MEMO

TO:	Urban Pesticides Committee	**DATE:**	June 18, 2007
FROM:	Kelly D. Moran	**PROJECT:**	47a
SUBJECT:	Urban Use of the Insecticide Fipronil—Water Quality Implications		

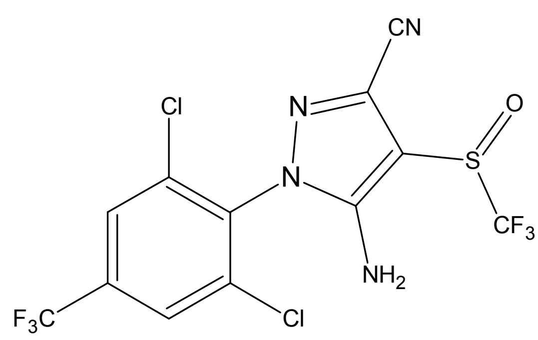
Fipronil is of interest for surface water quality because it is highly toxic to aquatic organisms and its use patterns include applications around buildings to control ants and on pets to control fleas. These use patterns have been associated with past incidents of aquatic toxicity in urban creeks and municipal wastewater treatment plant effluent. This memorandum reviews scientific information relevant to understanding the potential water quality implications of increased fipronil use. Based on this information, the memorandum provides recommendations for California water quality agencies and other entities involved in management of pesticides and water quality.

Background

Fipronil is a relatively new insecticide. The first phenylpyrazole insecticide to enter the marketplace, fipronil was first registered in California in the late 1990s.

The formal chemical name for fipronil is 5-amino-1-[2,6-dichloro-4-(trifluromethyl)phenyl]-4-[(trifluromethyl)sulfinyl]-1*H*-pyrazole. Its chemical structure (see Figure 1 below) is chiral, which means that the structure has a mirror image "handedness" to it (in the way a right hand differs from a left hand). The two mirror image versions of the structure are called "enantiomers." Commercial products contain an approximately equal mixture of the two enantiomers.

Figure 1. Structure of Fipronil



The chemical and environmental fate properties of fipronil are summarized in Table 1 (on the next page). Fipronil is only slightly soluble in water. Once in a water body, it can move from the aqueous phase onto solids and into sediments. The quickest decomposition route in water is via photolysis (decomposition due to exposure to light),

Table 1. Fipronil Chemical Properties and Environmental Fate Data

Property	Value
Solubility in Water (ppm) pH 5 pH 9	 1.9 2.4
Log K_{ow}	3.5
K_{oc} (average value)	825
Vapor Pressure (25º C)	3.7×10^{-4} mPa
Aqueous Photolysis Half-Life (Days) pH 5.5	0.33
Hydrolysis Half-Life (22º C) pH 5.5 pH 7.0 pH 9.0	 >100 days >100 days 32 days
Soil Anaerobic Half-Life	18-22 days*
Soil Aerobic Half-Life	188 days
Aerobic Aquatic Half-Life	1-5 days*

Source: Gunasekara and Troung 2007.
*Formulated product data; half-life depends on formulation.

which occurs where sunlight can penetrate the water. Its aquatic sediment half life was reported by California Department of Pesticide Regulation (DPR) to be 14.5 days (Gunasekara and Troung 2007).

A variety of compounds are formed when fipronil degrades in the environment. These compounds, which also have insecticidal activity (Gunasekara and Troung 2007), include desulfinyl fipronil, fipronil sulfone, fipronil sulfide, and desulfinylfipronil amide. Because some fipronil degradates do not immediately decompose (in fact, some are more environmentally stable than fipronil itself) and some have relatively significant aquatic toxicity, their presence and toxicity needs to be considered in environmental evaluations of fipronil. Environmental fate data for fipronil degradates are greatly needed—almost no data were identified in this review.

