5	105	3.36
	G-30033	0.10 ppb (LOQ)	5	99.9	6.60
	G-28279	0.10 ppb (LOQ)	5	104	5.20
	G-28273	0.10 ppb (LOQ)	5	106	5.30
	Metolachlor	0.10 ppb (LOQ)	5	92.5	5.11
	Ametryn	0.10 ppb (LOQ)	5	96.3	0.94
	Prometryn	0.10 ppb (LOQ)	5	96.4	2.58
	GS-11354	0.10 ppb (LOQ)	5	99.6	2.76
	GS-11355	0.10 ppb (LOQ)	5	100	3.57
	GS-26831	0.10 ppb (LOQ)	5	98.9	3.62

Appendix C – Independent Laboratory Data

Summary of Method Validation Recoveries from Surface (River) Water							
Matrix	**Analyte**	**Spike level (ppb)**	**Sample size (n)**	**Range of Recoveries (%)**	**Mean % ± std. dev.**	**RSD (%)**	**95% C.I.**
Surface (River) Water	Atrazine	0.1	5	75 - 97	87 ± 7.9	9.0	±9.8
		1.0	5	95 - 110	103 ± 6.8	6.6	±8.5
	Simazine	0.1	5	83 - 94	87 ± 4.6	5.3	±5.7
		1.0	5	92 - 102	100 ± 4.5	4.5	±5.6
	G-30033	0.1	5	77 - 98	89 ± 8.9	10	±11
		1.0	5	89 - 108	101 ± 7.4	7.3	±9.2
	G-28279	0.1	5	65 - 102	77 ± 15	19	±18
		1.0	5	83 - 98	91 ± 7.0	7.8	±8.8
	G-28273	0.5	5	86 - 111	98 ± 9.4	9.7	±12
		5.0	5	92 - 107	101 ± 5.9	5.8	±7.3
	Ametryn	0.1	5	81 - 102	91 ± 8.6	9.5	±11
		1.0	5	105 - 115	110 ± 3.6	3.3	±4.5
	Prometryn	0.1	5	92 - 108	100 ± 6.3	6.4	±7.9
		1.0	5	109 - 114	111 ± 1.9	1.7	±2.4
	GS-11354	0.1	5	86 - 101	94 ± 5.4	5.8	±6.7
		1.0	5	95 - 106	103 ± 4.4	4.3	±5.5
	GS-11355	0.1	5	84 - 92	89 ± 3.4	3.9	±4.3
		1.0	5	95 - 108	103 ± 4.8	4.7	±5.9
	GS-26831	0.1	5	74 - 106	89 ± 14	15	±17
		1.0	5	90 - 111	101 ± 8.0	7.9	±9.9
	Metolachlor	0.1	5	81 - 109	94 ± 10	11	±13
		1.0	5	102 - 120	110 ± 8.9	8.0	±11

Summary of Method Validation Recoveries from Ground (Well) Water							
Matrix	**Analyte**	**Spike level (ppb)**	**Sample size (n)**	**Range of Recoveries (%)**	**Mean % ± std. dev.**	**RSD (%)**	**95% C.I.**
Ground (Well) Water	Atrazine	0.1	5	91 - 104	98 ± 4.8	4.9	±5.9
		1.0	5	102 - 109	106 ± 2.9	2.7	±3.6
	Simazine	0.1	5	93 - 106	98 ± 5.1	5.2	±6.3
		1.0	5	104 - 108	106 ± 1.7	1.6	±2.1
	G-30033	0.1	5	88 - 105	96 ± 8.0	8.3	±9.9
		1.0	5	104 - 109	107 ± 1.9	1.8	±2.4
	G-28279	0.1	5	102 - 120	113 ± 7.5	6.6	±9.3
		1.0	5	102 - 106	104 ± 1.8	1.7	±2.2
	G-28273	0.5	5	95 - 119	106 ± 9.3	8.7	±12
		5.0	5	100 - 106	103 ± 2.8	2.7	±3.5
	Ametryn	0.1	5	95 - 102	98 ± 3.0	3.1	±3.8
		1.0	5	101 - 110	105 ± 3.7	3.5	±4.6
	Prometryn	0.1	5	96 - 102	98 ± 2.2	2.2	±2.7
		1.0	5	100 - 104	102 ± 1.5	1.5	±1.8
	GS-11354	0.1	5	102 - 110	106 ± 3.5	3.3	±4.3
		1.0	5	101 - 104	103 ± 1.3	1.3	±1.6
	GS-11355	0.1	5	96 - 114	109 ± 7.5	6.9	±9.4
		1.0	5	104 - 110	107 ± 2.2	2.1	±2.8
	GS-26831	0.1	5	95 - 115	107 ± 8.1	7.6	±10
		1.0	5	104 - 112	107 ± 3.3	3.1	±4.1
	Metolachlor	0.1	5	94 - 102	97 ± 3.0	3.0	±3.7
		1.0	5	99 - 102	101 ± 1.3	1.3	±1.6

Summary of Method Validation Recoveries from Finished (Tap) Water							
Matrix	**Analyte**	**Spike level (ppb)**	**Sample size (n)**	**Range of Recoveries (%)**	**Mean % ± std dev**	**RSD (%)**	**95% C.I. (±)**
Finished (Tap) Water	Atrazine	0.1	5	91-102	96 ± 4.3	4.5	5.4
		1.0	5	94-101	98 ± 3.1	3.2	3.9
	Simazine	0.1	5	91-96	94 ± 2.3	2.4	2.9
		1.0	5	93-97	95 ± 1.5	1.6	1.9
	G-30033	0.1	5	94-101	98 ± 3.2	3.3	4.0
		1.0	5	97-100	98 ± 1.1	1.2	1.4
	G-28279	0.1	5	74-93	82 ± 8.4	10	10
		1.0	5	92-96	94 ± 1.6	1.8	2.0
	G-28273	0.5	5	85-101	93 ± 7.2	7.7	8.9
		5.0	5	96-103	100 ± 2.9	2.9	3.6
	Metolachlor	0.1	5	63-97	87 ± 14	16	17
		1.0	5	96-100	97 ± 1.7	1.7	2.1