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Review of the Environmental Fate and Use Patterns of Fipronil in California

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Background

This document is intended as a supplement to the Department of Pesticide Regulation's (DPR's) 2007 environmental fate review of fipronil (Gunasekara et al., 2007). More recent journal articles addressing national use trends, environmental fate, and impact to non-target organisms have recently been published (Bonmatin et al., 2015; Pisa et al., 2015; Simon-Delso et al., 2015). A comprehensive summary of California monitoring data and relative toxicity has also been documented (Budd et al., 2015). Finally, the fipronil occurrence and fate of fipronil through the wastewater treatment process has been reported (Sadaria et al., 2017). Herein, key findings are summarized; however, for a more in depth discussion of specific topics each of the above studies should be referenced.

Introduction

Fipronil (5-amino-1[2,6-dichloro-4-(trifluoromethyl)pheyl]-4[(trifluoromethyl)sulfinyl]-1H-pyrazole-3-carbonitrile) is a phenylpyrazole insecticide first synthesized by Rhone-Poulenc Ag Company (now Bayer Crop Science) in 1987 (Council, 2000) and registered for use in the United States in 1996. The insecticide controls a broad spectrum of insects at larval and adult stages by inhibiting the nervous system by binding to the GABA receptors and to glutamate receptors coupled to chloride channels (Simon-Delso et al., 2015). As of May 2017, there were 134 fipronil products registered for use in the state of California, 92 of which are formulated in pet products. Other than flea and tick treatment in pets, registered uses include structural pest control, turf grass pest control, and consumer products intended for indoor use (gels and baits) (CDPR, 2017). In the state of California, fipronil is not registered for uses in production agriculture.

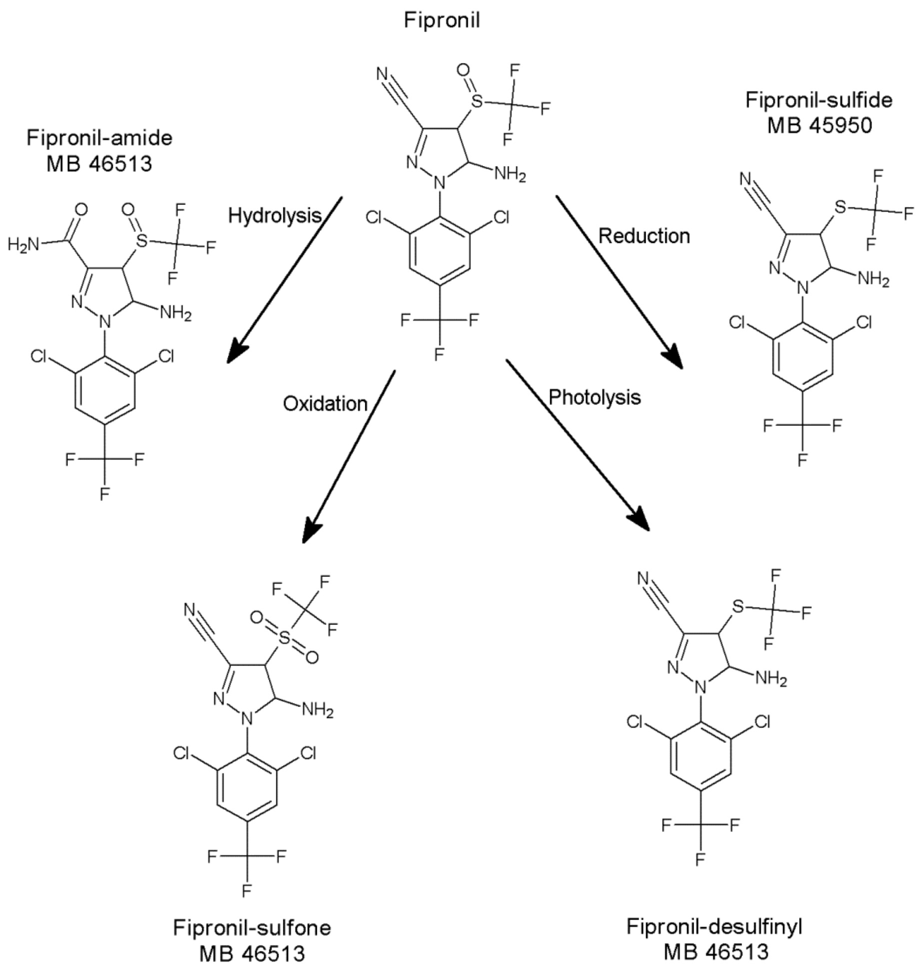

Figure 1. Fipronil, major degradates, and dominant degradation pathway.

