Using Integrative Passive Samplers to Monitor Current-Use and Legacy Pesticides in San Francisco Bay, CA

Kelly L. Smalling and Kathryn M. Kuivila

USGS California Water Science Center
Sacramento, CA

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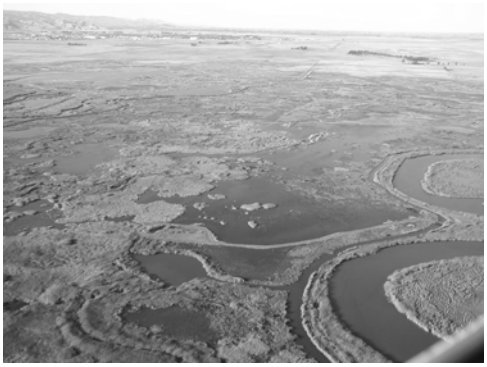
1

Suisun Marsh

- Largest contiguous estuarine marsh on US west coast
- Major, but often ignored, component of the SF Estuary
- Covers 116,000 acres, including managed wetlands, upland grasses, tidal wetlands, channels and sloughs
- Intensely altered and managed for more than 100 years, mostly as a non-tidal freshwater wetland for waterfowl

Importance of Suisun Marsh

- Recognized as valuable tidal brackish environment and important habitat for native fish
- Supports at least 43 plant and animal species of special concern
- Best place left in the estuary to restore large areas of tidal marsh



