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Fipronil Monitoring and Model Scenarios

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Abstract

The California Department of Pesticide Regulation (DPR) Surface Water Protection Program (SWPP) has identified fipronil as a contaminant of concern in California surface waters. Fipronil has been detected in approximately half of all monitoring samples at concentrations above toxicity thresholds set by the US Environmental Protection Agency (USEPA). Currently there are two fipronil-containing products registered in California that have been identified as contributing to urban runoff concentrations. Presented is a modeling approach to evaluate the effects of altering application practices with the potential to reduce fipronil runoff from residential areas of California. Using the USEPA acute benchmark as a reduction goal, fipronil concentrations in urban receiving waters of California would need to be reduced by 59% (based on monitoring results) to 78% (based on modeling results). Tested scenarios include narrow application band, reduction of fipronil mass applied, and restriction of areas that can be treated. Less applied mass with narrow band proportionally reduces fipronil urban runoff. For example, model-predicted fipronil concentration in urban receiving water is reduced by 92% with "oneinch up and one-inch out" using pin stream application, compared to label-suggested band of one foot. In addition, fipronil runoff potential is sensitive to applications to the garage door/driveway interface. Exclusion of driveway/garage door uses results in concentration reduction by 43%, while the applied mass is only decreased by 16%. A research contract with the University of California at Riverside has been initiated to test modeled application scenarios on runoff potential and bioefficacy.

1.0 Introduction

Fipronil, a phenylpyrazole insecticide, was first approved for use in California by the DPR in 1997. According to a recent review (Ensminger, 2014), there are 94 fipronil products actively registered in California. Based on the latest Pesticide Use Reporting (PUR) database, 71,617 pounds of active ingredient of fipronil are used in 2013, majority (99.2%) of them are for structural pest control. Spatially, more than half of the total fipronil uses are observed in the four counties of Los Angeles (15.8%), Sacramento (12.4%), Riverside (12.1%), and San Bernardino (11.2%). Based on DPR monitoring results in northern and southern California during 2008-2013, fipronil (with detection frequency of 49%), fipronil sulfone (43%), and fipronil desulfinyl (33%) are frequently detected in storm drain outfalls and receiving waters of California residential areas (Budd et al., 2015). Compared to USEPA aquatic life chronic benchmark (USEPA, 2015), 46% of receiving water samples have fipronil concentrations above its' benchmark values. Outdoor applications, especially those to impervious surfaces such as driveways, are considered as significant sources for off-site movement of fipronil and its' degradates to urban receiving waters. Therefore, surface water monitoring of fipronil by DPR and other organizations has focused on runoff originating from residential areas.

Recent studies have shown that application practices could reduce fipronil runoff from urban homes by restricting treated areas, altering spray methods, and timing (Greenberg et al., 2010; Greenberg et al., 2014; UCIPM, 2014; DaSilva, 2015a). DPR is conducting additional research efforts to better understand the occurrence and potential reduction of fipronil in urban runoff. As a part of this effort, a modeling approach is applied to estimate the effects of scenarios on fipronil runoff from residential areas of California. The specific objectives of the modeling effort is: (1) to develop a baseline model simulation for reasonable and conservative representation of fipronil residues as observed in the monitoring studies, and (2) to incorporate altered application practices as scenarios in the model, and evaluate their effects as relative changes to the baseline simulation results.

2.0 Monitoring

DPR conducts surface water sampling to monitor for environmental contamination of water bodies due to pesticides. Monitoring efforts for fipronil have focused on urban surface waters due to suspected contributions from treated urban landscapes. DPR's Surface Water Protection Program has collected over five hundred water samples from storm drains receiving runoff from residential landscapes and from urban water bodies (e.g., creeks) throughout California since 2008 to determine the presence and concentrations of fipronil and five fipronil degradates. Statewide, fipronil has been detected above reporting limits in 49% of water samples (Budd et al., 2015). Furthermore, 15% of samples contained fipronil concentrations at levels above the USEPA acute aquatic benchmark, and 48% above the chronic aquatic benchmark. The acute and chronic benchmarks represents a concentration that when exceeded is expected to cause toxicity to aquatic invertebrates over short-term and long-term exposure periods, respectively.

