Pesticide Sequestration in Passive Samplers (SPMDs): The Effect of Biofouling and Deployment Time in a Tropical Watershed

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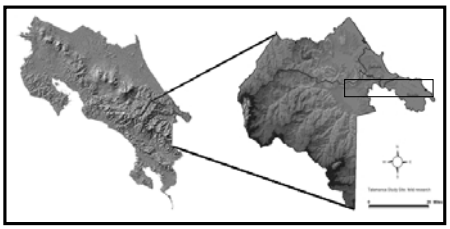
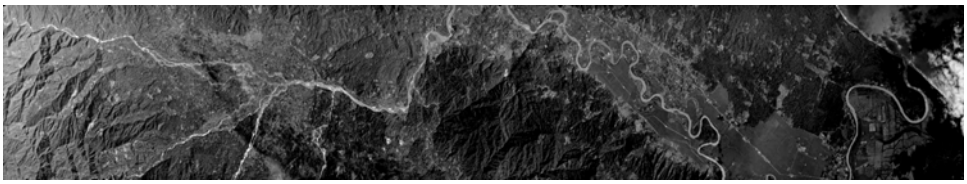
Talamanca, Costa Rica



Lower Sixaola River Watershed (~700 Km^2): Extensive plantations of export banana and plantain (>300 km^2)



Indigenous Plantain Farmers, National Plantain Cooperatives, Multinational Companies

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Year-Round Pesticide Application in Export Banana and Plantain

- Aerial application of fungicides every 8 days
  - Difenoconazole
  - Bitertanol
  - Mancozeb
  - Tridemorph
- Nematicide applications every 3 to 4 months
  - Terbufos
  - Oxamyl
  - Ethoprofos
- Herbicides every 2 to 6 months
  - Glyphosate
  - Paraquat
  - Diuron
- Chlorpyrifos-impregnated blue bags on all fruit
- Estimated 50 kg a.i./ha per year (compare to 3 kg a.i./ha in US)

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Current pesticide application practices are a concern

- lack of safe-handling practices
- no regulatory infrastructure
- no adequate facilities for agrochemical storage, transport, and waste disposal
- river and groundwater resources are used for consumption, fishing activities, and household use
- effect on human health, flora and fauna is unknown

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SPMD Use

1. Monitoring of pesticide presence/absence in freshwater/marine resources
2. Estimation of bioavailable fraction and organism exposure
3. Estimate time-weighted average pesticide concentrations in stream/estuaries

Data is being used for:
Ecological Risk Assessment of Current Pesticide Use
Regional Public Health and Human Rights Initiatives
Integrated Freshwater, Marine and Terrestrial Conservation Planning

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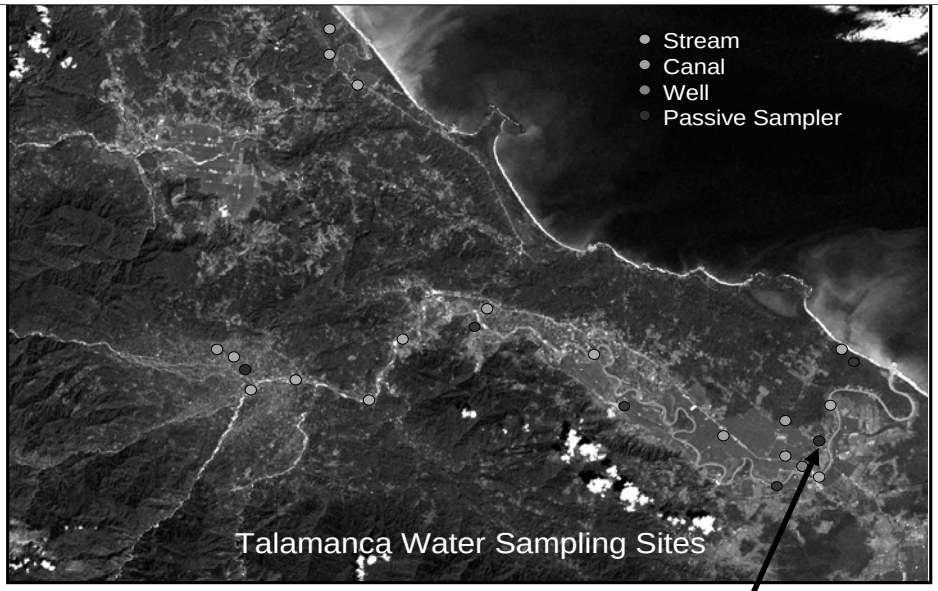