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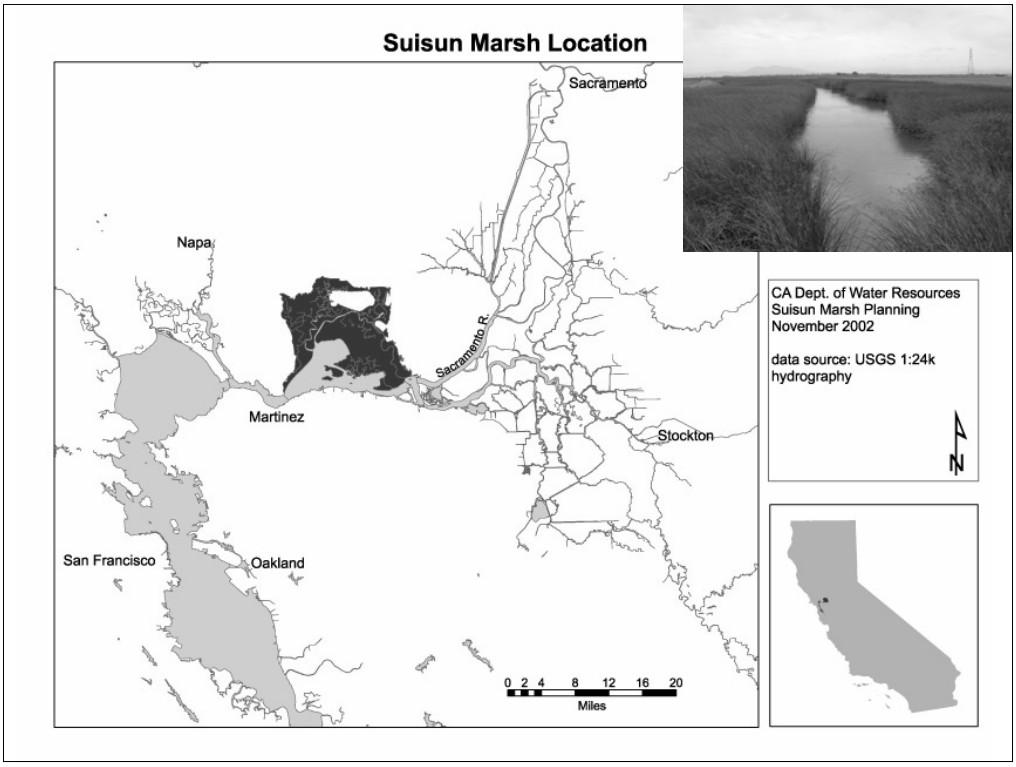
Suisun Marsh Location
Sacramento
Napa
Sacramento R.
Martinez
Stockton
San Francisco
Oakland
0 2 4 8 12 16 20
Miles
