

PS/SS: Fipronil and its Degradation Products in San Francisco Bay Surface Water and Sediments

Estimated Cost: \$19,000

Oversight Group: Emerging Contaminants Work Group

Proposed by: Katie Harrold, SFEI

Background

Fipronil is a relatively new pesticide which was introduced for use in 1993 and registered for use in the US in 1996 (US EPA 1996). It is a phenylpyrazole insecticide and works by disrupting nerve function via GABA (γ -aminobutyric acid type A) receptors. In California, fipronil is used primarily for structural application and pet treatment (Gunasekara *et al.* 2007) and is not currently registered for agriculture use. Use of fipronil is expected to increase as the use of other insecticides is restricted, especially as users switch away from pyrethroids. Thirty-seven current use products containing fipronil are registered in California (DPR 2009).

Fipronil degrades into several compounds, some of which are persistent and also toxic including fipronil sulfide, fipronil sulfone, and fipronil desulfinyl (Gunasekara *et al.* 2007). The lowest reported LC₅₀ for fipronil is 0.14 $\mu\text{g L}^{-1}$ in mysid shrimp (US EPA 1996). A species of estuarine copepods (*Amphiascus tenuiremis*) has also been found to be highly sensitive to fipronil, with a developmental delay of two days and 71% reduction in egg extrusion when exposed to 0.22 $\mu\text{g L}^{-1}$ (Chandler *et al.* 2004). Larval flies (*Chironomus tentans*), one of the few species tested with sediment exposure, are also sensitive, with LC_{50s} of 0.13 $\mu\text{g fipronil/g organic carbon}$, 0.16 $\mu\text{g fipronil sulfide/g organic carbon}$, and 0.12 $\mu\text{g fipronil sulfone/g organic carbon}$ (Maul 2008). Moran (2007) concluded that there is a potential for adverse aquatic effects in California surface waters and recommended monitoring for fipronil and fipronil degradates because of their high toxicity and increasing use in urban areas.

Limited monitoring has occurred in California to date. Since 2002 the National Water-Quality Assessment Program (NAWQA) has monitored urban streams that discharge into the Sacramento and San Joaquin Rivers and detected fipronil sulfide at 5 – 18 ng/L, fipronil sulfone at 6 – 13 ng/L, and fipronil at levels of detection with estimated concentrations of 5 – 100 ng/L; (USGS 2009). The US Geological Survey and National Park Service conducted a survey of urban creeks in the Golden Gate National Recreation Area, including the Presidio, and detected fipronil and fipronil sulfone below detection levels with estimated concentrations of 0.8 and 1.4 ng/L, respectively (Hladik and Orlando 2008). The Gan research group at UC-Riverside has been conducting a study of urban runoff in Sacramento and Orange Counties and reports regularly finding fipronil, fipronil sulfide, fipronil sulfone, and fipronil desulfinyl in Sacramento County runoff and finding fipronil and fipronil degradates at concentrations greater than 0.14 $\mu\text{g L}^{-1}$ in Orange County runoff (Oki *et al.* 2008). As part of a California Sediment Quality Objectives assessment of the Delta, fipronil and its degradates were analyzed in 75 sediment samples from the Lower Delta and all samples were below detection (MDL 20 ng/g dw) (Lowe 2009).

Applicable RMP Objectives and Management Questions

1. Are chemical concentrations in the Estuary potentially at levels of concern and are associated impacts likely?
 - A. Which chemicals have the potential to impact humans and aquatic life and should be monitored?
 - B. What potential for impacts on humans and aquatic life exists due to contaminants in the Estuary ecosystem?

The objective of this study is to determine if fipronil and its stable degradates, specifically fipronil sulfide, fipronil sulfone, and fipronil desulfinyl, are present in the Bay at concentrations within range of effects thresholds. Fipronil concentrations have been detected at concentrations exceeding known effects levels in urban streams draining into the Sacramento River (Oki *et al.* 2008), but monitoring has not occurred in ambient Bay water or sediments.

Relationship of the Study to the ECWG Priority Question and Current RMP List of Emerging Contaminants

The Emerging Contaminant Workgroup is focused on answering the following question: “What emerging contaminants have the greatest potential to adversely impact beneficial uses in the Bay?” Fipronil has been highlighted as a new insecticide with relatively little monitoring or toxicity data available. However, several studies have found it to be toxic to estuarine species and also detected in urban runoff at concentrations exceeding these thresholds (US EPA 1996; Chandler *et al.* 2004; Oki *et al.* 2008). Fipronil is more toxic to grass shrimp (*Palaemonetes pugio*) than either atrazine or imidacloprid (Key *et al.* 2007). Sediment toxicity is of great concern in the Bay, but the cause(s) of the observed toxicity have not been determined and it is possible that fipronil is contributing to sediment toxicity in the Bay. Pesticides are by design intended to be toxic to organisms, so any drift, leaching, or runoff of active ingredient from application sites has the potential of impacting non-target organisms. Fipronil and its degradates have been found in urban runoff and fipronil is included in the TDC Environmental list of pesticides of concern for urban surface waters developed for SFEP and the Regional Water Quality Control Board (TDC Environmental 2008). Additionally, use is expected to increase further as users move away from pyrethroids.

Approach

Fipronil and its degradates will be analyzed in sediment and ambient surface water samples collected at half of the random 2010 Status and Trends monitoring sites. Sediment samples can be analyzed by EBMUD or CDFG by GC/MS (Smalling and Kuivila 2008). CDFG can also analyze surface water samples by GC/MS (Hladik *et al.* 2008). Alternatively, AXYS has an archived method that can achieve much lower MDLs although it will take additional work to get the method up and running.

Analysis Options

	Sediment			Water		
	MDL	RL	Cost	MDL	RL	Cost
AXYS	0.4 pg/g *			5 – 10 pg/L *		
EBMUD	~10 ppb dw		\$0 †	-	-	-
CDFG	25 ppb dw	50 ppb dw	\$433	~0.1 µg/L	~0.02 µg/L	\$306

* estimated DL, matrix effects will likely affect the MDL; method currently archived

† if fipronil can be incorporated into current analyses there will be no additional cost

Proposed Budget

Task	Estimated Cost
Water analysis (\$306/sample × 9 samples)	\$2754
Sediment analysis (\$0/sample × 20 samples)	\$0
Project Management	\$600
Data Management	\$5,400
Data analysis and reporting	\$9,000
Miscellaneous expenses	\$1,000
Total	\$18,754

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