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OFFICE OF
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MEMORANDUM

SUBJECT: EFED Comments on "Response to Data Evaluation Reports for Environmental Monitoring and Modeling Studies Related to Fipronil Uses for Fire Ant Control"

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The registrants (Bayer CropScience and BASF) have submitted a report, entitled "Response to Data Evaluation Reports for Environmental Monitoring and Modeling Studies Related to Fipronil Uses for Fire Ant Control", in response to EFED Data Evaluation Records (DERs). The DERs evaluate five studies. Three of five studies (MRIDs 46490301, 46490302, and 46490303) concern Vegetative Buffer Strip (VBS) studies. MRID 46936101 is a study of the degradation kinetics of fipronil and its major metabolites in simulated outdoor ponds. MRID 46733903 is a fipronil estuarine monitoring study after application to an adjacent area of turf. The Previous EFED modeling of this use resulted in acute and chronic risk quotients that exceed levels of concern for aquatic invertebrates for fipronil and one of its degradates (MB 46136).

EFED Response Summary

The chemical properties of fipronil and the nature of the fire ant treatment contribute to risk. Both fipronil and its degradates of concern are persistent and accumulate over time in aquatic and terrestrial environments. The fire ant treatment use contributes to risk because the treatment is applied to the soil surface with only a "for best results" recommendation on the label that the treatment be watered in after application. Fipronil remaining on the surface or watered in to the uppermost soil layers would be susceptible to runoff and erosion during rainstorms if dissolved or bound to soil particles or organic material entrained in runoff water.

Conversely, other aspects of the fire ant treatment tend to reduce the exposure potential. The treatment would often be applied to areas with established vegetation such as grass or established turf where the established vegetation would tend to reduce runoff potential by slowing runoff velocities and, thereby, create the opportunity for greater deposition of suspended material and infiltration of dissolved material.

Specific Responses to Comments

1. EPA MRID 46490301 AND 46490302

CITATION: Braun, D., J. Cappy, and J. W. White. 2004. Effect of Vegetative Buffer Strips on Fipronil Runoff Losses from Warm-Season CHIPCO Choice Treated Turfgrass and Simulated Rainfall. Sponsored by Bayer CropScience, RTP, NC. Performed by Stone Environmental, Montpelier, VT; White Environmental, Lexington, KY; Bayer CropSciences, RTP, NC; and AgVise Laboratories, Northward, ND. MRID 4690301.

CITATION: Braun, D. C., J. Cappy, and J. W. White. 2004. Effect of Vegetative Buffer Strips on Fipronil Runoff Losses from Cool Season CHIPCO Choice Treated Turfgrass under Simulated Rainfall. Sponsored by Bayer CropScience, RTP, NC. Performed by Stone Environmental, Montpelier, VT; White Environmental, Lexington, KY; Bayer CropSciences, RTP, NC; and AgVise Laboratories, Northward, ND. MRID 46490302.

1.1 EPA Reviewer Comment 1 in DER

A fixed small plot field study: buffer zone (4.0) ratio was used in the study. Available data suggest the effectiveness of the buffer zone is dependent on numerous factors including runoff flow rate and depth, soil type, antecedent moisture, source area size, rainfall intensity and quantity, etc. (USDA/NRCS, 2000). Sediment filter strip design also is dependent on the rainfall amount and intensity. The Universal Soil Loss Equation rainfall-erosivity factor for the Southeastern United States ranges from 250 to 350 (EPA, 1985t). Under these 'conditions, effective sediment trapping in filter strips is expected for source area:filter ratios of < 50 (USDA/NRCS, 2000). This information suggest effective sediment trapping would be expected for the proposed source area: buffer ratio of 4.0. More importantly, the use of a low field area to buffer area ratio may bias the assessment of buffer effectiveness.