CA Dept. of Water Resources
Suisun Marsh Planning
November 2002
data source: USGS 1:24k
hydrography
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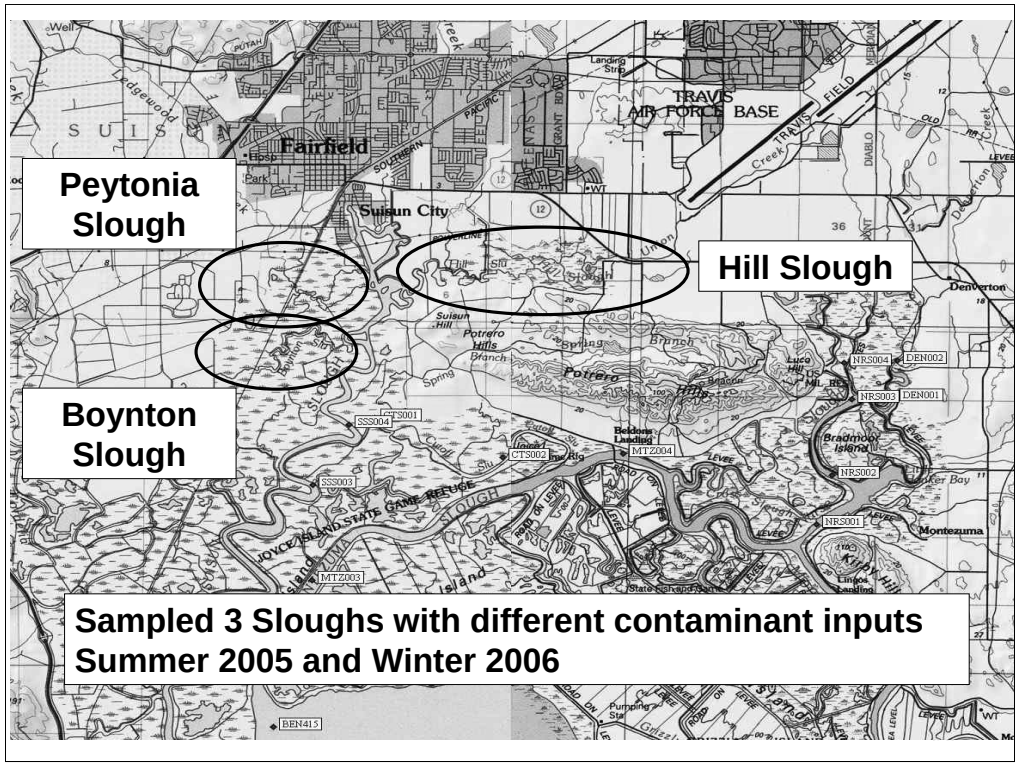
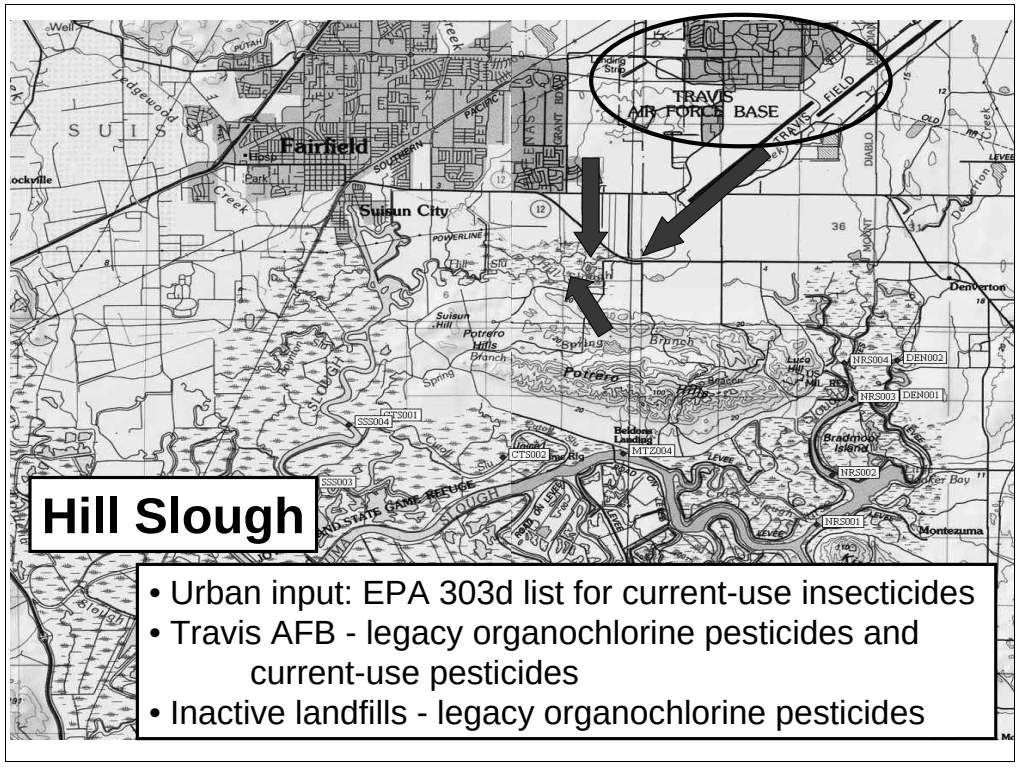


