Data Evaluation Report of Surface Water Monitoring Study

PMRA Submission Number {.....} EPA MRID Number 46733902

Data Requirement: PMRA Data Code:
EPA DP Barcode:
OECD Data Point:N/A
EPA Guideline: N/A

Test material:
Common name: Fipronil
IUPAC name: 5-amino-1-(2,6-dichloro-α,α,α-trifluoro-*p*-tolyl)-4-trifluoromethylsulfinylpyrazole-3-carbonitrile
CAS name: 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethyl)sulfinyl]-1*H*-pyrazole-3-carbonitrile

Primary Reviewer: James Hetrick, Ph.D **Signature:** James A. Hetrick
Date: 5/1/08

Secondary Reviewer: Thuy Nguyen
EPA **Signature:** Thuy Nguyen
Date: 5/6/08

EPA PC Code: 129121

CITATION: Mosier, Dwight G. 2005. Fipronil Water Monitoring Study following Application of Chipco Topchoice® to a Golf Course Turf at College Station, Texas. Sponsored by Bayer Crop Science, RTP, NC. Performed by Bayer Crop Science, Stillwell, KS; Biological Research Service, College Station, TX; AgVise Laboratories, Northward, ND; and Stone Environmental, Inc. Montpelier, VT. MRID 46733902.

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EXECUTIVE SUMMARY:

The fipronil water monitoring study (MRID 46733902) provides supplemental data on the runoff potential of fipronil and its degradation products (MB46136, MB46513, and MB 46950) and its impact on fipronil residue occurrence in surface water from use of Chipco Topchoice® on a turf in College Station,TX. This study was submitted to fulfill a condition of registration regarding runoff concerns of fipronil residues from broadcast use of fipronil for control of fire ants. The registrant did not provide any concurrent biological monitoring of the aquatic environment to assess the impact of fipronil and its degradation products on aquatic invertebrates. The study is deemed supplemental because there is an incomplete description of the storage stability study. To upgrade the study, the registrant should provide a detailed description of the storage stability study because these data were used to justify sample storage times for various fipronil monitoring studies.

The runoff monitoring study was conducted at a golf course near College Station (Brazos County), Texas. The site was a 2.1 acre site of established turf bordered by drainage canals. Runoff from the site is moved into a concrete drainage canal and an adjoining pond with a 1.5 acre surface area. The pond has a single discharge outlet. Samples were taken daily from 0 to 2 days post-treatment, 10 day intervals from 10 to 100 days post-treatment, 20 day intervals from 120 to 180 days post-treatment. Additionally, samples were taken within 24 hours after significant rainfall events (≥ 0.5 inch). There were no fipronil residue detections (≥ 0.004 µg/L) in the 2002 drainage canal and outlet water samples. There was no clear explanation for the lack of fipronil residue detections in 2002 because the rainfall events for the 35 days post-treatment and the last 3 months of study exceeded the historical average precipitation. In 2003, fipronil was detected (0.020 to 0.021 µg/L) in drainage and outlet samples at 34 days and 46 days post-treatment. No fipronil degradation products were detected in drainage canal and pond water samples. Fipronil detections in 2003 were correlated with rain events on day 31- 34 post-treatment (2.77 inches) and 45 days post-treatment (1.1 inches). The fipronil degradation product, MB46136, was detected (0.101 µg/kg) in the 90 day post-treatment sediment sample in 2003. No other fipronil residues were detected in composite sediment samples.

I. MATERIALS AND METHODS

GUIDELINE FOLLOWED: The SETAC-Europe: Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides (March 1995; pp. 1, 34) is not applicable.

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COMPLIANCE: This study was conducted in compliance with USEPA FIFRA Good Laboratory Practices (40 CFR Part 160), which are consistent with the OECD Principles of GLP (p. 3). Signed and dated GLP, Data Confidentiality, Quality Assurance, and Certificate of Authenticity statements were provided (pp. 2-3, 5-6).

A. MATERIALS:

The objective of this study is to assess the runoff potential of fipronil and its degradation products from golf course turf use of Chipco Topchoice® insecticide for control of fire ants.

1. Study Description

The runoff monitoring study was conducted at a golf course near College Station (Brazos County), Texas. The site was a 2.1 acre site of established turf bordered by drainage canals. Runoff from the site is moved into a concrete drainage canal and an adjoining pond with a 1.5 acre surface area. The pond has a single discharge outlet. The maximum slope in the watershed was 10%.

The soils on the site are classified as a Burlewash (fine, smectitic, thermic Ultic Paleustalfs)-Singleton (fine, smectitic, thermic, Udic Paleustalfs). Soil physicochemical properties for surface samples (0-6 inches) are shown in **Table I, pp 52**. The soils the watershed are classified as C/D hydrologic group soils.

Water samples were taken from the drainage canels upstream from the treatment area. The drainage water quality is shown in **Table II, p 53**. Grab samples water samples were taken from 4 sampling points along a drainage canal that transected through the fipronil treatment area (**Figure 1, pp 49**). Samples were taken daily from 0 to 2 days post-treatment, 10 day intervals from 10 to 100 days post-treatment, 20 day intervals from 120 to 180 days post-treatment. Additionally, samples were taken within 24 hours after significant rainfall events (≥ 0.5 inch). Rainfall event sampling in 2002 occurred on 1, 4, 6, 19, 20, 21, 51, 116, 118, 119, 125, 131, 154, 162, 167, and 170 day post-treatment. In 2003, rainfall event sampling occurred on 14, 24, 32, 33, 34, 45, 92, 114, 130, 146, 147, and 150 days post-treatment. All samples were taken 6 feet from the drainage canal edge using telescopic extension arm. Water samples were stored refrigerated at the test site (35-40^{0}F) prior to transfer to the analytical facility.

Four random sediment samples were taken at each sampling location. In 2003, sediment samples were taken immediately before the fipronil treatment, 90 and 180 days post-treatment. The four random samples were composited and then a subsample was taken. Subsamples of sediment were placed on blue ice and then transported to laboratory for frozen storage until chemical analysis.

A rain gauge was used to collect on-site precipitation. The on-site precipitation accounted for 35.90 inches in 2002 and 18.20 inches in 2003 (**Table III, pp 26; Appendix E, pp 65 to 79**).

2. Site Preparation and Maintenance

The height of turf on the site was maintained at 0.5 to < 1.0 inch. There is no additional information on the site maintenance history.

3. Pesticide Application

The fipronil application area accounts for 2.057 acres of established turf. Chipco Topchoice® insecticide was broadcast applied on June 25, 2002 at 0.0120 lbs ai/A and May 12, 2003 at 0.0122 lbs ai/A. The maximum label application rate is 0.0125 lbs ai/A. Applications were made using calibrated drop spreaders. A 15 foot buffer was maintained around the drainage canals and in-turf drains.

4. Analytical

A total of 84 water samples (a total of 104 samples in 2003 and 2004) were analyzed during this study. Water samples were stored frozen for a maximum time period of 725 days (**Appendix F, pp 79-85**). Reviewer Note: The registrant referenced storage stability data for a maximum of 750 days (**Tables IX and X, pp. 34**). There was an incomplete description of the storage stability studies.

Residues of fipronil in water samples were analyzed using a LC/MS/MS method entitled Insecticides, Fipronil: Method of Analysis for Possible Residues of Fipronil, MB46513, MB45950, and MB46136 in Water- Revisions 4 (May 21, 2002). This method has a detection limit (MDL) of 0.004 µg/L and limit of quantification (LOQ) of 0.010 µg/L. (**Reviewer Note**: The method procedure requires filtration for cloudy extracts. The extracts are filtered through a nylon filtration disk after an acetoanitrile extraction of surface water.)

Method verification in duplicate samples of drainage canal water with no fortification (controls) and duplicate samples of drainage canal water fortified at 0.01 and 0.10 ng/mL showed recoveries of 99.6% for fipronil (n=4), 93.7% for MB46513 (n=4), 93.4% for MB45950 (n=4), and 95.3% for MB46136 (n=4) (**Table IV, pp 27**). Procedural recoveries were conducted using drainage canal water at the 0.010, 0.05, 0.10 and 0.100 ng/mL. Average recoveries were 91% (n=31) for fipronil, 98% (n=31) for MB46513, 96% (n=31) MB45950, and 99% for MB46136 (**Table V, pp 27**). Field spike fortifications were conducted in fortified drainage canal water at the 0.02 ug/L and 0.20 µg/L. Fortification studies were conducted on December15, 2003 and March 15, 2004. Average recoveries in the March 15, 2004 fortifications ranged 85 to 89% for fipronil, 74 to 92% for MB46513, 61 to 91% for MB45950, and 66 to 92 % for MB46136

(**Table VIII, pp 30**). Average recoveries in the December 13, 2003 fortications ranged 66 to 85% for fipronil, 69 to 93% for MB46513, 67 to 89 % for MB45950, and 67 to 94 % for MB46136 (**Table VII, pp 29**).

