

Fipronil

TIER 3
MODERATE
CONCERN

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Quick Summary

Fipronil is a broad-spectrum insecticide with growing use to control pests around structures and fleas on pets. Fipronil and its multiple stable degradation products have been detected in Bay Area urban runoff, urban creeks, and Bay sediment. Nationally, fipronil has been detected in urban runoff, municipal wastewater effluent, water and sediment in urban creeks, and in estuary sediment. Observed concentrations are approaching and in some cases exceeding effect thresholds, suggesting an increasing potential for fipronil to pose risks to aquatic ecosystems.

What Is It?

- Synthetic broad-spectrum insecticide first approved for use in the late 1990s.
- A slow acting toxicant that insects can carry back to and share with colonies.
- Fipronil has at least four stable degradation products, three of which (fipronil sulfide, fipronil sulfone, and desulfinyl fipronil) can readily be measured with standard chemical analysis techniques.
- Fipronil and its stable degradation products are lethal to sensitive aquatic organisms (e.g., crustaceans and aquatic insects) at concentrations <1 microgram per liter ($\mu\text{g/L}$) (TABLE 1). Chronic toxicity to the crustacean *Americamysis bahia* has been reported at concentrations less than 0.003 $\mu\text{g/L}$ (USEPA 2007). For some aquatic species – such as *Americamysis bahia* – fipronil’s degradation products are more toxic than fipronil itself.

What Is It Used For?

- In 2003, the California Department of Pesticide Regulation (DPR) began to allow professional applicators to spray fipronil around buildings to control nuisance insects (the only significant outdoor use). Other uses are pet flea “spot-on” treatments, containerized insect control baits, and termite control solutions for injection into soil beneath structures.
- Not used on landscaping except in Southern California’s Coachella Valley, where professional applicators are authorized to make limited use of fipronil solely to control fire ants.
- No agricultural use in California.
- Total California sales were about 18,000 kg in 2011 and have tripled since 2003 (CDPR 2013).



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How Is It Getting Into the Bay?

- Urban stormwater, which flows directly into the Bay untreated, is a pathway to the Bay due to use of fipronil outdoors around buildings.
- In samples from Bay Area storm drains and creeks in two watersheds collected between 2008 and 2011, Ensminger et al. (2013) measured fipronil concentrations up to 0.46 µg/L. Nine percent of Bay Area fipronil detections exceeded the US Environmental Protection Agency (USEPA) chronic aquatic invertebrate protection benchmark of 0.011 µg/L (USEPA 2013). Urban runoff concentrations measured in the Sacramento, Orange County, and San Diego regions were higher – up to 10 µg/L.
- In an intensive two-year sampling program in Sacramento and Orange Counties, median concentrations of fipronil plus its three degradation products in runoff were 0.014 to 0.441 µg/L (Gan et al. 2012).
- Applications to control insects around buildings involve spraying impervious surfaces, like building walls and walkways, from which fipronil and its degradation products can be washed into gutters and storm drains. In laboratory simulations, fipronil and its degradation products appeared in runoff from concrete surfaces at concentrations >140 µg/L one day after application, >30 µg/L two weeks after application, and >1 µg/L 56 days after application (Thuyet et al. 2012; Jiang et al 2010).

- Although there are no local monitoring data, municipal wastewater treatment plant effluent is probably also a pathway to the Bay.
- Fipronil and its degradation products were detected in both filtered effluent and effluent solids from eight of nine Columbia River Basin (Washington and Oregon) municipal wastewater treatment plants (Morace 2012). All fipronil detections exceeded USEPA’s chronic aquatic invertebrate protection benchmark of 0.011 µg/L (USEPA 2013).
- The only indoor use of fipronil is a “spot-on” treatment for fleas and ticks on pets, which could subsequently be washed into the sewer system when the pet is bathed. Other possible pathways to the sewer system include post-application cleanup activities, seepage into underground sewer lines from subterranean termite treatments, spills, and improper disposal.

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TABLE 1

Toxicity thresholds for fipronil and its degradation products. All concentrations in µg/L.

CHEMICAL NAME	AMERICAMYSIS BAHIA		LOWEST USEPA PESTICIDE AQUATIC LIFE BENCHMARKS
	LC50	LOWEST OBSERVED EFFECT CONCENTRATION	
Fipronil	0.14	0.005	0.011 (invertebrates, chronic)
Fipronil Sulfone (MB46136)	0.56	0.0026	0.037 (invertebrates, chronic)
Fipronil Sulfide (MB45950)	0.077	0.0087	0.11 (invertebrates, chronic)
Desulfinyl Fipronil (MB46513)	1.5	–	0.59 (fish, chronic)

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What Happens to It in the Bay?

General Properties

- The fate of fipronil in the Bay has not been studied, but predictions can be made based on information from other studies. Fipronil and its stable degradation products are likely to occur in both water and sediment in the Bay. Partitioning into sediment and breakdown by exposure to sunlight and microbial activity likely determine fipronil's ultimate fate in the Bay.
- In sediment, because the presence of organic carbon significantly reduces the uptake of fipronil and its degradation products by organisms, toxicity thresholds are expressed on the basis of sediment organic carbon content (e.g., micrograms of fipronil per gram of organic carbon).
- Limited data exist to characterize the fate of fipronil degradation products, which may have half-lives (time required for a 50% reduction) as long as 700 days in aquatic environments (USEPA 2007).