Map of the sloughs and their relationship with surrounding area



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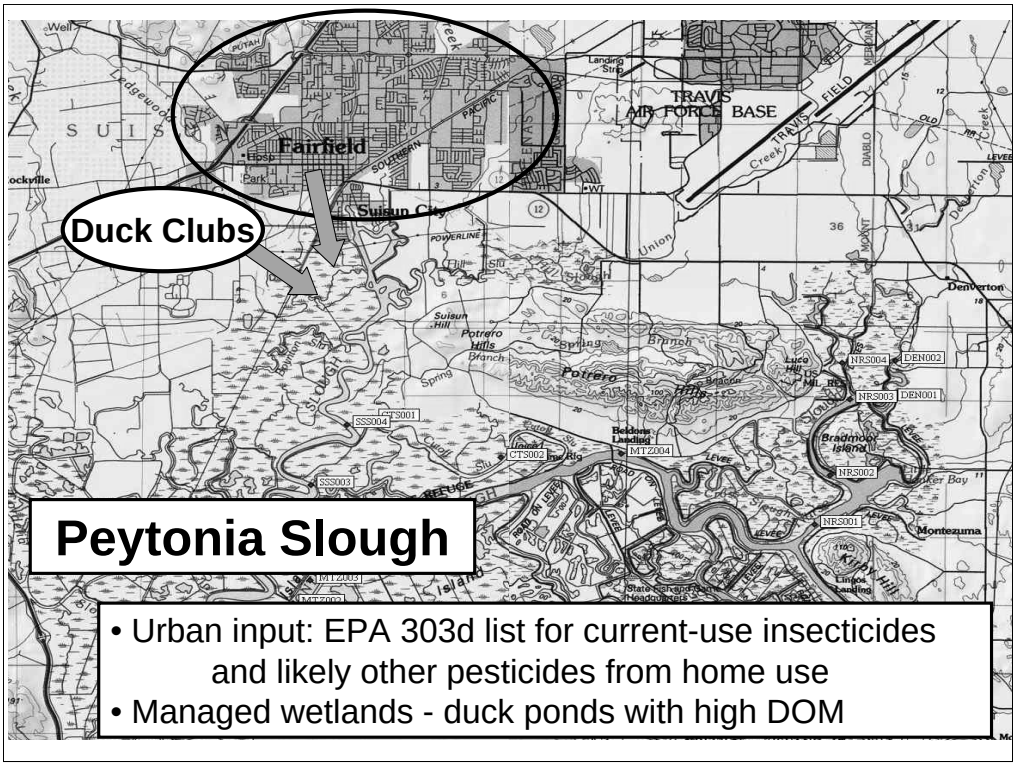