Residues of fipronil in sediment samples were analyzed using a LC/MS/MS method entitled Method of Analysis for Possible Residues of Fipronil, MB46513, MB45950, and MB46136 in Sediment (November 19, 2003). This method has method detection limit (MDL) of 0.030 µg/kg and limit of quantification (LOQ) of 0.100 µg/kg. Procedural recoveries from fortified sediment at 0.2 µg/kg was 86% (n=2) for fipronil,101% (n=2) for MB46513, 119% (n=2) for MB45950, and 114% (n=2) for MB46136 (**Table XI, pp 35**).

B. REPORTED RESULTS

1. Fipronil Residues in Water Samples

There were fipronil residue detections (≥ 0.004 µg/L) in the 2002 drainage canal and outlet water samples (**Table XII, pp. 36-39**). In 2003, fipronil was detected (0.020 to 0.021 µg/L) in drainage and outlet samples at 34 days and 46 days post-treatment (**Table XIII, pp 40-42, Table VI, pp 28, Table XIV, pp 43**). No fipronil degradation products were detected in drainage canal and pond water samples.

Fipronil detections in 2003 was correlated with rain events on day 31- 34 post-treatment (2.77 inches) and 45 days post-treatment (1.1 inches) (**Figure 3, pp 33**). There was no clear explanation for the lack of fipronil residue detections in 2002 because the rainfall events for the 35 days post-treatment and the last 3 months of study exceeded the historical average precipitation (**Figure 2, pp 33**). The first major rainfall event in 2002 accounted for 4.76 inches at 35 days post-treatment.

2. Fipronil Residues in Sediment Samples

The fipronil degradation product, MB46136, was detected (0.101 µg/kg) in the 90 day post-treatment sample in 2003 (**Table XV, pp 43**).

C. REVIEWER COMMENTS

1. The fipronil water monitoring study (MRID 46733902) provides supplemental data on the runoff potential of fipronil and its degradation products (MB46136, MB46513, and MB 46950) and its impact on fipronil residue occurrence in surface water from use of Chipco Topchoice® on a turf in College, TX. This study was submitted to fulfill a condition of registration regarding runoff concerns of fipronil residues from broadcast use of fipronil for control of fire

ants. The registrant did not provide any concurrent biological monitoring of the aquatic environment to assess the impact of fipronil and its degradation products on aquatic invertebrates.

2. The study is deemed supplemental because there is an incomplete description of the storage stability study. The registrant referenced storage stability data for a maximum of 750 days. **The registrant should provide a detailed description of the storage stability study because these data were used to justify sample storage times for various fipronil monitoring studies.**

Soil

On 22 October 2003, five soil samples were obtained from the top 6 inches of soil within the treatment area for characterization analyses. These samples were held at the Principle Field Investigators storage facility then shipped to Agvise Laboratories for analysis, where they were received on 12 January 2004. The results of the soil characterization analyses are listed in Table I. Copies of the laboratory reports are included in this Appendix.

Table I: Soil Characterization

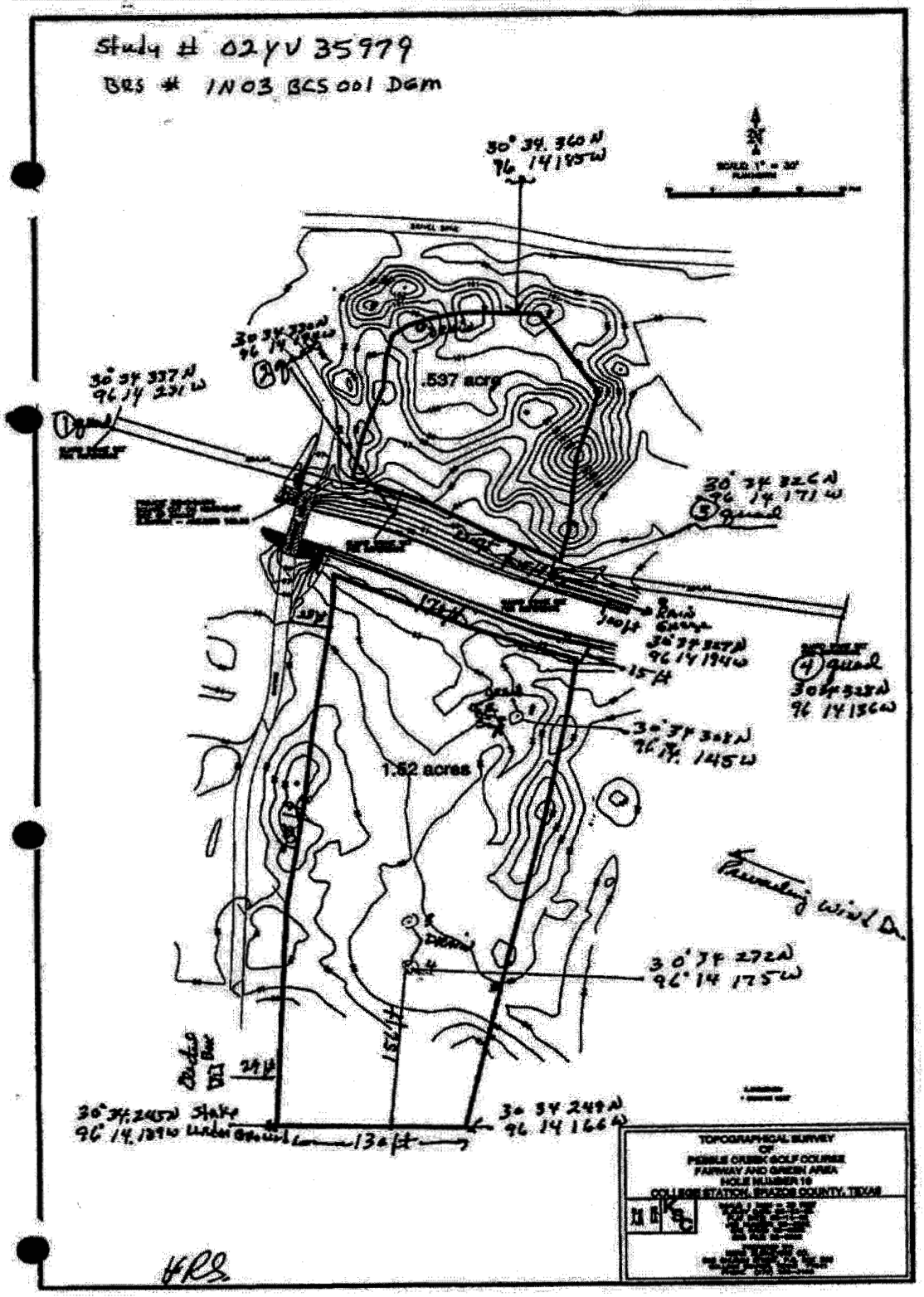
Parameter	Sample									
	ST-01 6"		QUAD 1 6"		QUAD 2 6"		QUAD 3 6"		QUAD 4 6"	
Sand (%)	60		62		58		60		60	
Silt (%)	22		20		24		24		22	
Clay (%)	18		18		18		16		18	
USDA Textural Class (hydrometer method)	Sandy Loam		Sandy Loam		Sandy Loam		Sandy Loam		Sandy Loam	
Bulk Density (disturbed) (gm/cc)	1.09		1.11		1.11		1.08		1.03	
Cation Exchange Capacity (meq/100 g)	16.4		14.6		19		15.3		18.7	
% moisture at 1/3 bar	27		20.6		23.9		24.7		33.6	
% moisture at 15 bar	12.3		10.4		12.8		11.7		16.7	
% Organic Matter	3.9		2.7		4.3		3.1		3.5	
pH (1:1 soil:water)	7.9		8.1		7.8		8		8	
Phosphorus (ppm)	16		20		22		32		14	
Nitrogen ((%)	0.059		0.121		0.158		0.148		0.134	
Soluble Salts (mmhos/cm)	1.38		1.33		1.5		1.43		1.63	
Base Saturation:	**%**	**ppm**	**%**	**ppm**	**%**	**ppm**	**%**	**ppm**	**%**	**ppm**
Calcium	53.8	1760	56.9	1660	60.1	2280	54	1650	48.4	1810
Magnesium	10.9	215	10	175	9.8	224	10.5	193	12.4	278
Sodium	28.7	1080	26	873	23.4	1020	28.4	1000	34.6	1490
Potassium	4.6	295	4.3	246	4.1	301	4.5	266	4.2	305
Hydrogen	2	3	2.7	4	2.5	5	2.6	4	0.4	1

Water

Prior to application each year, three, 2-gallon water samples were collected upstream from the drainage canal away from the application area. These samples were collected on 24 June 2002 and 11 May 2003 then shipped to Bayer CropScience on 15 July 2002 and 3 June 2003. A subsample was taken and forwarded to Agvise Laboratories on 4 May 2005 for characterization. The results are listed in Table II. A copy of the laboratory report is included in the Appendix.