An additional concern is the offsite transport of fipronil degradation by-products to urban surface waters. Fipronil degrades fairly quickly in surface waters to one of three dominant metabolites: fipronil sulfone, fipronil sulfide and fipronil desulfinyl. The degradation pathway is driven by various environmental conditions. Two of its' degradates, fipronil sulfone and fipronil desulfinyl, are also commonly detected in 43% and 33% of all samples, respectively. Fipronil sulfone concentrations were found at levels above the acute aquatic benchmark in 1% of the samples and above the chronic aquatic benchmarks in 37% of samples. Recent research suggests that fipronil degradates are more toxic to certain aquatic test species than the parent compound at lower concentrations than established benchmark levels (Weston and Lydy, 2014).

A subset of locations have been developed as long term monitoring stations (LTMS) which have the largest associated data set for trend analysis. Samples are collected at storm drains before any dilution effects have occurred and within receiving waterbodies that serve as primary habitat for aquatic species. Forty-six percent of samples collected at receiving water LTMS contained fipronil concentrations potentially toxic to sensitive aquatic organisms, indicating that fipronil is not fully mitigated by stream dilution effects to levels below ecological concerns.

Other research efforts have also detected fipronil at high frequencies in surface waters receiving urban runoff. Weston et al. (2014) detected fipronil in 88% of samples collected within sixteen California watersheds receiving urban runoff (Weston and Lydy, 2014). In another California study, fipronil was detected in 66 - 100% of samples collected at six residential storm drains

(Gan et al., 2012). In a nationwide survey between 2002 and 2011, Stone et al. (2014) detected fipronil in 70% of 125 monitored streams, several of which were in California (Stone et al., 2014). Currently there is very little sediment monitoring data associated with fipronil. The Stream Pollution Trends Monitoring Program (SPoT) recently began monitoring fipronil and degradates within sediments collected in urban streams in 2014. Fipronil has been detected frequently and at concentrations that are of concern to aquatic benthic communities (Brian Anderson, personal communication), indicating sediment deposits may serve as a long-term source of fipronil within surface water ecosystems.

3.0 California Use Patterns

There are currently 134 fipronil products registered with the DPR for use in California. Fipronil is not registered for use in production agriculture in the state. The majority of registered products are designated for flea control on pets. An evaluation of product labels showed that only two of the fipronil-containing products currently registered for outdoor use have the potential to contaminate surface waters; Termidor SC Termiticide/Insecticide and Taurus SC Termiticide/Insecticide. Both are liquid soluble concentrate products used to control termite, ant, and other insect pests (Ensminger, 2014). According to DPR's PUR system, statewide fipronil use between 2009 and 2013 by professional applicators exceeded 255,000 pounds, 99% of which represented structural pest control applications.

4.0 Modeling

The following section describes the methodology and results of modeling efforts to predict concentrations of fipronil in urban runoff under various application scenarios.

4.1 Simulation design

The urban module (Luo, 2014a) and degradate module (Luo et al., 2015) in the registration evaluation (RegEval) model by DPR's SWPP are used in this study. Modeling results are reported as daily time series of pesticide concentrations in a receiving water body, which is simulated as USEPA standard pond. Model simulations are conducted for the 30-year period during 1961-1990 based on the meteorological data for exposure assessment models (USEPA,

2006). The modeling approach is consistent with USEPA registration evaluations and risk assessments. Estimated environmental concentration (EEC) is derived as the 1-in-10-year peak value of the model-predicted concentration time series. Moving averaging could be used in the evaluation of chronic risks. In this report, "daily EEC" is calculated based on predicted daily concentrations and used in the acute risk characterization, while "21-d EEC," which is defined as the 1-in-10-year peak value of the 21-d moving averages of predicted concentrations, is used for chronic risk assessment. The RegEval urban module was designed to represent statewide conservative conditions for California urban environment. Therefore, modeling results will be compared with all available monitoring data in California.