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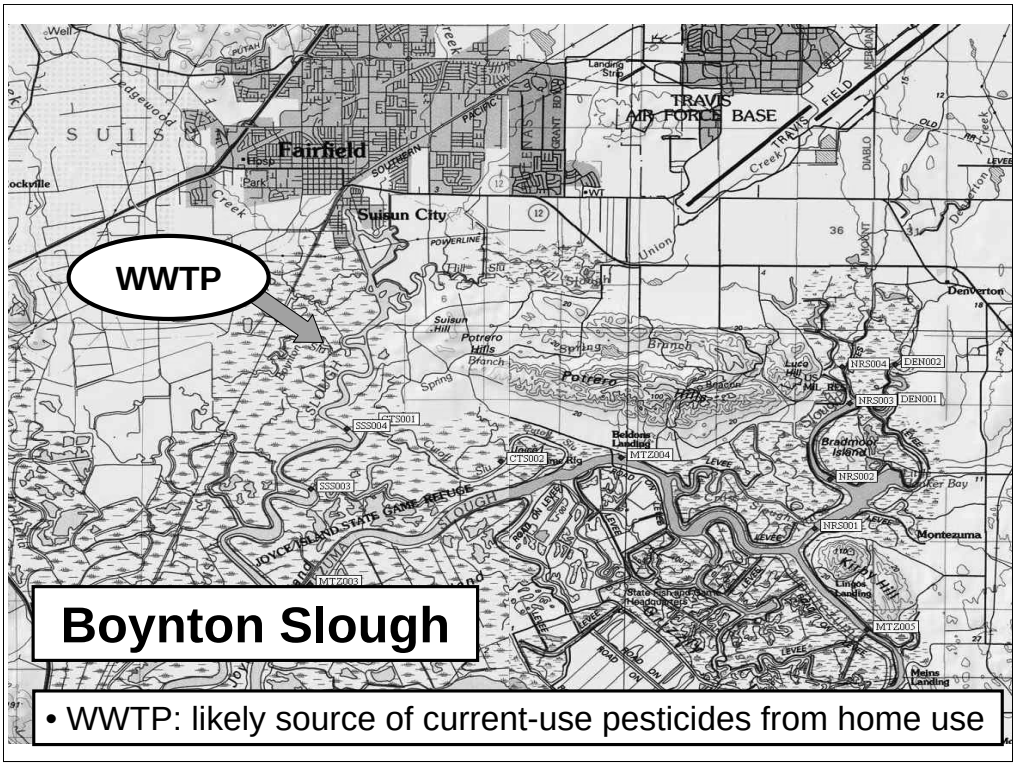


Map of the sloughs and their relationship with surrounding area

Why Passive Samplers?

- Integrate over time
- Interested in a wide range of pesticides (log K_{ow} = 1.5-7)
  - Combined SPMDs and POCIS to cover the range of K_{ow}
- Monitoring legacy organochlorines and pyrethroids

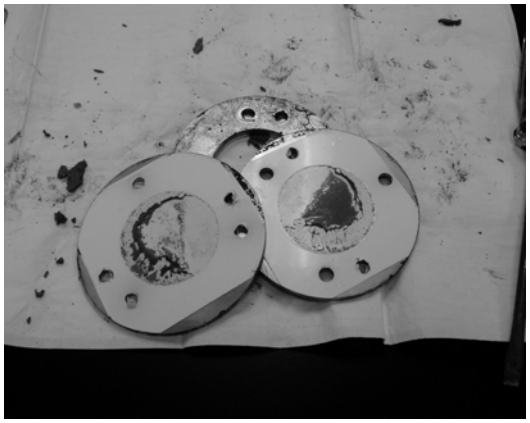
Polar organic chemical integrative sampler (POCIS)