Fipronil Products, Sales, and Use

Table 2 (on the next page) lists the twenty-five fipronil-containing products that were registered for use in California as of October 2006. These products include professional products (termite and nuisance insect control products) as well as consumer products (baits and pet flea control products). Fipronil is sold commercially under a variety of brand names, including Termidor, Maxforce FC, Frontline, and Chipco Choice. Two fipronil-containing pet treatment products are formulated with another insecticide (S-methoprene); other products contain only fipronil and confidential ingredients (which are commonly called "inert ingredients"). Most products have less than 0.5% fipronil by weight. Some products are containerized baits or gels intended to be applied in indoor cracks and crevices. A few products have fipronil concentrations between 9% and

Table 2. California-Registered Fipronil Products, 2006

Registration Number	Product Name	% Fipronil (by weight)
432-1219-AA	Ceasefire Fire Ant Bait Insecticide	0.00015
432-896-AA	Chipco Choice Insecticide	0.1
432-1217-AA	Chipco Topchoice Insecticide	0.0143
64240-32-AA	Combat 12 Month 1	0.05
64240-42-AA	Combat Ant Killing Gel	0.001
64240-30-ZA	Combat Outdoor Ant Stakes	0.01
64240-33-ZE	Combat Plus Quick Kill Formula 1	2.15
64240-33-ZA	Combat Plus Quick Kill Formula 1 Roach	0.03
64240-33-ZB	Combat Quick Kill Formula 1	0.03
64240-34-ZA	Combat Quick Kill Formula 2	0.03
64240-30-ZB	Combat Quick Kill Formula 3	0.01
65331-4-AA	Frontline Plus For Cats	9.8
65331-5-AA	Frontline Plus For Dogs	9.8
65331-1-AA	Frontline Spray Treatment	0.29
65331-2-AA	Frontline Top Spot For Cats	9.7
65331-3-AA	Frontline Top Spot For Dogs	9.7
7969-212-AA-7	Garden Tech Over 'N Out! Fire Ant Killer	0.0103
432-1264-AA	Maxforce Carpenter Ant Bait Gel	0.001
432-1256-AA	Maxforce FC Professional Insect Control	0.01
432-1257-AA	Maxforce FC Professional Insect Control	0.05
432-1258-AA	Maxforce FC Professional Insect Control	0.03
432-1259-AA	Maxforce FC Professional Insect Control	0.01
432-1264-ZA	Maxforce FC Professional Insect Control	0.001
432-1259-ZA	Maxforce FC Select Professional Insect	0.01
7969-210-AA	Termidor SC Termiticide/Insecticide	9.1

Source: DPR Product/Label Database (DPR, 2006c).

10%—these include one professional product for control of termites and nuisance insects and four products for pet flea treatments.

The approved uses of fipronil in California are listed in Table 3 (on the next page). In California, all registered uses of fipronil products are urban. (However, in the last few years, a few emergency exemptions for uses not listed in the table have been granted for limited agricultural use.) Fipronil is commonly used by professionals for underground injection to control termites. In 2003, DPR agreed to allow application of fipronil outdoors around structures to control ants, which could expose it to runoff.

The State of California annually compiles statewide pesticide sales volumes, by amount of active ingredient, based on the payment of a fee that provides the majority of DPR's funding. DPR sales data are based on a fee paid by the pesticide manufacturer when products are shipped. Data are generally released 10 to 12 months after the end of the

Table 3. Registered Sites of Use for Fipronil in California, 2006

Type	Specific Sites
Buildings/Outdoor	Household or Domestic Dwellings, Cracks & Crevices, Household or Domestic Dwellings (Outdoor), Buildings and Structures (Non-Ag Outdoor)
Animals	Cats, Dogs, Dogs (Puppies), Dogs (Adult), Cats (Adult), Laboratory, Research Animals
Lawn/Garden/Turf	Landscape Maintenance, Soil Applied-Soil Surface, Ornamental Turf, Ornamental Lawns, Lawns, Ornamental Sod Farm (Turf), Ornamental Grasses, Turf, Golf Course (Fairways, Greens, Rough)
Food/Feed	Processed Food and Feed Products, Storage Areas & Processing Equipment, Feed/Food Storage Areas, Dairy Farm Milk Handling Facil. & Equip. Food Processing/Handling Plant/Area, Bottling Plants (Includes Beverage Bottles), Creameries, Dairies, Cheese Plants, etc., Feed Mills, Feed Stores, Feed Processing Plants, Eating Establishments, Eating Establishments (Food Handling/Serving Area), Food Marketing, Storage & Distribution Facilities
Indoor	Storage Areas (Unspecified), Household or Domestic Dwellings (Indoor), House or Domestic Dwelling Indoor Non-Food Area, Wall Voids, Wood (Injection), Window Sills, Cracks & Crevices, Wall Void, Wood (Injection), Food Processing/Handling Plant/Area (Nonfood Area), Hospitals & Related Institutions, Nursing Homes, Hospital Critical & Semi-Critical Items, Schools, Commercial, Institutional or Industrial Equipment Commercial Storages or Warehouses, Commercial/Institutional/Industrial Buildings. (Nonfood-Fumigation), Schools (Indoor)
Large outdoor areas	Uncultivated Non-Ag Areas, Recreational Areas, Tennis Courts, Parks, Etc., Utility Rights-of-Way, Yards, Substations, etc., Paved Areas, Pre-Paving Applications, Private Roads, Walkways, Lanes, Patios, etc., Commercial, Institutional or Industrial Areas, Refuse and Solid Waste Sites, Zoos
Vehicles/Facilities	Commercial Transport Facilities, Ships, Boat Premises, etc., Railway Trains, Aircraft, Buses

