Stakeholder Meeting

Central Valley Pyrethroid Pesticides Total Maximum Daily Load and Basin Plan Amendment

23 October 2014

Outline

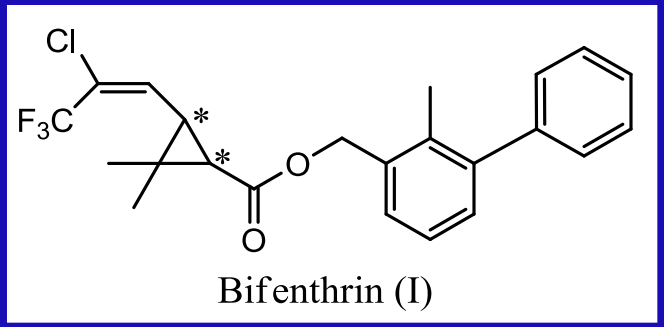
- **Project Schedule**
- **Water Quality Objectives Alternatives**
- **Bioavailability Background and Options**

Project Schedule

Milestone	Estimated Date
CEQA Scoping Meeting	*October 2012*
Stakeholder Meetings	*Sept,* **Oct,** Nov **2014**
Draft Staff Report for Peer Review	December 2014
Draft Staff Report for Public Comment	Feb/March 2015
Stakeholder Workshop	March 2015
Regional Board Information Item	March 2015
Regional Board Hearing	June 2015
State Board Approval	Late 2015
Office of Administrative Law Approval	Early 2016
USEPA Approval	2016

Pyrethroids Background

- **Priority pyrethroids**
  - Bifenthrin
  - Cyfluthrin
  - Lambda-cyhalothrin
  - Cypermethrin
  - Esfenvalerate
  - Permethrin
- **Additive toxicity**



Bifenthrin (I)

Water Quality Objectives

Limits or levels of water quality constituents or characteristics which are established for the reasonable protection of beneficial uses of water or prevention of nuisance within a specific area

- Narrative or numeric

Water Quality Objectives

Considerations in adopting WQOs (§13241, Porter-Cologne)

1. Past, present, probable future BU's
2. Environmental characteristics of hydrographic unit
3. Water quality conditions reasonably achievable
4. Economic considerations
5. Need to develop housing
6. Need to develop & use recycled water

Water Quality Objectives

- Sacramento and San Joaquin River Basins
- WQOs would apply in waters with designated or existing aquatic life beneficial uses (WARM/COLD)

Water Quality Objectives

Alternatives

Aqueous concentrations

→ Additive toxicity

1. No change to narrative objectives
2. No pyrethroids in water
3. UC Davis criteria
4. CDFG criteria (US EPA method)
5. Criteria with EPA method & UCD datasets
6. EPA OPP benchmarks

Water Quality Objectives

Aqueous concentrations

No change to narrative objectives

- Regional Board continues using available criteria and guidelines to assess attainment of narrative objectives (303(d) assessment)
- Regional Board is planning to use UC Davis criteria to assess pyrethroids data on next 303(d) update
- Values can change in future updates

Water Quality Objectives

Aqueous concentrations

No pyrethroids in water

- This would maintain “natural” conditions
- Any detection would be an exceedance
- Relies on antidegradation policies
  - Board would have to determine that any pyrethroids in waters are not to the maximum benefit of the people of California

Water Quality Objectives

Aqueous concentrations

UC Davis criteria

- Acute and chronic criteria for 6 pyrethroids
  - Additive
- Derived to protect aquatic life
- Scientific methodology uses high quality toxicity data for multiple species, similar to EPA method

Water Quality Objectives

Aqueous concentrations

CDFG (CDFW) criteria

- Acute criteria for 2 pyrethroids (permethrin, cypermethrin)
  - Incomplete data for bifenthrin, esfenvalerate
- Derived to protect aquatic life
- EPA 1985 method

Water Quality Objectives

Aqueous concentrations

Criteria derived with EPA method

- Used UC-Davis criteria toxicity data sets
- Acute criteria for bif, lcy, per. Chronic for lcy.
  - Data sets incomplete for remaining pyrethroids
- Derived to protect aquatic life
- EPA 1985 method