used to monitor hydrophilic contaminants in water

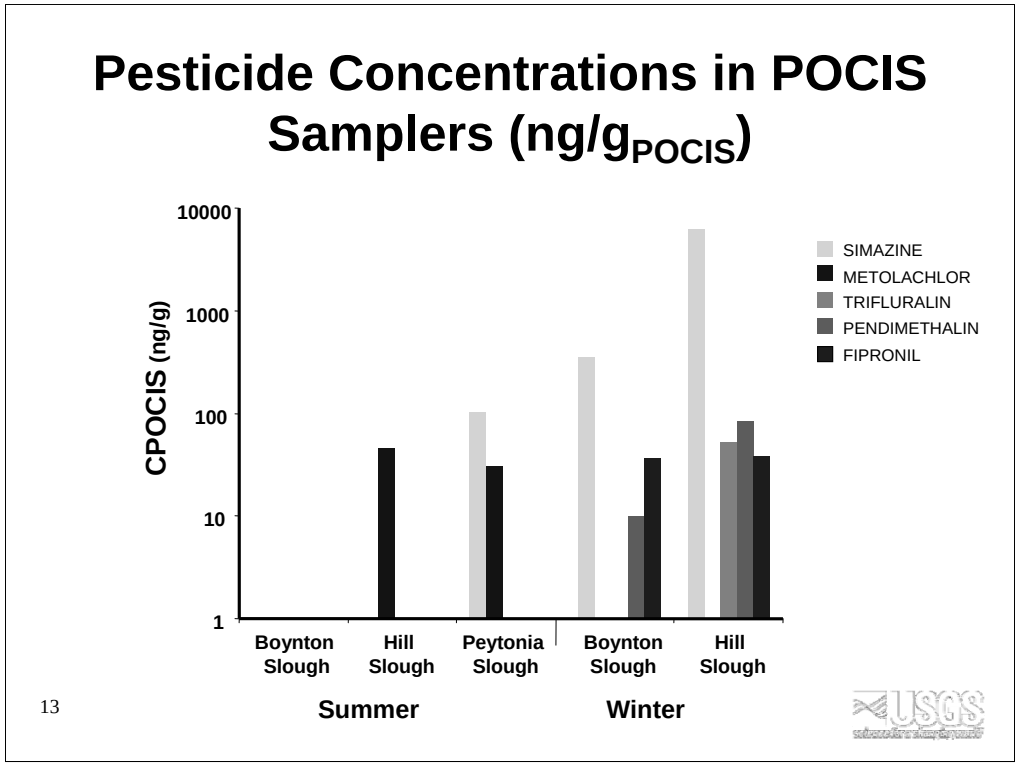
- Easy to extract and analyze
- Contaminants with log K_{ow} <4
- Integrates over time

SPMD/POCIS deployment/retrieval

POCIS Extraction/Analysis



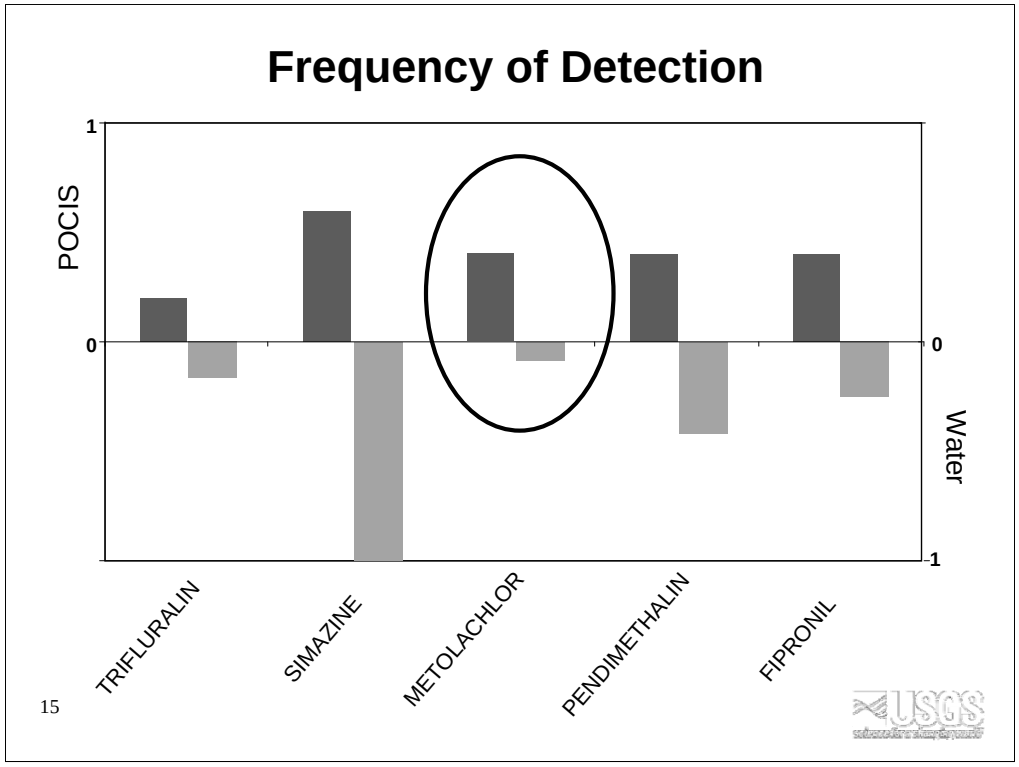
- Rinsed HLB sorbent into glass columns with MeOH
- Extracted w/ 1:1:8 MeOH:EtOAc:DCM
- Filtered particulates using GF/F.
- Removed matrix with carbon SPE cartridges
- Analyzed by GC/MS for ~ 50 pesticides