Two sets of model simulations are conducted in this study: [1] baseline simulation and [2] scenario analysis. The objective of baseline simulation is to generate reasonable and conservative representations of the current condition of fipronil level in urban receiving waters in California (according to monitoring results). For scenario analysis, proposed scenarios are incorporated by adjusting numerical values of relevant model input parameters. Effects of application practices on fipronil runoff are evaluated based on the relative changes of modeling results between scenario analysis and baseline simulation.

4.2 Physiochemical properties and toxicity data

Fipronil and three of its' degradates, sulfide (MB45950), sulfone (MB46136), and desulfinyl (MB46513), are selected for modeling simulation. Fipronil amide is not included due to the lack of USEPA aquatic life benchmark (USEPA, 2015). Degradate formation pathways (Figure 1) and formation fraction (Table 1) are based on a modeling study submitted by Bayer Crop Science and reviewed by USEPA (USEPA, 2008a). The same simulation engine (Pesticide Root-Zone Model, or PRZM) is used in the Bayer's study and this study.

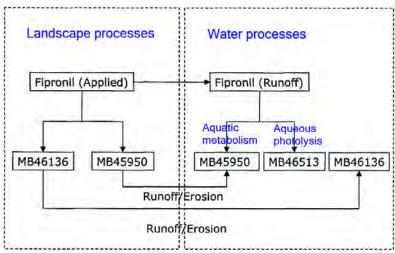


Figure 1. A schematic diagram of modeled fipronil transport and transformation processes, adapted from USEPA MRID Number 46936102 (USEPA, 2008a).

| Table 1. 1 allways and fractions (by mass) of fipform degradate formation. | | | | | |
|----------------------------------------------------------------------------|----------|-----------|-----------|------------|--|
| | Fipronil | Fipronil | Fipronil | Fipronil | |
| | | sulfide | sulfone | desulfinyl | |
| | | (MB45950) | (MB46136) | (MB46513) | |
| Soil, overall | - | 0.05 | 0.2 | - | |
| Aqueous photolysis | - | - | - | 1.0 | |
| Aquatic metabolism | - | 1.0 | - | - | |

Table 1. Pathways and fractions (by mass) of fipronil degradate formation.

Notes: data are based on USEPA MRID Number 46936102 (USEPA, 2008a). Formation pathways for MB45950 and MB46513 in aquatic environment were identified but their formation fractions were not reported. Here their formation fractions are conservatively set to be 100% (or 1.0 in the above table).

Chemical properties and reaction half-lives of the simulated chemicals (Table 2) are taken from registrant-submitted data which have been evaluated by DPR or USEPA (USEPA, 2008a, b; DaSilva, 2015). The lowest values of USEPA aquatic life benchmark, for acute and chronic toxicity tests, are used for risk characterization (Table 3). For example, acute benchmark values of fipronil are reported as 14.5 ppb (fish), 0.11 ppb (invertebrates), and 140 ppb (nonvascular plants). Therefore, the lowest value of 0.11 ppb is used for characterizing acute risks of fipronil in this study.

| | Fipronil | Fipronil | Fipronil | Fipronil |
|-------------------------------------|----------|-----------|-----------|------------|
| | - | sulfide | sulfone | desulfinyl |
| | | (MB45950) | (MB46136) | (MB46513) |
| Water solubility (mg/l) | 2.15 | 1.1 | 0.16 | 0.95 |
| KOC (<i>l</i> /kg[OC]) | 837.5 | 3658 | 4096.5 | 1306.5 |
| Hydrolysis half-life (HL, d) | - | - | - | - |
| Aerobic soil metabolism HL (d) | 126 | 730 | 730 | - |
| Anaerobic soil metabolism HL (d) | 131 | - | - | - |
| Aerobic aquatic metabolism HL (d) | 14.5 | 42.8 | 21 | 16 |
| Anaerobic aquatic metabolism HL (d) | - | - | - | - |
| Molecular weight (g/mol) | 473.2 | 421 | 451 | 389 |
| Henry's law constant (atm*m3/mol) | 8.5e-10 | 8.6e-9 | 2.1e-8 | 1.6e-8 |
| Vapor pressure (torr) | 2.8e-9 | 1.7e-8 | 5.7e-9 | 3.0e-8 |
| Aqueous photolysis HL (d) | 0.33 | - | - | - |
| Soil photolysis HL (d) | 34 | - | - | - |