1.2 BCS/BASF Response

This study was conducted to evaluate the effectiveness of a 15 ft grass buffer in reducing fipronil residues in runoff. The study plots and treatments were designed in a way to isolate the effectiveness of a grass buffer in mitigating fipronil residues in runoff. The expected runoff volume and sediment load from each treatment - with and without the effect of buffer are same. Any difference that was noted was due to experimental variations. With such a design, where relative difference was measured the treated field to buffer area ratio may not play a major role in the outcome of the study. Considering the mechanism of vegetated buffers reducing chemical loads, the width of the buffer would play a major role in reducing dissolved chemicals because it would offer more area for infiltration. Whereas, the width of the buffer beyond a certain limit would offer no added benefit for trapping sediment bound chemicals (typically having moderate to high sorption coefficient). There are several studies in the literature that would show that field to buffer area is not highly correlated to sediment trapping.

The USDA publication on runoff buffers (USDA, 2000) is intended for agricultural lands. The BCS study was designed to evaluate the effectiveness of grass buffer to trap fipronil residues in runoff from treated turf areas. That is, the buffer area is essentially untreated turf area. The runoff velocity from a treated turf area is expected to be significantly lower than from an agricultural field.

Arora *et al.* (2003) studied the effect of two (15:1 and 30:1) field-buffer ratio on two weakly sorbed herbicides and one highly-sorbed insecticide. Though they observed that the lower field to buffer ratio (15: 1) treatments provided numerically higher pesticide reduction, the reductions were not statistically significant at $a = 0.1$. The authors also reviewed existing vegetated buffer studies and noted that the first few meters of the buffer tend to trap about 50% of the sediment load, which may be reason for the lack of significant differences between trapping efficiencies between the 15:1 and 30:1 treatments.

Liu *et al.* (2008) reviewed the 80 different experiments from the literature on efficacy of vegetated buffers on sediment trapping and developed statistical models to investigate the major factors affecting sediment trapping. The authors concluded that sediment trapping by the buffers is predominantly influenced by buffer width and slope. Their analysis of existing results also showed that buffer widths beyond 10 m did not improve the sediment trapping regardless of area to buffer ratio.

Therefore, the small scale runoff studies conducted by BCS satisfy the objectives of the study. The trapping efficiencies range from 64% to 77% and are representative of expected reduction from non-treated buffers in turf areas. Yet, these reductions can be used as conservative estimates in exposure assessments.

EPA Response to Registrant Comments in Section 1.2
The Agency appreciates the extra information.

1.3 EPA Reviewer Comment 2
The registrant did not attempt to conduct separate analysis of fipronil residues on entrained sediments and dissolved in runoff water. This analysis would be useful in understanding the importance of fipronil sorption on entrained sediments.

1.4 BCS/BASF Response

The extraction procedure extracted fipronil residues from the runoff water, which contained total suspended solids. Extracting the sediment separately from the dissolved phase does not add value to the study because of the following reasons:

1. The sediment loads from the turf plots were very low. The total suspended solids load ranged from 17 to 61 ppm in the cool season grass study (MRID: 46490302) and 27 to 50 ppm in the warm season grass study (MRID: 46490301).
2. Based on the sorption characteristics of fipronil (Koc range from 427 to 1248), one can estimate the percent of fipronil that will be sorbed in the sediment phase. Considering an average Koc value of 727 and organic matter content of the soils at the study sites, approximately 6% to 18% of fipronil in the runoff load would have been in the sorbed phase at the cool season grass study (MRID: 46490302). In the warm season grass study (MRID: 46490301) approximately 11% to 26% can be expected to be in sorbed phase.
3. When the runoff water reaches a water body, the fipronil residues re-equilibrate between water and sediment phase and hence knowing the sorbed portion at the edge of the runoff plots does not provide meaningful information on sediment dwelling organisms' exposure to fipronil residues in the water body.

EPA Response to Registrant Comments in Section 1.4

The Agency appreciates the additional analysis. However, the Agency would rather see studies conduct separate analysis of fipronil residues on entrained sediments and dissolved in runoff water rather than estimates based on a range of Koc values from other soils.

