Data Evaluation Report of Modeling Calibration from Runoff Plots

PMRA Submission Number {.....} EPA MRID Number 46936102

Test material: 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.
EPA
Signature: James G. Hetrick
Date: 3/12/08

Secondary Reviewer: Thuy Nguyen
EPA
Signature:
Date: 3/6/08

CITATION: Tang, Z. and T.S. Ramanarayanan. 2006. Modeling Fate and Transport of Granular Formulations to Turf: Calibration of Small-Scale Runoff Studies. Sponsored by Bayer Crop Science, RTP, NC. Performed by Bayer Crop Science, Stillwell, KS, MRID 46936102.

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EXECUTIVE SUMMARY:

The non-guideline study provides ancillary data on the calibration of the PRZM model to small-scale runoff (SSR) studies. The registrant calibrated the PRZM model using the program **P**arameter **EST**imation (PEST), Version 8. The reviewer is not familiar with the PEST model. More importantly, the reviewer could not replicate the model calibration process because the PEST model is not currently available in the Agency. Therefore, the review cannot comment on the adequacy of the calibration process.

The registrant calibrated the PRZM model to the registrant sponsored SSR studies on warm season grass (MRID 46490301) and cool season grass (MRID 46490302). The model calibration process used the **PEST** model to optimize PRZM input parameters (field capacity, wilting point, water storage in the surface horizon, runoff volume, sediment loads, soil erosion parameters, half-life of fipronil and its degradation products, and organic carbon partitioning coefficient) for prediction of fipronil residue losses on sediment and in runoff. The registrant deemed the calibration acceptable when the calibrated/ observed ratio (C/O ratio) of fipronil loss in runoff ranged from 0.5 to 2.0.

The calibrated/observed ratio (C/O ratio) for fipronil mass in runoff ranged from 0.90 to 1.04. In contrast, the C/O ratio of fipronil degradation product mass in runoff was generally lower than parent fipronil. The C/O ratio ranged from 0.05 to 0.10 for MB 45950 and 0.59 to 1.53 for MB 46136. The calibration process consistently underestimated the mass of MB 45950 in sediment and runoff. The C/O ratio for total mass of fipronil residues in runoff and sediment ranged from 0.87 to 1.04

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

COMPLIANCE: This study was not conducted in compliance with USEPA FIFRA Good Laboratory Practices (40 CFR Part 160).

A. Material and Methods:

The objective of the study was to calibrate an exposure assessment model for small-scale fipronil runoff studies (SSRO) for warm season grass (MRID 46490301) and cool season grass (MRID 46490302).

PRZM/EXAMS modeling was calibrated using the **P**arameter **EST**imation (PEST), Verision 8. PEST optimizes the modeling using a nonlinear weighted least squares. Calibrated parameters include field capacity, wilting point, water storage in the surface horizon, runoff volume, sediment loads, soil erosion parameters, half-life of fipronil and its degradation products, and organic carbon partitioning coefficient (**Tables 2-8**). The registrant did a step-wise calibration process. Calibration performance was determined using the percent error calculation for runoff and erosion load for each runoff event. The calibration was deemed acceptable when the ratio of estimated to observed values ranged from 0.5 to 2.0.

Soil characteristics used in PRZM modeling are shown in **Table 2.**
Descriptions of SSROs are provided in the data evaluation records for MRID 46490301 and MRID 46490302.

B. Results and Discussion

The calibrated curve number, USLE factors (C, K, and LS), and soil wilting point for the test plots were comparable to published values. The calibrated field capacity was higher than the measured field capacity for the test soils. The registrant believes a discrepancy in measured and calibrated field capacity may be attributed to lower water potentials for actual field soil samples or because the field capacity was measured using disturbed soil samples. The percent error in calibrated sediment loads ranged from -25.9% to 50% (**Table 7**) The sediment load was consistently underestimated in the first runoff event and overestimated in the second runoff event.

