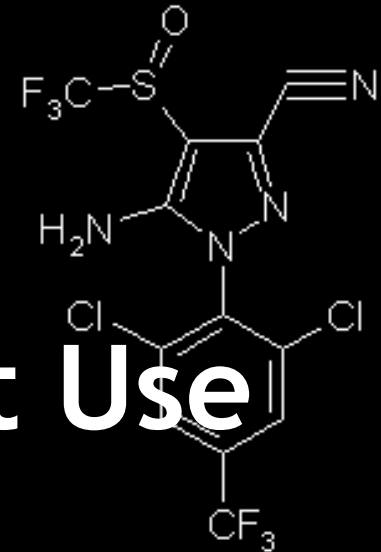
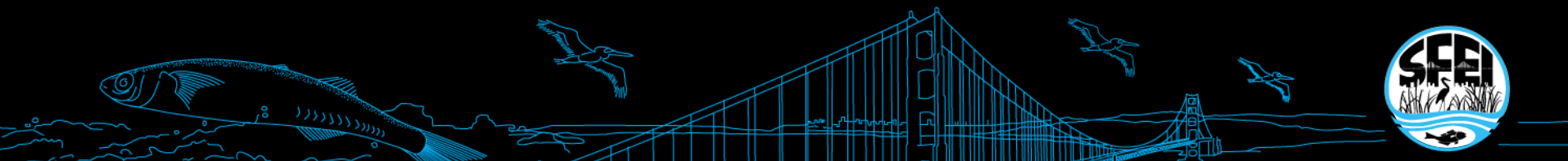


Fipronil & Current Use

Pesticides

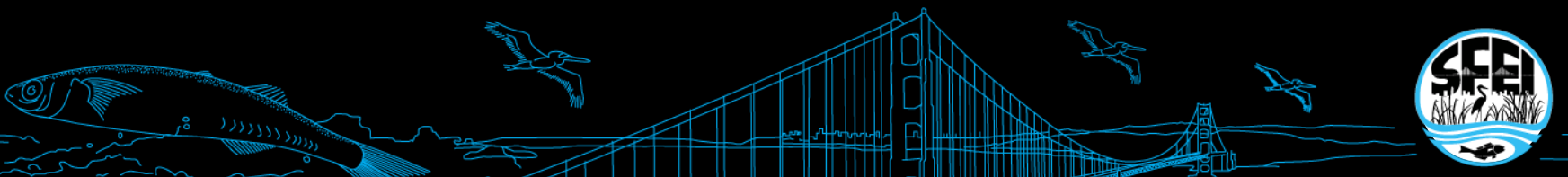


RMP Emerging Contaminants Workgroup
April 5th, 2013



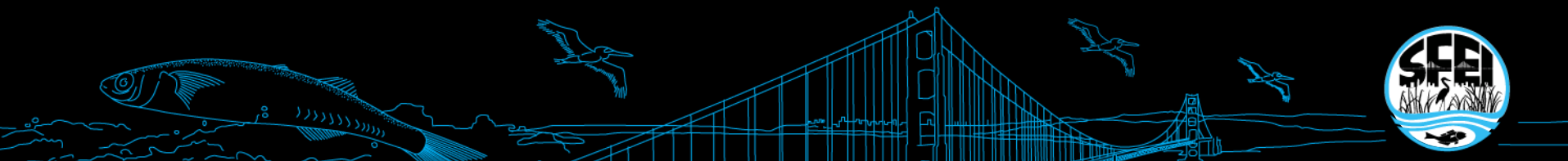
Needs

- Current Use Pesticides
 - Fipronil - should we add water matrix?
 - What other pesticides should we consider?
 - In what matrices?
- RMP CUP Workshop meeting May/June
 - No final decisions today, guidance/info