Table 2. Physiochemical properties of fipronil and degradates.

Notes: [1] blank cells: data not available (for half-life, the value will be set to "stable"). [2] fipronil data are taken from SWPP registration evaluation for FUSE (DaSilva, 2014, draft). [3] degradate data are taken from USEPA MRID Number 46936102, 46936103 (USEPA, 2008a, b).

Table 3. USEPA aquatic life benchmark (USEPA, 2015).

| | Fipronil | Fipronil sulfide (MB45950) | Fipronil sulfone (MB46136) | Fipronil desulfinyl (MB46513) |
|------------------------------------|----------|----------------------------------|----------------------------------|-------------------------------------|
| The lowest acute benchmark (ppb) | 0.11 | 1.065 | 0.36 | 10 |
| The lowest chronic benchmark (ppb) | 0.011 | 0.11 | 0.037 | 0.59 |

5.3 Label rate, application method, and other input data

According to fipronil product review (Ensminger, 2014), two of the 94 registered fipronil products in California have potential to contaminate surface waters: Termidor® SC Termiticide/ Insecticide and Taurus® SC Termiticide/ Insecticide. The labels are similar for both products. Modeling will be focused on the outdoor use of the two products for ant and other arthropod control, since outdoor use is associated with larger contribution to surface water contamination compared to pre/post-construction applications. Specifically, spray to perimeter foundation with "1-ft up & 1-ft out" method is modeled (Table 4). **Table 4.** Decision tree for fipronil products and application methods modeled in this study, based on fipronil product review (Ensminger, 2014).

| | 94 registered fipronil products in CA | | | | |
|---------------|---------------------------------------------|------------------------------|--------------|----------------|--|
| Risk to | Termidor® SC Terr | | Other | | |
| surface water | Taurus [®] SC Termit | ticide/ Insecticide | | products (with | |
| | | | | limited | |
| | | | | potential of | |
| | | | | surface | |
| | | | 1 | runoff) | |
| Use pattern | Outdoor pest contro | bl | Pre/post- | - | |
| | | | construction | | |
| Application | A low-pressure | A low-pressure coarse | | | |
| method | general surface | banded surface spray up to | | | |
| | spray to perimeter | 18 inches in width around | | | |
| | foundations | doors, windows, vents, | | | |
| | (where the | pipes, foundation cracks, or | - | - | |
| | foundation meets any exterior openings etc. | | | | |
| | the ground) "one- | | | | |
| | foot up and one- | crack and crevice spray, or | | | |
| | foot out." | into voids | | | |
| Modeling | | - | - | - | |

Label rate is calculated as 0.38 kg/ha (Figure 2), estimated from the following statement in the label: *Apply 2 quarts of 0.06% finished spray of Taurus SC per 160 linear feet*. Total number of applications is set as 2 ("*Do not exceed a maximum of 2 applications per year*"). Interval between the two applications is set as 30d.

| Rate Calculator | | | | |
|------------------------------------------------|-----------------|--------|---------------|---------------------------------|
| Fraction of AI in the prod | 9.1 | | | |
| (for liquid formulation on | ly) lb.[Al] per | gallor | n [product]: | 0.8 |
| Dilution required. Ret | trieve data fr | om mi | xing instruct | ions in the label: |
| Product quantity (oz): | | | | 0.8 |
| Water volume (gal): | | | | 1 |
| Application rate, based on the final form u | used in appli | cation | s (product o | r spr a y dilution): |
| 0.5 | gal. 👻 | per | 320 | ft2 🔻 |
| Application rate for mode | el use (kg [A |]/ha): | | 0.3814903 |
| | | | Calculate | e Apply |

Figure 2. Data used for calculating label rate by the "rate calculator" in SWPP RegEval model.

