Data Evaluation Report of Modeling Fate and Transport from Turf

PMRA Submission Number {......}   EPA MRID Number 46936103

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

Secondary Reviewer: Thuy Nguyen   Signature: *Thuy L. Try*
EPA   Date: 5/2/08

CITATION: Tang, Z. and T.S. Ramanarayanan. 2006. Modeling Fate and Transport of Fipronil and Its Metabolites in Surface Water Following Application of Chipco Topchoice® to Turf. Sponsored by Bayer Crop Science, RTP, NC. Performed by Bayer Crop Science, Stillwell, KS, MRID 46936103.

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EXECUTIVE SUMMARY:

The non-guideline study provides ancillary data on the prediction of fipronil concentrations for the Pickens, Arkansas water monitoring study (MRID 46733905) using calibrated PRZM/EXAMS modeling. The model calibration process is not described in the study.

The registrant used a calibrated PRZM/EXAMS model to estimate both seasonal and long-term concentrations of fipronil and its degradation products in the pond for the Pickens, Arkansas water monitoring study (MRID 46733905). They calibrated the model by changing the curve number to 79. Also, site specific soil and precipitation were used in the modeling. Pesticide applications were simulated for April 15th, April 30th, May 15th, and May 30th.

There was a positive correlation of observed and predicted concentrations of fipronil (r = 0.94) and total fipronil residues (r = 0.92) in the pond water during the actual study period. Long-term PRZM/EXAMS simulations were conducted to estimate long-term aquatic exposure to total fipronil and its degradation products. Time series for the application date scenarios show the highest fipronil concentration is approximately 1.8 ug/L. The maximum fipronil concentration in the monitoring study (0.39 ug/L) accounted for the 77rd percentile annual peak concentration for the April 15th and May 15th applications, 73rd percentile annual peak concentration for the April 30th application, and 80th percentile annual peak concentration for the May 30th application.

The registrant also evaluated a time series of soil pore water concentrations to assess the potential for fipronil accumulation in soil. The registrant believes there is no observable accumulation of total fipronil residues in the soil pore water; therefore, the potential for year to year accumulation of fipronil residues is low.

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 predict the temporal distribution of fipronil water concentrations for the Pickens, Arkansas water monitoring study (MRID 46733905) using calibrated PRZM/EXAMS modeling.

PRZM-EXAMS modeling was conducted to estimate fipronil residues in surface water. The modeling strategy assumes MB 46136 and MB 45950 are the only soil degradation products of fipronil (**Figure 4**). The degradation product MB 46513 was assumed to form only in aqueous environments. PRZM/EXAMS modeling was calibrated to provide the best fit of observed and predicted water concentrations of fipronil and its degradation products. The model was calibrated by modifying the curve number to 79.

The model was parameterized using site specific properties. The runoff area and pond size were modified to represent the runoff site. Precipitation data for actual field simulation were taken from Monticello, AR (Coopertative Station ID 034900) NOAA weather station. Long-term precipitation data from 1961 to 1990 were taken from Dumas, AR (Cooperative Station ID 036253) NOAA weather station. Evapotranspiration was estimated according to the PRZM users manual. Soils were characterized to a depth of 15 cm. Average values of bulk density, field capacity, wilting point, and organic carbon were used to represent the soil. The USLE erodibility (K) factor, LS factor, and Manning's roughness coefficient were derived from the PRZM manual. A C factor of 0.001 was derived from PRZM calibration study (Tang and Ramanarayanan, 2006, MRID 46936102). The chemical application method was set to 4 with an incorporation depth of 0.1 cm.

Environmental fate properties of fipronil and its degradation products are shown in **Table 3**. The aerobic soil metabolism rate of fipronil was calibrated to 15 days. This half-life was selected to represent the field dissipation half-life of fipronil. A half-life of 730 days was selected to represent the persistence of MB45950 and MB46136. The registrant stated a 15-foot untreated area (buffer) was not considered in the modeling.

Pesticide applications were simulated according to the actual pesticide application dates in the Pickens, AR water monitoring study. Additionally, long-term PRZM/EXAMS simulations considered single application dates of April 15th, April 30th, May 15th, and May 30th. Pesticide applications were assigned days with no precipitation.

B. Results and Discussion

There was a positive correlation of observed and predicted concentrations of fipronil (r = 0.94) and total fipronil residues (r = 0.92) in the pond water during the actual study period (**Figures 6 and 7**).

Long-term PRZM/EXAMS simulations were conducted to estimate long-term aquatic exposure to total fipronil and its degradation products. Time series for the application date scenarios show the highest fipronil concentration is approximately 1.8 ug/L **(Figures 8, 9, 10, and 11)**. The maximum fipronil concentration in the monitoring study (0.39 ug/L) accounted for the 77rd percentile annual peak concentration for the April 15th and May 15th applications, 73rd percentile annual peak concentration for the April 30th application, and 80th percentile annual peak concentration for the May 30th application.

The registrant also evaluated a time series of soil pore water concentrations to assess the potential for fipronil accumulation in soil **(Figure 12)**. The registrant believes there is no observable accumulation of total fipronil residues in the soil pore water. Therefore, the potential for year to year accumulation of fipronil residues is low.

C. Review Comments

1. The registrant assumed the MB 46513 does not form in the turf environment. Field dissipation studies of fipronil, however, indicate above ground uses of fipronil with foliar applications (e.g., turf) can result in the formation of MB 46513. This may explain the underestimation of predicted concentrations as shown in **Appendix D**.

2. The registrant calibrated the PRZM/EXAMS model to the water monitoring study in Picken, AR. There is no description on the exact procedure used to calibrate the model. More importantly, there is no discussion on the criteria used to evaluate the calibration process.

3. The registrant presented time series for soil pore water concentrations of total fipronil. The reviewer assumes these data were taken from the PRZM simulation. Sediment pore water concentrations would be taken from the PRZM/EXAMS simulation.

The registrant presented long-term time series for soil pore water concentrations. They concluded the data shows the fipronil residues do not accumulate in the soil pore water. The registrant should clarify if the time series represents soil pore water or sediment pore water.

4. The registrant provided the output files in Appendix B. The reviewer notes the files are difficult to evaluate because of misalignment of the columns.

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pond study, kinetics modeling was performed to characterize the degradation of fipronil in a sediment-water system. The calibrated hydrologic and chemical fate parameters from the calibration work of SSRO, and aquatic degradation characteristics obtained from kinetic modeling of simulated pond, were used to facilitate the parameterization of models employed in this study.