Metolachlor in 3 samples

POCIS Field Validation

- Collected water samples at beginning and end of each deployment
- Current-use pesticides detected in both water samples at a site (pendimethalin, simazine)
- Other pesticides were only detected in one of the samples at a site (hexazinone, oxyfluorfen)



Metolachlor detected more frequently in POCIS compared to the water

Water sampling missed metolachlor input that the POCIS caught

Simazine detected more frequently in water that POCIS

Detection limits of simazine in POCIS are probably slightly higher because the samples needed to be cleaned-up to remove matrix interferences

All other compounds were detected in about the same frequency when you compare the water to the POCIS

Comparison of Water Analysis with POCIS

- If detected in water, results of POCIS agreed well (pendimethalin, simazine, trifluralin)
- Some pesticides detected at low concentrations in POCIS but at or below detection limit in water (metolachlor)
- Transient compounds do not show up in POCIS (hexazinone)
- Good indicator of water concentration over time
  - Eliminates the need to catch definitive pesticide ‘pulses’
  - Does not over estimate

PROBLEMS ??

Biofouling and sediment build-up may hinder uptake in environments with high-suspended sediment loads

Semi-permeable membrane devices (SPMDs)

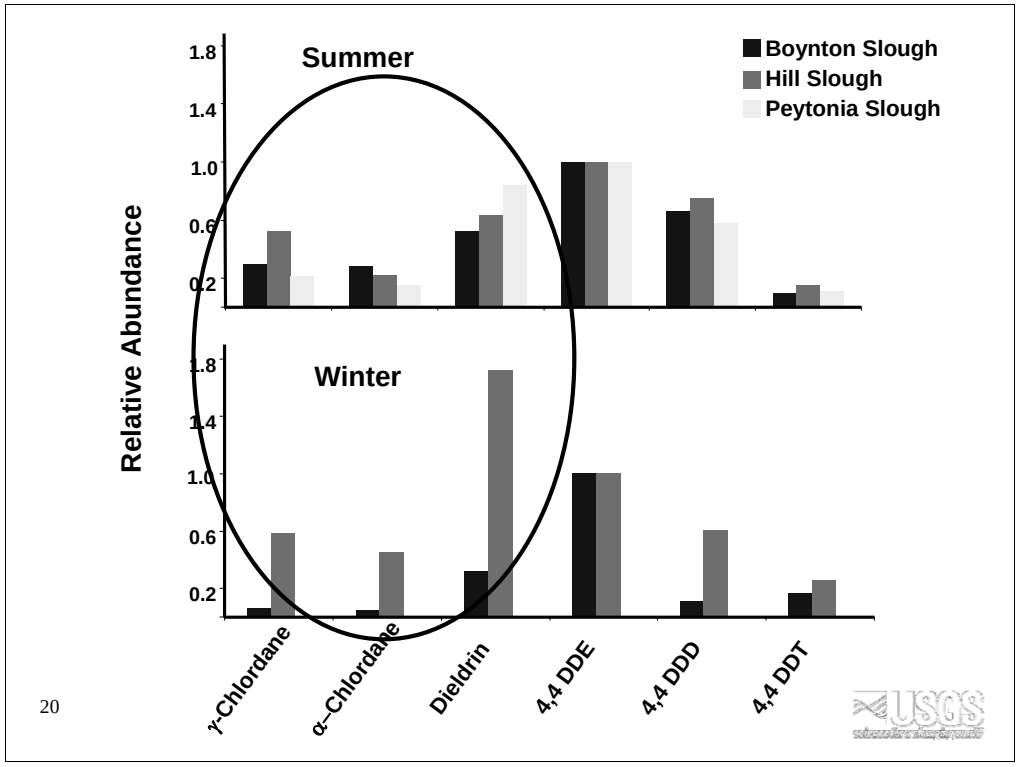
used to monitor hydrophobic contaminants in water

