Special Study Proposal: Fipronil and Degradates in WWTP Influent and Effluent

Summary: Fipronil is a moderate concern (Tier III) CEC for the Bay. Recent RMP-funded monitoring of 24-hour composite samples of influent and effluent from eight Bay wastewater treatment plants (WWTPs) assessed dissolved phase concentrations of fipronil and degradates. A lack of information concerning levels of particle-associated contaminants limits the conclusions that can be drawn from existing data concerning the effects of treatment on contaminant discharges. The proposed study aims to fill this data gap, by analyzing total water samples of influent and effluent. Findings are likely to influence ongoing efforts within the California Department of Pesticide Regulation aimed at reducing environmental contamination and ecological impacts of fipronil and its degradates.

Estimated Cost: $30,000

Oversight Group: ECWG

Proposed by: Rebecca Sutton and Jennifer Sun (SFEI)

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	***Due Date***
Task 1. Project Management (write and manage sub-contracts, track budgets)	Winter 2015 – Summer 2016
Task 2. Develop detailed sampling plan	Summer 2015
Task 3. Field Sampling	Early fall 2015
Task 4. Lab analysis	Fall 2015
Task 5. QA/QC and data management	Winter 2015
Task 6. Draft report (manuscript)	3/31/2016
Task 7. Final report (submitted manuscript)	6/30/2016

Background

Fipronil, a broad-spectrum insecticide widely used to control fleas, termites, and ants, is considered a moderate concern contaminant for San Francisco Bay (Sutton et al. 2013). Fipronil and its degradates (including fipronil sulfide, fipronil sulfone, and fipronil desulfinyl) are highly toxic to aquatic organisms (CVWB 2012). It has been detected in stormwater in the Bay Area and elsewhere, but few measurements exist regarding its presence in wastewater (Ensminger 2012; Weston and Lydy 2014; Heidler and Halden 2009). Potential sources of fipronil to wastewater include wash off from pets treated with topical fipronil flea-control pesticides, seepage into sewers from belowground application of fipronil to control termites, improper disposal, and post-application cleanup.

To evaluate the importance of the wastewater pathway and investigate the potential impacts of treatment technologies on levels of fipronil and degradates to the Bay, the RMP funded a 2015 Special Study to analyze 24-hour composite samples of influent and effluent from eight Bay wastewater treatment plants (WWTPs). The findings of this study do not indicate wastewater treatment significantly reduces levels of dissolved fipronil (Table 1).

Table 1: Influent and effluent concentrations (ng/L) of fipronil and its three degradates from the eight WWTPs. The concentrations only include the contaminants present in the dissolved phase.

WWTP	Influent (ng/L)	Effluent (ng/L)
SFO	10	ND
Palo Alto	78	53
Fairfield Suisun	85	57
San Leandro	119	63
EBMUD	76	86
San Mateo	52	112
San Jose-Santa Clara	135	113
Central Contra Costa	168	121

However, the analyses were conducted on the dissolved phase of the samples only, and did not characterize the particle-associated contaminant load. Fipronil and its degradates have K_{ow}s ranging from three to four (Gunasekara 2007), suggesting particle-bound contamination may be an important factor.

The USGS conducted a similar study in the Columbia River Basin: effluent grab samples from nine WWTPs were collected and analyzed (Morace 2012). The samples were also filtered before analysis and the dissolved concentrations of fipronil were comparable to the RMP 2015 special study levels. The USGS found that the concentration of fipronil on the filtered solids was negligible compared to the concentration in the dissolved phase, suggesting that particle-bound fipronil may not be an important loading pathway to the Bay. However, influent contains a significantly higher amount of solids than effluent and filtered influent samples may not characterize the total fipronil load to WWTPs.

In 2012 and 2013 fipronil stormwater samples were collected from six Bay Area creeks. The stormwater samples were also lab filtered and the dissolved phase was analyzed. The highest Bay Area effluent concentrations were five times the concentrations in stormwater. The level of suspended solids is considerably higher in stormwater than in effluent; comparing effluent and stormwater concentrations is less useful until total water concentrations are available for both matrices. Lacking Bay Area stormwater total water concentrations, data from the California Department of Pesticide Regulation on stormwater measurements in other regions may provide useful upper and lower bounds (Budd et al. 2015).

Study Objectives and Applicable RMP Management Questions

This study will provide data essential to determining the impact of wastewater treatment on fipronil discharges to the Bay. Currently available RMP data are limited to the dissolved phase, and suggest treatment does not significantly modify levels of fipronil and degradates in discharges. However, given K_{ow}s of 3-4, particle-associated contamination may be important, particularly for influent. Fipronil is classified as a moderate concern (Tier III) contaminant for the Bay, and greater knowledge of pathways can guide management actions to reduce pollution.

Management questions to be addressed by monitoring fipronil and degradates in WWTP effluent are the same as those of the overall RMP program, as shown in Table 2.

Table 2. Study objectives and questions relevant to RMP management questions.