DPR's Pesticide Use Reporting (PUR) database contains application records for pesticides applied by professional applicators. The majority of fipronil applications (>99%) by professionals are structural application (CDPR, 2017). Products purchased directly by consumers (i.e., pet products, gels, and baits) are not reported in the PUR, however, pesticide mass can be evaluated through an internal sales database (CDPR, 2016). The mass of fipronil introduced to the environment statewide for structural application is between 1.5 and 5.6 times higher than for use in pet products (Figure 2).

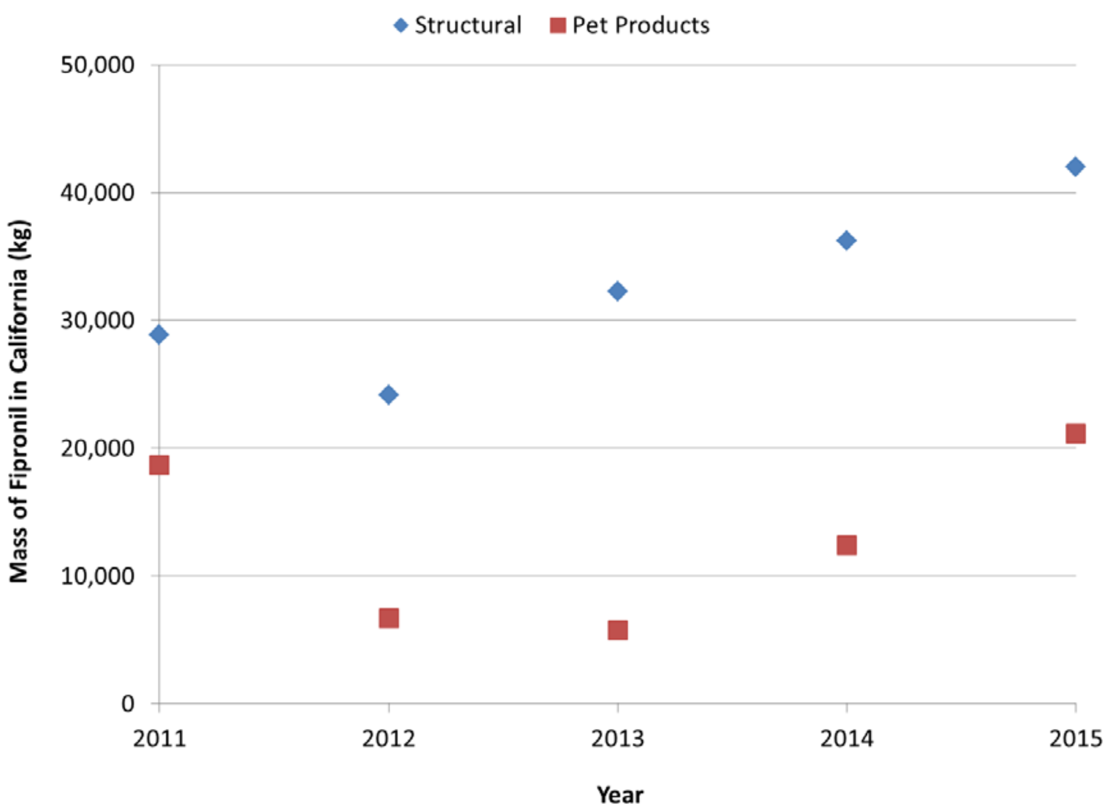

Figure 2- Comparison of fipronil use amounts based on professional application reported in the PUR and mass sold as pet products (CDPR, 2016; CDPR, 2017).

Physical-chemical properties

Fipronil is a systemic pesticide able to translocate in plants and animals for increased efficacy to target organisms (Dyk et al., 2012; Pisa et al., 2015). Fipronil has low solubility in water and has a moderate affinity for organic matrices. Fipronil is stable in the pH range of ambient waters (pH 5 and 7) and will slowly hydrolyze at a pH of 9 (DT_{50} 28 days) (Council, 2000). Fipronil is relatively stable to heat and is expected to have negligible losses to volatilization based on a low Henry's law coefficient.

Table 1. Physicochemical properties of fipronil.