- Samples only dissolved form
- Contaminants with log K_{ow} >4
- Integrates over time

SPMD Extraction/Analysis

- Dialyzed 24 hrs in hexane (EST)
- Matrix/lipid removed by GPC (98:2 DCM:MeOH)
- Clean-up/fractionation
  - 5 g Florisil (5% deactivated)
  - 5 g activated silica gel
  - Collected 2 fractions
- Analyzed by GC/MS (25 current-use) and GC/ECD (26 legacy OCs)

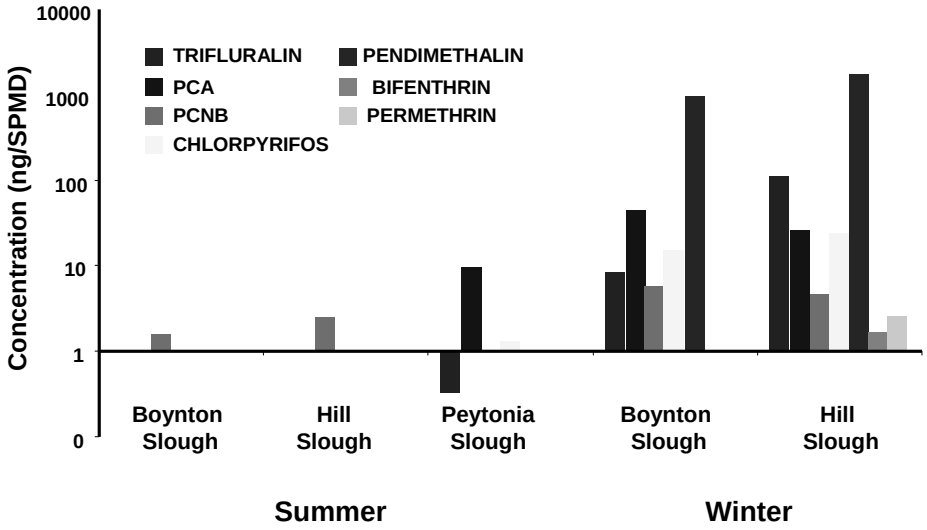
19



Red circle shows input from Travis AFB

Other OCs were detected by ECD but have not been verified by MS

Current-use Pesticides in SPMDs



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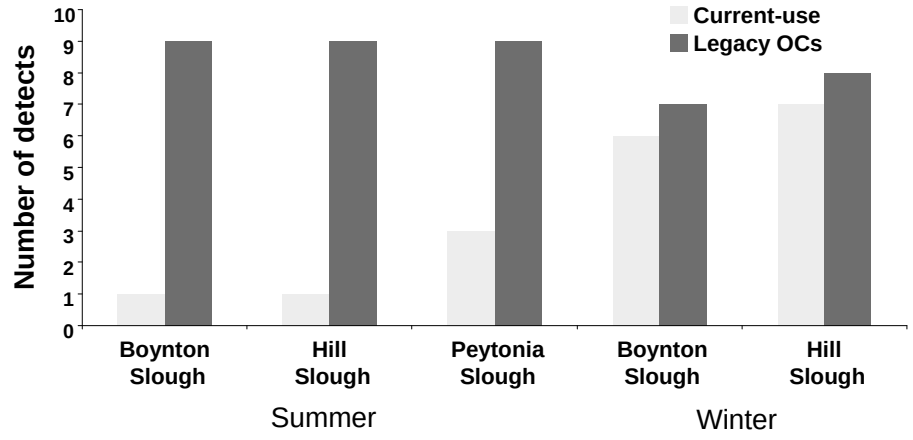
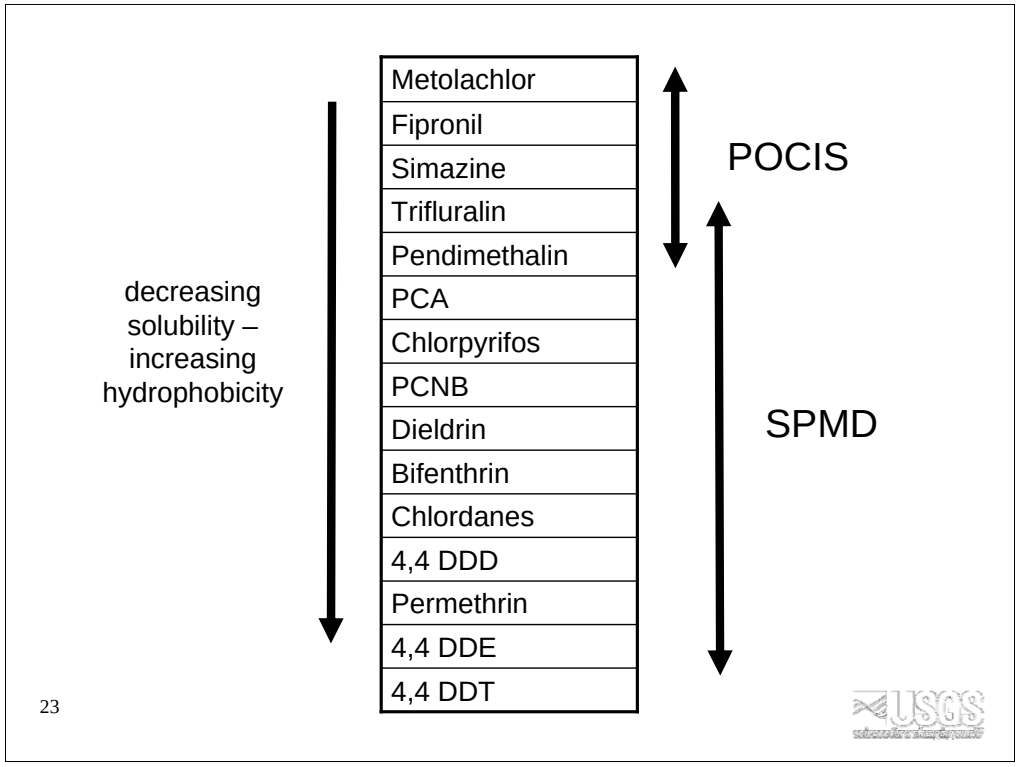


- Constant source of legacy OCs to the estuary year around
- Occurrence of current-use pesticides dependent on use and run-off
  - Greater number of detects in the winter compared to the summer

22

USGS

PS lost in winter


Metolachlor
Fipronil
Simazine
Trifluralin
Pendimethalin
PCA
Chlorpyrifos
PCNB
Dieldrin
Bifenthrin
Chlordanes
4,4 DDD
Permethrin
4,4 DDE
4,4 DDT
POCIS
SPMD
decreasing solubility – increasing hydrophobicity
23

Pyrethroids in SPMDs

- Of interest due to increasing use and high toxicity to fish
- Should work since log K_{ow} > 4
- But size and shape hinder their passing through the SPMD membrane
- Also more difficult to remove pyrethroids from SPMDs, resulting in high background of extracted samples

Using Passive Samplers for Pesticides

- Useful to combine POCIS (more polar/hydrophilic) with SPMDs (more hydrophobic/less water soluble)
- Good indicator for concentrations below typical MDLs
- Integrate over time – eliminate complexity due to episodic pulses
- **ALWAYS TEST** – potential problems with pyrethroids

25

Future Directions

- Laboratory uptake studies to validate effectiveness of passive samplers for current-use pesticides
- Specifically focus on pyrethroids and uptake/extraction from SPMDs
- Future deployments of samplers in other areas where dissolved pesticides are of concern

Acknowledgments

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