Patterns of Occurrence in the Bay and in Other Aquatic Ecosystems

- The RMP measured fipronil and its degradation products in Bay sediment in 2002-2003 and 2009-2012. The highest concentrations, up to 0.56 ppb for individual fipronil compounds, were measured in Lower South Bay. Toxicity data for saltwater benthic (sediment-dwelling) species are limited. One laboratory study found reduced reproduction in a saltwater benthic crustacean with addition of 30 ppb to sediment (Chandler et al. 2004). The highest concentrations observed in the Bay exceed the EC50 for immobilization (level causing immobilization in 50% of test organisms) of a freshwater benthic species, *Chironomus tentans*.
- Fipronil and its degradation products were detected in 100% of sediment samples collected in 2007-2009 from the Ballona Creek estuary (Los Angeles, CA). The highest measured fipronil concentration was 6 ppb. In most samples, the degradation product fipronil sulfone was present at higher concentrations, up to 9.8 ppb. In some cases, the total toxic potency of fipronil plus degradation products, exceeded the EC50 for *Chironomus tentans* (Bay et al. 2010).
- In 2012 monitoring of four Bay Area urban creeks, fipronil was detected in 100% of samples, at concentrations from 0.006 to 0.020 µg/L. Thirty-six percent of these discrete samples exceeded USEPA's chronic aquatic life protection benchmark of 0.011 µg/L (USEPA 2013).

- A recent review of California urban watershed fipronil monitoring data published between 2003 and 2012 found that fipronil was detected in 39% of water samples and 19% of sediment samples. Average observed levels of fipronil in water (0.09 µg/L) exceeded USEPA's chronic aquatic invertebrate protection benchmark of 0.011 µg/L, while average concentrations of fipronil degradation products were on the same order of magnitude as their lowest respective USEPA chronic aquatic protection benchmarks (0.037-0.590 µg/L) (Ruby 2013).

Trends in the Bay and Nationally

- In RMP sediment monitoring, higher concentrations of fipronil compounds were generally found in more recent (2009-2012) samples, compared to 2002-2003 samples, in which they were often not detected.
- Based on data from 10 nationwide urban sites, USGS identified a "widespread significant upward trend" in detection frequency and concentrations of fipronil and two degradation products from 2000-2008 (Ryberg et al. 2010).
- Since fipronil is an alternative to the pyrethroid insecticides, usage is likely to increase in response to regulatory restrictions on pyrethroids.

Is There a Risk of Harm in the Bay?

- Available monitoring data indicate that concentrations of fipronil and its degradation products could potentially be approaching effect levels for sensitive test organisms, particularly at the Bay margins, near discharge points.
- The persistence of fipronil degradation products could lead to accumulation in sediment.

Concentrations of fipronil and its degradation products could potentially be approaching effect levels for sensitive test organisms, particularly at the Bay margins, near discharge points

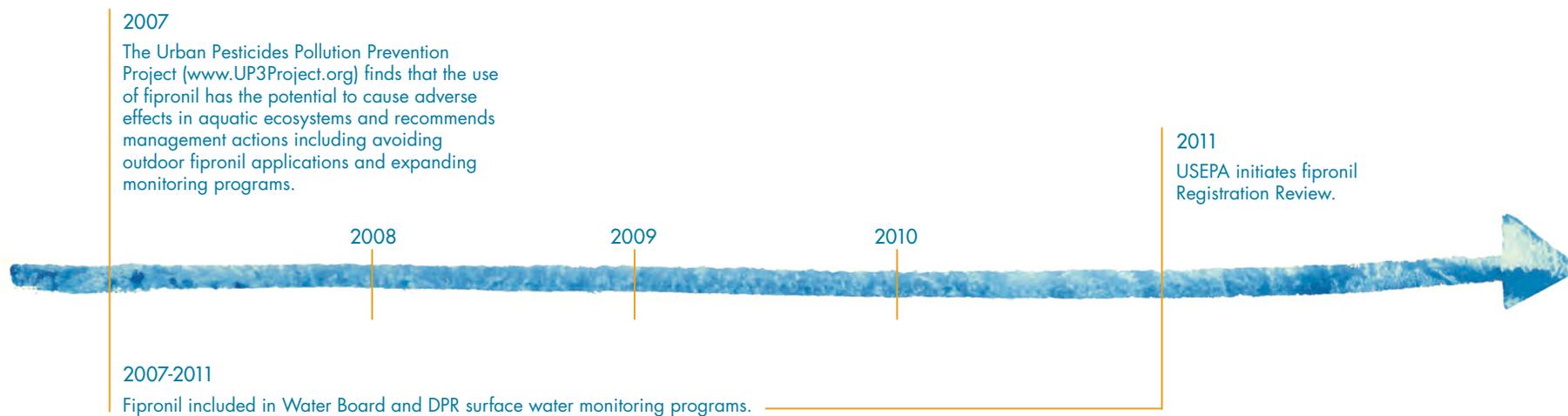
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Key Information Gaps

- Aquatic toxicity and environmental fate data, particularly for fipronil degradation products.
- Monitoring data for fipronil and its stable degradation products in Bay water and sediment (particularly near discharge points, including Bay margins), urban creek sediment, and municipal wastewater effluent.
- Toxicity identification evaluation methods that allow evaluation of the potential for linkage between fipronil exposures and incidents of toxicity to testing organisms.
- Application rates and techniques that maintain pest control efficacy while reducing the quantity of fipronil in urban stormwater runoff.



Management Timeline



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