Quebrada Caña Experimental Creek

Objective: determine effect of biofouling and deployment time on pesticide sequestration in SPMDs

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Caña Creek Site Characteristics

- Year-round environmental loading of pesticides: particularly chlorpyrifos and difenoconazole
- Year-round water temperature 25-30 °C
- Suspended solids carbon content = 3.5 %
- pH = 7.5 – 8.0, Conductivity = 0.2 mS
- Large fluctuations in stream turbidity, dissolved oxygen, flow regime
- Site of frequent fish kills

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Field Methods

- Two study periods: February 2006 (166mm rain)
  June 2006 (80mm rain)
- 2 or 3 SPMD membranes removed at 4, 15 and 28 days
  Visual estimation of biofouling on site
- Stream measurements made every 2 days
  TSS, Flow (Q=V*A), EC, pH, DO, Temp, etc.
- 4 Liters of surface water samples collected weekly
- 4 Liters Filtered for Suspended Sediments (TSS)
  collected every 2 days, 4-5 g dry weight/month

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Laboratory Methods

- Weight of SPMD membrane before and after surface cleaning (to estimate of biofouling by weight of biofilm)
- Dialysis/Extraction of SPMDs from EST methods
- Water and TSS extraction EPA method 3535, 3510
- Internal Standard (Etiom) with membrane blanks
- Quantification with GC-FPD, ECD and GC-MS
- No cleanup step, no PRC compounds
- Characterization of suspended sediments (mineralogy, % carbon, chlorophyll a)

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Pesticides Above MQLs

SPMDs: chlorpyrifos (log Kow 4.7- 4.9)
difenoconazole (log Kow 4.2)
terbufos (log Kow 3.7-4.5)
Replicate precision +/- 0.02 ng/membrane

Water: difenoconazole (log Kow 4.2)
diuron (log Kow 2.8)
Replicate precision +/- 1μg/L

Suspended sediments: no compounds detected (MDL<0.02 μg/ml)
samples < 4 grams dry weight per ml
carbon content of 3.5%
C:N ratio of 10
Smectitic clays, organic matter, algae

SPMDs increased ability to detect chlorpyrifos and terbufos in streams

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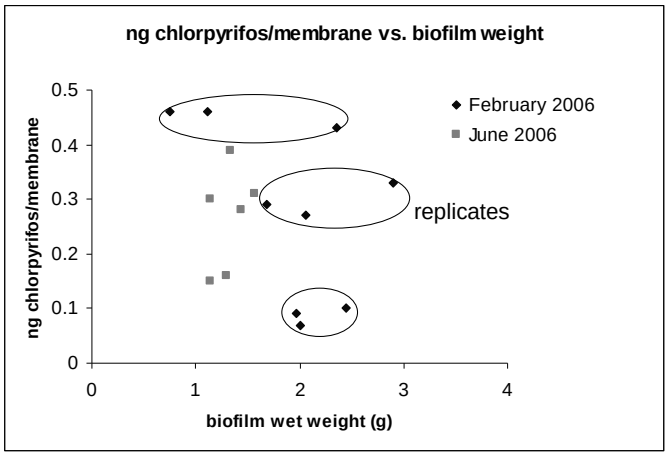
SPMD-Chlorpyrifos and Biofilm Weight



No significant correlation between chlorpyrifos in each membrane and biofilm weight