1.5 EPA Reviewer Comment 3

Fipronil residue concentrations in this study are edge-of-field concentrations in runoff waters from a treated site. They do not account for any off-site attenuation or dilution due to site specific hydrology or topography. The reviewer notes the reported concentrations are expected to be most representative of first-order streams, where water quality characteristics are dominated by runoff.

1.6 BCS/BASF Response

BCS agrees with the comment that fipronil residues concentration measured in these studies are edge-of-field concentrations and not necessarily the exposure concentrations in water bodies. It should be noted that we cannot generalize that these concentrations represent first-order streams. The concentration in a stream reach would depend on the land use composition of the catchment it is draining and the proportion of the catchment that was treated with over-the-ground fipronil treatments.

EPA Response to Registrant Comments in Section 1.6

The Agency and registrant appear to be in agreement. Therefore, no response is needed.

2. EPA MRID 4649303

CITATION: Braun, D., J. Cappy, and J. W. White. 2004. Effect of Vegetative Buffer Strips on Fipronil Runoff Losses from Tall Fescue Under Simulated Rainfall. Sponsored *by Bayer CropScience, RTP, NC. Performed by Stone Environmental, Montpelier, VT; White Environmental, Lexington, KY; Bayer CropSciences, RTP, NC; and AgVise Laboratories, Northward, ND. MRID 46490303.*

2.1 EPA Reviewer Comments 1 - 3
Same comments as those for MRIDs 46490301 and 46490302.

2.2 BCS/BASF Response
Same responses as those for MRIDs 46490301 and 46490302.

EPA Response to Registrant Comments in Section 2.2
See Comments in EPA Response to comments in Section 1.2.

2.3 EPA Reviewer Comment 4
The registrant did not provide any method verification, procedural method verification, or field spike verification for the analytical methods. Additionally, the registrant did not provide any storage stability data. These data are needed to upgrade the study.

2.4 BCS/BASF Response
This study was conducted as a preliminary (non-GLP) study to verify the functionality of field equipment, instrumentation, samplers and other field logistics. Hence, the analysis did not include method verification, concurrent recovery, and field-spike verification. These were conducted for the two main studies (MRID: 46490301 and 46490302). It should be noted that this study was conducted in Chatham County, North Carolina in December 2001, when fipronil is not expected to be applied. Fipronil for fire-ant control is expected to be applied in spring, during which the turf density in the buffer area is expected to be high. Therefore, the results from this study are not representative of the conditions when fipronil products are expected to applied for fire-ant control BCS understands the supplementary nature of this study, and requests EPA not to use the results from this study for exposure and risk assessments.

EPA Response to Registrant Comments in Section 2.4
The Agency will treat this study as supplemental information.

3. EPA MRID 46936101
CITATION: Tang, Z. and T.S. Ramanarayanan. 2006. Degradation of Fipronil and Its Major Metabolites Following Application of Chipco TopChoice® Leachate to Outdoor Simulated Ponds: Kinetics modeling. Sponsored by Bayer CropScience, RTP, NC. Performed by Bayer CropScience, Stillwell, KS, MRID46936101

3.1 EPA Reviewer Comment 1
The registrant did not discuss the implications of redox potentials on the formation of MB 45950 and MB 46136. The modeling strategy assumes the total system redox potential is anaerobic because MB 45950 is the major degradation product from biological degradation. Under aerobic conditions, MB 46136 is expected to be the major

degradation product. The reviewer does not understand how the outdoor pond could be anaerobic and still maintain any viable population of invertebrates for toxicity testing.

3.2 BCS/BASF Response

There is abundant evidence that the ponds in the simulated pond study used for the kinetic analysis remained oxygenated throughout the course of the study. Dissolved oxygen concentrations, measured regularly, ranged between 3.8 and 10.3 mg/L, with a minimum percent of saturation of 48% (3.8 mg/L at 27 QC). In addition, there was a diverse and abundant population of pelagic species which are associated with aerobic conditions.