Management Question	Study Objective	Example Information Application
1) Are chemical concentrations in the Estuary at levels of potential concern and are associated impacts likely?	Compare measured concentrations to toxicity thresholds, ambient Bay measurements, and influent/effluent measurements in other regions.	Are findings consistent with the current designation of fipronil as a moderate concern CEC with potential to cause low level impacts to Bay wildlife? Do data indicate a need for management actions?
2) What are the concentrations and masses of contaminants in the Estuary and its segments? 2.1 Are there particular regions of concern?	Compare levels discharged by WWTPs in different embayments.	Could relative wastewater discharges cause regional variations in ambient Bay fipronil?
3) What are the sources, pathways, loadings, and processes leading to contaminant-related impacts in the Estuary? 3.1. Which sources, pathways, etc. contribute most to impacts?	Obtain information on the potential effects of wastewater treatment on effluent discharged to the Bay. Evaluate wastewater pathway relative to stormwater.	Are there indications that any treatment technologies employed by participating WWTPs can reduce levels of fipronil or degradates discharged to the Bay?
4) Have the concentrations, masses, and associated impacts of contaminants in the Estuary increased or decreased? 4.1. What are the effects of management actions on concentrations and mass?	Review new results alongside available data from previous RMP studies for indications of trends in contamination over time.	Are discharges of fipronil and degradates increasing?
5) What are the projected concentrations, masses, and associated impacts of contaminants in the Estuary?	Review measured results alongside available projections of use and anticipated changes to wastewater treatment.	Which anticipated changes or actions are likely to have the greatest impact on fipronil pollution? Are additional/different actions needed?

This monitoring effort would most directly address question 3, characterizing contaminant discharges from the effluent pathway. It will also provide an indication of whether any of the broad range of treatment types employed by participating WWTPs are useful in reducing discharges to the Bay. Results may provide some information useful to addressing questions 1, and 4, characterizing fipronil pesticide contamination and its potential for impacts at the current time and relative to past data. Inferences regarding regional or future pollution patterns could involve interpretation of the data within the context of regional use data and potential changes in wastewater treatment technologies, all of which may play a role in addressing questions 2 and 5.

In addition, the study will address the emerging contaminants priority question: What emerging contaminants have the potential to adversely impact beneficial uses of the Bay? The RMP's tiered risk and management action framework lists fipronil as a moderate concern (Tier III) contaminant; CECs in this category may be recommended for Special studies of fate, effects, and sources, pathways, and loadings, and may be recommended for inclusion in Status and Trends Monitoring (Sutton et al. 2013). This proposal will improve our knowledge of an important pathway of fipronil contamination to the Bay.

Approach

Effluent Sampling

24-hour composite samples of WWTP influent and effluent voluntarily provided by eight Bay WWTPs will be collected. A replicate sample and a field blank will be collected as well, for a total of 20 samples. Sampling will occur in the summer of 2016, when inflow and infiltration are insignificant. WWTPs will provide measurements of total suspended solids on the day of sample collection.

The eight WWTPs that volunteered to provide samples for the previous study of fipronil are expected to participate in this study, and include facilities employing secondary and advanced treatment, and located in South, Central, and North Bay. Previous participants include: Central Contra Costa Sanitary, East Bay MUD, Fairfield Suisun, Palo Alto, SFO, San Jose, San Leandro (EBDA member), San Mateo. As with the previous RMP fipronil monitoring project, participating dischargers are not guaranteed anonymity. Measurements for each discharger will be reported individually.

Analytical Methods

Samples will be analyzed by Dr. Rolf Halden (Arizona State University) or a comparable laboratory. Per sample analytical costs range from $200 to $300, depending on the matrix.

Dr. Halden's lab employs isotope dilution liquid chromatography tandem mass spectrometry (ID-LC-MS/MS), and can perform total water analyses (as opposed to dissolved phase analyses). Instrument detection limits for fipronil and degradates were previously reported at 10 ng/L, with the exception of desulfinyl fipronil (IDL 500 ng/L). Lower detection limits are preferred, and are now available in the range of 41 - 480 pg/L (Halden, personal communication).

Budget

The following budget represents estimated costs for this proposed special study (Table 3). Efforts and costs can be scaled up or down by changing the number of WWTPs sampled. Pro bono collaborations between the Halden lab and individual WWTPs may be leveraged to further reduce costs.

Table 3. Proposed Budget.

Expense	Estimated Hours	Estimated Cost
Labor		
Project Staff	156	14,400
Senior Management Review	8	1600
Project Management	0	NA*
Contract Management	0	NA*
Data Technical Services		6000
GIS Services	4	400
Creative Services	10	750
IT Services	0	
Communications	0	
Operations	0	
Subcontracts		
Name of contractor		
Dr. Halden or comparable lab		5700**
Direct Costs		
Equipment		400
Travel		350
Printing		0
Shipping		400
Other		0
Grand Total		
		30,000

*services included in the base RMP funding
**costs may be reduced due to existing, independent collaborations between the Halden lab and individual WWTPs

<u>Budget Justification</u>

Field Costs
Field costs include staff time and vehicle miles required to visit WWTPs and collect samples, as well as sample containers and shipping. Increased efficiency is possible through scheduling visits to multiple WWTPs on the same day.

Laboratory Costs
Analytical costs per sample are estimated to be $300. For 19 samples, including influent, effluent, a duplicate for each matrix, and a blank, the total analytical costs will be $5,700

Data Management Costs
Standard data management procedures and costs will be used for this project.

Reporting

Results will be reported to the RMP committees in the form of a draft manuscript for publication in a peer-reviewed journal by 3/31/17.[1] Comments will be incorporated into the manuscript submitted by 6/30/17.

References

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[1] This report will be distributed by email, instead of posting to the website, so as not to jeopardize potential journal publication.

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