Table II: Water Characterization

Parameter	Sample
pH	7.8
Calcium (ppm)	66
Magnesium (ppm)	9.4
Sodium (ppm)	144
Hardness mq equivalent CaC03/L	204
Conductivity (mmhos/cm)	1.07
Sodium Adsorption Ratio	4.39
Total Dissolved Solids (ppm)	812
Turbidity (NTU)	21.1



conditions conducive to runoff occurred 24, 31, 32, 33, 34 and 45 DAT in amounts of 0.55, 0.47, 0.94, 0.77, 0.59 and 1.10 inches, respectively. Other onsite rainfall events that potentially created conditions conducive to runoff in 2003 occurred 92, 114, 130, 146 and 150 DAT in amounts of 0.94, 1.75, 0.6, 2.50 and 3.30 inches, respectively.

A total of 35.95 and 18.20 inches of precipitation were recorded onsite during the study periods in 2002 and 2003, respectively. Both years, supplemental irrigation in the amounts of 0.1 to 0.2 inches were applied daily to the test site when rainfall was less than 0.30 inches. Historical and study period precipitation data are summarized in Table III. The daily rainfall, irrigation and temperature data are presented in Appendix E.

Table III. 30 Year Monthly Average and Monthly On-Site Precipitation

Month	30 Year Monthly Average (1973-2002)*	On-Site Precipitation Data (2002)*	On-Site Precipitation Data (2003)*
May	4.98 in		1.14 in
June	4.04 in	1.94 in (26-30 June 2002)	4.89 in
July	2.11 in	8.98 in	1.22 in
August	2.62 in	2.40 in	1.13 in
September	3.90 in	1.06 in	2.92 in
October	4.18 in	8.11 in	6.90 in
November	3.26 in	6.62 in	0.0 in (1-8 Nov. 2003)
December	3.35 in	6.84 in	

* From NOAA Weather Station (411889), College Station, TX.

5.4 Water Analysis

5.4.1 Method Verification

The analytical method for water has been validated internally and has undergone a successful independent laboratory validation. The results of these studies are presented in separate reports (References 2 and 4).

The analytical method was verified prior to beginning analysis of the field samples using a fortification solution of a mixture of fipronil and its metabolites. The verification set consisted of 2 control samples of onsite pre-application bulk water, 2 samples of onsite water fortified at the LOQ (0.01 ng/mL), 2 samples of onsite water fortified at 10XLOQ (0.10 ng/mL). Results of the method verification were satisfactory and are shown in Table IV. In addition, all quantitative data for the method verification is provided in Appendix I.

2002 Critical Dates for Drainage Canal Water Sample Analyzed for Fipronil-Related Residues

Sample ID (35979-01-)	Sampling Event	Sampling Date	Shipping Date	Analysis Date
0001	Pre-Treatment	24-Jun-02	15-Jul-02	23-Aug-02
0003	Pre-Treatment	24-Jun-02	15-Jul-02	23-Aug-02
0005	Pre-Treatment	24-Jun-02	15-Jul-02	23-Aug-02
0007	Pre-Treatment	24-Jun-02	15-Jul-02	23-Aug-02
0011	0 DAT	25-Jun-02	15-Jul-02	23-Aug-02
0013	0 DAT	25-Jun-02	15-Jul-02	23-Aug-02
0015	0 DAT	25-Jun-02	15-Jul-02	23-Aug-02
0017	0 DAT	25-Jun-02	15-Jul-02	23-Aug-02
0019	1 DAT	26-Jun-02	15-Jul-02	23-Aug-02
0021	1 DAT	26-Jun-02	15-Jul-02	23-Aug-02
0023	1 DAT	26-Jun-02	15-Jul-02	23-Aug-02
0025	1 DAT	26-Jun-02	15-Jul-02	26-Aug-02
0027	2 DAT	27-Jun-02	15-Jul-02	26-Aug-02
0029	2 DAT	27-Jun-02	15-Jul-02	26-Aug-02
0031	2 DAT	27-Jun-02	15-Jul-02	26-Aug-02
0033	2 DAT	27-Jun-02	15-Jul-02	26-Aug-02
0035	3 DAT	28-Jun-02	15-Jul-02	26-Aug-02
0037	3 DAT	28-Jun-02	15-Jul-02	26-Aug-02
0039	3 DAT	28-Jun-02	15-Jul-02	26-Aug-02
0041	3 DAT	28-Jun-02	15-Jul-02	26-Aug-02
0161	Rain 1	1-Jul-02	15-Jul-02	21-Oct-02
0163	Rain 1	1-Jul-02	15-Jul-02	21-Oct-02
0043	10 DAT	5-Jul-02	15-Jul-02	26-Aug-02
0045	10 DAT	5-Jul-02	15-Jul-02	26-Aug-02
0047	10 DAT	5-Jul-02	15-Jul-02	26-Aug-02
0049	10 DAT	5-Jul-02	15-Jul-02	26-Aug-02
0051	20 DAT	15-Jul-02	15-Jul-02	26-Aug-02
0057	20 DAT	15-Jul-02	15-Jul-02	30-Sep-02
0165	Rain 2	16-Jul-02	14-Aug-02	21-Oct-02
0167	Rain 2	16-Jul-02	14-Aug-02	21-Oct-02
0169	Rain 2	16-Jul-02	14-Aug-02	19-Dec-02
0171	Rain 2	16-Jul-02	14-Aug-02	19-Dec-02
0059	30 DAT	25-Jul-02	14-Aug-02	30-Sep-02
0061	30 DAT	25-Jul-02	14-Aug-02	30-Sep-02
0063	30 DAT	25-Jul-02	14-Aug-02	30-Sep-02
0065	30 DAT	25-Jul-02	14-Aug-02	30-Sep-02
0067	40 DAT	4-Aug-02	14-Aug-02	30-Sep-02
0069	40 DAT	4-Aug-02	14-Aug-02	30-Sep-02
0071	40 DAT	4-Aug-02	14-Aug-02	30-Sep-02
0073	40 DAT	4-Aug-02	14-Aug-02	30-Sep-02
0075	50 DAT	14-Aug-02	10-Sep-02	30-Sep-02
0077	50 DAT	14-Aug-02	10-Sep-02	30-Sep-02
0079	50 DAT	14-Aug-02	10-Sep-02	30-Sep-02

2002 Critical Dates for Drainage Canal Water Sample Analyzed for Fipronil-Related Residues

Sample ID (35979-01-)	Sampling Event	Sampling Date	Shipping Date	Analysis Date
0081	50 DAT	14-Aug-02	10-Sep-02	30-Sep-02
0173	Rain 3	16-Aug-02	10-Sep-02	19-Dec-02
0175	Rain 3	16-Aug-02	10-Sep-02	19-Dec-02
0177	Rain 3	16-Aug-02	10-Sep-02	21-Oct-02
0179	Rain 3	16-Aug-02	10-Sep-02	28-Oct-02
0083	60 DAT	25-Aug-02	10-Sep-02	30-Sep-02
0085	60 DAT	25-Aug-02	10-Sep-02	30-Sep-02
0087	60 DAT	25-Aug-02	10-Sep-02	21-Oct-02
0089	60 DAT	25-Aug-02	10-Sep-02	21-Oct-02
0091	70 DAT	4-Sep-02	10-Sep-02	21-Oct-02
0093	70 DAT	4-Sep-02	10-Sep-02	21-Oct-02
0095	70 DAT	4-Sep-02	10-Sep-02	21-Oct-02
0097	70 DAT	4-Sep-02	10-Sep-02	19-Dec-02
0099	80 DAT	14-Sep-02	7-Oct-02	19-Dec-02
0101	80 DAT	14-Sep-02	7-Oct-02	19-Dec-02
0103	80 DAT	14-Sep-02	7-Oct-02	19-Dec-02
0105	80 DAT	14-Sep-02	7-Oct-02	19-Dec-02
0107	90 DAT	24-Sep-02	7-Oct-02	19-Dec-02
0109	90 DAT	24-Sep-02	7-Oct-02	19-Dec-02
0111	90 DAT	24-Sep-02	7-Oct-02	19-Dec-02
0113	90 DAT	24-Sep-02	7-Oct-02	19-Dec-02
0115	100 DAT	4-Oct-02	7-Oct-02	19-Dec-02
0117	100 DAT	4-Oct-02	7-Oct-02	19-Dec-02
0119	100 DAT	4-Oct-02	7-Oct-02	19-Dec-02
0121	100 DAT	4-Oct-02	7-Oct-02	19-Dec-02
0181	Rain 4	20-Oct-02	12-Nov-02	28-Oct-02
0183	Rain 4	20-Oct-02	12-Nov-02	28-Oct-02
0185	Rain 4	20-Oct-02	12-Nov-02	19-Dec-02
0187	Rain 4	20-Oct-02	12-Nov-02	19-Dec-02
0189	Rain 5	22-Oct-02	12-Nov-02	19-Dec-02
0191	Rain 5	22-Oct-02	12-Nov-02	19-Dec-02
0193	Rain 5	22-Oct-02	12-Nov-02	19-Dec-02
0195	Rain 5	22-Oct-02	12-Nov-02	19-Dec-02
0123	120 DAT	26-Oct-02	12-Nov-02	19-Dec-02
0125	120 DAT	26-Oct-02	12-Nov-02	19-Dec-02
0127	120 DAT	26-Oct-02	12-Nov-02	19-Dec-02
0129	123 DAT	26-Oct-02	12-Nov-02	14-Sep-04
0130	123 DAT	26-Oct-02	12-Nov-02	14-Sep-04
0131	142 DAT	14-Nov-02	17-Dec-02	14-Sep-04
0132	142 DAT	14-Nov-02	17-Dec-02	14-Sep-04
0133	142 DAT	14-Nov-02	17-Dec-02	14-Sep-04
0134	142 DAT	14-Nov-02	17-Dec-02	14-Sep-04
0135	142 DAT	14-Nov-02	17-Dec-02	14-Sep-04