2. SUBSTANCE UNDER CONSIDERATION

Degradation pathways of fipronil in the environment are summarized in Figure 2. Degradation of fipronil in the environment occurs via four competing pathways of oxidation, reduction, photolysis and hydrolysis. The toxicologically significant metabolites of fipronil (MB 46136, MB 45950, and MB 46513) continue to further degrade mainly via microbe-mediated hydrolysis (nitrile to amide to acid). Hydrolysis has been shown to be a detoxification process. The physiochemical and environmental fate properties of fipronil and its major metabolites related to this study are summarized in Table 1.

Table 1   Physical and Environmental Fate Properties Relevant to Environmental Behavior of Fipronil and Its Metabolites (Reference 3 expect otherwise noted)

Property	Fipronil	MB 46136	MB 45950	MB 46513
Molecular Weight (g/mol)	437	451	421	389
Water Solubility (mg/L)	2.4	0.16	1.1	0.95
Octanol/Water Partition Coefficient (log P)	3.5	3.8	3.7 (3.45)	3.4
Vapor Pressure(mm Hg @ 25°C)	2.8×10^{-9}	5.7×10^{-9}	1.7×10^{-8}	3.0×10^{-8}
Henry's Law Constant (atm-m^3/mol)	6.7×10^{-10}	2.1×10^{-8}	8.6×10^{-9}	1.6×10^{-8}
Soil Koc (L/kg)	427-1248	1448-6745	1695-5621	1150-1498
Laboratory Aerobic Soil Half-Life (days)]	18-308 [4 and 5]	>=700	>=700	630-693 [9]
Laboratory Aerobic Aquatic Half-Life (days) [6 and 7]	15-32			
Laboratory Aqueous Photolysis Half-Life (days) [8]	0.33			

Otherwise, they were from model-recommended estimates, related field dissipation studies, or model calibration. The PRZM/EXAMS model was calibrated based on a comparison of observed versus predicted pond water concentrations of fipronil and the three metabolites. The principle of the calibration is that all parameters should be adjusted within ranges either reported by actual measurements or in databases representing site-specific conditions. A detailed description of model parameterizations is given below.

Figure 4   A schematic diagram of modeled fipronil transport and transformation processes.
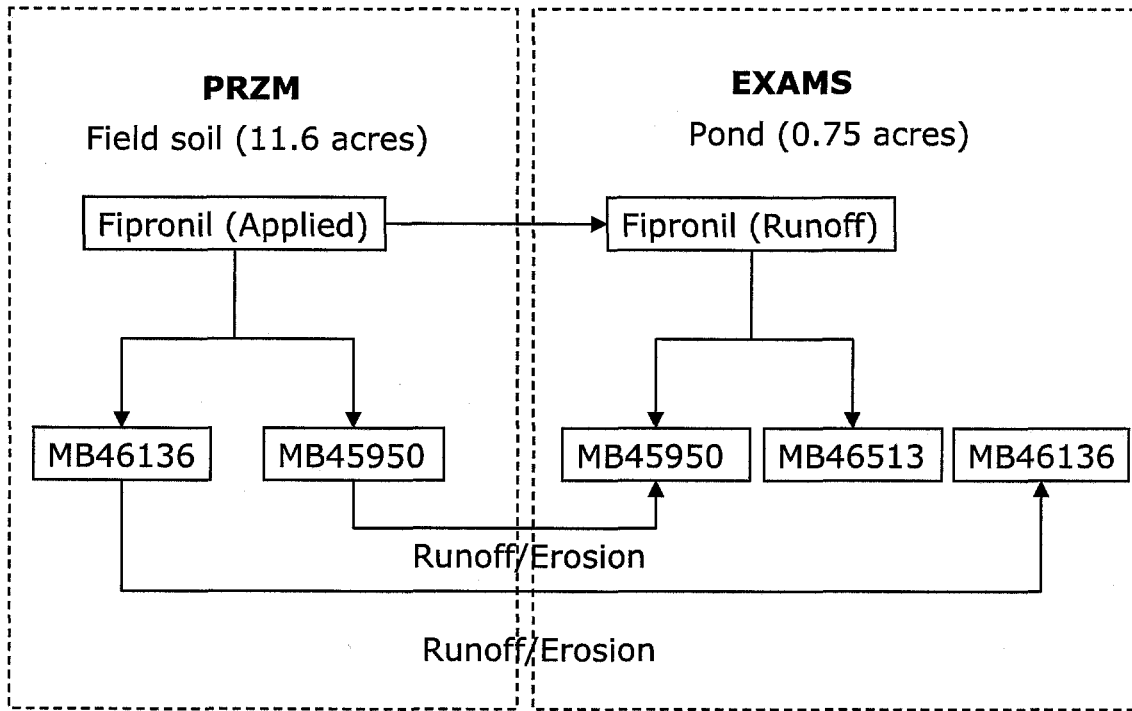
5.1   PRZM input

PRZM requires the following input data: meteorologic parameters, soil and hydraulic parameters, application, and chemical parameters. The required meteorologic data include daily precipitation, mean air temperature, and monthly daylight hours. Measured on-site precipitation was used for the monitoring period. Precipitation in other periods and mean air temperature were taken from a nearby NOAA weather station (Monticello, AR, cooperative station ID 034900). The precipitation for the simulation period is shown in Figure 5.   Monthly daylight hours for evaportranspiration estimation were from tabulated values in the model user manual [10].

The soils at the test site were characterized to a depth of 15 cm. The soil in the model was divided into three horizons with the depths of 10cm, 20cm, and 70cm. Horizon 1 to 3 was subdivided into 0.1, 2, and 2-cm-thick compartments, respectively. Soil bulk density and organic carbon content were from the field measurements. Water retention measurements at 1/3 bar and 15 bar pressure heads were used as field capacity and permanent wilting point. The average values of the measurements were used for these soil parameters (Table 2). PRZM was employed to simulate surface runoff in this study, and only the top soil horizon has an impact on surface

runoff simulation. Therefore, the soil properties were assumed the same for all three horizons although the measurements were mainly applicable for the top horizon.

Table 2   Soil Input Parameters Used in PRZM

Parameter	Value
Bulk Density (g/cm3)	1.10
Field Capacity (cm3/cm3)	0.282
Wilting Point (cm3/cm3)	0.116
Organic Carbon (%)	0.3

Universal soil loss equation erodibility (K) factor, LS factor and Manning's roughness coefficient were derived from the tables in the PRZM manual based on the site characteristics. A K factor of 0.43 was used as input. This value is close to the K factor value of 0.39 from STASGO soil survey data. A value of 0.001 of universal soil loss equation C factor was from the PRZM calibration study [1]. Curve number was calibrated to 79 which is within the range of curve numbers for C and D soils.