Water Quality Objectives

Aqueous concentrations

EPA OPP Aquatic Life Benchmarks

- Screening values
  - Not intended as Water Quality Objectives
  - Used in risk assessments for pesticide registration & to prioritize sites and pesticides that require further investigation
- Do not require a minimum data set
- Several are not protective based on available toxicity data

Water Quality Objectives

Aqueous concentrations (ng/L)

	UCD Criteria		CDFW Criteria		EPA Method-UCD data		Lowest OPP Benchmarks	
	A	C	A	C	A	C	A	C
Bifenthrin	4	0.6	-	-	0.48	-	75	1.3
Cyfluthrin	0.3	0.05	-	-	-	-	12.5	7.4
Lambda-cyhalothrin	1	0.5	-	-	0.92	0.39	3.5	2
Cypermethrin	1	0.2	2	-	-	-	195	69
Esfenvalerate	20*	3*	-	-	-	-	25	17
Permethrin	10	2	30	-	10	-	10.6	1.4

*Draft

Water Quality Objectives

Aqueous concentrations

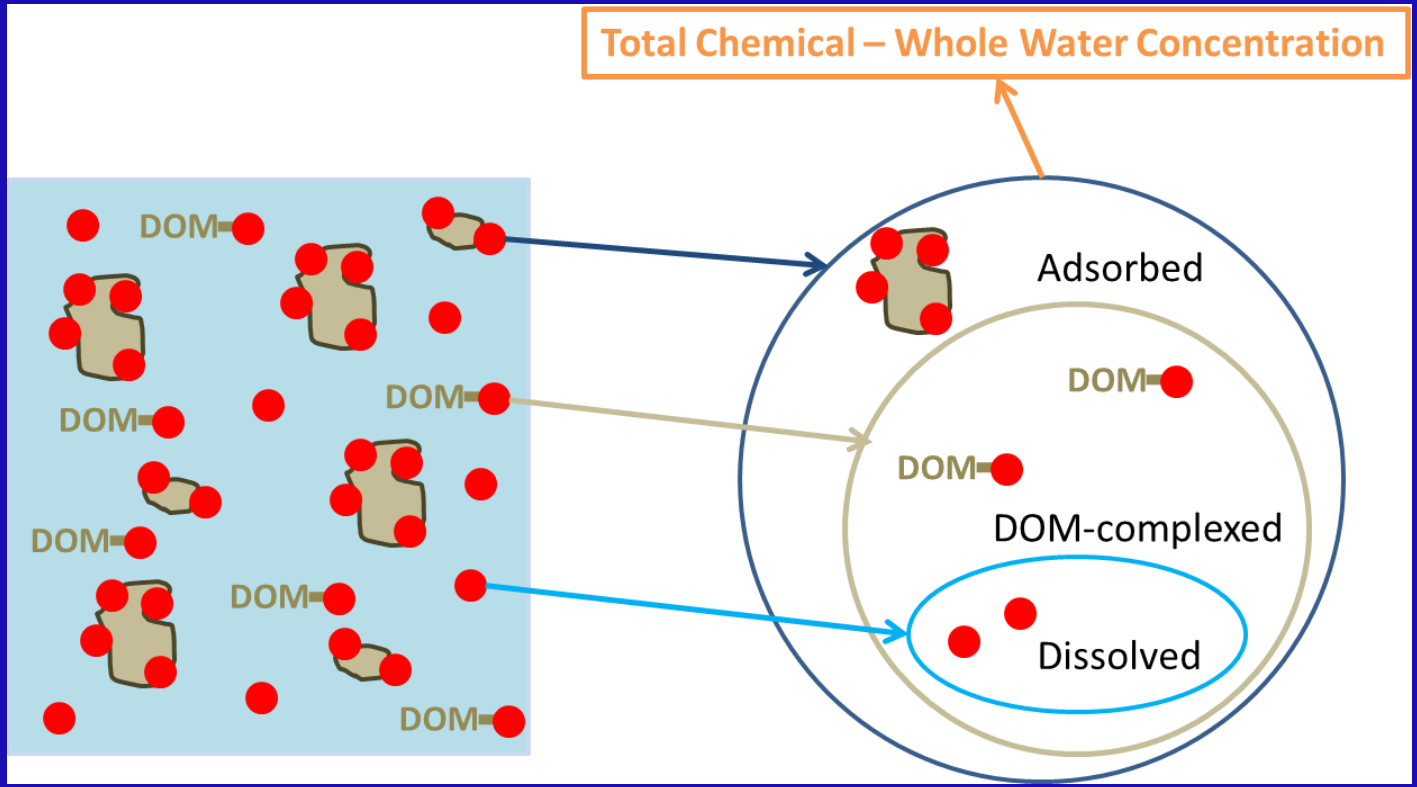
Additivity

$$Sum = \frac{C_{bif}}{O_{bif}} + \frac{C_{cyf}}{O_{cyf}} + \frac{C_{cyh}}{O_{cyh}} + \frac{C_{cyp}}{O_{cyp}} + \frac{C_{esf}}{O_{esf}} + \frac{C_{per}}{O_{per}}$$

Exceedance: $Sum > 1$

Attainment : $Sum \leq 1$

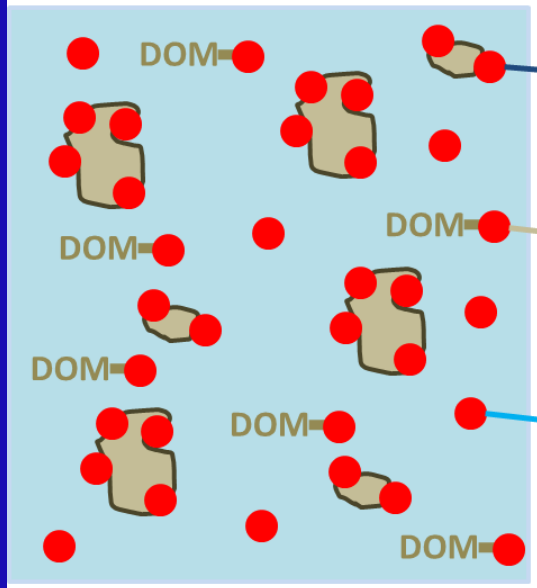
Bioavailability



Bioavailability

Total Chemical – Whole Water Concentration

?



Bioavailability

- Toxicity testing