The date of first application will be set as the 1st day of each month for each individual model run. Application timing is not specified in the label, but year-round fipronil uses are observed in PUR database (Figure 3). In baseline simulation, therefore, fipronil applications will be modeled for all 12 months from January to December. For conservative estimation, the maximum EEC will be reported: reported EEC =max (EEC with the first application on Jan 1st, EEC[Feb 1st], ..., EEC[Dec 1st]). Scenario analysis may set restrictions on months for fipronil application.

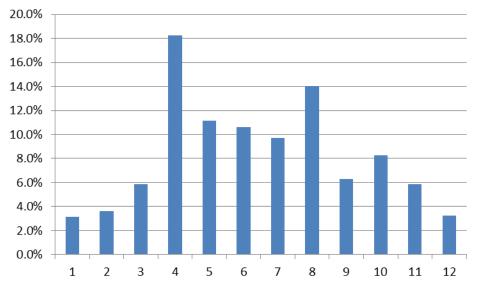


Figure 3. Monthly fipronil uses (2010-2012), presented as % over annual total uses (summation of all bars = 100%).

Application extent and water connectivity are considered for more realistic simulation in

California residential areas. Specifically, the following adjustments are incorporated in the model simulation,

- 75.9%: fraction of households treated with outdoor insecticide control products, based on survey results by Pyrethroid Working Group (PWG) (Winchell, 2013), reviewed by DPR (Luo, 2014b).
- 26.3%: probability of products containing fipronil used for treatment, based on PWG survey results (Winchell, 2013), reviewed by DPR (Luo, 2014b).
- 25.0% (Figure 3): fraction of residential lot where impervious surfaces have direct hydrologic connectivity to driveway and street gutters. Other portion of impervious surfaces will be first routed to adjacent pervious surfaces (e.g., lawns).

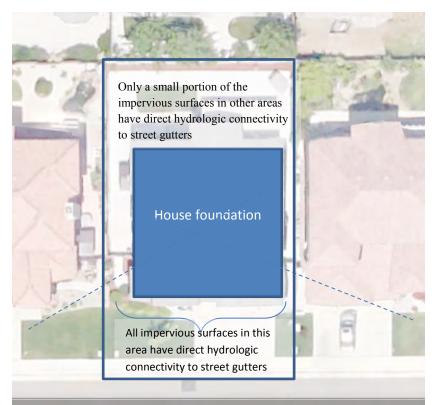


Figure 4. Hydrologic connectivity for impervious surfaces in front yard and other areas.

4.4 Monitoring data

Monitoring data compiled in the following two review reports are used in this study:

- "Review of Pyrethroid, Fipronil and Toxicity Monitoring Data from California Urban Watersheds" by California Stormwater Quality Association (CASQA) (Ruby, 2013), including some SWPP data in 2012 and before.
- "Monitoring fipronil and degradates in California surface waters 2008–2013" by DPR's SWPP (Budd et al., 2015).

There might be duplicated data in the two reviews, but not necessary to be identified because the modeling results are compared with the maximum measurements. In both reviews, monitoring data are summarized as maximum concentrations by site and by sampling study. At the site of Pleasant Grove Creek (PGC010) during 2008-2009 sampling period, e.g., the maximum concentration of fipronil was below detection limit during the dry season, and 0.107 ppb during the wet season (Ensminger and Kelley, 2011; Ruby, 2013). By combining the two reviews, there are 132 maximum values reported for fipronil (Table 5).

| period, reported in the two selected reviews. | | | | | |
|-----------------------------------------------|--------------------|-------------------------|-------|--|--|
| | CASQA (Ruby, 2013) | DPR (Budd et al., 2015) | Total | | |
| Receiving water | 29 | 29 | 58 | | |
| Storm drain | 45 | 29 | 74 | | |
| Total | 74 | 58 | 132 | | |

Table 5. Number of reported maximum concentrations of fipronil, by site and by sampling period, reported in the two selected reviews.