MB 46136 is generally found as an impurity in the formulated product. In order to account for that, in addition to fipronil active ingredient, MB 46136 was also applied at the rate of 3% of applied fipronil. It should be noted that the amount of MB 46136 in the formulation was not measured prior to the runoff study and the application of 3% of MB 46136 is an assumption based on discussions with Bayer CropScience product chemists. The chemical application method (CAM) parameter was set to 4, which is soil application, with an incorporation depth of 0.1 cm. The incorporation depth was not measured in the field, but derived from the calibration of PRZM against the SSRO study [1]. Being a granular application, an application efficiency of 100% with no spray drift was simulated.

Degradation rates of parent were calibrated to achieve an overall effective half-life of 15 days for parent fipronil. This is consistent with the half-life values of 12 to 15 days observed in a field dissipation study on turf with slit application [13]. Because the half-life values for MB 46136 and MB 45950 were not derived from laboratory metabolism studies or field dissipations studies, the half-life values of 730 days (two years) were used in the simulations for conservative reasons. The transformation rates of fipronil to the metabolites were from a kinetic study which derived 20 and 5 percent of parent fipronil for MB 46136 and MB 45950, respectively based on laboratory metabolism studies [3]. The same transformation rates were also used in the calibration of PRZM on the SSRO study. The calibrated half-lives in the soil and Koc for fipronil and its metabolites are shown in Table 3.

Table 3   Half-life and Koc Values for Fipronil and Three Metabolites Calibrated in PRZM and EXAMS

Substance	Koc	Half-life (days)		
		Aerobic Soil	Aerobic Aquatic	Aqueous photolysis
Fipronil	1248	15	32.1	0.33
MB950	5621	730	42.8	
MB513	1290		16.0	
MB136	5372	730	21.0	

5.2   EXAMS input

The operation of EXAMS involved three types of data inputs: environment, load, and chemical. The EFED standard farm pond scenario was slightly modified to serve as the environment data input. The modifications made to the parameters describing the physical characteristics of the pond, including surface area, depth, and volume. The daily loading value files generated by PRZM were used as the "load" data input. The chemical data input files were created mainly based on two sources: the environmental fate profiles of fipronil and its metabolites (Table 1), and model calibration based on kinetics modeling of a simulated pond study [2].

Metabolism and photolysis of parent fipronil were simulated as separate processes in EXAMS in order to represent the separate formation pathways of MB 45950 and MB 46513.The "yield" parameter for the aerobic metabolite process in which MB 45950 was formed was calculated based on the kinetic analysis of a simulated pond study (2). The transfer file between PRZM and EXAMS is presented in Appendix B. For parent fipronil, photolysis was obtained from the result of an aqueous photolysis study (Table 1). The K_{oc} values of each substance calibrated in the PRZM model were used in the EXAM model. The degradation rates of fipronil and the three metabolites were derived from minimal calibration based on the kinetic modeling of the simulated pond study. Table 3 showed aquatic half-lives calculated from the calibrated degradation rates.

5.3   Comparison of calibrated and observed results

Although the model calibrations were carried out for each individual substance, total fiprole concentrations that include fipronil, MB 46136, MB 45950 and MB 46513 are of interest. Therefore, the simulated fipronil and total fiprole concentrations using the calibrated PRZM/EXAMS model were compared to those observed values, respectively, in the monitoring period in 2003 and 2004. Input files used for the simulations and corresponding output files are presented in Appendix A through Appendix C. The comparisons of the concentrations of each individual simulated substance to the corresponding observed values are presented in Appendix D.

Observed and simulated daily total fiprole concentrations and parent fipronil concentrations are presented in Figure 6 and Figure 7. The observed concentrations in each sampling date were represented by mean, minimum, and maximum concentrations of all sampling points. As shown in the figures, the simulated concentrations compared very well with
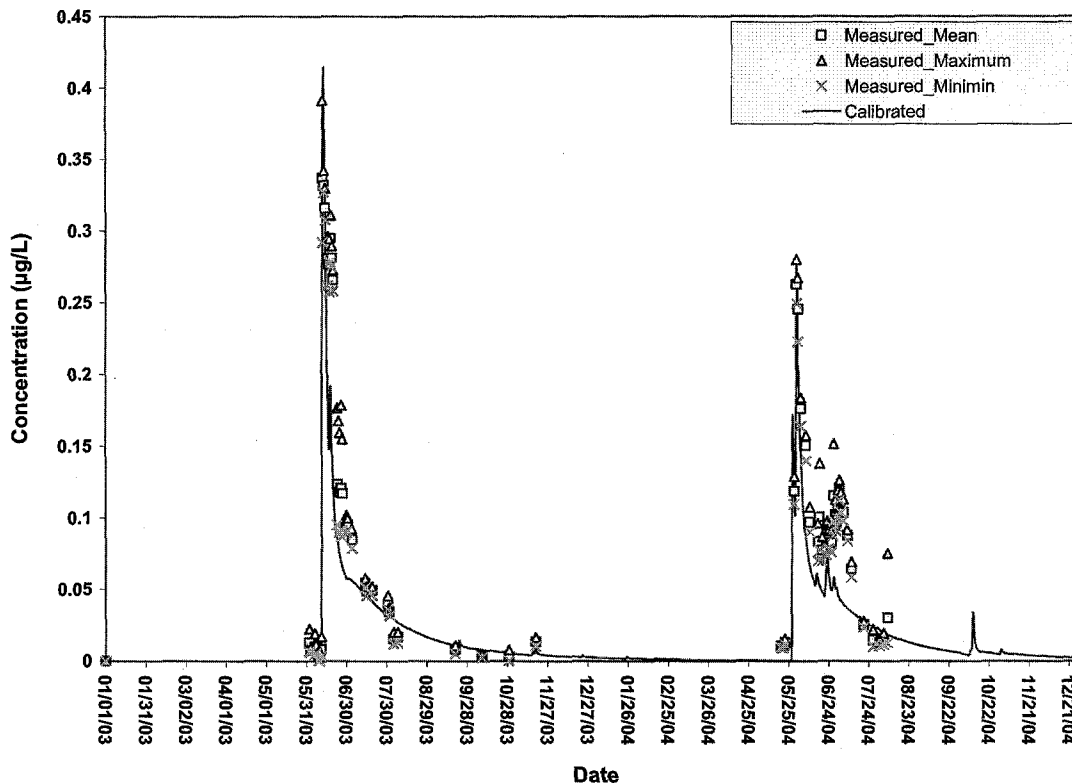
Figure 6   Simulated Parent Fipronil Concentrations Compared to the Measured
Concentrations in 2003 and 2004