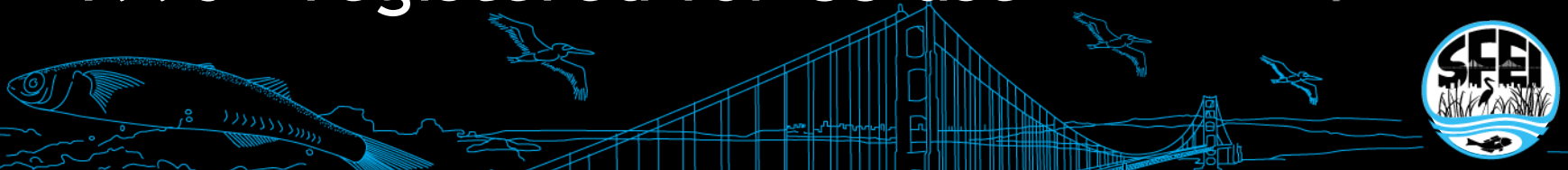
Fipronil

- Current use insecticide
 - Increased market share
 - Pyrethroids & other insecticides decreasing
 - Urban use
- Found in runoff & streams
- UP3 recommended including fipronil & degradates in water quality monitoring



Overview

- Phenylpyrazole insecticide
- Disrupts nerve function via GABA (γ-aminobutyric acid type A) receptors
- $\log K_{ow}$ 3.5
- 1987 - developed
- 1993 - introduced for use
- 1996 - registered for US use



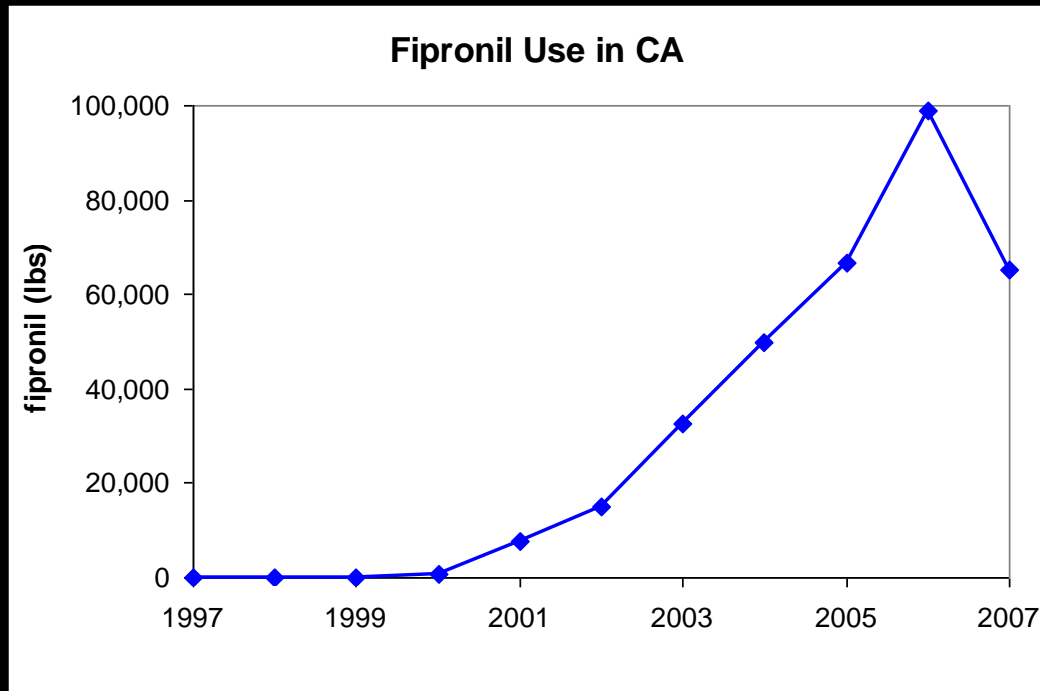
Uses

- Turf products
- Seed treatments
- Topical pet care products
- Gel baits (e.g., ants)
- Liquid termiticides
- Agriculture (not in CA DPR 2007)