Source: DPR Product/Label Database (DPR, 2006c).

reporting year. The most recent data available are for calendar year 2005 (DPR 2007b). According to DPR data, fipronil sales have been relatively stable since 2001, as shown in Table 4 (the anomalous 2002 value should be viewed with caution as it may reflect a reporting data error that was corrected in subsequent years). DPR sales data have potentially meaningful uncertainty (see pages 4-6 of TDC Environmental 2006 for more information); in fact, this review identified a reporting error that was corrected by the registrant (previous reports erroneously indicated sales of >1,000,000 pounds).

Table 4. Sales of Fipronil in California, 2000-2005
(Pounds of Pesticide Active Ingredient)

	2000	2001	2002	2003	2004	2005
Fipronil	1,857	19,002	32,191*	13,546	18,108	21,711

Source: DPR Sales data reports (DPR 2001, 2002, 2003, 2005, 2006b, 2007b)

Certain pesticide applications[1] are required to be reported to the County Agricultural Commissioner, who, in turn, reports the data to DPR. In general, the pesticide uses that require reporting are agricultural uses or urban applications made by licensed pest control operators (who are called "professionals" in this memorandum). DPR prepares annual summary reports on the basis of these data.

Almost all fipronil (>99%) reported used in 2004 and 2005 was for structural pest control (DPR 2006a; DPR 2007a).[2] The structural pest control reporting category includes aboveground applications (e.g., spraying around a building to control ants), indoor applications, and underground injection (e.g., injection of pesticides into holes drilled into the ground to control termites). Outdoor applications, which have the greatest potential to be washed into surface waters, may include containerized baits, gels (e.g., in cracks and crevices), and broadcast applications around structures.

DPR pesticide use reporting data have uncertainty (see pages 7-8 of TDC Environmental 2006 for more information). An example of the types of errors that may occur was identified during this review. While exploring the question of why reported fipronil use exceeded reported sales, DPR discovered that a few professional structural pest control applicators were apparently reporting the amount of diluted product applied, rather than the amount of actual formulated product used. Because fipronil concentrate is typically diluted 150 times, this reporting error caused use to be over-reported by some 150 times. This seemingly minor error had significant consequences—nearly 30% of the entire reported use of fipronil in California in 2005 was reported under one professional applicator's license number. With the assistance of the appropriate County Agricultural Commissioner, DPR was able to confirm that this applicator was indeed reporting use of diluted material rather than the product itself (Farnsworth 2007).

All instances of this error were not able to be identified, so DPR's reported use data for fipronil could not be corrected to reflect actual fipronil use. Therefore, fipronil reported use data are not included in this memorandum. Recognizing the importance of accurate pesticide use reporting, the Pest Control Operators of California, which is the professional organization for structural pest control applicators, is making its members aware of this issue (Van Steenwyk 2007).

Without accurate reported use data, retail sales cannot be estimated. Pesticides sold at retail are primarily used by California residents. The two types of fipronil products generally available at retail outlets are baits (usually containerized) and pet flea treatments.