- Tissue residue analysis
- Directly measure freely dissolved concentration
- Estimate freely dissolved concentrations via partition coefficients
- Filter samples to remove particles

Bioavailability

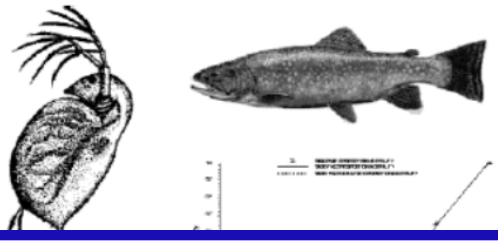
- Toxicity Testing

EPA
United States
Environmental Protection
Agency

Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms

Fifth Edition

October 2002



EPA 600/R-99/064
MARCH 2000

Methods for Measuring the Toxicity and Bioaccumulation of Sediment-associated Contaminants with Freshwater Invertebrates

Second Edition

Bioavailability

- Tissue residue analysis

SETAC PRESS

Environmental Toxicology and Chemistry, Vol. 32, No. 9, pp. 2026–2034, 2013

Printed in the USA

ACCUMULATION OF PESTICIDES IN PACIFIC CHORUS FROGS (*PSEUDACRIS REGILLA*) FROM CALIFORNIA'S SIERRA NEVADA MOUNTAINS, USA

KELLY L. SMALLING,*† GARY M. FELLERS,‡ PATRICK M. KLEEMAN,‡ and KATHRYN M. KUIVILA†
†California Water Science Center, US Geological Survey, Sacramento, California
‡Western Ecological Research Center, US Geological Survey, Point Reyes National Seashore, Point Reyes, California

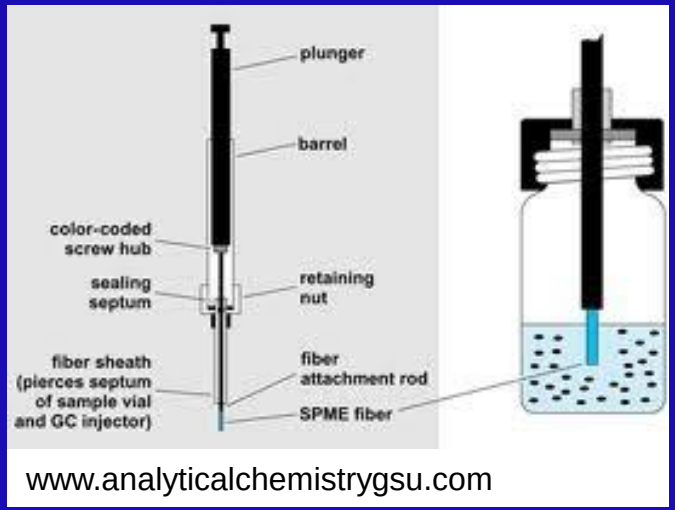
(Submitted 30 January 2013; Returned for Revision 28 March 2013; Accepted 30 April 2013)