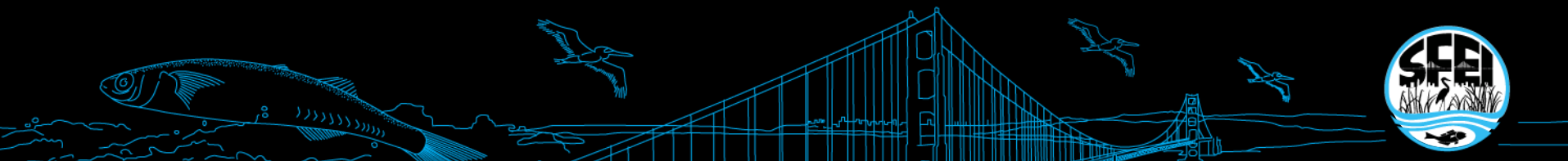
Use - CA

- ~38,000 lbs use in CA in 2010 (CADPR 2011)
- Not registered for ag. use in CA
 - Emergency exceptions
- 37 products registered in CA (DPR 2009)

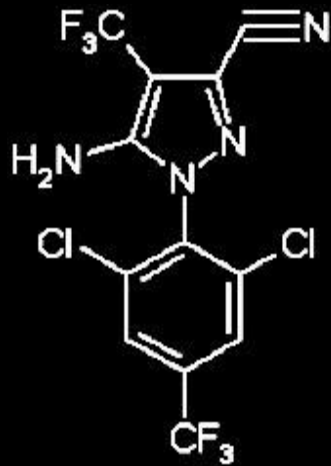


Existing Regulations

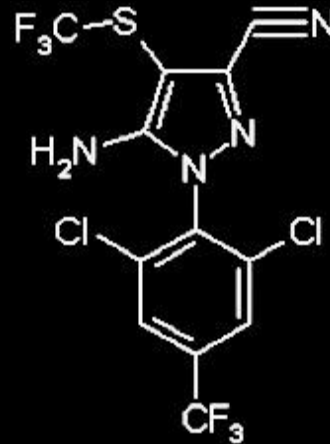
- No EPA WQC or SQC
- LA surface freshwater TMDL
 - 4.6 $\mu\text{g L}^{-1}$ acute
 - 2.3 $\mu\text{g L}^{-1}$ chronic



Degradates



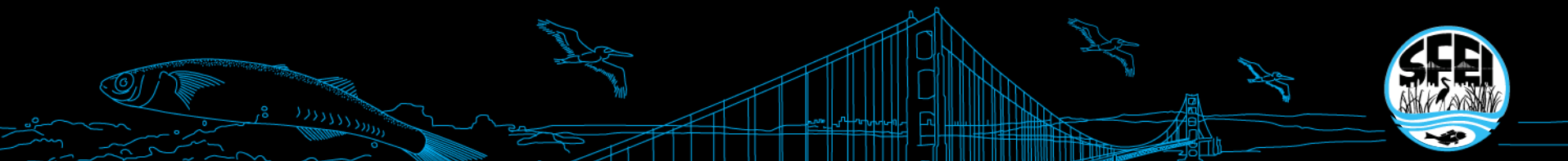
fipronil
desulfinyl



fipronil
sulfide



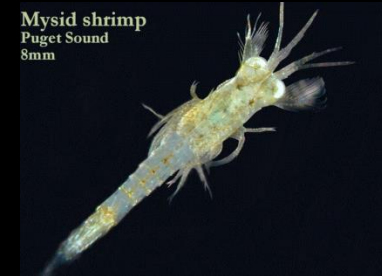
fipronil
sulfone



Toxicity

- Water

- 410 ng/L *Chironomus tentans* LC₅₀
- 140 ng/L Mysid shrimp LC₅₀ (US EPA 1996)



- Sediment

- *Chironomus tentans* (Maul 2008)

	Fipronil	fipronil sulfide	fipronil sulfone
LC50	130	160	120
EC50 _{immob}	100	60	40

ng/g organic carbon



- Are sediment criteria \leq in some marine species?