[1] The following pesticide uses must be reported: pesticide uses for the production of any agricultural commodity, except livestock; for the treatment of post-harvest agricultural commodities; for landscape maintenance in parks, golf courses, and cemeteries; for roadside and railroad rights-of-way; for poultry and fish production; any application of a restricted material; any application of a pesticide designated by DPR as having the potential to pollute ground water when used outdoors in industrial and institutional settings; and any application by a licensed pest control operator.

[2] The reporting errors discussed in the next paragraph do not change this conclusion (reported use other than structural us is <1% of fipronil sales).

Aquatic Toxicity

Fipronil and its degradates are highly toxic to aquatic species. Aquatic toxicity data for fipronil were obtained from the U.S. EPA Ecotox database (U.S. EPA, 2006), the U.S. EPA Pesticide Fact Sheet for fipronil (U.S. EPA 1996) and a DPR summary on fipronil (Gunasekara and Troung 2007). This information was subject to scientific review and the data from U.S. EPA and DPR must meet the quality assurance standards of the agencies.[3] Table 5 (on the next page) summarizes fipronil and degradates aquatic toxicity data for standard aquatic toxicity testing species, which were selected on the basis of methodology previously used for the San Francisco Estuary Project (see Section 9 of TDC Environmental 2003). As Table 5 shows, although an incomplete set of aquatic toxicity data is available, it is clear that fipronil is highly toxic to aquatic species. Although very limited data are available for fipronil degradates, available data suggest that they are also highly toxic to aquatic species.

The toxicity of the two fipronil enantiomers differs significantly. Chemical enantiomers have identical chemical properties, but may interact with organisms differently because some molecules in organisms also have "handedness", which may cause them to interact differently with the two different enantiomers' handedness. Konwick et al. (2005) explored whether there is a difference in biological activity of the two fipronil enantiomers by measuring the toxicity of the each individual fipronil enantiomer to *Ceriodaphnia dubia*. In 48-hour LC_{50} tests they found that the (+) enantiomer was about twice as toxic as the commercial product and the (-) enantiomer was about half as toxic as the commercial product. This difference could be environmentally important if the two enantiomers decompose at different rates.

Fipronil adversely affects crustaceans at concentrations that have been measured in environmental samples. Various studies have documented lethality and sub-lethal toxicity to crustaceans at very low concentrations. Fipronil treatment of rice seed was linked to a decline in crawfish production in receiving waters (U.S. EPA 2002a and 2002b). In response to this linkage, U.S. EPA Region 6 prepared Total Maximum Daily Loads (TMDLs) for six Louisiana water bodies that caused the state to greatly limit fipronil use in those watersheds (the fipronil product for rice was eventually voluntarily removed from the market). "Environmentally realistic concentrations" of fipronil (0.25 to 0.63 μg/l) were reported to have adverse effects on reproduction of a common estuarine copepod (*Amphiascus tenuiremis*) (Cary et al. 2004; Chandler et al. 2004).

Sediment toxicity data are needed for fipronil and its degradates. Although fipronil and its degradates are likely to move into the sediment layer in a water body, no sediment toxicity data were identified in the reviewed aquatic toxicity data sources. Chandler et al. (2004) reported that spiked sediment exposures of 65 to 300 micrograms per kilogram (μg/Kg) (dry weight) yielded significantly reduced reproduction rates for the copepod *Amphiascus tenuiremis*.

[3] This memorandum relies on the database quality assurance procedures; the original data sources for the aquatic toxicity data compiled in this report were not re-reviewed.

Table 5. Fipronil and Degradates Aquatic Toxicity Data Summary (µg/l)