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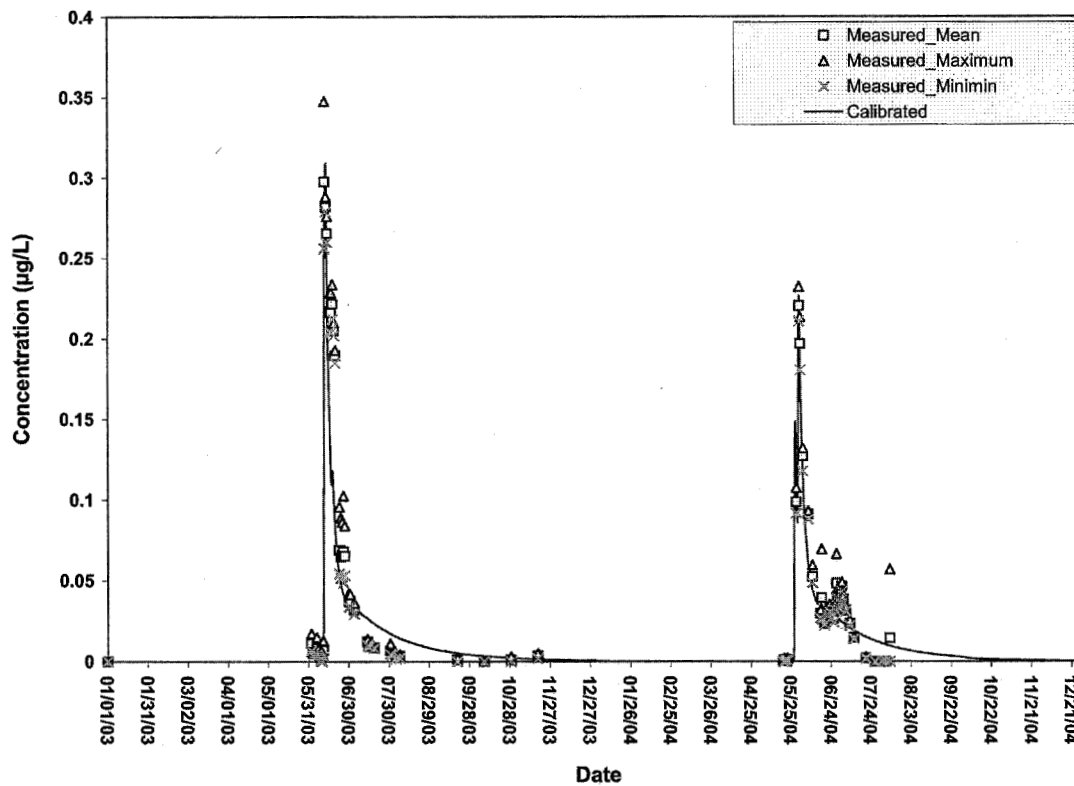
Figure 7   Simulated Total Fiprole Concentrations Compared to the Measured
            Concentrations in 2003 and 2004

5.4   Long-term simulations

One of the objectives of this work was to predict long-term temporal distribution of
aquatic exposure at this site. Long-terms simulations using the calibrated PRZM/EXAMS model
covered the period of 1961 to 1990 with thirty years of weather data. Historical daily weather
data such as precipitation and air temperature were obtained from National Oceanic and
Atmospheric Administration (NOAA) cooperative weather stations closest to the site (Dumas,
AR, cooperative station ID 032300). The weather data were then screened for missing values and
filled from the nearest weather station where the data was available (ROHWER_2_NNE, AR,
cooperative station ID 036253). The compound was assumed to be applied once a year with the
maximum allowable application rate in the label. The simulations were conducted in four
scenarios based on the dates of application, April 15, April 30, May 15, and May 30, which
covered the product application window in Arkansas. It was assumed the application was not
made on wet days. In other words, application was manually postponed in the input file, when
there is rain on the above desired application dates until a dry day. Input files used for the long-
term simulations are presented in Appendix A.

Did not apply with rainfall

Results (Figure 8 through Figure 11) showed that the highest annual peak concentration was less than 1.2 ppb for 30-year simulations in all the four scenarios. The measured maximum total fiprole concentration 0.39 µg/L corresponded to the 77rd, 73rd, 77th, and 80th percentile of annual peak concentrations for applications that occurred on April 15, April 30, May 15, and May 50, respectively.