Concentrations in CA

- Urban streams feeding Sac. & San J. (NAWQA 2009)
 - Fipronil at DL est. 5 - 100 ng/L
 - Fipronil sulfide 5 - 18 ng/L
 - Fipronil sulfone 6 - 13 ng/L
- Golden Gate Nat'l Rec Area Urban Streams (Hladik & Orlando 2008)
 - Fipronil ~0.8 ng/L
 - Fipronil sulfone ~1.4 ng/L
- Urban Runoff - Sac. & Orange Counties (Oki et al. 2008)
 - Fipronil & degradates detected in Sac.
 - >140 ng/L (Mysid shrimp LC₅₀) in OC
- SQO Lower Delta Sediment (Lowe 2009)
 - Fipronil & degradates <20 ng/g dw

Water tox

- Mysid 140 ng/L
- Copepod 220 ng/L

Sediment tox

- Midge 100 ng/g org. C

Concentrations SF Region

- Urban streams in Bay Area (all ND to < 20ng/L)
 - Fipronil
 - Fipronil desulfinyl
 - Fipronil sulfide
 - Fipronil sulfone
- Bay Sediments (RMP S&T 2009-2012)
 - Fipronil 0.004- 0.05 ng/g dw
 - Fipronil desulfinyl <0.005 - 0.16 ng/g dw
 - Fipronil sulfide <0.005 - 0.09 ng/g dw
 - Fipronil sulfone <0.01 - 0.56 ng/g dw
 - Bay OC ~1% so max may approach EC₅₀