Species Name	Common Name	Test	Fipronil	Desulfinyl fipronil	Fipronil sulfone	Fipronil sulfide	Desulfinyl fipronil amide
Invertebrates							
Ceriodaphnia dubia	Water flea	48-H LC50	17.7[a]	355[d]			
Daphnia magna	Water flea	48-H LC50	100[b]				
		48-H EC50	29-190[b]				
		Life cycle NOEC	9.8[c]				
		Life cycle LOEC	20[c]				
		21-Day EC50		230[a]	4.5[a]	27[a]	
		48-Day EC50			29[a]	100[a]	
Daphnia pulex	Water flea	48-H LC50	9-83				
Hyalella azteca	Scud	*					
Gammarus lacustris	Scud						
Gammarus fasciatus	Scud						
Americamysis bahia	Opossum shrimp	96-H LC50	0.14[a,b]	1.5[d]			
		Life cycle NOEC	<0.005[c]				
		Life cycle LOEC	0.005[c]				
Penaeus sp.	Shrimp						
Crassostrea virginica	American oyster	96-H EC50	770[b]				
Crassostrea gigas	Pacific oyster						
Vertebrates							
Pimephales promelas	Fathead minnow						
Oncorhynchus mykiss	Rainbow trout	96-H LC50	250[a], 39-246[b]	31[a]	39[a]		
		Early Life Stage NOEC	6.6[a]				
		Early Life Stage LOEC	15[a]				
Salvelinus fontinalis	Brook trout						
Lepomis macrochirus	Bluegill	96-H LC50	83[a] 25-83[b]	20[a]	25[a]		
Cyprinodon variegatus	Sheepshead minnow	96-H LC50	130[a,b]				
Menidia beryllina	Inland silverside						
Plants							
Selenastrum capricornutum	Green algae						
Skeletonema costatum	Diatom	120-H EC50	140[b]				

*Blanks indicate that there was no data for this species in the data sources that were reviewed. Salt water species are in the shaded areas of the table.
Sources: [a]DPR (Gunasekara and Troung 2007), [b]ECOTOX (U.S. EPA 2006), [c]U.S. EPA New Pesticide Fact Sheet (U.S. EPA 1996), [d]Konwick et al. 2005, [e]U.S. EPA 2001.

Fipronil bioaccumulates in fish. Data submitted to U.S. EPA indicates that fipronil bioaccumulates in fish, with a bioconcentration factor of about 300 (U.S. EPA 1996).

Water Quality Criteria

U.S. EPA does not have water quality or sediment quality criteria for fipronil. In a series of TMDLs prepared by U.S. EPA Region 6 for Louisiana surface waters (U.S. EPA 2002a and 2002b), U.S. EPA used numeric targets of 4.6 µg/l (acute) and 2.3 µg/l (chronic). These targets were based on adjustment of the lowest 48-hour LC_{50} values for invertebrate species indigenous to Louisiana, and the lowest 96-hour LC_{50} values for vertebrate species indigenous to Louisiana. In developing these targets, U.S. EPA used adjustment factors of 0.1 for acute criteria and 0.05 for chronic criteria, based on state-specific procedures.

Chemical Analysis

In 2003, the U.S. Geological Survey (USGS) published a method that it has used for some monitoring projects under the National Water Quality Assessment (NAWQA) program. This method (USGS 2003) covers fipronil and four major degradates. It has a initial method reporting limits of >0.010 µg/l for all compounds. This is lower than all but the lowest aquatic toxicity values reported in Table 5. There are issues with recovery of fipronil and one degradate from samples that limit data accuracy at low concentrations (USGS 2003). USGS chemists in Sacramento have developed improved methods for both water column and sediment analyses, both of which are being prepared for journal publication (Hladik 2007).

Informal surveys by the UP3 Project have not found commercial laboratories advertising the capability of measuring environmentally relevant concentrations of fipronil and its degradates in water or sediment.

Surface Water Monitoring Data

Limited monitoring data for fipronil are available. This is not surprising given the lack of a generally accepted chemical analysis method prior to publication of the USGS method just a few years ago. No fipronil monitoring data were found in the DPR Surface Water Database.

Fipronil was not among the primary USGS NAWQA analytes, but has been included in some USGS NAWQA monitoring completed since the USGS developed its chemical analysis method. Konwick et al. (2005) summarized unpublished nationwide data from the USGS NAWQA. Fipronil concentrations reportedly ranged from 0.01 and 0.07 µg/l. In surface waters that receive rice field runoff, USGS measured fipronil concentrations of 0.83 to 5.3 µg/l (Demcheck and Skrobialowski 2003). Measured degradate concentrations were often on the same order of magnitude as the concentrations of fipronil itself.