Long-term total fiprole concentration in soil pore water was also simulated. As an example, the simulation result for application occurred on April 15 is presented in Figure 12. The results for application occurred on the other dates (April 30, May 15, and May 30) can be found in Appendix E. The figures clearly show that fiprole (parent and metabolites) does not tend to accumulate in soil pore water. The carry-over concentration from one season to the next is very low.
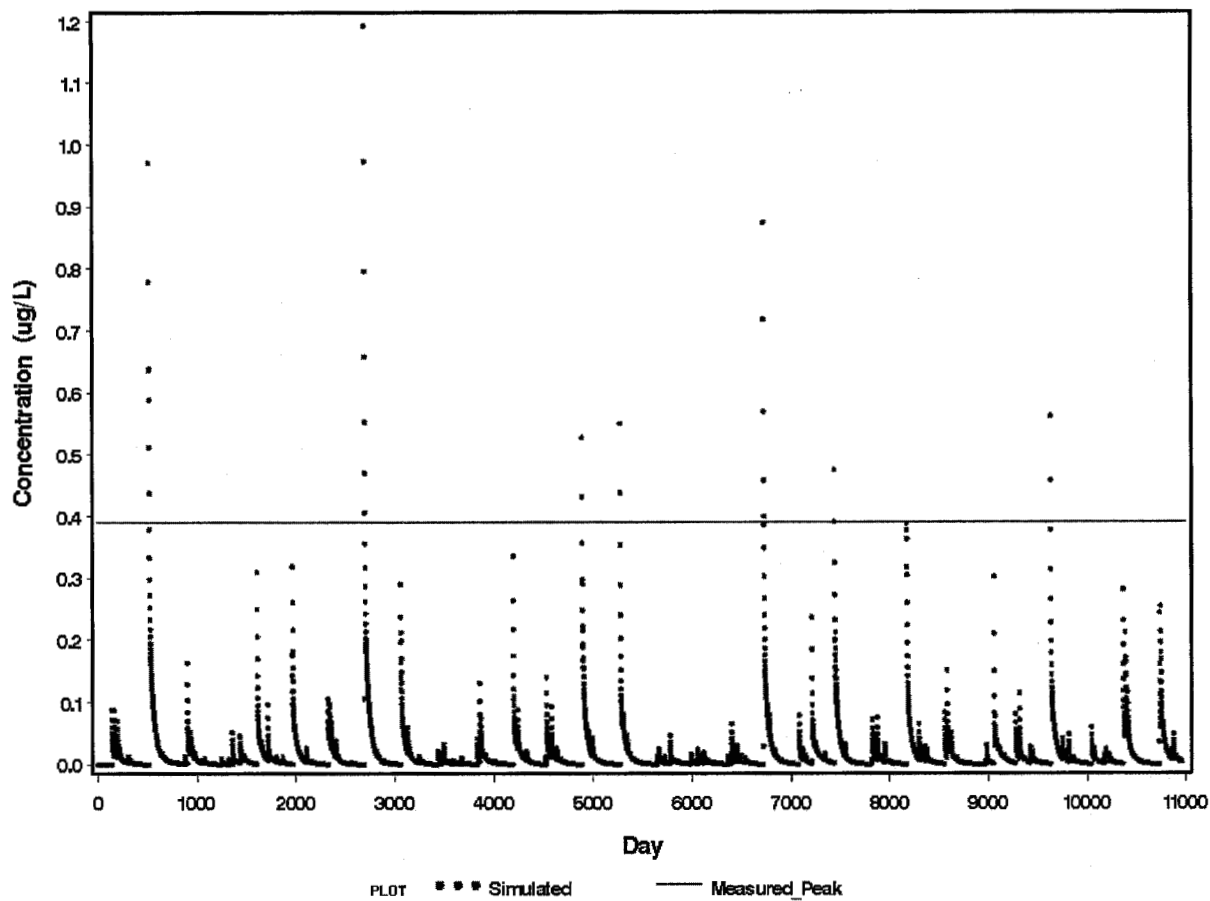
Figure 8   Long-term Simulated Total Fiprole Concentrations in Water with Application Date April 15
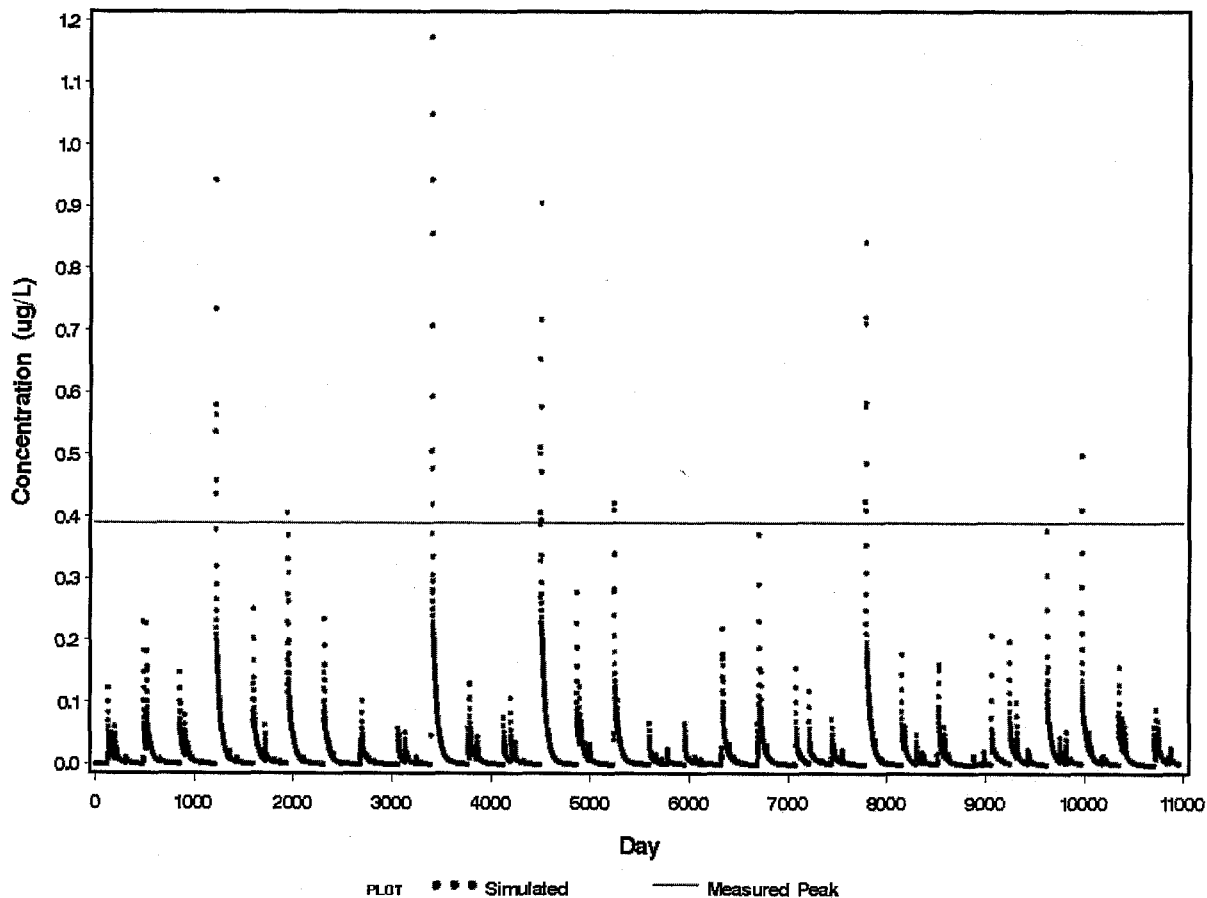
Note the red line is the maximum measured total fiprole concentration (0.39 ppb)