4.5 Modeling scenarios

Scenarios (Table 6) are proposed by SWPP staff and tested for their effects on the potential prevention and reduction of fipronil runoff from residential areas. Generally, the following three types of scenarios and their combinations are simulated: [1] narrow band of application, [2] reduction of applied mass, and [3] restriction of treated areas (by reducing or excluding the driveway and garage door for application). Similar to the baseline simulation, scenario analysis generates daily EEC and 21-d EEC. The relative changes of EEC's between the scenario analysis and baseline simulation are reported.

| T | - | T 1 | |
|----------|-----|------------|------------|
| Table | 6. | Tested | scenarios. |
| | ~ • | | |

| Run | Scenarios | Mec | hanisı | ms |
|-----|-----------------------------------------------------------------------|-----|--------|-----|
| ID | | [1] | [2] | [3] |
| А | Baseline simulation (i.e., perimeter treatment, "1-ft up, 1-ft out" @ | | | |
| | | | | |
| В | Pin stream application, "1-in up, 1-in out" @ label rate | | | |
| D | Narrow band, 50% mass of A, e.g., "6-in up, 6-in out" @ label rate | | | |
| F | No applications to the garage door; spot treatment to the driveway | | | |
| | edge (4 ft ² @ label rate) | | | |
| G | No applications to the garage door and driveway edge | | | |
| BG | B and G combined | | | |

Notes: mechanisms involved in the scenarios include: [1] narrow band (or spot treatment), [2] reduced fipronil mass (in term of total mass applied per year), and [3] restriction of treated area. Model run ID is assigned by following the ID of application method to be tested in DPR's contract project #14-C0102 (CDPR, 2014).

4.6 Baseline simulation

Baseline simulation results for individual chemicals are summarized for daily EEC and 21-d EEC (Table 7). Compared to monitoring results, daily EEC of fipronil (0.5 ppb in receiving water) is higher than (57 out of the 58, 98%) the maximum values observed in receiving waters, and lower than (15 of the 74, 20%) the maximum observed concentrations in storm drains (Figure 5). Very high concentrations were reported at storm drains, e.g., 10.0 ppb by Gan et al.

(2012). Those are not compared with modeling results (in urban receiving water), but considered as an upper bound for reasonable model predictions.

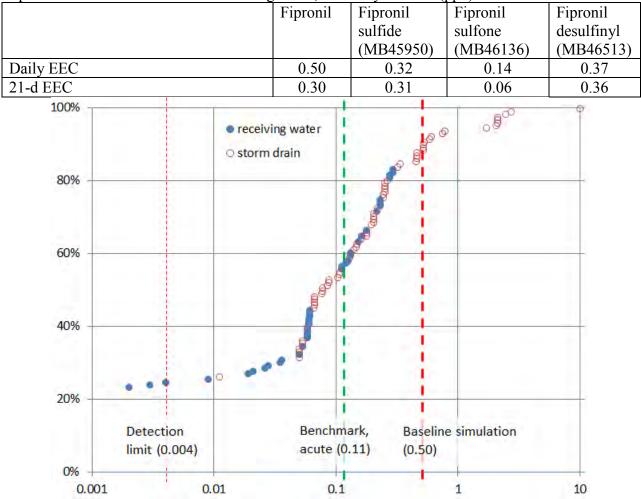


Table 7. Baseline simulation ("1-ft up and 1-ft out", 2x appl., 30d interval) results: predicted fipronil concentrations in urban receiving water, 1-in-10 year EEC (ppb).

Figure 5. Probability plot of observed maximum concentrations (ppb) of fipronil, by sites and by monitoring study period, in California urban areas.