California NAWQA data was obtained from the USGS NAWQA data warehouse (USGS 2006). These data include recent samples from a few dozen urban and agricultural locations in about a dozen California counties. Fipronil concentrations ranged from below reporting limits (which varied, but are typically on the order of 0.01 µg/l) to 0.080 µg/l. Degradates were also measured. The highest concentrations of degradates were as follows: desulfinyl fipronil – 0.016 µg/l; desulfinyl fipronil amide – below 0.01 µg/l; fipronil sulfide – 0.015 µg/l; and fipronil sulfone – 0.024 µg/l. In this very limited data set, the highest concentrations of fipronil and its degradates were found in a Sacramento area urban creek (Arcade Creek).

In 2006, DPR compiled nationwide USGS monitoring data for fipronil and its degradates (Gunasekara and Troung 2007). The highest concentrations that DPR found in this data set were: fipronil – 0.117 µg/l (Louisiana); desulfinyl fipronil – 0.158 µg/l (California); desulfinyl fipronil amide –0.011 (Louisiana) µg/l; fipronil sulfide – 0.015 µg/l (Louisiana); and fipronil sulfone – 0.038 µg/l (Colorado).

The limited available monitoring data show concentrations that are generally lower than most of the available aquatic toxicity data. The highest concentrations exceed toxicity thresholds for the most sensitive species (*Americamysis bahia*). Agricultural uses, which are not currently allowed in California, have been linked to higher fipronil surface water concentrations expected to be harmful to aquatic life (U.S. EPA 2002a and 2002b).

<u>Fipronil degradates occur in sediments as well as in the water column</u>. A USGS NAWQA special study of fipronil in waters in Louisiana rice-producing areas found that while fipronil was not accumulating in sediment in the study area, its degradates were present (Demcheck and Skrobialowski 2003). Fipronil sulfide concentrations ranged from 0.64 to 24.8 µg/Kg. Desulfinyl fipronil (concentrations up to 10.5 µg/Kg) and fipronil sulfone (concentrations up to 7 µg/Kg) were also detected.[4] Due to the lack of sediment toxicity data, it is not possible to determine the environmental relevance of these fipronil degradate sediment concentrations.

<u>Under ordinary conditions, fipronil does not appear to migrate to surface water from underground injection applications</u>. According to U.S. EPA, because fipronil has a low mobility in soil, it is not expected to leach from soil after application (U.S. EPA 1996). An Australian study of the mobility of fipronil and its degradates after underground injection treatment to soil around buildings similarly concluded that fipronil was unlikely to migrate long distances under ordinary soil conditions (Ying et al. 2006).

<u>Conclusions</u>

<u>*Conclusion 1*</u>*: Use of fipronil has the potential to cause adverse effects in aquatic ecosystems.* Uncontained above ground fipronil applications make fipronil and its degradates available to be washed to storm drains and creeks without any treatment. Improper disposal to gutters and storm drains is also possible. Discharges to sewage treatment plants are another potential pathway to surface water. Both improper disposal and washing treated pets can lead to discharges to sewage treatment plants. Increased use of fipronil, particularly outdoors around buildings, may occur if the market shifts toward fipronil as a substitute for organophosphorous insecticides (like diazinon and chlorpyrifos) or the pyrethroids.

Limited available surface water monitoring data show concentrations that are generally lower than most of the available aquatic toxicity data. Due to the lack of sediment toxicity data, it is not possible to determine the environmental relevance of fipronil and

[4] The source did not say whether sediment concentration data were provided on the basis of wet or dry weight.

degradates sediment concentrations. Available data (both monitoring data and aquatic toxicity data) are too few to determine whether current use patterns and levels may be associated with incidents of acute or chronic toxicity to aquatic organisms or non-compliance with toxicity-related NPDES permit requirements. Increased outdoor use of fipronil increases the risk of surface water toxicity problems. Available data are insufficient to determine at what use level toxicity problems would occur.

<u>Conclusion 2</u>: *The chemical fate and aquatic toxicity of fipronil and its degradates are not fully characterized. Critical data gaps exist.* Although the available data were sufficient for a weight of evidence analysis, neither the aquatic toxicity of fipronil and its degradates nor the environmental fate of fipronil degradates can be fully characterized with available information. The most important data gaps are for aquatic toxicity, where more data for fipronil, data for degradates, and sediment toxicity data are needed. Filling gaps for the standard aquatic toxicity testing species listed in Table 5—including chronic toxicity data—is a priority. Exploration of cumulative toxicity of fipronil in combination with its degradates and with other pesticides commonly present in urban surface waters (e.g., pyrethroids) is also needed to understand the environmental significance of fipronil's use.