Figure 9   Long-term Simulated Total Fiprole Concentrations in Water with Application
             Date April 30
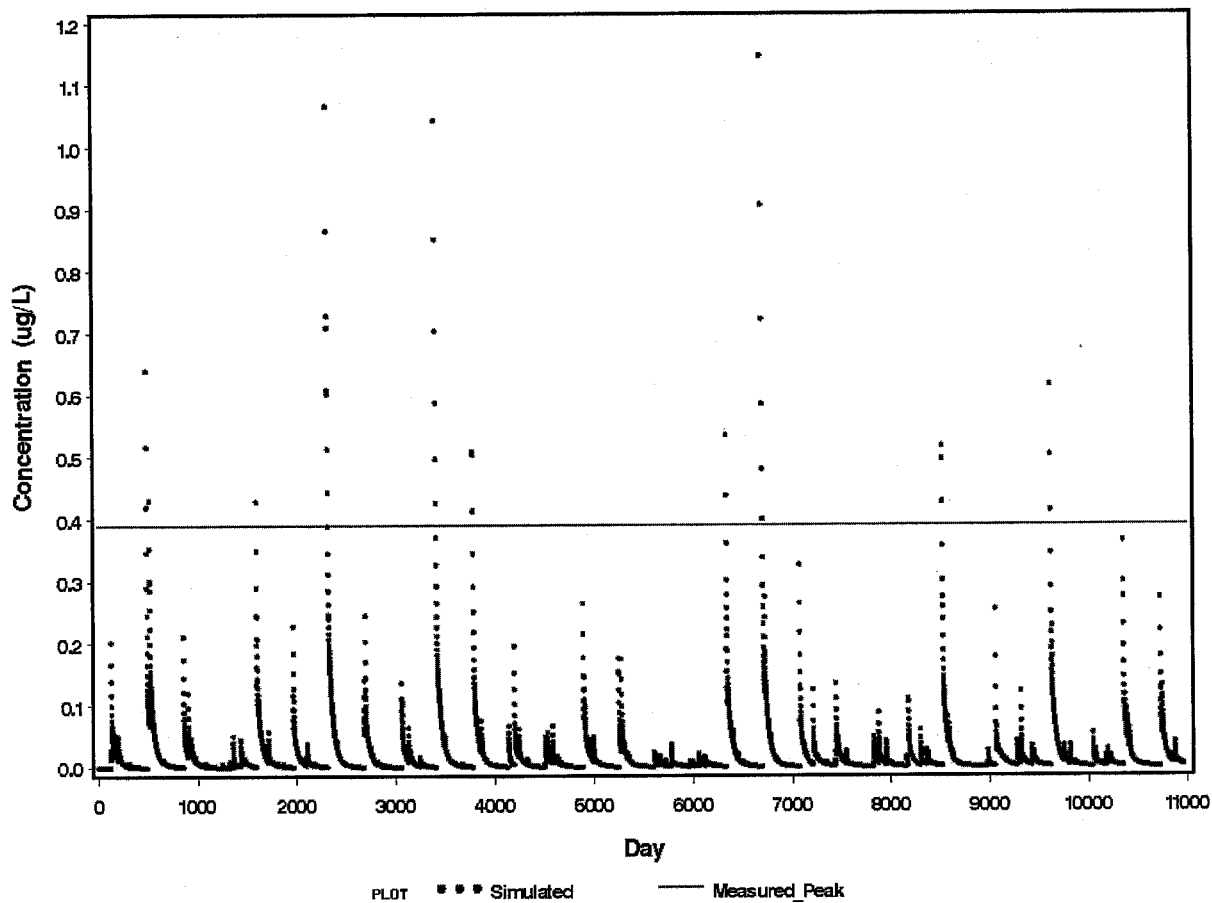
Note the red line is the maximum measured total fiprole concentration (0.39 ppb)

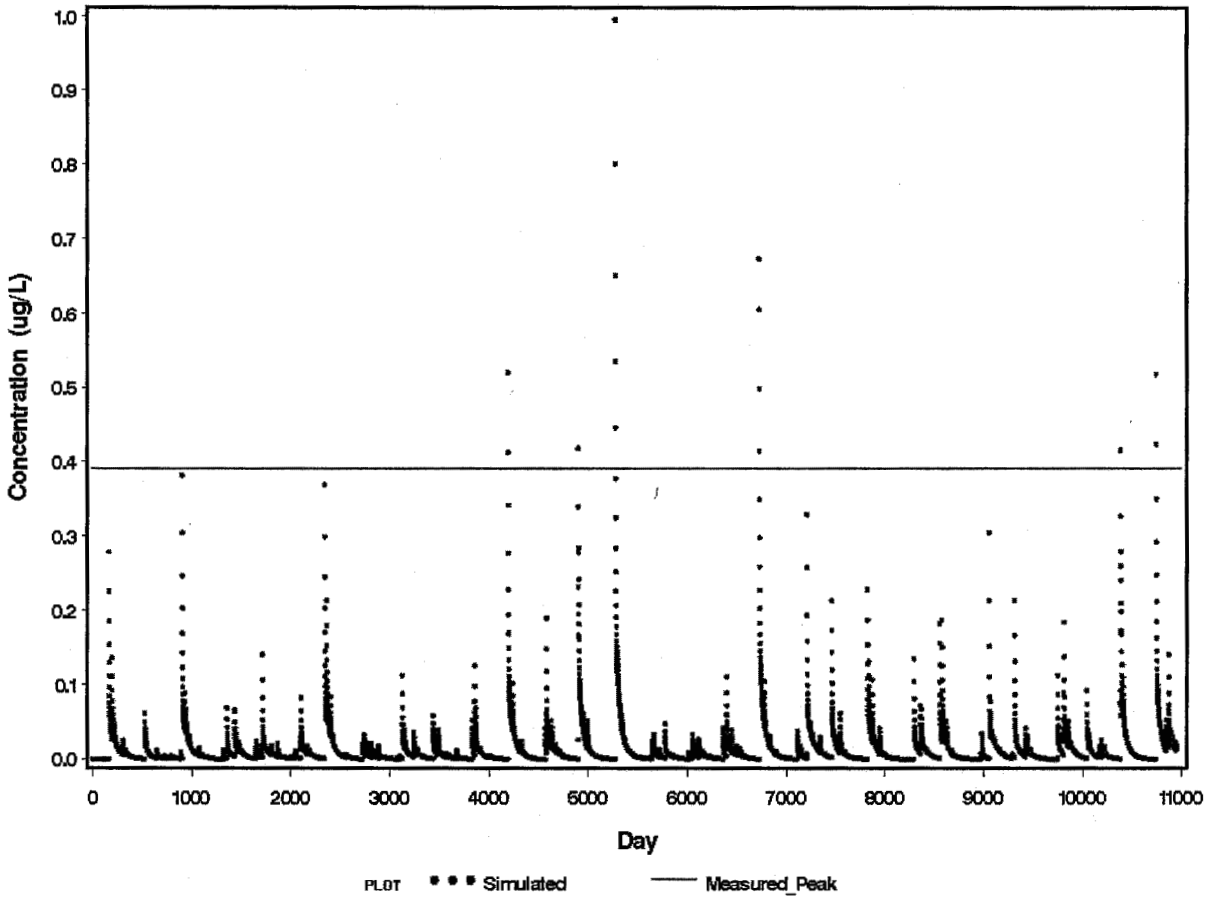Figure 10 Long-term Simulated Total Fiprole Concentrations in Water with Application Date May 15

Note the red line is the maximum measured total fiprole concentration (0.39 µg/L)

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Figure 11   Long-term Simulated Total Fiprole Concentrations in Water with Application
Date May 30