Property		Fipronil	Units
Chemical Abstract Service registry number (CAS)[1]		120068-37-3	na
Molecular[1] weight		437.15	g/mol
Solubility[1]	water	1.9, 2.4	mg/L, 20°C, pH 5, pH 9
	acetone	545.9	g/L, 20°C
	dichloromethane	22.3	g/L, 20°C
	hexane	0.028	g/L, 20°C
	toluene	3.0	g/L, 20°C
Melting Point[1]		200–201	°C
Density[1]		1.48–1.63	g/mL 20°C
Vapor Pressure		3.7×10^{-4}	mPa @ 25°C
Henry's constant[1]		3.7×10^{-5}	Pa*m^3/mol
Octanol-water partition coefficient[1]		4.0	log K_{ow}
Aqueous photolysis[1]		0.33	days; pH=5
Hydrolysis half-life[2]		>100 >100 32.08 4.75 0.45 (11 hrs) 0.1 (2.4 hrs)	days, pH =5.5 days, pH=7.0 days, pH=9.0 days, pH=10 days, pH=11 days, pH=12
Aerobic soil half-life[4]		188	days
Anaerobic soil half- life[3,4]		18.3–91	days
Anaerobic water half-life[1]		0.92–5.2	days

[1] (Council, 2000)
[2] (Bobé et al., 1998)
[3](Lin et al., 2009)
[4](Ngim and Crosby, 2001)

USEPA aquatic life benchmarks have been adopted for fipronil and three degradates (Table 2). The Central Valley Regional Water Quality Control Board through a contract with UC Davis is in the process of developing water quality criteria for fipronil and degradates. The values, currently in draft form for public comment, report sub-ng/L water quality criteria for fipronil sulfide and fipronil sulfone (Table 2).

Table 2. Summary of US EPA aquatic life benchmarks and water quality standards. Invertebrates are the most sensitive taxon for US EPA aquatic benchmarks with the exception of fipronil desulfinyl where fish are the most sensitive taxon (denoted with *) There are not sufficient toxicity tests available to provide a species sensitivity distribution to calculate water quality objectives for fipronil amide or fipronil desulfinyl amide.

Chemical	US EPA Chronic Aquatic Life Benchmark (ng/L)[1] to most sensitive taxon	US EPA Acute Aquatic Life Benchmark (ng/L)[1] to most sensitive taxon	UC Davis Water Quality Objective acute (ng/L)[2]	UC Davis Water Quality Objective chronic (ng/L)[2]
Fipronil	11	110	14	2.2
Fipronil amide	na	na	na	na
Fipronil sulfide	110	1,065	0.58	0.13
Fipronil desulfinyl	590*	10,000*	na	na
Fipronil sulfone	37	360	1.3	0.17
Fipronil desulfinyl amide	na	na	na	na

[1]USEPA Aquatic Life Benchmarks (USEPA, 2014)
[2]UC Davis water quality criteria (Bower and Tjeerdema, 2017)

Environmental Fate

Water

Fipronil applied in urban areas for structural pest control is transported offsite during dry season lawn irrigation and during storm events (Budd et al., 2015; Weston et al., 2009). DPR's Surface Water Protection Program (SWPP) has conducted monitoring for fipronil and degradates at urban environments since 2008. From 2008-2015 detection frequencies for fipronil, fipronil sulfone, and fipronil desulfinyl were 49, 43 and 33% respectively, with relatively higher concentrations in southern California. Receiving water samples exhibited fipronil concentrations above the lowest USEPA chronic aquatic benchmark 46% of the time. Sulfone and desulfinyl were most commonly detected degradates frequently at concentrations exceeding their lowest

USEPA chronic aquatic life benchmarks. Annual mass flux was greater during dry season than that during storm season (Budd et al., 2015). Fipronil persists at the site of application. A study measuring dust in urban environments reported occurrence of fipronil desulfinyl and fipronil sulfone in addition to the parent (Richards et al., 2016). Parent fipronil is expected to transform to degradation products prior transport off site to surface water environments.

Concentrations of fipronil and degradates have been reported in raw wastewater and treated wastewater effluent (Heidler and Halden, 2009; Sadaria et al., 2017; Supowit et al., 2016). Removal during wastewater treatment process is minimal resulting in constant discharge of fipronil and degradates to receiving waters. A minor increase in degradates occurs during treatment for fipronil sulfone, sulfide, and amide with a negligible decrease in total fiprole load (Sadaria et al., 2017) . Treated wastewater effluent contains fipronil and degradates at concentrations that exceed USEPA aquatic benchmarks, however some dilution will occur once discharged to surface water and thus a direct comparison isn't appropriate. Washoff of fipronil from treated pets to wastewater catchment has been reported (Teerlink et al., 2017), and indirect transfer from clothing, bedding, humans, and indoor surfaces in contact with treated pets has been proposed (Sadaria et al., 2017).