Abstract: Pesticides are receiving increasing attention as potential causes of amphibian declines, acting singly or in combination with other stressors, but limited information is available on the accumulation of current-use pesticides in tissue. The authors examined potential exposure and accumulation of currently used pesticides in pond-breeding frogs (*Pseudacris regilla*) collected from 7 high elevations sites in northern California. All sites sampled are located downwind of California's highly agricultural Central Valley and receive inputs of pesticides through precipitation and/or dry deposition. Whole frog tissue, water, and sediment were analyzed for more than 90 current-use pesticides and pesticide degradates using gas chromatography–mass spectrometry. Two fungicides, pyraclostrobin and tebuconazole, and one herbicide, simazine, were the most frequently detected pesticides in tissue samples. Median pesticide concentration ranged from 13 μg/kg to 235 μg/kg wet weight. Tebuconazole and pyraclostrobin were the only 2 compounds observed frequently in frog tissue and sediment. Significant spatial differences in tissue concentration were observed, which corresponded to pesticide use in the upwind counties. Data generated indicated that amphibians residing in remote locations are exposed to and capable of accumulating current-use pesticides. A comparison of *P. regilla* tissue concentrations with water and sediment data indicated that the frogs are accumulating pesticides and are potentially a more reliable indicator of exposure to this group of pesticides than either water or sediment. *Environ Toxicol Chem* 2013;32:2026–2034. © 2013 SETAC

Keywords: Current-use pesticides Amphibian Sierra Nevada *Pseudacris regilla* Accumulation