Note the red line is the maximum measured total fiprole concentration (0.39 ppb)

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Figure 12   Long-term Simulated Total fiprole Concentrations in Soil Pore Water with Application Date April 15
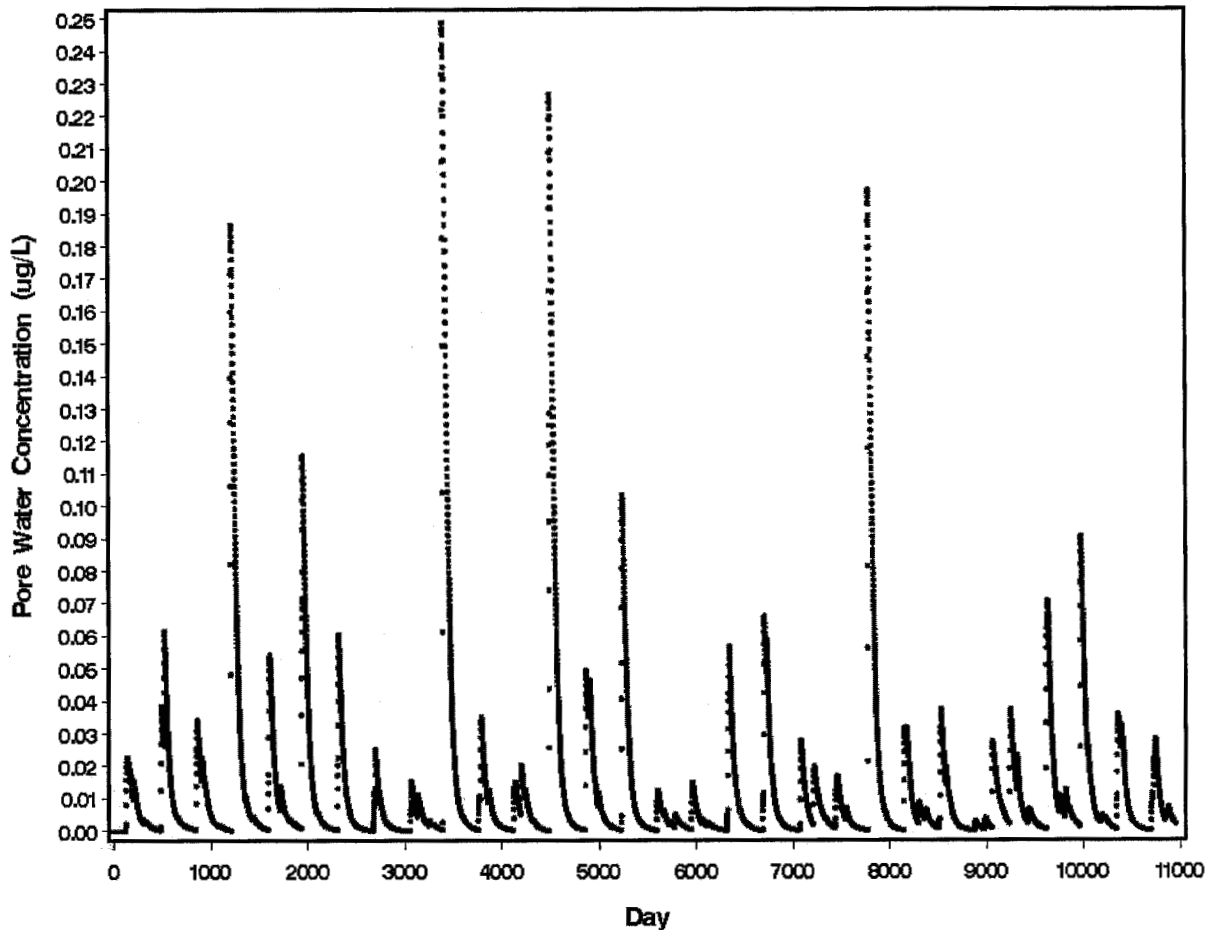
6. CONCLUSION