The calibrated/observed ratio (C/O ratio) for fipronil mass in runoff ranged from 0.90 to 1.04 (**Tables 9 and 10**). In contrast, the C/O ratio of fipronil degradation product mass in runoff was generally lower than parent fipronil. The C/O ratio ranged from 0.05 to 0.10 for MB 45950 and 0.59 to 1.53 for MB 46136. The calibration process consistently underestimated the mass of MB 45950 in sediment and runoff. The C/O ratio for total mass of fipronil residues in runoff and sediment ranged from 0.87 to 1.04.

The registrant believes the calibration exercise demonstrates the PRZM model "described the fate and transport of fipronil and its relevant metabolites for granular applications on turf. They believe the calibrated parameters may be useful for estimating fipronil runoff from other relevant turf studies.

C. Review Comments

1. The registrant assumed the MB 46513 does not form in the turf environment. Field dissipation studies, however, indicate above ground uses of fipronil with foliar applications (e.g., turf) can result in the formation of MB 46513.

2. The registrant calibrated the PRZM/EXAMS modeling using a step-wise calibration process for eight model input parameters. Although the reviewer is not familiar with the PEST model, re-parameterization of model input parameter ignores inherent autocorrelations among the parameters.

3. Extrapolation of the calibrated modeling cannot be justified because the PRZM modeling was calibrated to specific use sites.

Table 1 Physical Properties Relevant to Environmental Behavior of Fipronil and Its Metabolites (Pugsley, R. F., et al., 1999 expect otherwise noted)

Property	Fipronil	MB 46136	MB 45950
Molecular Weight (g/mol)	437	451	421
Water Solubility (mg/L)	2.4	0.16	1.1
Octanol/Water Partition Coefficient (log P)	4.00/3.5	3.8	3.7 (3.45)
Vapor Pressure(mm Hg @ 25°C)	2.8×10^{-9}	5.7×10^{-9}	1.7×10^{-8}
Henry's Law Constant (atm-m^3/mol)	6.7×10^{-10}	2.1×10^{-8}	8.6×10^{-9}
Soil Koc (L/kg)	427-1248	1448-6745	1695-5621
Laboratory Aerobic Soil Half-Life (days)	18-308*	>=700**	>=700**

* Reference Waring, A.R. (1993) and Humphreys, et al., 1994.

**These values were not experimentally derived from laboratory studies on the metabolites, but were suggested based on studies with parent fipronil in which reliable degradation rates for the metabolites could not be calculated.

Table 2 Soil Characteristic Parameters used in PRZM

Depth interval(cm)	Warm season turf			Cool season turf		
	Texture	Bulk density (g/cm3)	OC (%)	Texture	Bulk density (g/cm3)	OC (%)
0 - 10	Sandy clay loam	0.88	1.86	Sandy loam	1.27	0.64
10 - 30	Sandy clay loam	1.13	0.46	Sandy loam	1.26	0.52

Table 3 Optimal Field Capacity and Permanent Wilting Point at Top Soil Layer from Water Storage Calibration

Parameter	Warm season turf			Cool season turf		
	Measured	Pedo-transfer function	Calibrated	Measured	Pedo-transfer function	Calibrated
Field capacity (%)	17.78	24 - 32	32	9.31	17-25	15.16
Permanent wilting point (%)	12.33	7-13	13	5.8	6-13	5.8

Table 4 Calibrated and Measured Soil Water Storage for the Top 10 cm Soil

Soil water storage	Warm season turf		Cold season turf	
	Measured range (cm)	Calibrated (cm)	Measured range (cm)	Calibrated (cm)
Before application	1.85 – 1.90	1.85	1.21 – 1.53	1.52
2 days after and before rainfall	2.24 – 2.65	2.12	1.32 – 1.51	1.34
Day 6	1.93 – 2.31	2.01	1.01 – 1.29	1.24
Day 9 and before rainfall			1.06 – 1.40	1.06
Day 10 and before rainfall	1.79 – 1.98	1.89		