2002 Critical Dates for Drainage Canal Water Sample Analyzed for Fipronil-Related Residues

Sample ID (35979-01-)	Sampling Event	Sampling Date	Shipping Date	Analysis Date
0136	142 DAT	14-Nov-02	17-Dec-02	14-Sep-04
0137	142 DAT	14-Nov-02	17-Dec-02	14-Sep-04
0138	142 DAT	14-Nov-02	17-Dec-02	14-Sep-04
0139	163 DAT	5-Dec-02	17-Dec-02	14-Sep-04
0140	163 DAT	5-Dec-02	17-Dec-02	14-Sep-04
0141	163 DAT	5-Dec-02	17-Dec-02	14-Sep-04
0142	163 DAT	5-Dec-02	17-Dec-02	14-Sep-04
0143	163 DAT	5-Dec-02	17-Dec-02	14-Sep-04
0144	163 DAT	5-Dec-02	17-Dec-02	14-Sep-04
0145	163 DAT	5-Dec-02	17-Nov-02	4-Dec-04
0197	Rain 6	25-Oct-02	12-Nov-02	19-Dec-02
0199	Rain 6	25-Oct-02	12-Nov-02	19-Dec-02
0201	Rain 6	25-Oct-02	12-Nov-02	19-Dec-02
0203	Rain 6	25-Oct-02	12-Nov-02	19-Dec-02
0205	Rain 7	5-Nov-02	12-Nov-02	19-Dec-02
0207	Rain 7	5-Nov-02	12-Nov-02	19-Dec-02
0209	133 DAT	5-Nov-02	12-Nov-02	4-Dec-04
0211	133 DAT	5-Nov-02	12-Nov-02	4-Dec-04
0213	Rain 8	10-Dec-02	17-Nov-02	4-Dec-04
0215	Rain 8	10-Dec-02	17-Nov-02	4-Dec-04
0149	185 DAT	27-Dec-02	10-Feb-03	4-Dec-04
0151	185 DAT	27-Dec-02	10-Feb-03	4-Dec-04

2003 Critical Dates for Drainage Canal Water Sample Analyzed for Fipronil-Related Residues

Sample ID (35979-)	Sampling Event	Sampling Date	Shipping Date	Analysis Date
2001	Pre-Treatment	11-May-03	3-Jun-03	28-Oct-04
2002	Pre-Treatment	11-May-03	3-Jun-03	28-Oct-04
2003	Pre-Treatment	11-May-03	3-Jun-03	28-Oct-04
2004	Pre-Treatment	11-May-03	3-Jun-03	28-Oct-04
2005	0	12-May-03	3-Jun-03	28-Oct-04
2006	0	12-May-03	3-Jun-03	28-Oct-04
2007	0	12-May-03	3-Jun-03	28-Oct-04
2008	0	12-May-03	3-Jun-03	28-Oct-04
2009	1	13-May-03	3-Jun-03	28-Oct-04
2010	1	13-May-03	3-Jun-03	28-Oct-04
2011	1	13-May-03	3-Jun-03	28-Oct-04
2012	1	13-May-03	3-Jun-03	28-Oct-04
2013	2	14-May-03	3-Jun-03	28-Oct-04
2014	2	14-May-03	3-Jun-03	28-Oct-04
2015	2	14-May-03	3-Jun-03	28-Oct-04
2016	2	14-May-03	3-Jun-03	28-Oct-04
2017	3	15-May-03	3-Jun-03	24-Sep-03
2018	3	15-May-03	3-Jun-03	24-Sep-03
2019	3	15-May-03	3-Jun-03	24-Sep-03
2020	3	15-May-03	3-Jun-03	24-Sep-03
2057	13	25-May-03	3-Jun-03	24-Sep-03
2058	13	25-May-03	3-Jun-03	24-Sep-03
2059	13	25-May-03	3-Jun-03	24-Sep-03
2060	13	25-May-03	3-Jun-03	24-Sep-03
2065	15	27-May-03	3-Jun-03	24-Sep-03
2066	15	27-May-03	3-Jun-03	24-Sep-03
2067	15	27-May-03	3-Jun-03	24-Sep-03
2068	15	27-May-03	3-Jun-03	24-Sep-03
2097	23	4-Jun-03	8-Jul-03	24-Sep-03
2098	23	4-Jun-03	8-Jul-03	24-Sep-03
2099	23	4-Jun-03	8-Jul-03	24-Sep-03
2100	23	4-Jun-03	8-Jul-03	24-Sep-03
2101	24	5-Jun-03	8-Jul-03	24-Sep-03
2102	24	5-Jun-03	8-Jul-03	24-Sep-03
2103	24	5-Jun-03	8-Jul-03	24-Sep-03
2104	24	5-Jun-03	8-Jul-03	24-Sep-03
2450	24	5-Jun-03	8-Jul-03	3/24/2004*
2133	32	13-Jun-03	8-Jul-03	24-Sep-03
2134	32	13-Jun-03	8-Jul-03	24-Sep-03
2135	32	13-Jun-03	8-Jul-03	24-Sep-03

* Pond Outlet Sample

2003 Critical Dates for Drainage Canal Water Sample Analyzed for Fipronil-Related Residues

Sample ID (35979-)	Sampling Event	Sampling Date	Shipping Date	Analysis Date
2136	32	13-Jun-03	8-Jul-03	24-Sep-03
2458	32	13-Jun-03	8-Jul-03	3/24/2004*
2137	33	14-Jun-03	8-Jul-03	24-Sep-03
2138	33	14-Jun-03	8-Jul-03	24-Sep-03
2139	33	14-Jun-03	8-Jul-03	24-Sep-03
2140	33	14-Jun-03	8-Jul-03	24-Sep-03
2459	33	14-Jun-03	8-Jul-03	3/24/2004*
2141	34	15-Jun-03	8-Jul-03	24-Sep-03
2142	34	15-Jun-03	8-Jul-03	24-Sep-03
2143	34	15-Jun-03	8-Jul-03	24-Sep-03
2144	34	15-Jun-03	8-Jul-03	24-Sep-03
2460	34	15-Jun-03	8-Jul-03	3/24/2004*
2177	43	24-Jun-03	8-Jul-03	24-Sep-03
2178	43	24-Jun-03	8-Jul-03	24-Sep-03
2179	43	24-Jun-03	8-Jul-03	24-Sep-03
2180	43	24-Jun-03	8-Jul-03	24-Sep-03
2189	46	27-Jun-03	8-Jul-03	24-Sep-03
2190	46	27-Jun-03	8-Jul-03	24-Sep-03
2191	46	27-Jun-03	8-Jul-03	24-Sep-03
2192	46	27-Jun-03	8-Jul-03	24-Sep-03
2472	46	27-Jun-03	8-Jul-03	3/24/2004*
2217	53	4-Jul-03	8-Jul-03	24-Sep-03
2218	53	4-Jul-03	8-Jul-03	24-Sep-03
2219	53	4-Jul-03	8-Jul-03	24-Sep-03
2220	53	4-Jul-03	8-Jul-03	24-Sep-03
2479	53	4-Jul-03	8-Jul-03	3/24/2004*
2293	72	23-Jul-03	2-Sep-03	24-Sep-03
2294	72	23-Jul-03	2-Sep-03	24-Sep-03
2295	72	23-Jul-03	2-Sep-03	24-Sep-03
2296	72	23-Jul-03	2-Sep-03	24-Sep-03
2337	83	3-Aug-03	2-Sep-03	19-Nov-03
2338	83	3-Aug-03	2-Sep-03	19-Nov-03
2339	83	3-Aug-03	2-Sep-03	19-Nov-03
2340	83	3-Aug-03	2-Sep-03	19-Nov-03
2373	92	12-Aug-03	2-Sep-03	19-Nov-03
2374	92	12-Aug-03	2-Sep-03	19-Nov-03
2375	92	12-Aug-03	2-Sep-03	19-Nov-03
2376	92	12-Aug-03	2-Sep-03	19-Nov-03
2518	92	12-Aug-03	2-Sep-03	12/1/2003*
2377	93	13-Aug-03	2-Sep-03	19-Nov-03