Water tox

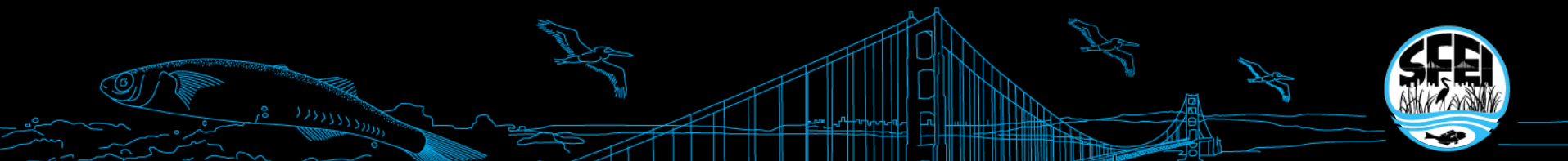
- Mysid 140 ng/L
- Copepod 220 ng/L

Sediment tox

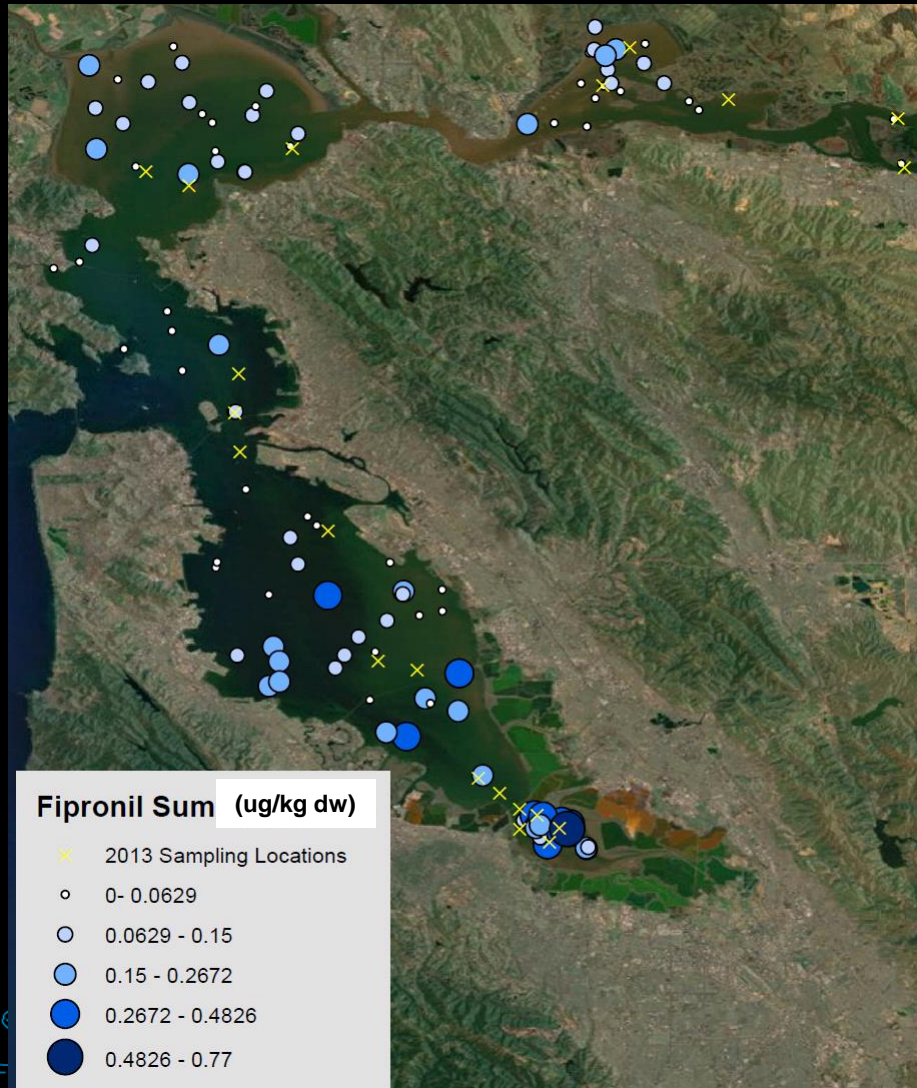
- Midge 100 ng/g org. C

Previously Proposed

- Fipronil, fipronil sulfide, fipronil sulfone, fipronil desulfinyl
- GC/MS
- Half of S&T sites
 - 20 sediment - EBMUD - currently added
 - 9 water - CDFG ?? Not implemented
 - Now we have sed data, add water sites?



RMP Sed Data & Water Sites



- Highest conc. In SB/LSB
 - Pick sites nearest high sediment concentrations?

Analysis Costs

- Fipronil, fipronil desulfinyl, fipronil sulfide, fipronil sulfone

	Sediment			Water		
	MDL	RL	Cost	MDL	RL	Cost
AXYS				5 - 10 pg/L ⁺		<\$400
EBMUD	~10 ppb dw		\$0 *	-	-	-
CDFG				~0.01 µg/L	~0.02 µg/L	\$376