Table 5 Calibrated and Measured Runoff for the Simulated Rainfall Events

Rainfall event	Warm season turf				Cool season turf			
	Rainfall (cm)	Runoff (cm)		Percent error (%)	Rainfall (cm)	Runoff (cm)		Percent error (%)
		Measured	Calibrated			Measured	Calibrated	
First	6.45	2.26	2.471	9.3	4.47	2.46	2.26	-8.10
Second	6.25	2.19	2.109	-3.7	5.54	2.59	2.84	9.60

Table 6 Optimal Erosion Input Parameters from Sediment Loads Calibration

Parameter	Calibrated		Model manual for grass	EPA standard scenarios
	Warm season turf	Cool season turf		
C factor	0.001	0.001	0.004	0.001-0.326
K factor	0.24	0.24	0.25	
LS factor	0.50	0.58	0.58	
Manning's	0.25	0.25	0.17-0.30	0.023, 0.11

Table 7 Calibrated and Measured Sediment Load for the Simulated Rainfall Events

Sediment load	Warm season turf			Cool season turf		
	Measured (g)	Calibrated (g)	Percent error (%)	Measured (g)	Calibrated (g)	Percent error (%)
First event	43.7	32.4	-25.9	71.4	55.2	-22.7
Second event	16.6	24.9	50	37.0	48.6	31.4

Table 8 Calibrated Soil Half-life and K_{oc} Values

Parameter	Warm season turf	Cool season turf	Lab - determined	
			Range	Average
Half life - fipronil (day)	82	139	18-308	
K_{oc} – fipronil	563	918	427-1248	803
K_{oc} – MB 45950	1695	1695	1695-5621	3911
K_{oc} – MB 46136	1448	5329	1448-6745	4209

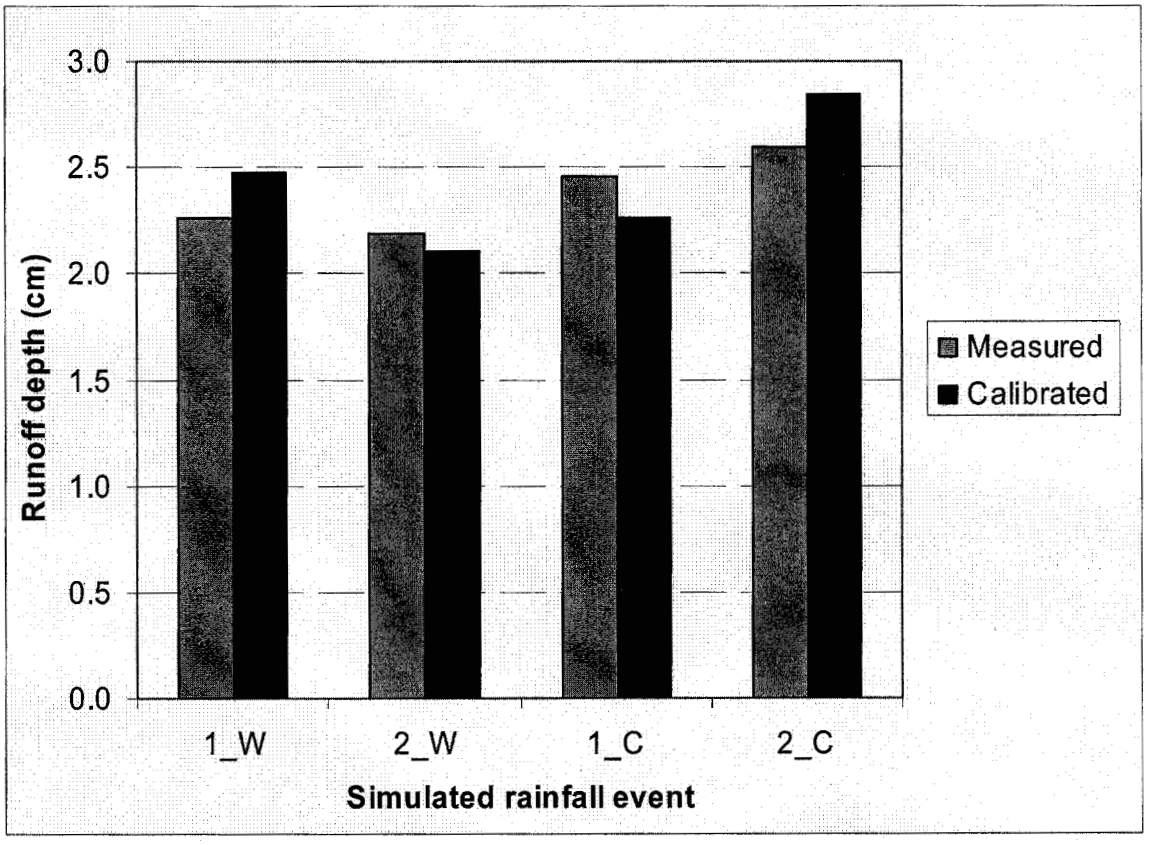
Table 9 Calibrated and Measured Chemical Loads for the Warm Season Turf Scenario