A comprehensive comparison of the relative contribution of fipronil from outdoor urban runoff and from wastewater treatment plants has not yet been reported. When considering total fiproles, or the sum of fipronil and all degradates, a greater proportion of total fiproles are comprised of degradates in samples from the environment than immediately following tertiary wastewater treatment process.

Soil

The half-life of fipronil in soil varies greatly and is dependent on moisture content, oxidation state, temperature, and soil composition (Brennan et al., 2009; Lao et al., 2010; Lin et al., 2009). Fipronil is least stable under anaerobic soil conditions, and degradation products are stable under anaerobic and aerobic conditions (Table 3). Environmental monitoring results consistently report more frequent detection and greater concentrations of degradation products in soil than those of parent fipronil (Brennan et al., 2009; Hintzen et al., 2009; Lin et al., 2009). Under aerobic conditions, or low moisture content, fipronil sulfone is the dominate degradation product (Hintzen et al., 2009; Lao et al., 2010). Under high moisture or anaerobic conditions fipronil sulfide is the dominant form (Demcheck and Skrobialowski, 2003; Lao et al., 2010).

Sorption of fipronil and degradates is positively correlated with clay content and organic carbon content (Brennan et al., 2009; Singh et al., 2014). The majority of fipronil and degradates remain in the upper 0-5 cm of undisturbed soil columns, ~15% of fipronil moved to 5-10 cm indicating some mobility (Chatterjee and Gupta, 2010). Although some mobility has been reported for fipronil and degradates, the affinity for organic matter is unlikely to result in groundwater contamination concerns.

Table 3. Organic carbon normalized partition coefficients for fipronil and major degradates.

Chemical	**Log K_{oc}**	**Aerobic soil Half-live (days)**	**Anaerobic soil half-live (days)**
Fipronil	2.7 –4.5[1, 2,3]	188	18.3–91[3,4]
Fipronil sulfide	3.6–5.61[1,3]	195-352[3]	>280[3]
Fipronil sulfone	3.5–6.2[1,3]	502-589[3]	>280[3]
Fipronil desulfinyl	3.1[3]	217-497[3]	>280[3]

[1](Brennan et al., 2009)
[2](Ying and Kookana, 2001)
[3](Lin et al., 2009)
[4](Ngim and Crosby, 2001)

Air

Fipronil does not readily volatilize and is not expected in air (Table 1).

Toxicity

Fipronil and its' degradates are particularly toxic to freshwater midges (*Chiromonids*). During storm sampling of urban creeks 70% of the *Chironomus dilutus* were immobilized and effects attributed to fipronil and fipronil sulfone concentrations (Weston et al., 2015). Using joint probability analysis curve to investigate the impact from environmental concentrations of fipronil and degradates indicate that the LC50 for the most sensitive 5% of the species is exceeded 8.5-18.8% of the time for two sites studied, or 75-78% of the time for when using the more conservative NOEC (Wu et al., 2015).

Wagner et al. reported a positive correlation between gross deformity (tail curvature) at 200 μg/L and delayed hatching at LOEC 600 μg/L in Japanese Medaka (*Oryzias latipes*) (Wagner et al., 2017). The 24-hour chronic LC_{10} concentrations for larval fathead minnow (*Pimephales promelas*) was 306 μg/L (Beggel et al., 2010). Experiments comparing swimming performance and growth between the active ingredient and formulated products found enhanced effects with the formulations (Beggel et al., 2010). Fipronil is toxic to larval fish at concentrations higher than typically reported in the environment (Baird et al., 2013). Baird et al., experiments were setup with fipronil spiked sediments, indicating the importance of sediment concentrations to aqueous exposure (2013). The same study hypothesizes that the system source for fipronil sulfone is the fipronil exposed fish.

Summary

Fipronil is a phenylpyrazole insecticide that exhibits neuro-toxic activity by blocking the GABA-regulated chloride channels of neurons. Fipronil and degradates are frequently detected in California surface waters at concentrations that exceed USEPA chronic aquatic benchmarks. Detections are likely from offsite runoff due to applications in structural pest control and from pet products making their way through wastewater treatment plants. In soil, fipronil degrades readily under anaerobic conditions. Degradation products are relatively persistent, however, not mobile. Fipronil and degradates are highly toxic to aquatic organisms. Test species *Chironomus dilutus* is particularly sensitive to toxicity from fipronil and fipronil degradates.

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