* Pond Outlet Sample

2003 Critical Dates for Drainage Canal Water Sample Analyzed for Fipronil-Related Residues

Sample ID (35979-)	Sampling Event	Sampling Date	Shipping Date	Analysis Date
2378	93	13-Aug-03	2-Sep-03	19-Nov-03
2379	93	13-Aug-03	2-Sep-03	19-Nov-03
2380	93	13-Aug-03	2-Sep-03	19-Nov-03
2405	100	22-Aug-03	2-Sep-03	19-Nov-03
2406	100	22-Aug-03	2-Sep-03	19-Nov-03
2407	100	22-Aug-03	2-Sep-03	19-Nov-03
2408	100	22-Aug-03	2-Sep-03	19-Nov-03
2526	100	22-Aug-03	2-Sep-03	12/1/2003*
2409	120	9-Sep-03	29-Oct-03	19-Nov-03
2410	120	9-Sep-03	29-Oct-03	19-Nov-03
2411	120	9-Sep-03	29-Oct-03	19-Nov-03
2412	120	9-Sep-03	29-Oct-03	19-Nov-03
2413	140	29-Sep-03	29-Oct-03	19-Nov-03
2414	140	29-Sep-03	29-Oct-03	19-Nov-03
2415	140	29-Sep-03	29-Oct-03	19-Nov-03
2416	140	29-Sep-03	29-Oct-03	19-Nov-03
2417	160	19-Oct-03	29-Oct-03	1-Dec-03
2418	160	19-Oct-03	29-Oct-03	1-Dec-03
2419	160	19-Oct-03	29-Oct-03	1-Dec-03
2420	160	19-Oct-03	29-Oct-03	1-Dec-03
2421	180	8-Nov-03	12-Nov-03	1-Dec-03
2422	180	8-Nov-03	12-Nov-03	1-Dec-03
2423	180	8-Nov-03	12-Nov-03	1-Dec-03
2424	180	8-Nov-03	12-Nov-03	1-Dec-03
2537	90	9-Aug-03	2-Sep-03	4/1/2004**
2538	90	9-Aug-03	2-Sep-03	4/1/2004**
2539	180	8-Nov-03	12-Nov-03	8/17/2004**
2540	180	8-Nov-03	12-Nov-03	8/17/2004**
2541	180	8-Nov-03	12-Nov-03	8/17/2004**
2542	180	8-Nov-03	12-Nov-03	8/17/2004**

* Pond Outlet Sample

** Sediment Sample

Table IX. Concurrent Recoveries of Fipronil, MB46513, MB45950 and MB46136 Spiked at 1.0 ppb and Analyzed with Storage Stability Samples.

	Concurrent Recovery			
Storage Period	Fipronil	MB46513	MB45950	MB46136
Day 0	93	96	86	93
Week 1	67	64	73	86
Month 1	74	91	105	112
Month 3	86	63	60	72
Month 6	90	93	92	90
Month 9	75	79	78	84
Month 12	94	93	88	90
Month 25	97	101	103	106

Table X. Storage Stability Recovery Summary for Fipronil, MB46513, MB45950 and MB46136.[1]

	Percent Recovery			
Storage Period	Fipronil	MB46513	MB45950	MB46136
Day 0	103	100	107	103
	100	98	101	101
	99	97	100	100
Average	**101**	**98**	**103**	**101**
Week 1	116	114	93	92
	112	111	93	94
	125	128	103	102
Average	**118**	**118**	**96**	**96**
Month 1	104	95	82	79
	116	96	90	88
	115	100	86	80
Average	**112**	**97**	**86**	**82**
Month 3	115	156	142	124
	119	167	162	128
	115	159	160	124
Average	**116**	**161**	**155**	**125**
Month 6	106	97	97	96
	106	102	95	93
	99	100	93	92
Average	**104**	**100**	**95**	**94**
Month 9	99	90	94	89
	103	95	96	88
	101	92	95	87
Average	**101**	**92**	**95**	**88**
Month 12	100	100	102	103
	98	105	108	108
	100	104	109	110
Average	**99**	**103**	**106**	**107**
Month 25	104	102	95	96
	100	99	96	94
	103	98	99	98
Average	**102**	**100**	**97**	**96**

[1] Corrected for concurrent recoveries.

Table IV. Water Method Verification Results

Sample Identification	Fortification Level (ng/mL)	Percent Recovery			
		Fipronil	MB46513	MB45950	MB46136
35979-01-Bulk-UTC-1	0	ND	ND	ND	ND
35979-01-Bulk-UTC-2	0	ND	ND	ND	ND
35979-01-Bulk-10 ppt-1	0.01	101.6	94.1	93.8	103.7
35979-01-Bulk-10 ppt-2	0.01	108.5	105.1	97.6	103.9
35979-01-Bulk-100 ppt-1	0.10	94.7	88.7	90.6	87.3
35979-01-Bulk-100 ppt-2	0.10	93.7	87.1	91.7	86.5
Mean Recovery		**99.6 n=4**	**93.7 n=4**	**93.4 n=4**	**95.3 n=4**

5.4.2 Procedural Recoveries

Each sample set contained at least one control sample (pre-application bulk water) fortified with a mixture of fipronil, MB46513, MB45950 and MB46136. The fortification levels were 0.005, 0.010 or 0.100 ng/mL. The procedural recoveries are summarized in Table V. In addition, all quantitative data for the procedural recoveries are included in Appendix I.

Table V. Mean Procedural Recoveries from Fortified Bulk Water

Analyte	Fortification Level (ng/mL)	Number	Mean Percent Recovery
Fipronil	0.01	5	98
	0.05	4	86
	0.10	18	89
	1.00	4	89
	Mean	**31**	**91**
MB46513	0.01	5	101
	0.05	4	104
	0.10	18	95
	1.00	4	93
	Mean	**31**	**98**
MB45950	0.01	5	96
	0.05	4	99
	0.10	18	93
	1.00	4	94
	Mean	**31**	**96**
MB46136	0.01	5	103
	0.05	4	102
	0.10	18	96
	1.00	4	95
	Mean	**31**	**99**

Table VIII. Recoveries from Field Fortified Water Samples

Fortification Level (ng/mL)	Replicate	Percent Recovery			
		Fipronil	MB46513	MB45950	MB46136
0	A	ND	ND	ND	ND
	B	ND	ND	ND	ND
0.02	A	85	72	60	65
	B	84	71	61	67
	C	82	74	55	61
	D	90	80	66	71
	Mean	**85**	**74**	**61**	**66**
0.2	A	80	87	86	87
	B	92	92	92	91
	C	90	96	96	99
	D	94	92	91	91
	Mean	**89**	**92**	**91**	**92**

[1] Analyzed on March 15, 2004

5.4.5 Storage Stability

The majority of the water samples from the College Station, TX site were analyzed within approximately 90 to 120 days of collection each year. A few were analyzed late to evaluate and confirm the stability of fipronil-related residues in frozen water with a storage interval extending beyond 180 days. The analytical results are included in the study file. The recovery results summarized in Tables IX and X demonstrate the stability of fipronil and its metabolites in frozen water stored for up to 25 months.

5.5 Sediment Analysis

5.5.1 Method of Analysis

During the course of this study, a method of analysis was developed for the sediment samples. The acceptable recoveries observed in the sample set demonstrated the capability of the method to extract fipronil-related residues from sediment. The procedural recoveries in this study are provided in Table XI.

5.5.2 Analytical Results of Sediment Samples

No sediment samples were collected in 2002. In 2003, sediment samples were collected 90 and 180 days after application of the test substance and were analyzed for potential accumulation of fipronil-related residues in the drainage canal sediment. The 90 and 180-day sediment samples did not contain parent fipronil residues in any of the samples. The only fipronil-related metabolite detected was MB46136 at 0.10 ppb in one out of four replicates of sediment collected 90 days after application. The results are summarized in Table XV and Appendix H.

MB45950, and MB46136 to yield concentrations of 0.02 ng/mL and 0.20 ng/mL. During the analytical phase it was discovered that the recovery results from the 0.20 ng/mL dose was lower than expected in that the averages fell below the acceptable level of 70% (Table VII). Recoveries from the low dose (0.02 ng/mL) were acceptable as they ranged from 85 to 93%. To confirm the initial recovery results, a second set of field recovery samples were prepared on 12 February 2004 via the same method used on 14 November 2002, except with a new mixture of fipronil, MB46513, MB45950, and MB46136 to yield concentrations of 0.02 ng/mL and 0.20 ng/mL. The second set of samples were analyzed on 15 March 2004. Recovery results from this second set of samples revealed that fipronil and all three metabolites, at the high dose (0.2 ng/mL), and fipronil at the low dose (0.02 ng/mL), fell within the acceptable range of 70 to 120% (Table VIII). Average recoveries for MB46513, MB45950 and MB46136 in this second set were 74, 61 and 66%, respectively. All quantitative data for the field recovery samples are included in Appendix I.