	Measured (mg)	Calibrated (mg)	Ratio (calibrated / measured)	Percent applied (based on calibrated)
Fipronil mass				
First event	4.1	4.2	1.02	4.5
Second event	2.3	2.1	0.91	2.3
MB 45950 mass				
First event	0.02	0.002	0.10	0.002
Second event	0.05	0.005	0.10	0.005
MB 46136 mass				
First event	0.15	0.2	1.3	0.2
Second event	0.27	0.16	0.59	0.2
Total fiprole mass				
First event	4.27	4.40	1.03	4.7
Second event	2.62	2.27	0.87	2.4

Table 10 Calibrated and Measured Chemical Loads for the Cool Season Turf Scenario

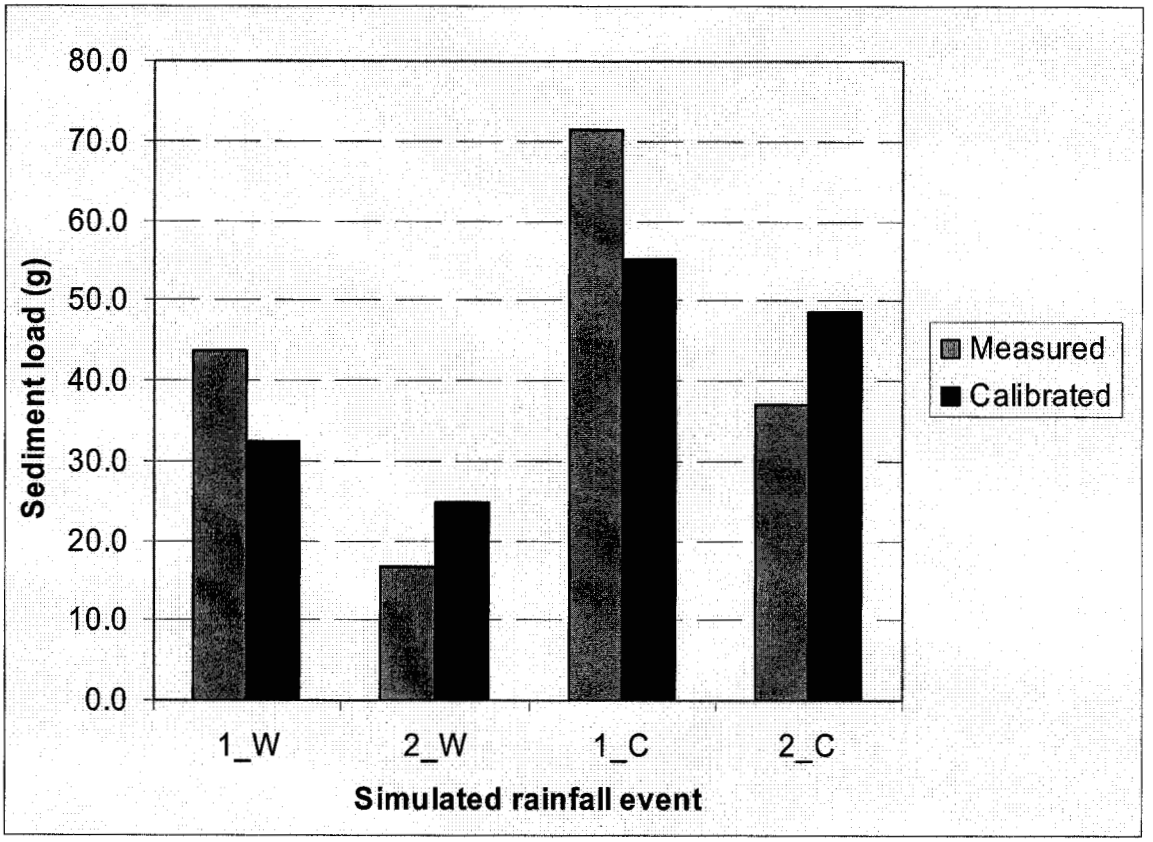
	Measured (mg)	Calibrated (mg)	Ratio (calibrated / measured)	Percent applied (based on calibrated)
Fipronil mass				
First event	7.2	7.4	1.04	6.1
Second event	6.2	5.6	0.90	4.5
MB 45950 mass				
First event	0.06	0.004	0.07	0.003
Second event	0.21	0.011	0.05	0.009
MB 46136 mass				
First event	0.15	0.23	1.53	0.2
Second event	0.32	0.26	0.81	0.2
Total fiprole mass				
First event	7.41	7.63	1.04	6.3
Second event	6.73	5.87	0.87	1.9