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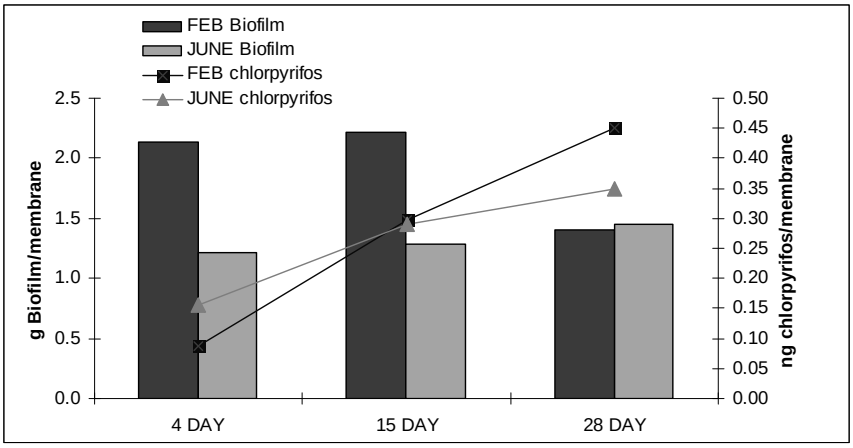
SPMD-Chlorpyrifos and Biofilm Weight



- Increased sequestration of chlorpyrifos over time during both months
- More overall chlorpyrifos sequestration and more biofilm by weight in February compared to June

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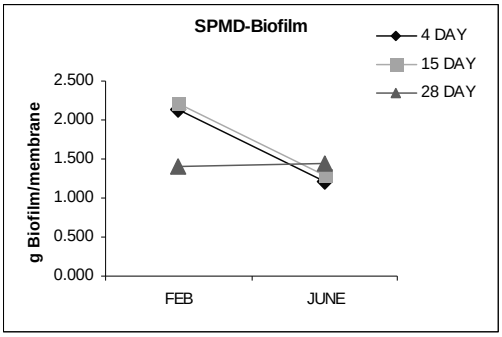
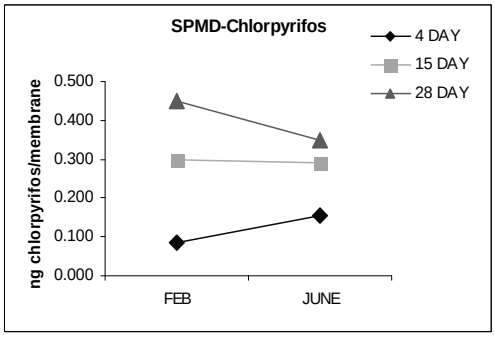
SPMD-Chlorpyrifos and Biofilm Weight

Two-way ANOVA ($p<0.05$)

- Average biofilm weight on membranes was significantly different between two study periods (higher in February)





- Significant differences in SPMD-chlorpyrifos among three deployment times (4, 15, 28 days) AND in the interaction between study period and deployment time
- Interaction effects are due to 4 day and 28 day deployments

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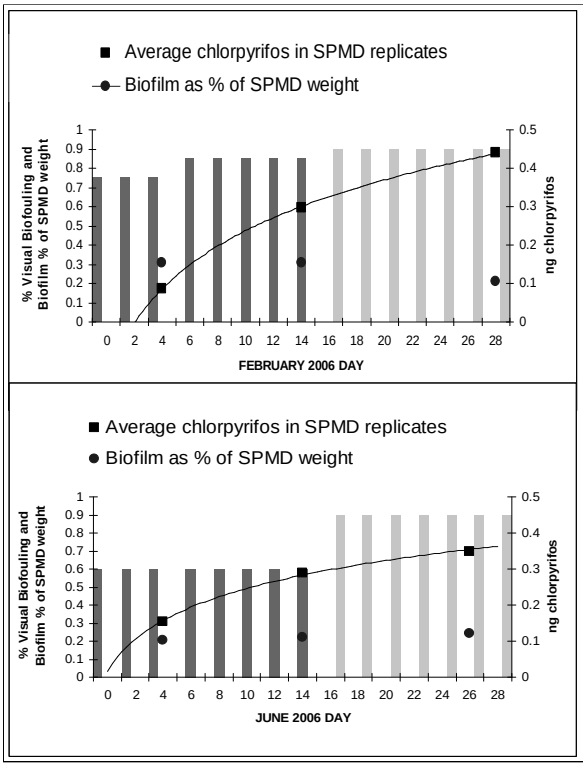

