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Review of Fipronil Mitigation Strategies for the Protection of Surface Water

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Introduction

Fipronil (5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethyl)sulfinyl]-1*H*-pyrazole-3-carbonitrile) is a phenylpyrazole insecticide used throughout California for structural pest control in urban areas, in addition to topical flea and tick treatments for cats and dogs. Since its registration for use in the U.S. in 1996, use in California has continued to rise; currently there are 109 products containing fipronil registered in CA.

Due to frequent detections of fipronil in surface waters of California and fipronil's high toxicity to aquatic organisms, mitigation efforts are underway to minimize runoff from sites applied with fipronil-containing ant and termite products and to reduce overall water concentrations. In addition, fipronil's four degradates (fipronil sulfone, fipronil desulfinyl, fipronil sulfide and fipronil amide) are of concern; these have been found to be persistent and highly toxic.

According to the University of California Integrated Pest Management (UC IPM) Program there are many ways applicators and home owners can mitigate offsite movement of fipronil. For example, reducing applications near storm drains or areas where runoff may occur will help reduce the amount of fipronil entering storm drains and waterways. In addition, many changes to application methods and sites are advised. For instance, reducing applications to sloped areas and adjusting spray methods from a fan spray nozzle to a pinpoint spray nozzle or using bait stations will also reduce offsite movement (UC IPM, 2011). However, improving irrigation systems in order to reduce runoff is also essential. Below, various studies considering mitigation techniques and runoff modeling are summarized.

The objective of this review is to assess current literature and summarize current fipronil use and potential mitigation techniques for fipronil, in order to better understand offsite movement into surface waters.

Current Fipronil Application Techniques

Fipronil is commonly used to control various ant species. Bait stations and gels, for example, are formulated with roughly 0.01% a.i. and can be placed on the exterior of homes and buildings. In

Coachella Valley, CA, the use of granular products (approx. 0.01–0.1% a.i.) is allowed for the control of Red-Imported Fire Ants. These products (e.g., Chipco Choice Insecticide and Senture Insecticide) can be applied to outdoor settings such as turf, landscape beds and/or outdoor nurseries and have the potential to runoff with irrigation and precipitation.

Products that are more likely to contaminate surface water are those formulated as soluble concentrates (e.g., Termidor SC Termiticide/Insecticide and Taurus Termiticide/Insecticide); these widely-used products allow pre/post construction application to control ants, termites and other arthropods. These outdoor applications consist of a surface spray to exterior openings or perimeter foundations. Impervious surfaces may increase fipronil concentrations in runoff from rainfall or other contact with water.

Dust formulated products (e.g., Termidor Dry California) may be applied outdoors; however, these product are directly injected at the site of termite activity. Underground injection is likely not a pathway for fipronil contamination of surface runoff; however, it could be a potential pathway into urban wastewater. At this time, the scope of this review will be strictly limited to evaluating surface water contamination and its mitigation.

Experimental Conditions and Results

Study #1. Greenberg et al. (2010) – Pin-stream application technique and spray-free zones

As pesticides are often applied to the exteriors of houses, post-treatment runoff is of concern. To investigate the extent at which runoff occurs, Greenberg et al. (2010) looked at various application methods as potential management practices. Homes containing irrigated front lawns were treated once with either one or two insecticides, during the summer months of 2007 to avoid wash-off from rain. Daily irrigation occurred and water samples were collected (1, 4 and 8 weeks post-application) once the runoff hit the street curb.

In 2007, houses were treated using conventional treatments such as, perimeter + spot and/ or spot using conventional fan-spray nozzles. In 2008, an additional study was conducted using pin-stream spray (narrow 5.1 cm band) and spray-free zones (located within 4.6 m of a street and 1.5 m from the sidewalk or driveway) in addition to conventional treatments. Water samples were collected 1 and 7 days post-application via runoff and at 14 days solely from a concrete driveway flush. In both studies, fipronil and its metabolites were analyzed for.