Figure 3 Calibrated and Measured Runoff Depth for Both the Warm Season Turf and the Cool Season Turf Scenarios



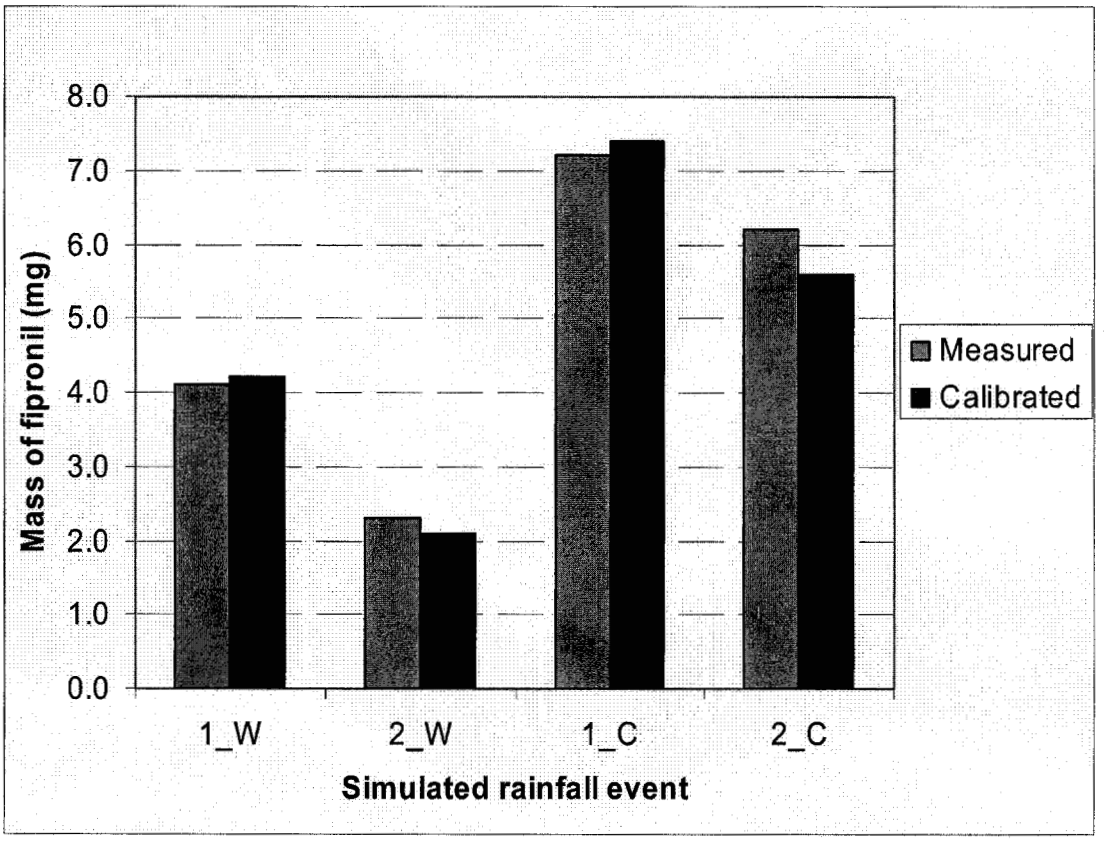
Note: 1_W: first simulated rainfall event for the warm season turf scenario
2_W: second simulated rainfall event for the warm season turf scenario
1_C: first simulated rainfall event for the cool season turf scenario
2_C: second simulated rainfall event for the cool season turf scenario

