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

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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
Sampled 3 Sloughs with different contaminant inputs Summer 2005 and Winter 2006

Map of the sloughs and their relationship with surrounding area
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Peytonia Slough

- Urban input: EPA 303d list for current-use insecticides and likely other pesticides from home use
- Managed wetlands - duck ponds with high DOM
Map of the sloughs and their relationship with surrounding area

- WWTP: likely source of current-use pesticides from home use
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
Pesticide Concentrations in POCIS Samplers (ng/g\textsubscript{POCIS})

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
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)
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

Concentration (ng/SPMD)

TRIFLURALIN
PENDIMETHALIN
PCA
BIFENTHRIN
PCNB
PERMETHRIN
CHLORPYRIFOS

Boynton Slough
Hill Slough
Peytonia Slough
Boynton Slough
Hill Slough

Summer
Winter
- 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

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

decreasing solubility – increasing hydrophobicity

POCIS
SPMD
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
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
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