As potential mitigation techniques, Greenberg et al. (2010) employed pin-stream applications, which are not common for house perimeter treatments, in addition to having spray-free zones around sidewalks and driveways. Employing these techniques resulted in an overall decrease in fipronil runoff in comparison to a spot treatment and perimeter spray. Data from the driveway flush (14 days post-application), had no detectable insecticide within the runoff when the pin-stream and spray-free zones were implemented. However, runoff from the spot treatment, without the spray-free zone, had significantly higher fipronil detections. Overall, these studies indicate that use of non-conventional application methods, in addition to limiting the amount applied on the perimeter of the structure, has the potential to reduce pesticide concentrations in irrigation runoff.

Efficacy of the treatments in controlling ants was also determined. In the 2007 study, fipronil applied as a perimeter spray was more efficacious (fan nozzle, 77% reduction in ants) than as a spot treatment (fan nozzle, 46% reduction). However in the 2008 study, perimeter and spot treatments using a pin-stream nozzle reduced ants by 80-82%. In addition, implementing spray-free zones reduced fipronil's ability to control ants; roughly 8% of ants were reduced by this method.

Studies #2 and 3. Jiang et al. (2010) and Jiang et al. (2014) – Effects of formulation, surface type, and application type on wash-off

Concrete disks, prepared in glass jars, were spiked with fipronil (267.4 µg/ disk) and exposed to environmental conditions for 0 (no outdoor exposure), 2, 7, 14, 28, 56 and 112 days. Simulated rainfall/irrigation was conducted by washing each disk with water for 10 min. Disks after 56 d of exposure were extracted to measure residual pesticides adhered to the concrete itself. Jiang et al. (2010) found 35% of the initially applied fipronil to rapidly wash off on day zero (no environmental exposure), whereas environmental conditions decreased the concentrations measured in wash-off by the end of the experiment. However, fipronil was shown to be persistent when in contact with concrete, thus increasing its potential to contaminate runoff. *This study showed that liquid formulations had lower wash-off potentials than granular/powder formulations (Jiang et al., 2010).*

In a subsequent study, the runoff potential of a professional-use formulated fipronil soluble concentrate product, in combination with bifenthrin and permethrin was investigated. Pesticide mixtures (50 mL) were applied to concrete slabs which were exposed to dry summer temperatures for up to 89 days (Jiang et al., 2014). Concrete slabs were subjected to simulated rainfall (1, 7, 20, 47 and 89 days post-application) either as a single precipitation event or repeated irrigation events and runoff water was collected each time. At 89 days post-application, fipronil was still detectable (mean ± standard deviation = 0.18 ± 0.06 µg/ L) and remained efficacious. *This study concluded that there are various options that can be employed to reduce pesticide runoff, including 1) crack/spot treatments instead of broadcast applications, 2) limiting use on hardscapes away from water contact, and 3) minimize or avoid using granular/dust formulations on hardscapes, which may wash off rapidly (Jiang et al., 2014).*

Study #4. Luo et al. (2014) – Product-specific wash-off characterization and prediction

Although various studies measured the concentration of fipronil in runoff of treated concrete slabs, many did not characterize the parameters influencing such runoff. In particular, Luo et al. (2013) modeled runoff containing fipronil, in order to identify the influence factors such as chemical properties, formulation and rainfall duration have on pesticide transport from concrete. Concrete surfaces, applied with formulated pesticides were subjected to simulated rainfall and runoff was collected (similar to previous studies mentioned here). Within one day post-application, approximately 5% of the applied fipronil was detected in the wash-off.