Figure 4 Calibrated and Measured Sediment Load for Both the Warm Season Turf and the Cool Season Turf Scenarios



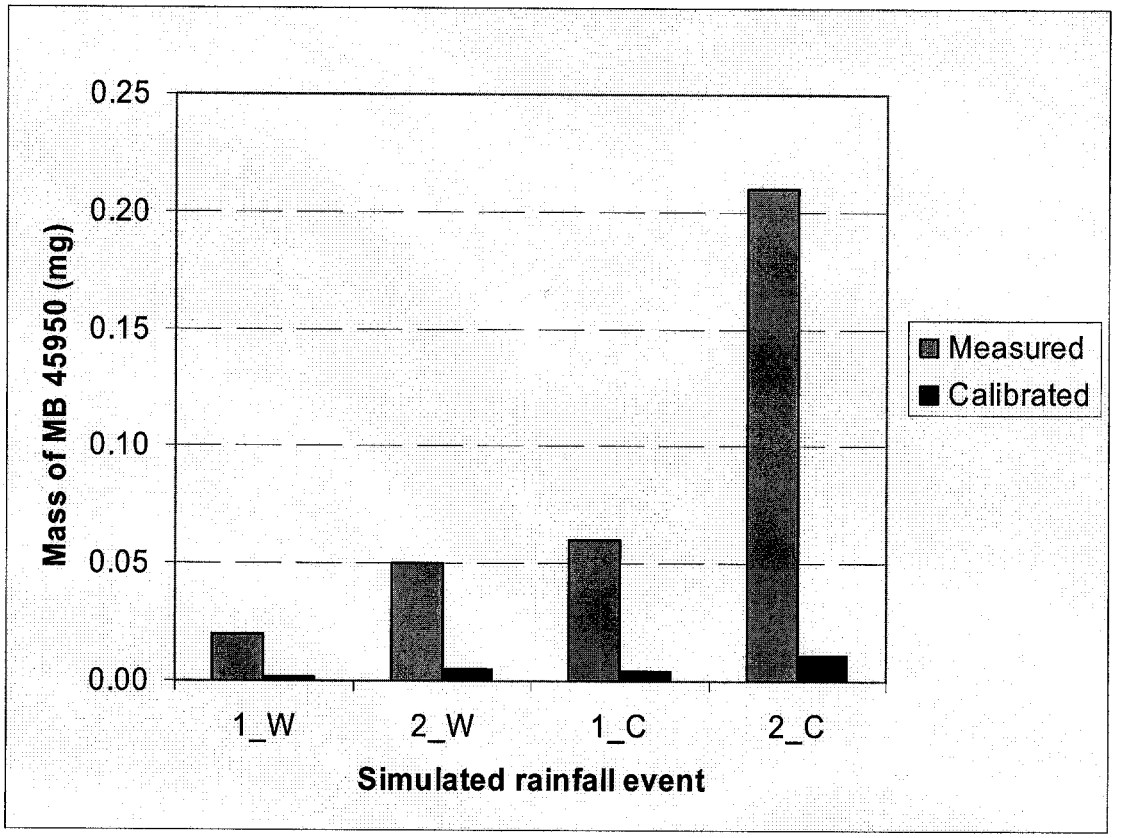
Note: 1_W: first simulated rainfall event for the warm season turf scenario
2_W: second simulated rainfall event for the warm season turf scenario
1_C: first simulated rainfall event for the cool season turf scenario
2_C: second simulated rainfall event for the cool season turf scenario

