Results of Round Robin Testing (Water and Sediment)

Public Meeting for
CALFED Funded Project ERP-02-P42
April 25, 2007

Joint Project Between:
U.S. Geological Survey
California Department of Fish and Game
California Department of Pesticide Regulation
California Department of Food and Agriculture

Refresher on Method Developed

Lab	Medium	Extraction Method	Volume	Analysis Method	MDLs
USGS	Water	Filtered sample; HLB cartridge with bottle rinse	1 L	GC/MS	2-5 ng/L
	Sediment (bed and suspended)	MASE/Carbon Alumina/GPC	5 g (dry weight)	GC/MS	1-5 ng/g
CDFG	Water	Whole water; liq/liq extraction	1 L	GC-ECD & GC/MS	1-5 ng/L
	Sediment (bed)	ASE/GPC/ Florisil	5 g (dry weight)	GC-ECD & GC/MS	1-4 ng/g
	Tissue	ASE/GPC/ Florisil	10 g (fresh weight)	GC-ECD & GC/MS	1-5 ng/g estimated
CDFA	Water	Whole water; liq/liq extraction, florisil clean-up	1L	GC/MS & GC-ECD	1- 8 ng/L (MRL 5-15 ng/L)
	Sediment (bed)	Solvent shake, florisil clean-up	20 g (wet weight)	GC/MS & GC-ECD	0.1 – 0.9 ng/g (MRL 1-1.5 ng/g)

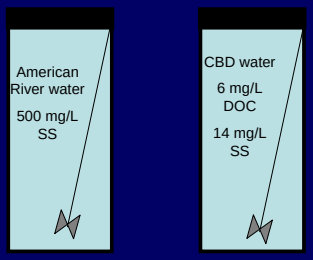
Other Methods Issues

- Isomers
  - Moving towards specific isomers
  - Obtaining specific isomers
- Standard Stability
  - Found <10% change of 6 months
- Sample Stability
  - Water
    - Need to be analyzed within a couple of days, preferably 24 hours
  - Sediment
    - Samples stable for over 1 year

Inter-Lab Comparisons Water

2 waters spiked at two different concentrations (10 and 100 ng/L)

Transferred to 1 L bottles (continuous stirring)



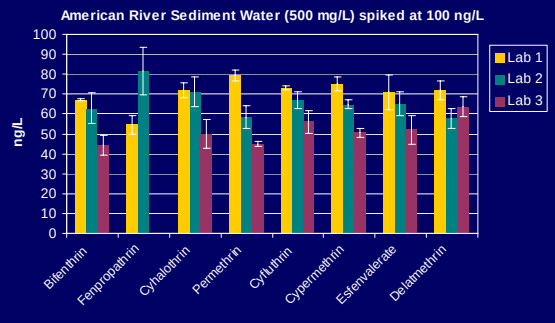
Inter-Lab Comparisons Water

- 2 concentrations: 10 ng/L and 100 ng/L
- Each lab received samples and spiking solution (2 ng/mL)
- Samples extracted within 48 hours (2 used liquid:liquid and one used SPE + filter extract)
- GC-ECD and MS detection
- No detects in blanks for any of the labs

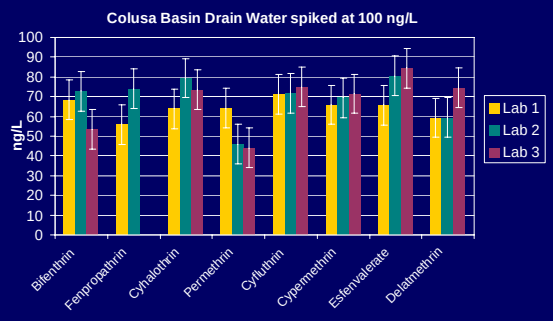
Inter-Lab Comparisons Water

- Spiking Solution
  - Sent out spiking solution (used by USGS) to labs
  - Agreed on concentration of spike (± 10%)
- Low Level Water Samples (10 ng/L)
  - 10 ng/L
  - One lab: below MRL
  - Lab # 1 ~3-9 ng/L
  - Lab # 2 ~ 3-8 ng/L

Inter-Lab Comparisons Water



Inter-Lab Comparisons Water



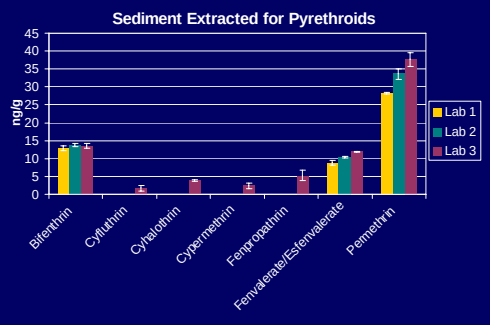
Inter-Lab Comparisons Water

- 10 ng/L did not work well, too low with 500 mg/L sediment
- Sediment water (500 mg/L),
  - Highest suspended sediment concentration
  - Fairly good agreement but concentrations measured were lower than expected (50-70%)
- Colusa Basin Drain
  - Better recovery (>70%) and all concentrations with one standard deviation
  - Composition more similar to most waters sampled

Pyrethroid Inter-Lab Comparisons Sediment

- Sediment collected from Salinas area by DPR
- All labs received 2 1-L jars of sediment
- Extractions were completed within one month
- One lab used shaking, one microwave and one pressurized solvent extraction
- Organic Carbon = 3.2%

Pyrethroid Inter-Lab Comparisons Sediment



Pyrethroid Inter-Lab Comparisons Sediment

- Slight differences in concentrations due to extraction methods
- Sonication has been shown the quantify 30% less than heated or pressurized extractions for OC and OP pesticides on aged sediments
- Also retain less matrix

Summary

- Methods have been developed for pyrethroids in
  - Water
  - Sediment
  - Colloids
  - Biota
- MDLs
  - Near toxicity levels
  - At 1/10th the LC_{50} were not achieved with standard instruments (that include confirmation)
  - Need more sensitive instruments GC-MS/MS

Current Time Table for Reports

- Analytical methods validated
  - July 1, 2007
- Draft final report
  - Oct 1, 2007
- Final report
  - Dec 31, 2007