Note: The three dashed lines represent (from left to right): [1] 0.004 ppb: DPR detection limit (Ensminger, 2013). Non-DPR monitoring studies may be associated with different detection limits. Therefore, non-detects are considered in calculating the probabilities (about 25% in total), but not displayed in the plot; [2] 0.11 ppb: the lowest value of USEPA acute benchmarks (Table 3); and [3] 0.50 ppb: baseline simulation result in urban receiving water (Table 7).

By following the approach previously used in model validation (Luo, 2014a, c), modeling results are compared with the average of the top 3 observed concentrations. For fipronil, the average of top 3 observations in receiving water is 0.27 ppb (Table 8). Please note that SWPP urban module is based on modeling scenarios, rather than field-specific settings, for pesticide transport

simulation. Modeling results are expected to represent conservative conditions in urban receiving waters of California, but may not be directly comparable to measurements in a specific monitoring site. Temporally, in addition, relatively high concentrations such as the daily EEC's are predicted by the model during rainfall events, which is consistent with monitoring results (Budd et al., 2015).

| | Fipronil | Fipronil sulfide (MB45950) | Fipronil sulfone (MB46136) | Fipronil desulfinyl (MB46513) |
|-------------------------------------------------------|----------|----------------------------------|----------------------------------|-------------------------------------|
| Baseline simulation results of daily EEC (Table 7) | 0.50 | 0.32 | 0.14 | 0.37 |
| Average of top 3 concentrations in receiving water | 0.27 | 0.007 | 0.13 | 0.11 |
| Average of top 3 concentrations in storm drain | 5.07 | 0.23 | 1.35 | 0.92 |

Table 8. Predicted and observed concentrations (ppb) for fipronil and its' degradates.

Modeling results for fipronil degradates also conservatively estimated their concentrations as observed in receiving water (Table 8). With reported formation fractions for fipronil sulfone (MB46136), the model generates conservative but realistic results compared to monitoring data (Figure 6). Fipronil sulfide (MB45950) and fipronil desulfinyl (MB46513) may be significantly overestimated, because of the assumption of 100% formation fractions in aquatic environment when actual data are not available (see Table 1 for more info).

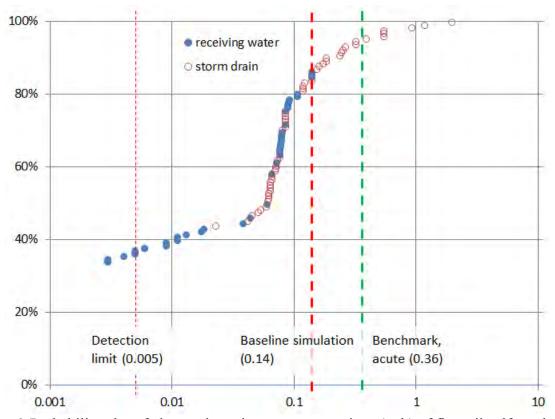


Figure 6. Probability plot of observed maximum concentrations (ppb) of fipronil sulfone, by sites and by monitoring study period, in California urban areas. Notes: The three dashed lines represent (from left to right): [1] 0.005 ppb: DPR detection limit (Ensminger, 2013). Please note that non-DPR monitoring studies may be associated with different detection limits. Therefore, nondetects are considered in calculating the probabilities (about 30% in total), but not displayed in the plot; [2] 0.14

ppb: baseline simulation result in urban receiving water (Table 7); and [3] 0.36 ppb: the lowest value of USEPA acute benchmarks (Table 3).

By considering fipronil and its' degradates together, the 1-in-10 year, daily average total (parent+degradates) risk quotient, RQ=sum(EEC[daily]/benchmark[acute]) = 4.7, in comparison with fipronil-only RQ = 4.5. For daily data, degradates contribute $0\sim86\%$ of total RQ, which is higher but generally comparable to monitoring results of $0\sim62\%$ (Budd et al., 2015). As mentioned before, this could be explained by the overestimations on fipronil sulfide (MB45950) and fipronil desulfinyl (MB46513).