An evaluation of the fate, transport and dissipation of fipronil in surface water was conducted through numerical modeling at a monitoring site close to Pickens, AR. The monitoring site represented an actual use scenario of established golf course turf with an on-site commercial pond. Surface runoff from this site enters the pond primarily from two shallow drainage furrows (swales). The linked PRZM/EXAMS model was used in this study. The model was calibrated based on a comparison of observed versus predicted pond water concentrations of fipronil and the three metabolites in 2003 and 2004. The calibrated PRZM/EXAMS model provided good estimates for the concentrations of total fiprole and parent fipronil based on measured concentrations for study periods in 2003 and 2004. The R^2 for the calibrated PRZM/EXAMS model is 0.84 for total fiprole and 0.88 for parent fipronil.
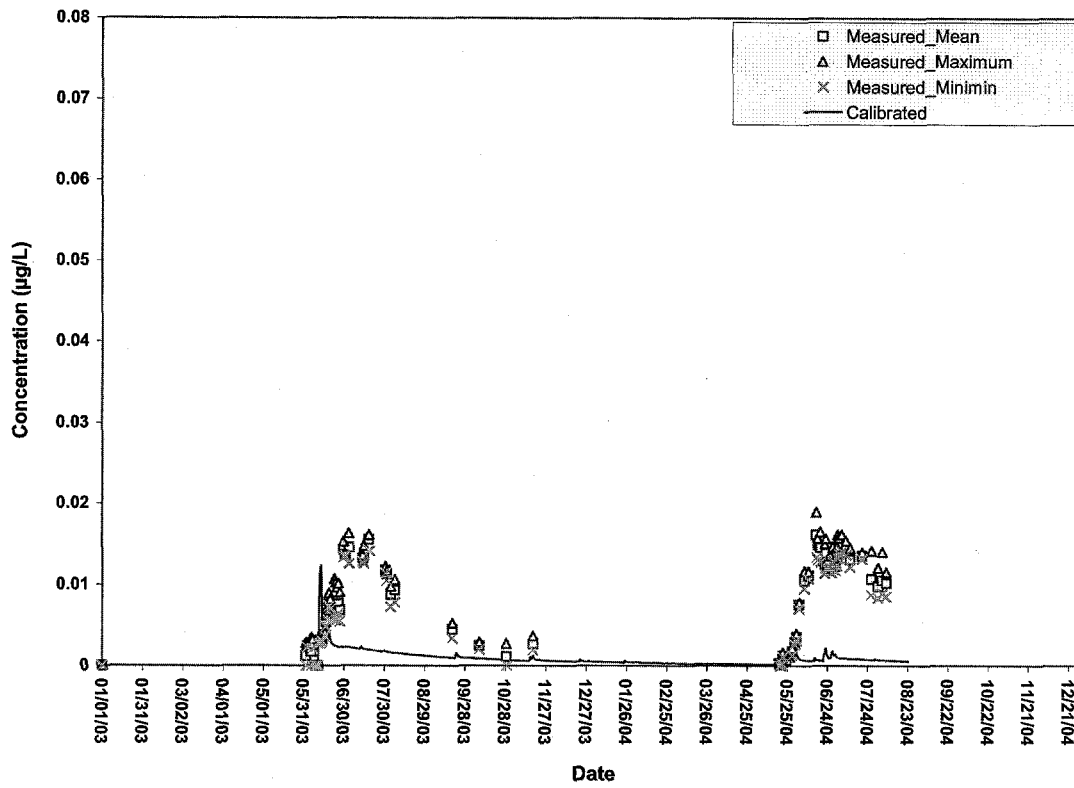
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The simulated compared to the measured concentrations of metabolite MB 46360 in 2003 and 2004
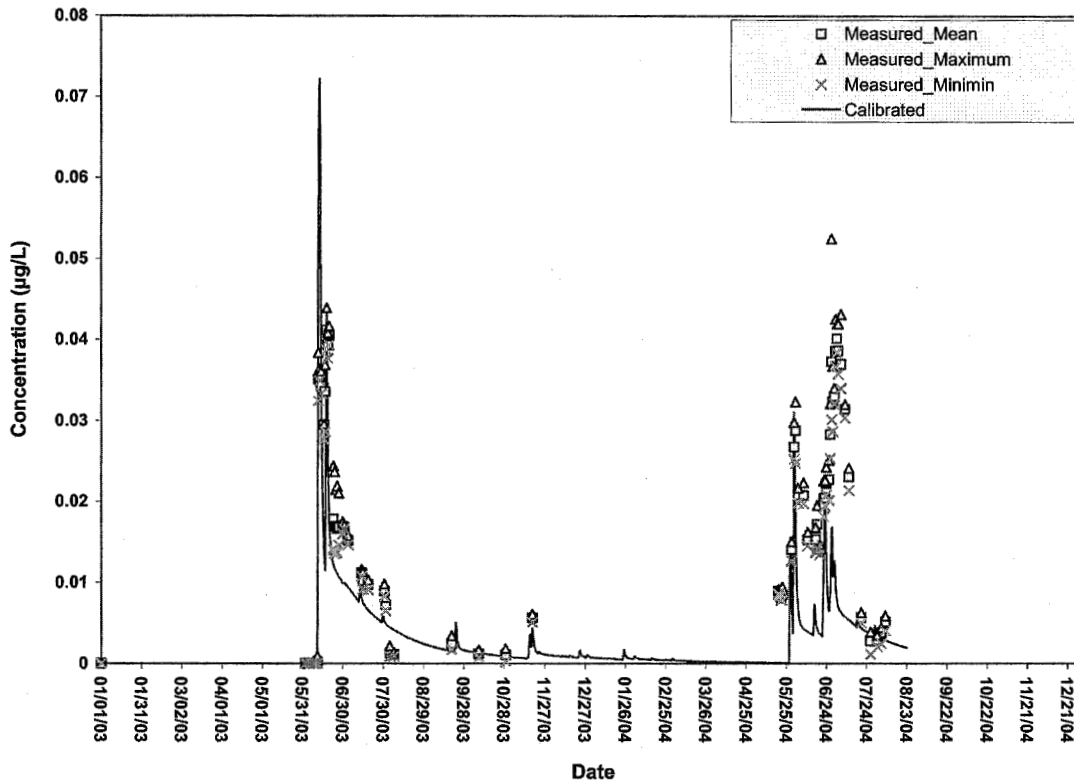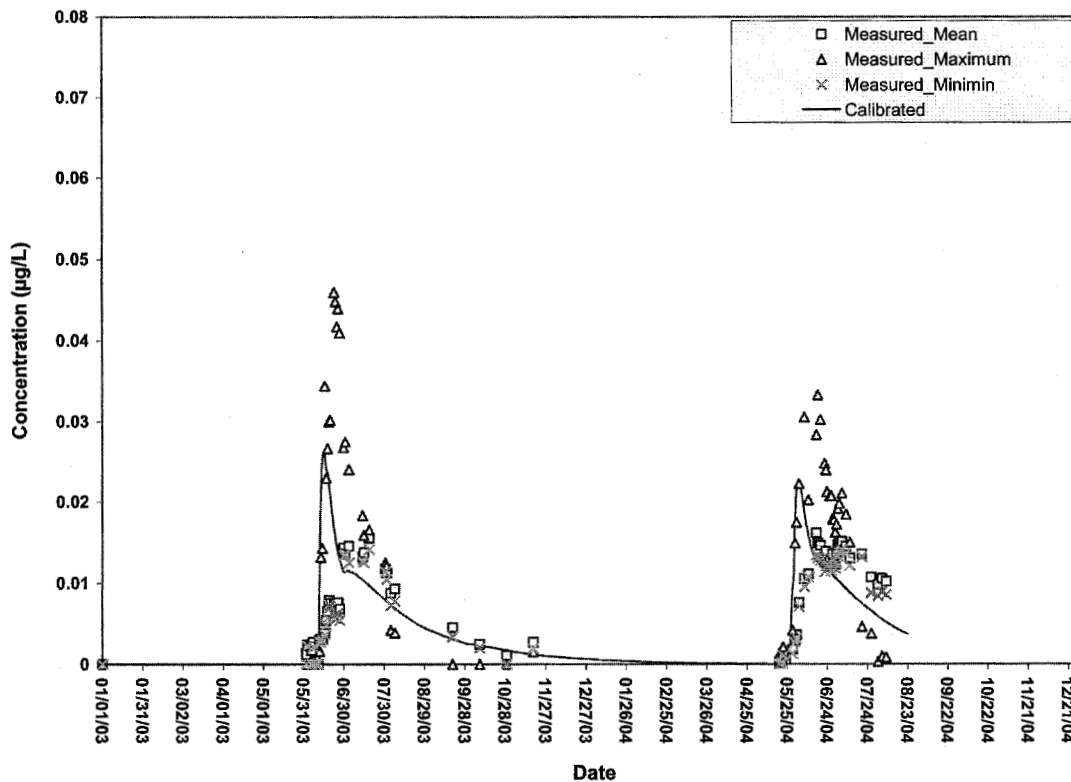
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The simulated compared to the measured concentrations of metabolite MB 45950 in 2003 and 2004

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The simulated compared to the measured concentrations of metabolite MB 46513 in 2003 and 2004