Visual Biofouling

- Changes in visual biofouling estimates more reflective of changes in chlorpyrifos sequestration over time
- Visual biofouling estimates were not related to biofilm weight
- Type of biofilm may be important
- Feb TSS had more clay
  June TSS had more algae

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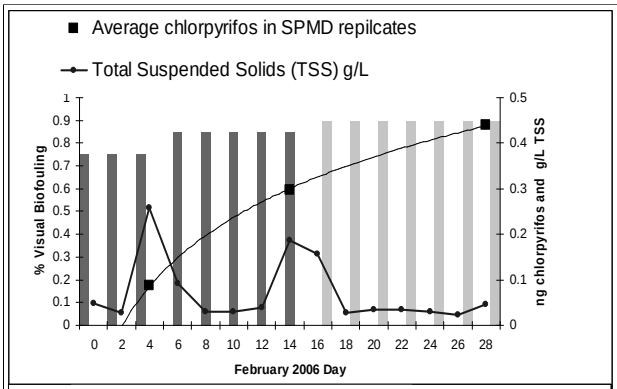

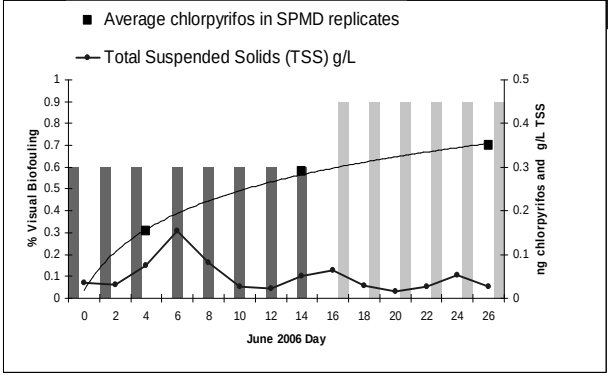

Biofouling and TSS

- Visual biofouling rates reflective of measured TSS (turbidity)
- Higher TSS in rainy season (Feb) vs. drier period (June)
- WHY MORE UPTAKE IN FEBRUARY? Membrane uptake not affected by TSS, water concentration, or sorbed compounds
- Slow desorption from biofilm? But no detections in TSS samples (MDL=0.2μg/ml)

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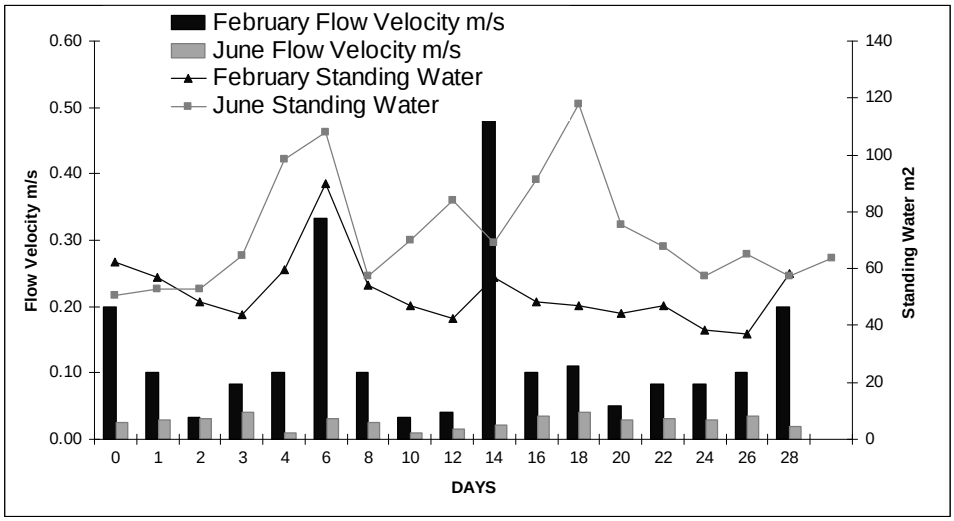