4.7 Scenario analysis

The predicted fipronil concentrations (i.e., simulated EEC's) from Table 7 and the observed fipronil concentrations from Table 8 are higher than the USEPA benchmarks (TOX, Table 3). The amount of reduction required to achieve benchmark levels can be calculated as:

"Required" reduction = $1 - \frac{\text{Benchmark}}{\text{EEC(Baseline simulation)}}$

Based on the monitoring and modeling results, the required reductions are calculated in Table 9.

Table 9. Estimated reductions of fipronil concentrations to achieve USEPA aquatic life benchmark levels.

| | Based on baseline simulation (daily | Based on monitoring data |
|-----------------------|-------------------------------------|----------------------------|
| | concentrations as statewide | (grab samples for selected |
| | conservative estimation) | sites and sampling dates) |
| For acute benchmark | -78% (=1-0.11/0.50) | -59% (=1-0.11/0.27) |
| For chronic benchmark | -96% (=1-0.011/0.30) | - |

Notes: 0.50 ppb = daily EEC (Table 7), 0.30 ppb = 21 - d EEC (Table 7), 0.27 ppb = the average of top 3 observations in receiving water (Table 8), 0.11 and 0.011 are, respectively, the lowest USEPA acute and chronic aquatic life benchmarks (Table 3).

DPR is considering use limitations of outdoor applications of fipronil. Analysis was conducted to predict relative changes of fipronil concentration under various scenarios, and identify use practices for further investigations. Relative changes for daily EEC and 21-d EEC are similar for the tested scenarios, thus only those for daily EEC are presented (Table 10). For the scenarios with varying application band widths, the predicted reduction of daily EEC is generally proportional to the applied mass of fipronil. Spatial resolution in simulating terrestrial processes of pesticides has been improved in SWPP urban module (Luo, 2014a) relative to the original PRZM, but still not sufficient for tracking the inch-by-inch changes of band width, e.g., from 12 inches to 6 inches and to 1 inch. In reality, application spray swath may have effects on the pesticide offsite movement. Results of field experiments can be used to improve the model by identifying locations where refined spatial resolution is required. Modeling results (Table 10) also showed that fipronil runoff potential is sensitive to fipronil mass by 16%, but the daily EEC is decreased by 43%. Effects of combined scenarios, e.g., reduction of application band plus exclusion of driveway/garage door, are also evaluated (Table 10).

| Run | Application spray swath | Relative change to the baseline simulation | |
|-----|----------------------------------------------------------------------------------------------------------------------------|--------------------------------------------|-----------|
| ID | | Fipronil mass | Daily EEC |
| В | "1-in up, 1-in out" | -92% | -92% |
| D | "6-in up, 6-in out" @ label rate | -50% | -50% |
| F | No applications to the garage door; spot treatment to the driveway edge (equivalent to 4 ft^2 @ label rate) | -15.9% | -42% |
| G | No applications to the garage door and driveway edge | -16.2% | -43% |
| BG | B and G combined | -93% | -95% |

Table 10. Relative changes of model predicted 1-in-10-year peak concentrations of fipronil concentrations in urban receiving water under various scenarios.

Note: residential driveway width is set as 25.5 ft, which is the average value observed (based on Google Earth) in the urban watersheds of selected DPR monitoring sites in both northern and southern California (local survey by Budd, et al., 2015, personal communication). Label application rate = 2 quarts of 0.06% finished spray per 160 linear feet, 1ft. up and 1 ft. out from foundation

DPR has entered into a research contract with Dr. Les Greenberg at the University of California at Riverside (Agreement Number 14-C0102) to evaluate runoff potential and bioefficacy of various application scenarios. The mass of fipronil in simulated runoff after each scenario will be compared to a baseline application of current label rates. DPR has received preliminary data pertaining to the fipronil runoff trials. DPR will utilize information gained from this research to evaluate various scenarios for use of fipronil products labeled for outdoor structural applications. The goal of these scenarios is to reduce fipronil transport from urban landscapes to surrounding surface waters.

5.0 References

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