Environmental fate data gaps are also significant. Almost no data characterizing fipronil's major degradates were identified. Since fipronil and its degradates partition into sediments in aquatic ecosystems, determining the degradates' fate in sediments as well as the water column is important. The most important sediment data gap is the aquatic sediment half life for fipronil degradates.

<u>Conclusion 3</u>: *There is little monitoring data for fipronil in California surface water.* Although the USGS has generated limited monitoring data in one large California watershed, no other monitoring data were identified for California surface water. No monitoring data was identified for urban runoff or municipal wastewater treatment plant effluent and biosolids.

Recommendations

<u>Recommendation 1</u>. *Continue to exercise discretion in use or recommendation of fipronil for urban outdoor above ground applications.* Above ground outdoor application of uncontainerized fipronil products should be avoided. Instead, encourage integrated pest management-based insect control methods that minimize pesticide releases to surface waters (e.g., use of containerized baits and barriers like caulking). Because containerized baits are unlikely to release significant quantities of pesticide active ingredients into runoff, it is not necessary to avoid fipronil in containerized baits. Similarly, use of fipronil by underground injection is unlikely to pose a threat to surface water quality under ordinary conditions.

<u>Recommendation 2</u>: *Fill aquatic toxicity data gaps.* There are limited aquatic toxicity data for standard aquatic toxicity testing species. Sediment toxicity data are lacking. Although several fipronil degradates appear to be highly toxic to aquatic organisms, there is almost no aquatic toxicity data for these degradates. Obtaining sediment toxicity data for both fipronil and its primary degradates and filling gaps for the standard aquatic toxicity testing species listed in Table 5—including chronic toxicity data—are priorities.

Cumulative toxicity of fipronil in combination with its degradates should be measured. The potential for additive or synergistic toxicity with other pesticides commonly present in urban surface waters (e.g., pyrethroids) should be explored, since it is very likely that fipronil co-occurs in surface waters with other commonly used pesticides (Lydy et al. 2004).

Recommendation 3: *Fill environmental fate data gaps.* Major gaps include the aquatic sediment half life for fipronil's degradates and basic characterization data for fipronil degradates.

Recommendation 4: *Support activities to improve chemical analytical capabilities for fipronil in surface water (water column and sediment), urban runoff, and municipal wastewater treatment plant effluent and biosolids*. Although the USGS has developed methods for measuring fipronil and its degradates in the water column, commercial laboratories have not adopted these methods. Improved water column methods and sediment methods are anticipated to be published by USGS soon (Hladik 2007). Transferring the USGS methods to commercial laboratories—or creating new methods that are feasible for commercial laboratories if these are not—is important, since contractors (rather than agency or university laboratories) perform the chemical analysis of most surface water quality samples collected in California.

Recommended detection limits (0.5 times the lowest aquatic toxicity data point):

- Fipronil and degradates in water—0.002 micrograms/liter
- Fipronil and degradates in sediment—30 µg/Kg (dry weight)

Recommendation 5. *Support activities to develop toxicity identification evaluation (TIE) capabilities for fipronil in water and sediment samples.* When toxicity is found in surface waters or sediments, TIEs are used to identify the cause of the toxicity. Because it is impractical to monitor for all pollutants that have the potential to cause aquatic toxicity, ambient toxicity monitoring is often conducted for surveillance purposes. When toxicity is found, TIE methods are needed to identify each likely cause. Given the potential for fipronil use to increase—particularly as a substitute for pyrethroids—development of TIE methods is recommended, to ensure that it is possible to determine whether fipronil is causing toxicity.

Recommendation 6: *Include fipronil and its degradates in water quality monitoring*. Because fipronil is highly toxic to aquatic organisms and is increasingly used in California urban areas, it should be included in surface water and sediment monitoring programs for waters receiving urban runoff. Since fipronil can be discharged to sewer systems, it is important to investigate whether environmentally meaningful levels of fipronil occur in municipal wastewater effluent or biosolids.

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