Feb: Higher flow velocity but less standing water

June: Lower flow velocity but more standing water

Increased uptake with higher flow velocity is consistent with Aqueous Boundary Theory

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Data Interpretation: Considerations of Stream Morphology

- High flow events may physically remove biofilm from membrane and change stream morphology
- Sedimentation and debris can block the stream mouth, reducing flow velocity but increasing standing water (depth and width)
- Increased turbidity (TSS) may affect compound availability and dissolved concentration
- Low flow velocities and high standing water conditions contribute to reduced uptake, compound dilution, increased volatilization, and potential stratification of compounds

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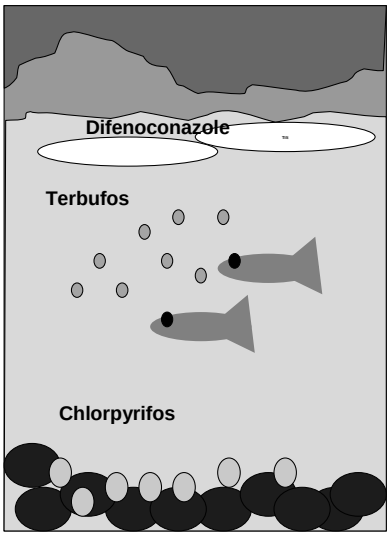
Stratification of Pesticides



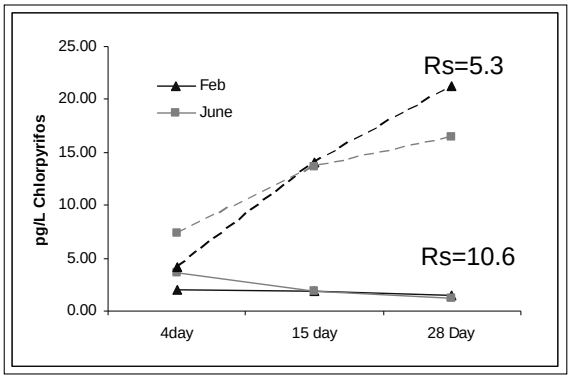
Field Uptake (Rsf) Values to calculate Cw?

$Cw = C_{spmd}/Rs*T$ vs. $Cw=C_{spmd}/K_{spmd}(1-\exp(-k_eT))$

Rsf = Rs(0.5) for heavy biofouling*

EX: Chlorpyrifos: Kow = 4.9, Rs =10.6 L/d, where $t^{1/2}$ = 12 days -curvilinear

or Rsf = 5.3 L/d where $t^{1/2}$= 26 Days - LINEAR



EX: Difenoconazole: Kow = 4.2, Rs=??? , Kspmd = ???

Assume water grab sample =12 day average, Rsf = 3.8 L/d

* Petty et al. 2000

Summary

- SPMDs allowed for detection of compounds previously undetected in routine water samples.
- Visual estimation of biofouling better than measurement of biofilm weight to estimate extent of biofouling.
- Higher visual biofouling and TSS (turbidity) in Feb study period showed more sequestration of SPMD chlorpyrifos likely due to increased flow velocities compared to June study period.
- Stream morphology may be important in for estimating final water concentrations due to complex relationships in stream discharge (standing water vs. flow velocity), turbidity and stratification of compounds during extended periods of low flow velocity.

Recommendations

- Continue field experiments on the effect of environmental variables (biofouling and flow) on field uptake rates (Rsf) of pesticides.
- Due to extent of biofouling, it is unlikely that SPMDs reached equilibrium conditions during either study period - in this case, deployments longer than 28 days are necessary.
- Need more detailed flow measurements (data loggers).
- Reality check: actual differences in chlorpyrifos uptake between study periods were relatively low.
- How to get PRCs to Costa Rica - Anyone?

¡MUCHAS GRACIAS!

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Environmental Sampling Technologies
International Network for the Improvement of Banana and Plantain (INIBAP)
Ministerio de Ambiente y Energía (MINAE)
Universidad Nacional

CATIE
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