Table VII. Recoveries from Field Fortified Water Samples

Fortification Level (ng/mL)	Replicate	Percent Recovery			
		Fipronil	MB46513	MB45950	MB46136
0	A	ND	ND	ND	ND
	B	ND	ND	ND	ND
0.02	A	83	85	82	88
	B	84	96	95	97
	C	81	80	77	85
	D	92	110	102	103
	Mean	**85**	**93**	**89**	**93**
0.2	A	59	59	61	62
	B	74	79	71	71
	C	68	72	77	75
	D	61	64	58	59
	Mean	**66**	**69**	**67**	**67**

[1] Analyzed on December 13, 2003

Table XI. Sediment Procedural Recovery Results

Sample Identification	Fortification Level (ng/mL)	Percent Recovery			
		Fipronil	MB46513	MB45950	MB46136
35979-Bulk-200 ppt	0.20	83	96	98	97
35979-200 ppt-2535A	0.20	88	106	139	130
Mean Recovery		**86 n=2**	**101 n=2**	**119 n=2**	**114 n=2**

Table XII. 2002 Analytical Results of Drainage Canal Water Samples

Days After Application	Sample ID	Collection Date	Analytical Results (ppb)			
			Fipronil	MB46513	MB45950	MB46136
Pre-Treatment	35979-01-0001	24 June 2002	ND	ND	ND	ND
Pre-Treatment	35979-01-0003	24 June 2002	ND	ND	ND	ND
Pre-Treatment	35979-01-0005	24 June 2002	ND	ND	ND	ND
Pre-Treatment	35979-01-0007	24 June 2002	ND	ND	ND	ND
0	35979-01-0011	25 June 2002	ND	ND	ND	ND
0	35979-01-0013	25 June 2002	ND	ND	ND	ND
0	35979-01-0015	25 June 2002	ND	ND	ND	ND
0	35979-01-0017	25 June 2002	ND	ND	ND	ND
1	35979-01-0019	26 June 2002	ND	ND	ND	ND
1	35979-01-0021	26 June 2002	ND	ND	ND	ND
1	35979-01-0023	26 June 2002	ND	ND	ND	ND
1	35979-01-0025	26 June 2002	ND	ND	ND	ND
2	35979-01-0027	27 June 2002	ND	ND	ND	ND
2	35979-01-0029	27 June 2002	ND	ND	ND	ND
2	35979-01-0031	27 June 2002	ND	ND	ND	ND
2	35979-01-0033	27 June 2002	ND	ND	ND	ND
3	35979-01-0035	28 June 2002	ND	ND	ND	ND
3	35979-01-0037	28 June 2002	ND	ND	ND	ND
3	35979-01-0039	28 June 2002	ND	ND	ND	ND
3	35979-01-0041	28 June 2002	ND	ND	ND	ND
6	35979-01-0161	01 July 2002	ND	ND	ND	ND
6	35979-01-0163	01 July 2002	ND	ND	ND	ND
10	35979-01-0043	05 July 2002	ND	ND	ND	ND
10	35979-01-0045	05 July 2002	ND	ND	ND	ND
10	35979-01-0047	05 July 2002	ND	ND	ND	ND
10	35979-01-0049	05 July 2002	ND	ND	ND	ND
20	35979-01-0051	15 July 2002	ND	ND	ND	ND
20	35979-01-0057	15 July 2002	ND	ND	ND	ND
21	35979-01-0165	16 July 2002	ND	ND	ND	ND
21	35979-01-0167	16 July 2002	ND	ND	ND	ND
21	35979-01-0169	16 July 2002	ND	ND	ND	ND
21	35979-01-0171	16 July 2002	ND	ND	ND	ND
30	35979-01-0059	25 July 2002	ND	ND	ND	ND
30	35979-01-0061	25 July 2002	ND	ND	ND	ND

Table XII. (continued). 2002 Analytical Results of Drainage Canal Water Samples

Days After Application	Sample ID	Collection Date	Analytical Results (ppb)			
			Fipronil	MB46513	MB45950	MB46136
30	35979-01-0063	25 July 2002	ND	ND	ND	ND
30	35979-01-0065	25 July 2002	ND	ND	ND	ND
40	35979-01-0067	04 August 2002	ND	ND	ND	ND
40	35979-01-0069	04 August 2002	ND	ND	ND	ND
40	35979-01-0071	04 August 2002	ND	ND	ND	ND
40	35979-01-0073	04 August 2002	ND	ND	ND	ND
50	35979-01-0075	14 August 2002	ND	ND	ND	ND
50	35979-01-0077	14 August 2002	ND	ND	ND	ND
50	35979-01-0079	14 August 2002	ND	ND	ND	ND
50	35979-01-0081	14 August 2002	ND	ND	ND	ND
52	35979-01-0173	16 August 2002	ND	ND	ND	ND
52	35979-01-0175	16 August 2002	ND	ND	ND	ND
52	35979-01-0177	16 August 2002	ND	ND	ND	ND
52	35979-01-0179	16 August 2002	ND	ND	ND	ND
60	35979-01-0083	25 August 2002	ND	ND	ND	ND
60	35979-01-0085	25 August 2002	ND	ND	ND	ND
60	35979-01-0087	25 August 2002	ND	ND	ND	ND
60	35979-01-0089	25 August 2002	ND	ND	ND	ND
70	35979-01-0091	04 Sept 2002	ND	ND	ND	ND
70	35979-01-0093	04 Sept 2002	ND	ND	ND	ND
70	35979-01-0095	04 Sept 2002	ND	ND	ND	ND
70	35979-01-0097	04 Sept 2002	ND	ND	ND	ND
80	35979-01-0099	14 Sept 2002	ND	ND	ND	ND
80	35979-01-0101	14 Sept 2002	ND	ND	ND	ND
80	35979-01-0103	14 Sept 2002	ND	ND	ND	ND
80	35979-01-0105	14 Sept 2002	ND	ND	ND	ND
90	35979-01-0107	24 Sept 2002	ND	ND	ND	ND
90	35979-01-0109	24 Sept 2002	ND	ND	ND	ND
90	35979-01-0111	24 Sept 2002	ND	ND	ND	ND
90	35979-01-0113	24 Sept 2002	ND	ND	ND	ND
100	35979-01-0115	04 October 2002	ND	ND	ND	ND
100	35979-01-0117	04 October 2002	ND	ND	ND	ND
100	35979-01-0119	04 October 2002	ND	ND	ND	ND

Table XII. (continued). 2002 Analytical Results of Drainage Canal Water Samples

Days After Application	Sample ID	Collection Date	Analytical Results (ppb)			
			Fipronil	MB46513	MB45950	MB46136
100	35979-01-0121	04 October 2002	ND	ND	ND	ND
117	35979-01-0181	20 October 2002	ND	ND	ND	ND
117	35979-01-0183	20 October 2002	ND	ND	ND	ND
117	35979-01-0185	20 October 2002	ND	ND	ND	ND
117	35979-01-0187	20 October 2002	ND	ND	ND	ND
119	35979-01-0189	22 October 2002	ND	ND	ND	ND
119	35979-01-0191	22 October 2002	ND	ND	ND	ND
119	35979-01-0193	22 October 2002	ND	ND	ND	ND
119	35979-01-0195	22 October 2002	ND	ND	ND	ND
120	35979-01-0123	26 October 2002	ND	ND	ND	ND
120	35979-01-0125	26 October 2002	ND	ND	ND	ND
120	35979-01-0127	26 October 2002	ND	ND	ND	ND
122	35979-01-0197	25 October 2002	ND	ND	ND	ND
122	35979-01-0199	25 October 2002	ND	ND	ND	ND
122	35979-01-0201	25 October 2002	ND	ND	ND	ND
122	35979-01-0203	25 October 2002	ND	ND	ND	ND
122	35979-01-0205	25 October 2002	ND	ND	ND	ND
122	35979-01-0207	25 October 2002	ND	ND	ND	ND
123	35979-01-0129	26 October 2002	ND	ND	ND	ND
123	35979-01-0130	26 October 2002	ND	ND	ND	ND
133	35979-01-0209	05 November 2002	ND	ND	ND	ND
133	35979-01-0211	05 November 2002	ND	ND	ND	ND
142	35979-01-0131	14 November 2002	ND	ND	ND	ND
142	35979-01-0132	14 November 2002	ND	ND	ND	ND
142	35979-01-0133	14 November 2002	ND	ND	ND	ND
142	35979-01-0134	14 November 2002	ND	ND	ND	ND
142	35979-01-0135	14 November 2002	ND	ND	ND	ND
142	35979-01-0136	14 November 2002	ND	ND	ND	ND
142	35979-01-0137	14 November 2002	ND	ND	ND	ND
142	35979-01-0138	14 November 2002	ND	ND	ND	ND
163	35979-01-0139	05 December 2002	ND	ND	ND	ND
163	35979-01-0140	05 December 2002	ND	ND	ND	ND
163	35979-01-0141	05 December 2002	0.010	ND	ND	ND
163	35979-01-0142	05 December 2002	ND	ND	ND	ND