Figure 5 Calibrated and Measured Mass of Fipronil in Runoff and Sediment for Both the Warm Season Turf and the Cool Season Turf Scenarios



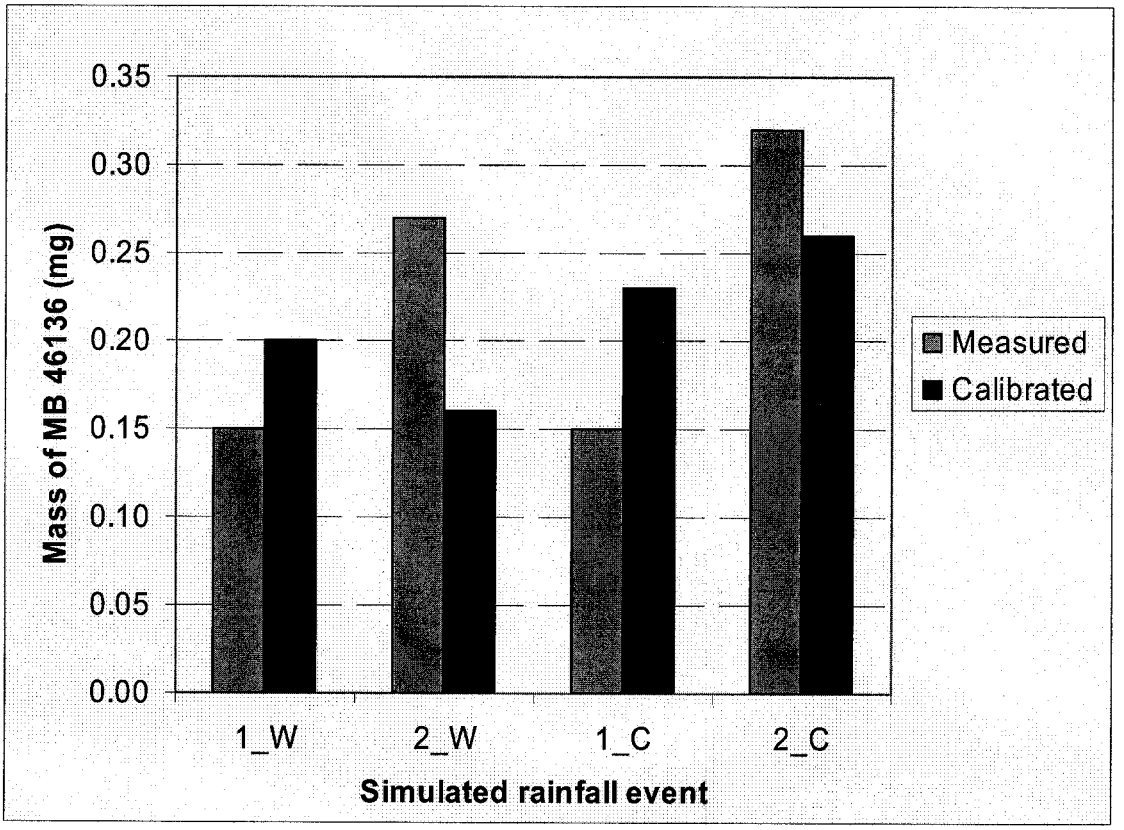
Note: 1_W: first simulated rainfall event for the warm season turf scenario
2_W: second simulated rainfall event for the warm season turf scenario
1_C: first simulated rainfall event for the cool season turf scenario
2_C: second simulated rainfall event for the cool season turf scenario

Figure 6 Calibrated and Measured Mass of MB 45950 in Runoff and Sediment for Both the Warm Season Turf and the Cool Season Turf Scenarios