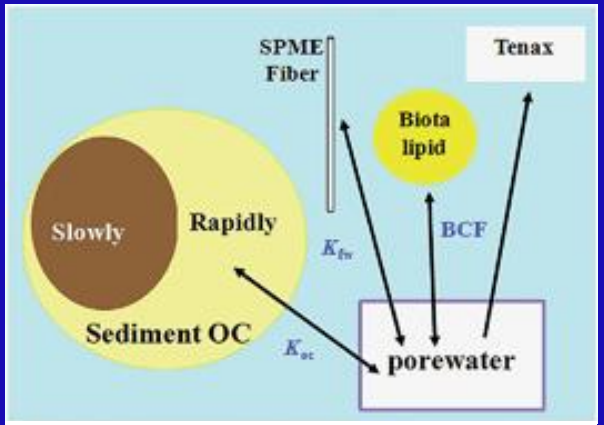
Bioavailability

- Direct measurement of freely dissolved concentrations



www.analyticalchemistrygsu.com

SPME



You et al. 2011. *J. Environ. Monit., 13, 792-800*

Tenax

Bioavailability

- Estimate freely dissolved concentration via partition coefficients

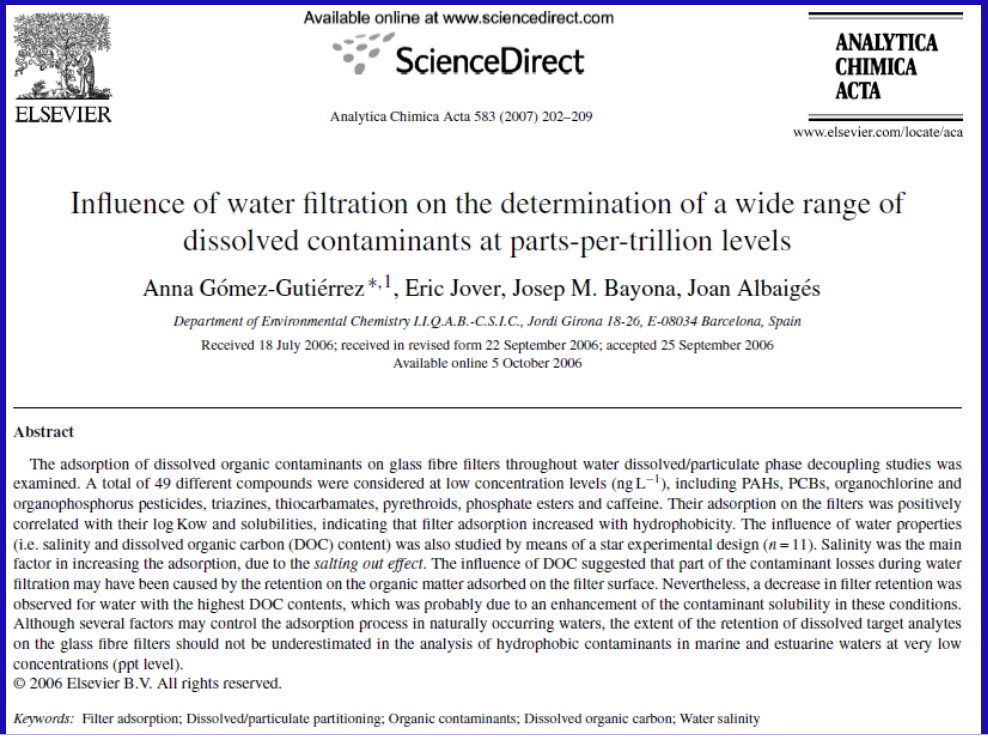
$$C_{dissolved} = \frac{C_{total}}{1 + ((K_{OC} \cdot [SS]) / \ foc) + (K_{DOC} \cdot [DOC])}$$

Measure:
C_{total} , [SS], [DOC], f_{OC}

Need:
K_{OC}
K_{DOC}

Bioavailability

- Sample filtration



Available online at www.sciencedirect.com
ScienceDirect
Analytica Chimica Acta 583 (2007) 202–209
ANALYTICA CHIMICA ACTA
www.elsevier.com/locate/aca

Influence of water filtration on the determination of a wide range of dissolved contaminants at parts-per-trillion levels

Anna Gómez-Gutiérrez *,1, Eric Jover, Josep M. Bayona, Joan Albaigés

Department of Environmental Chemistry I.I.Q.A.B.-C.S.I.C., Jordi Girona 18-26, E-08034 Barcelona, Spain

Received 18 July 2006; received in revised form 22 September 2006; accepted 25 September 2006
Available online 5 October 2006

Abstract

The adsorption of dissolved organic contaminants on glass fibre filters throughout water dissolved/particulate phase decoupling studies was examined. A total of 49 different compounds were considered at low concentration levels (ng L^{-1}), including PAHs, PCBs, organochlorine and organophosphorus pesticides, triazines, thiocarbamates, pyrethroids, phosphate esters and caffeine. Their adsorption on the filters was positively correlated with their log Kow and solubilities, indicating that filter adsorption increased with hydrophobicity. The influence of water properties (i.e. salinity and dissolved organic carbon (DOC) content) was also studied by means of a star experimental design ($n = 11$). Salinity was the main factor in increasing the adsorption, due to the *salting out effect*. The influence of DOC suggested that part of the contaminant losses during water filtration may have been caused by the retention on the organic matter adsorbed on the filter surface. Nevertheless, a decrease in filter retention was observed for water with the highest DOC contents, which was probably due to an enhancement of the contaminant solubility in these conditions. Although several factors may control the adsorption process in naturally occurring waters, the extent of the retention of dissolved target analytes on the glass fibre filters should not be underestimated in the analysis of hydrophobic contaminants in marine and estuarine waters at very low concentrations (ppt level).

Keywords: Filter adsorption; Dissolved/particulate partitioning; Organic contaminants; Dissolved organic carbon; Water salinity

Bioavailability

- Practical options:
  - Toxicity testing
  - Estimation of freely dissolved concentration via partition coefficients

Current Status & Next Steps

- Draft staff report under development
- E-mail updates sign up:

  http://www.waterboards.ca.gov/resources/email_subscriptions/reg5_subscribe.shtml

- Project website

  Central Valley Pyrethroid Pesticides TMDL and Basin Plan Amendment

Contact Info

Tessa Fojut

11020 Sun Center Drive #200

Rancho Cordova, CA 95670

Tessa.Fojut@waterboards.ca.gov