Table XII. (continued). 2002 Analytical Results of Drainage Canal Water Samples

Days After Application	Sample ID	Collection Date	Analytical Results (ppb)			
			Fipronil	MB46513	MB45950	MB46136
163	35979-01-0143	05 December 2002	ND	ND	ND	ND
163	35979-01-0144	05 December 2002	ND	ND	ND	ND
163	35979-01-0145	05 December 2002	ND	ND	ND	ND
168	35979-01-0213	10 December 2002	ND	ND	ND	ND
168	35979-01-0215	10 December 2002	ND	ND	ND	ND
185	35979-01-0149	27 December 2002	ND	ND	ND	ND
185	35979-01-0151	27 December 2002	ND	ND	ND	ND

Table XIII. 2003 Analytical Results of Drainage Canal Water Samples

Days After Application	Sample ID	Collection Date	Analytical Results (ppb)			
			Fipronil	MB46513	MB45950	MB46136
Pre-Treatment	35979-2001A	11 May 2003	ND	ND	ND	ND
Pre-Treatment	35979-2002A	11 May 2003	ND	ND	ND	ND
Pre-Treatment	35979-2003A	11 May 2003	ND	ND	ND	ND
Pre-Treatment	35979-2004A	11 May 2003	ND	ND	ND	ND
0	35979-2005A	12 May 2003	ND	ND	ND	ND
0	35979-2006A	12 May 2003	ND	ND	ND	ND
0	35979-2007A	12 May 2003	ND	ND	ND	ND
0	35979-2008A	12 May 2003	ND	ND	ND	ND
1	35979-2009A	13 May 2003	ND	ND	ND	ND
1	35979-2010A	13 May 2003	ND	ND	ND	ND
1	35979-2011A	13 May 2003	ND	ND	ND	ND
1	35979-2012A	13 May 2003	ND	ND	ND	ND
2	35979-2013A	14 May 2003	ND	ND	ND	ND
2	35979-2014A	14 May 2003	ND	ND	ND	ND
2	35979-2015A	14 May 2003	ND	ND	ND	ND
2	35979-2016A	14 May 2003	ND	ND	ND	ND
3	35979-2017A	15 May 2003	ND	ND	ND	ND
3	35979-2018A	15 May 2003	ND	ND	ND	ND
3	35979-2019A	15 May 2003	ND	ND	ND	ND
3	35979-2020A	15 May 2003	ND	ND	ND	ND
13	35979-2057A	25 May 2003	ND	ND	ND	ND
13	35979-2058A	25 May 2003	ND	ND	ND	ND
13	35979-2059A	25 May 2003	ND	ND	ND	ND
13	35979-2060A	25 May 2003	ND	ND	ND	ND
15	35979-2065A	27 May 2003	ND	ND	ND	ND
15	35979-2066A	27 May 2003	ND	ND	ND	ND
15	35979-2067A	27 May 2003	ND	ND	ND	ND
15	35979-2068A	27 May 2003	ND	ND	ND	ND
23	35979-2097A	04 June 2003	ND	ND	ND	ND
23	35979-2098A	04 June 2003	ND	ND	ND	ND
23	35979-2099A	04 June 2003	ND	ND	ND	ND
23	35979-2100A	04 June 2003	ND	ND	ND	ND
24	35979-2101A	05 June 2003	ND	ND	ND	ND
24	35979-2102A	05 June 2003	ND	ND	ND	ND

Table XIII. (continued). 2003 Analytical Results of Drainage Canal Water Samples

Days After Application	Sample ID	Collection Date	Analytical Results (ppb)			
			Fipronil	MB46513	MB45950	MB46136
24	35979-2103A	05 June 2003	ND	ND	ND	ND
24	35979-2104A	05 June 2003	ND	ND	ND	ND
32	35979-2133A	13 June 2003	ND	ND	ND	ND
32	35979-2134A	13 June 2003	ND	ND	ND	ND
32	35979-2135A	13 June 2003	ND	ND	ND	ND
32	35979-2136A	13 June 2003	ND	ND	ND	ND
33	35979-2137A	14 June 2003	ND	ND	ND	ND
33	35979-2138A	14 June 2003	ND	ND	ND	ND
33	35979-2139A	14 June 2003	ND	ND	ND	ND
33	35979-2140A	14 June 2003	ND	ND	ND	ND
34	35979-2141A	15 June 2003	0.021	ND	ND	ND
34	35979-2142A	15 June 2003	ND	ND	ND	ND
34	35979-2143A	15 June 2003	ND	ND	ND	ND
34	35979-2144A	15 June 2003	ND	ND	ND	ND
43	35979-2177A	24 June 2003	ND	ND	ND	ND
43	35979-2178A	24 June 2003	ND	ND	ND	ND
43	35979-2179A	24 June 2003	ND	ND	ND	ND
43	35979-2180A	24 June 2003	ND	ND	ND	ND
46	35979-2189A	27 June 2003	0.020	ND	ND	ND
46	35979-2190A	27 June 2003	0.021	ND	ND	ND
46	35979-2191A	27 June 2003	0.020	ND	ND	ND
46	35979-2192A	27 June 2003	0.020	ND	ND	ND
53	35979-2217A	04 July 2003	ND	ND	ND	ND
53	35979-2218A	04 July 2003	ND	ND	ND	ND
53	35979-2219A	04 July 2003	ND	ND	ND	ND
53	35979-2220A	04 July 2003	ND	ND	ND	ND
72	35979-2293A	23 July 2003	ND	ND	ND	ND
72	35979-2294A	23 July 2003	ND	ND	ND	ND
72	35979-2295A	23 July 2003	ND	ND	ND	ND
72	35979-2296A	23 July 2003	ND	ND	ND	ND
83	35979-2337A	03 August 2003	ND	ND	ND	ND
83	35979-2338A	03 August 2003	ND	ND	ND	ND
83	35979-2339A	03 August 2003	ND	ND	ND	ND

Table XIII. (continued). 2003 Analytical Results of Drainage Canal Water Samples

Days After Application	Sample ID	Collection Date	Analytical Results (ppb)			
			Fipronil	MB46513	MB45950	MB46136
83	35979-2340A	03 August 2003	ND	ND	ND	ND
92	35979-2373A	12 August 2003	ND	ND	ND	ND
92	35979-2374A	12 August 2003	ND	ND	ND	ND
92	35979-2375A	12 August 2003	ND	ND	ND	ND
92	35979-2376A	12 August 2003	ND	ND	ND	ND
93	35979-2377A	13 August 2003	ND	ND	ND	ND
93	35979-2378A	13 August 2003	ND	ND	ND	ND
93	35979-2379A	13 August 2003	ND	ND	ND	ND
93	35979-2380A	13 August 2003	ND	ND	ND	ND
100	35979-2405A	22 August 2003	ND	ND	ND	ND
100	35979-2406A	22 August 2003	ND	ND	ND	ND
100	35979-2407A	22 August 2003	ND	ND	ND	ND
100	35979-2408A	22 August 2003	ND	ND	ND	ND
120	35979-2409A	09 Sept 2003	ND	ND	ND	ND
120	35979-2410A	09 Sept 2003	ND	ND	ND	ND
120	35979-2411A	09 Sept 2003	ND	ND	ND	ND
120	35979-2412A	09 Sept 2003	ND	ND	ND	ND
140	35979-2413A	29 Sept 2003	ND	ND	ND	ND
140	35979-2414A	29 Sept 2003	ND	ND	ND	ND
140	35979-2415A	29 Sept 2003	ND	ND	ND	ND
140	35979-2416A	29 Sept 2003	ND	ND	ND	ND
160	35979-2417A	19 October 2003	ND	ND	ND	ND
160	35979-2418A	19 October 2003	ND	ND	ND	ND
160	35979-2419A	19 October 2003	ND	ND	ND	ND
160	35979-2420A	19 October 2003	ND	ND	ND	ND
180	35979-2421A	08 Nov 2003	ND	ND	ND	ND
180	35979-2422A	08 Nov 2003	ND	ND	ND	ND
180	35979-2423A	08 Nov 2003	ND	ND	ND	ND
180	35979-2424A	08 Nov 2003	ND	ND	ND	ND

5.4.3 Analytical Results of Water Samples

Samples from the drainage canal and adjoining pond outlet discharge were analyzed to evaluate the runoff of water containing fipronil related residues. The LOQ was 0.010 ng/mL, and the MDL was 0.004 ng/mL for fipronil and its metabolites, MB46513, MB45950, and MB46136. All quantitative data for the analysis of the drainage canal and pond outlet discharge samples is provided in Appendix J.