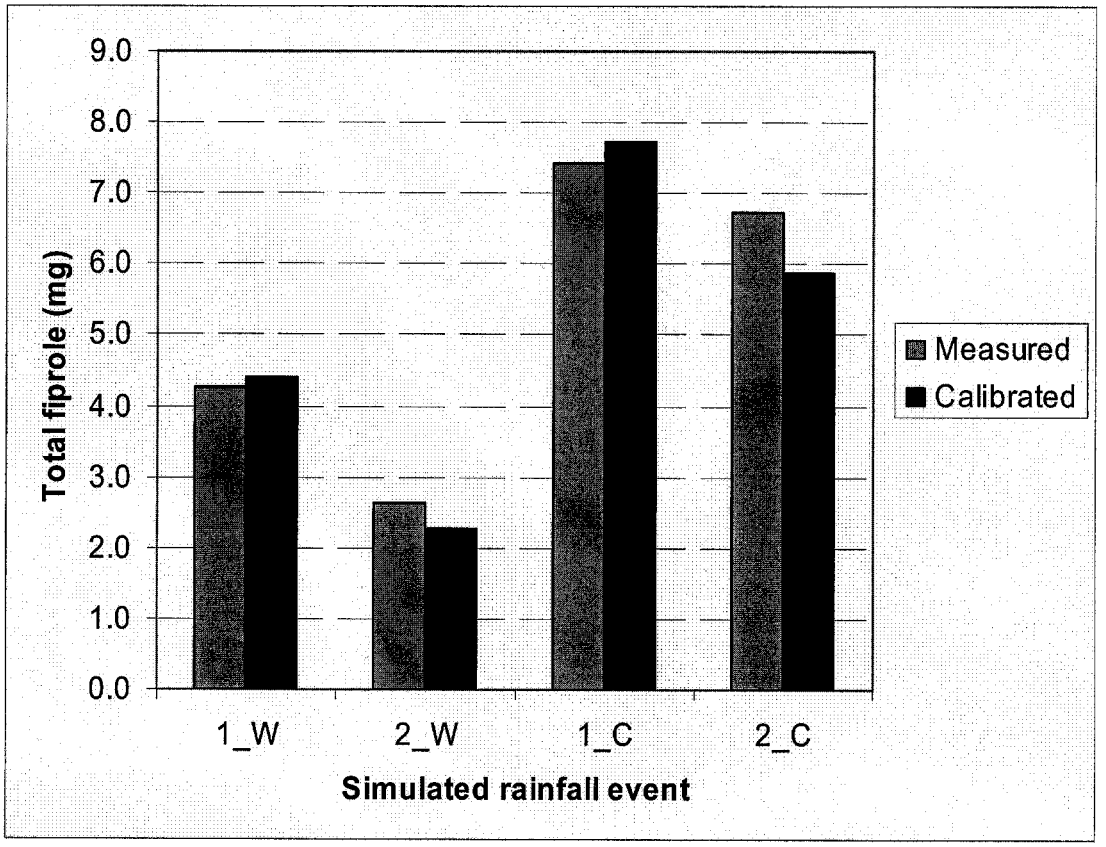
Note: 1_W: first simulated rainfall event for the warm season turf scenario
2_W: second simulated rainfall event for the warm season turf scenario
1_C: first simulated rainfall event for the cool season turf scenario
2_C: second simulated rainfall event for the cool season turf scenario

Figure 7 Calibrated and Measured Mass of MB 46136 in Runoff and Sediment for Both the Warm Season Turf and the Cool Season Turf Scenarios



Note: 1_W: first simulated rainfall event for the warm season turf scenario
2_W: second simulated rainfall event for the warm season turf scenario
1_C: first simulated rainfall event for the cool season turf scenario
2_C: second simulated rainfall event for the cool season turf scenario

Figure 8 Calibrated and Measured Mass of Total Fiprole in Runoff and Sediment for Both the Warm Season Turf and the Cool Season Turf Scenarios



Note: 1_W: first simulated rainfall event for the warm season turf scenario
2_W: second simulated rainfall event for the warm season turf scenario
1_C: first simulated rainfall event for the cool season turf scenario
2_C: second simulated rainfall event for the cool season turf scenario