MB 46136 was not formed in the pond. The ponds were dosed with leachate from a granular formulated product containing fipronil and MB 46136. Concentrations of MB 46136 were present in the treated pond water on day 0 and did not increase. By day 28, the concentration of MB 46136 present in the pond water was below the level of detection. These observations indicate that MB 46136 entered the pond directly from the product formulation along with the active ingredient fipronil, and did not form in the ponds. Therefore, the kinetics of MB 46136 was not included in the overall model but was modeled separately.

EPA Response to Registrant Comments in Section 3.2

The Agency appreciates the clarification.

3.3 EPA Reviewer Comment 2

The half-lives estimated from Model Maker are not unique values because they were derived using numerical integration methods. Estimates of half-life values may vary due different numerical techniques and convergence conditions.

3.4 BCS/BASF Response

The half-lives estimated from Model Maker were not derived using numerical integration methods. As described in the report (MRID 46936101), optimized model parameters (degradation/transformation rates) were calculated for the kinetics models by Model Maker using non-linear optimization procedures. The Marquardt algorithm of optimization was used with ordinary least squares.

The Marquardt algorithm, also called Levenberg-Marquardt algorithm, is a well accepted curve-fitting algorithm used in many software applications for generic curve-fitting solutions. It provides a numerical solution to the objective of minimizing a function, generally nonlinear, over a space of parameters of the function. In Model Maker, optimization allows the adjustment of parameter values to minimize the differences between predicted and observed values.

The estimation of the optimized parameters might be slightly different due to the selection of convergence criteria. However, it is statistically acceptable if the optimized parameters pass goodness of fit evaluation. The goodness of fit of the optimized parameters can be evaluated using visual comparison and statistical analysis of the optimization runs provided by Model Maker. In this report, the goodness of fit of the degradation/transformation rates derived was fully evaluated, and therefore, the calculated half-life values based on the derived degradation/transformation rates are statistically satisfactory.

EPA Response to Registrant Comments in Section 3.4

The Agency appreciates the clarification of the methods used by the Model Maker software. The fit to the degradate MB46136 data in Figure 5 of MRID 46936101 does not appear to be satisfactory. Potentially, the model chosen (single first-order decay) may have been mis-specified. Possibly, there was both some very limited production of MB46136 in the ponds as well as MB46136 in the fipronil formulation used to dose the ponds. In any case, the half-life estimate of MB46136 obtained in MRID 46936101 has significant uncertainty associated with it.

4. EPA MRID 46733903

CITATION: Wyatt, Daryl R. 2005. Fipronil Estuarine Monitoring Study following an Application of Chipco Topchoice® to a Golf Course at Gulf Breeze, Florida. Sponsored by Bayer Crop Science, RTP, NC. Performed by Bayer CropScience, Stillwell, KS and AgVise Laboratories, Northward, ND. MRID46733903.

4.1 EPA Reviewer Comment 1

The fipronil water monitoring study (MRID 46733903) provides acceptable data on the runoff potential of fipronil and its degradation products (MB46136, MB46513, and MB 46950) and its impact on fipronil residue occurrence in estuarine surface water from use of Chipco Topchoice® on a turf in Gulf Breeze, FL. 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.

4.2 BCS/BASF Response

According to the stepwise approach for the fipronil assessment provided to EPA (MRID 46936105), no biological monitoring was planned as a component of the water monitoring study (MRID 46733903). Instead, separate biological evaluations were performed, and submitted to the EPA. Studies included the simulated pond study (MRID 46733901) and the sediment recolonization study (MRID 47245001). These evaluations were higher tiered or semi-field approaches which allowed for the assessment of potential impacts of fipronil plus metabolites at concentrations which were based, in part, on the result of the water monitoring work.