A total of 85 and 104 samples collected in 2002 and 2003, respectively, were analyzed from the drainage canal and adjoining pond outlet discharge. Samples collected and analyzed were those at designated sampling periods in addition to those collected for several days following a significant rainfall event. This ensured that any fipronil-related residue arising from runoff would be detected. Additionally, 8 drainage canal sediment samples were analyzed in 2003.

None of the 2002 water samples analyzed contained detectable residues of parent fipronil or any metabolites. Water samples collected and analyzed in 2003 revealed that a detectable amount of the parent fipronil was present in one drainage canal sample collected 34 DAT, and all four drainage canal samples and one pond outlet sample collected 46 DAT (Table VI). These detects were caused by off site movement of fipronil when significant rainfall events occurred at or before the 34 and 46 DAT sampling dates. No analytes were detected anytime during the study period.

The analytical results for the fipronil detects in the drainage canal and pond outlet discharge are summarized in Figure 2, Table VI, and Tables XI to XIII.

Table VI. Detectable Residues in Drainage Canal and Pond Outlet

Sample ID	Date	Rainfall (in)	DAT	Fipronil (ppb)	MB46513 (ppb)	MB45950 (ppb)	MB46136 (ppb)
2141A[1]	15-June-03	2.77[3]	34	0.021	ND	ND	ND
2189A[1]	27-June-03	0[4]	46	0.020	ND	ND	ND
2190A[1]	27-June-03	0[4]	46	0.021	ND	ND	ND
2191A[1]	27-June-03	0[4]	46	0.020	ND	ND	ND
2192A[1]	27-June-03	0[4]	46	0.020	ND	ND	ND
2472A[2]	27-June-03	0[4]	46	0.021	ND	ND	ND

[1] Drainage Canal Water Samples
[2] Pond Outlet Discharge Water Sample
[3] Accumulative rainfall between June 12-15, 2003
[4] Water samples collected 1-day following a 1.1 inch rainfall

5.4.4 Analytical Results of Field Recovery Water Samples

Field recovery water samples were prepared to establish the stability of fipronil related residues during storage at the test site, subsequent transfer to the analytical facility, and further storage prior to analysis. Field recovery samples were prepared on 14 November 2002 by fortifying duplicate 100mL samples of pre-application (bulk) drainage canal water with a mixture of fipronil, MB46513,

Table XIV. 2003 Analytical Results of Pond Outlet Discharge Water Samples

Days After Application	Sample ID	Collection Date	Analytical Results (ppb)			
			Fipronil	MB46513	MB45950	MB46136
24	35979-2450A	05 June 2003	ND	ND	ND	ND
32	35979-2458A	13 June 2003	ND	ND	ND	ND
33	35979-2459A	14 June 2003	ND	ND	ND	ND
34	35979-2460A	15 June 2003	ND	ND	ND	ND
46	35979-2472A	27 June 2003	0.021	ND	ND	ND
53	35979-2479A	04 July 2003	ND	ND	ND	ND
92	35979-2518A	12 August 2003	ND	ND	ND	ND
100	35979-2526A	22 August 2003	ND	ND	ND	ND

Table XV. 2003 Analytical Results of Drainage Canal Sediment Samples

Days After Application	Sample ID	Collection Date	Analytical Results (ppb)			
			Fipronil	MB46513	MB45950	MB46136
90	35979-2535A	09 August 2003	ND	ND	ND	ND
90	35979-2536A	09 August 2003	ND	ND	ND	0.101
90	35979-2537A	09 August 2003	ND	ND	ND	ND
90	35979-2538A	09 August 2003	ND	ND	ND	ND
180	35979-2539A	08 Nov. 2003	ND	ND	ND	ND
180	35979-2540A	08 Nov. 2003	ND	ND	ND	ND
180	35979-2541A	08 Nov. 2003	ND	ND	ND	ND
180	35979-2542A	08 Nov. 2003	ND	ND	ND	ND

Figure 2: Fipronil-Related Residue Levels and Rainfall Data at the College Station, Texas Drainage Canal and Pond Test Site in 2002

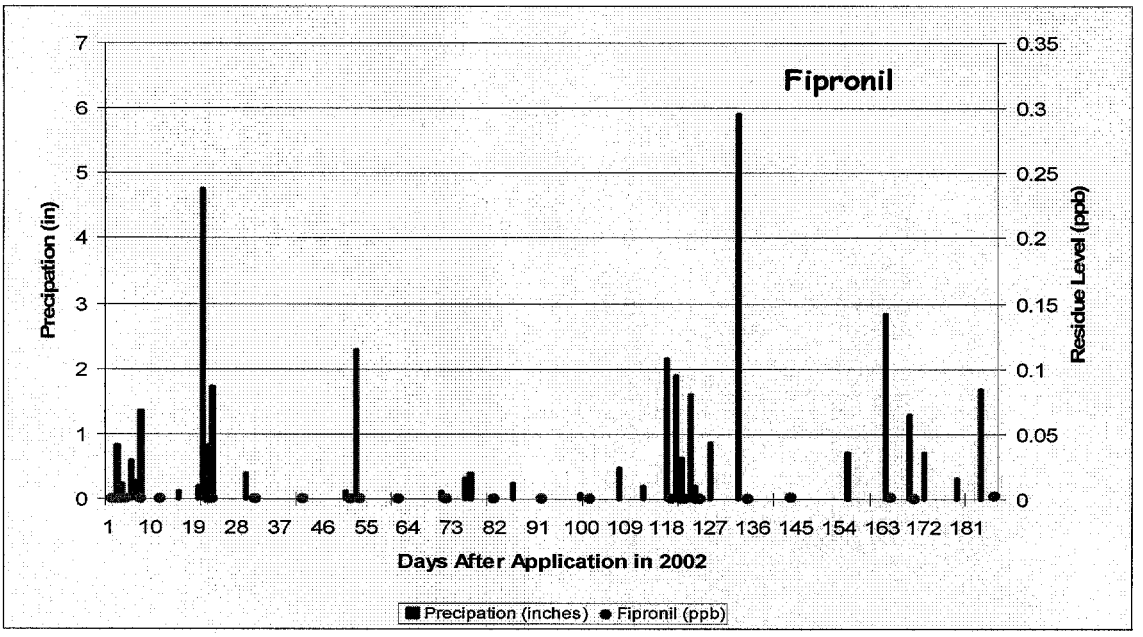
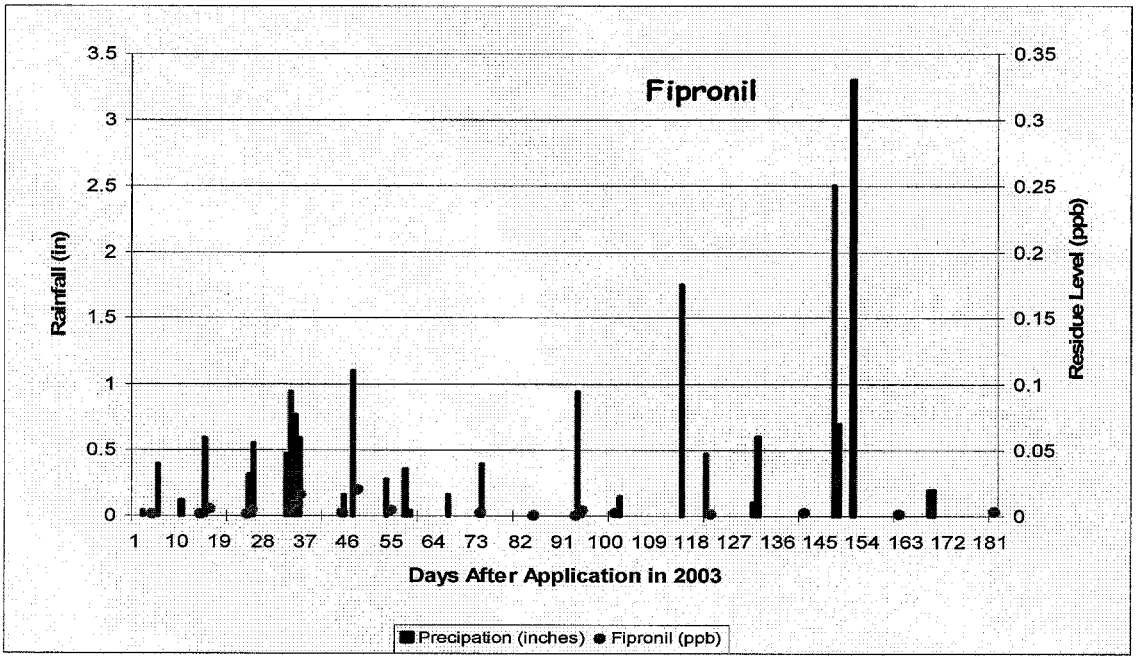


Figure 3: Fipronil-Related Residue Levels and Rainfall Data at the College Station, Texas Drainage Canal and Pond Test Site in 2003 *



***Note:** The only residue found that was greater than the LOQ in any drainage canal or pond outlet water sample in this 2-year study was parent fipronil at 34 and 46 DAT in 2003.