* Included with legacy pesticides analysis

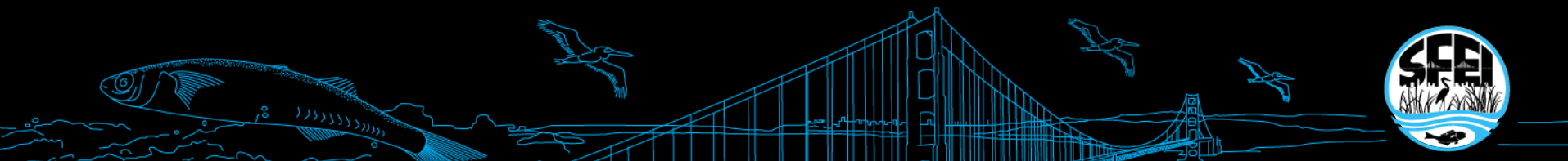
+ Method to be refined/validated



Budget

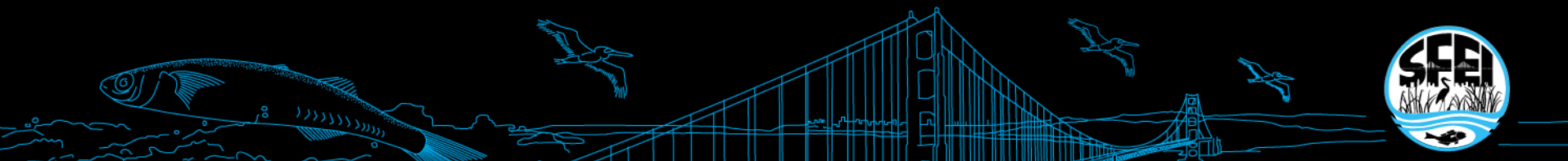
Task	Estimated Cost
Water analysis (\$376/sample × 9 samples)	\$3,384
Sediment analysis (\$0/sample × 20 samples)	\$0
Project Management	\$600
Data Management	\$5,400
Miscellaneous expenses	\$1,000
Total	\$10,384

w/o water samples other costs ~30% lower = ~\$5k



Fipronil Choices?

- Measure water
 - Are water tox thresholds (<140 ng/L) met?
- Continue sediment only?
 - Await sed tox data for more marine species
 - calculate porewater concentrations for tox?
 - Tributary concentrations already < saltwater toxicity thresholds
 - Ambient Bay concentrations likely even lower



Other Current Pesticides?

- 2008-2011 CA DPR urban survey (San Francisco, Sacramento, Orange County)
 - bifenthrin, **imidacloprid**, fipronil, fipronil sulfone, fipronil desulfinyl, carbaryl, and **malathion** found most often

yellow = not monitored RMP

blue = not in Bay matrices

- Easier to find in tributaries?
 - Pilot first in RMP trib sites if not required in MRP (stormwater) monitoring



Current Use Pesticides

- Imidacloprid

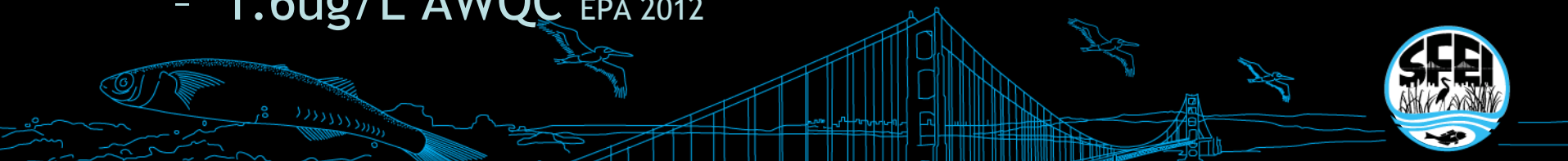
- $\log K_{ow}$ 3.7, max ~0.09 ug/L Sac 0.6 ug/L OC
Ensminger2013
- 0.9 ug/L LC_{50}

- Malathion

- $\log K_{ow}$ 2.9, max 0.19 ug/L SFB tribs Ensminger2013
- 28 ng/L chronic CA SWRCB, 100 ng/L CCC EPA

- Carbaryl

- $\log K_{ow}$ 2.4, <10-60 ng/L SFB tribs
- 1.6ug/L AWQC EPA 2012



Other Analytes?

- Great Lakes PP List / Howard & Muir 2010
 - Top 50 priorities (Top 10 Br, Cl, F, non-halogen, Si), mostly P&B(T?), HPV chemicals
 - Mostly not pesticides per se (intermediates/precursors), but some possibly analyzed by methods similar to current
- Discussions with labs on pilot screening level analysis development
 - Matrix? - if high K_{ow} look in sediments first



Possible Additions

- Try fipronils in water, or just sed only?
 - Trib concentrations only 5-10x DL so far
- Pilot to monitor other current use pesticides in **tribs** / other matrices?
 - **Imidacloprid, Malathion, Carbaryl**
- Pilot for some of Top 50 list?