EPA Response to Registrant Comments in Section 4.2

The Agency and registrant both agree that no concurrent biological monitoring of the aquatic environment to assess the impact of fipronil and its degradation products on aquatic invertebrates was provided.

4.3 EPA Reviewer Comment 2

The registrant referenced a storage stability study in a Texas runoff study (MRID 46733902). The Texas runoff study does not provide a detailed description of the storage stability study.

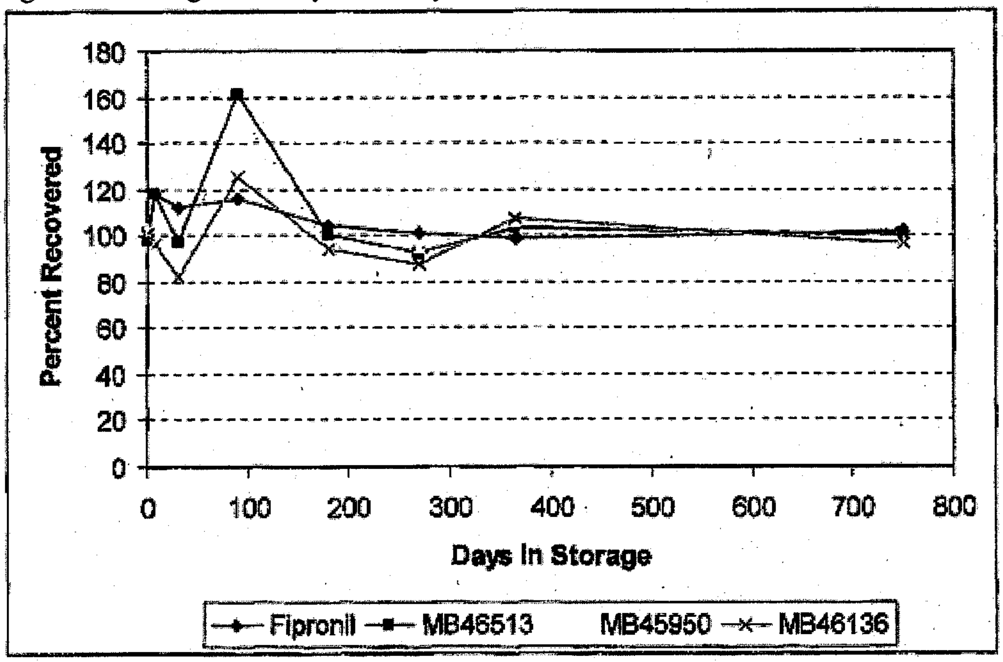
4.4 BCS/BASF Response

The storage stability information has been clearly summarized in Table X of the Texas runoff study report (MRID 46733902). The storage stability was tested for up to 25 months of storage in the freezer. The storage stability results are summarized in the table below and shown in the figure following that.

• Table 1: Summary of storage stability recovery

	Average Recoveries (% of applied)			
Storage Period	Fipronil	MB46513	MB45950	MB46136
Day 0	101	98	103	101
Week 1	118	118	96	96
Month 1	112	97	86	82
Month 3	116	161	155	125
Month 6	104	100	95	94
Month 9	101	92	95	88
Month 12	99	103	106	107
Month 25	102	100	97	96

Figure 1: Storage stability recovery



EPA Response to Registrant Comments in Section 4.4
The Agency appreciates the clarification and accepts that these data fulfill the storage stability study requirement.

5. REFERENCES

USDA 2000. Conservation buffers to reduce pesticide losses. U.S. Department of Agriculture, Natural resources Conservation Service, Washington, DC.

Arora, K., Michelson, S.K., Baker, J.L., 2003. Effectiveness of vegetated buffer strips in reducing Pesticide transport in simulated runoff. Trans. of the ASAE, 46(3): 635-644.

Liu X, Zhang, X., Zhang, M., 2008. Major factors influencing the efficacy of vegetated buffers on sediment trapping: A review and analysis. J. Environ. Qual. 37:1667-1674.