A wash-off model was developed to predict mass losses from concrete wash-off. Here, the model's predictions followed linearity as time between rainfall events increased. For fipronil, the

model's input parameters and output resulted in a coefficient of variance of 6%, thus the predicted and observed mass losses were correlated. *This study shows that besides knowing the chemical properties of the pesticide, certain product and application-related parameters (product formulation, product aging effects, concrete surface conditions and rainfall intensity) are important in considering pesticide risk assessment. Model based results may help to identify pesticide buildup and wash-off from artificial surfaces such as concrete. More importantly, product specific modeling results will help aid in mitigation processes such as restricting application amounts and contact areas.*

Study #5. Kroger and Moore (2008) – Effectiveness of wetland plant species in removing fipronil

Kroger and Moore (2008) investigated the efficacy of native and non-native wetland plant species in reducing fipronil and fipronil sulfone. Mesocosms, containing four different plant species, were dosed with fipronil and subjected to simulated storm runoff. Water and sediment samples were collected and analyzed for both fipronil and fipronil sulfone residues. The mesocosms reduced fipronil concentrations by 38-48%, but displayed an increase in fipronil sulfone by 96-328%. It should be noted that statistical significance could not be established between the control and treatments or among the treatments themselves. *The researchers speculated that the conversion of fipronil to its sulfone degradate in the oxidative aqueous environment and the sorption of fipronil to the test system accounted for the observed reduction. A longer residence time and an improved test system could improve the ability to see differences among treatments as well as between treatments and control. We are including this study in our review to document that the ability of wetland plants in removing fipronil was considered and explored.*

Study #6. Greenberg et al. (2014) – Monthly and bi-monthly application frequency using perimeter, pin-stream or crack and crevice sprays

Strategies to reduce fipronil use around homes for ant management were investigated by Greenberg et al. (2014). Ten houses were treated from July through October 2012, by either a bi-monthly (Protocol 1) or a monthly (Protocol 2) treatment.

Protocol 1 consisted of a perimeter spray (2 inch or 5.1 cm narrow band up and out) from the house foundation at the grade-wall junction and a pin-stream spray (applicator tip 0.6 m from the surface) at the garage door-driveway interface. Fipronil was applied with a backpack sprayer containing a cone nozzle. Protocol 2 used an 11.8 inch (30 cm) band width (up and out) when applying fipronil to the grade-wall junction. However, a crack and crevice application was used at the garage door-driveway expansion joint; the applicator tip was placed against the expansion joint. Here, fipronil was applied using a handheld tank sprayer with an adjustable cone tip. Subsequent applications replaced fipronil with either pyrethroids or botanical insecticides. Driveways were flushed and water samples were collected (1, 28, 65 and 98 days post-application) once the runoff hit the street curb. Samples were analyzed for fipronil.

Both application methods resulted in runoff concentrations below the fipronil EC₅₀ (10 µg/L) for Ceriodaphnia, however concentrations were greater than the acute invertebrate benchmark value (0.11 µg/L) set by the U.S. EPA. Overall runoff concentrations were higher in Protocol-1

houses compared to Protocol-2 houses although concentrations were not significantly different; however, a larger sample size is necessary to definitively establish the differences in runoff concentrations. Use of a lower pressure hand-held sprayer and a more localized application to cracks may have influenced the difference in runoff concentrations.

Summary

Fipronil and its degradates have been frequently detected in surface waters throughout California. Due to fipronil's rising popularity and increased use, there is concern that both fipronil and its degradates could adversely impact aquatic organisms and waterways (i.e. accumulate in sediments and/or concentrate within the water column). In order to minimize fipronil's movement to surface waters through post-application runoff, mitigation techniques are being evaluated. Techniques such as changing from broadcast to perimeter spray and from fan spray to pinpoint nozzles help minimize the amount of pesticide applied and therefore limiting the amount available to runoff. Although a new concept, urban mitigation employing vegetative ditches may eventually result in a successful reduction of fipronil loading into surface water bodies; however further experiments are required to warrant its effectiveness. Home owners can also proactively improve their irrigation schemes to limit wash-off of fipronil from treated surfaces to help mitigate the off-site movement of fipronil.

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