Non-Destructive Measurement of Pyrethroids on Fabrics: A Review for VCWG

Feb 19, 2014
Karl Malamud-Roam
The IR-4 Project
Collaboration

- IR-4 = U.S. Federal/State Program (est. 1963)
  - Goal: facilitate development of pest management tools in small markets
  - Public Health Pesticides (PHP) Program
- CDC: Mike Green & Steve Smith
- USDA: Uli Bernier
- U.S. DoD: Melynda Perry
- UC: Matt Hengle
Problem #1

- Clothing treated with permethrin often fail to provide adequate bite protection before the garment itself has failed.
- The pesticide treatment cannot be seen, smelled, or otherwise readily measured.
- Definitive chemical assays are destructive.
Problem #2

- Pyrethroid-treated Nets (ITN; LLIN) are critically important for malaria control, but
- it does not appear feasible now to routinely measure the concentration of pesticides on nets in the field.
Hypotheses

- Reliable methods of non-destructive determination of pyrethroids on fabrics (clothing, nets, etc.) are technically feasible;
- Such methods many be operationally useful;
- Operational use of such methods will require
  - definition of performance criteria,
  - technical optimization,
  - rigorous comparison of methods, &
  - definition of analytical role within programs.
Analytical Chemistry

- GC/HPLC = Extraction & Separation
- MS, MS/MS = Detection & Quantitation
- High precision for all known pesticides
- Destroys sample
- Expensive lab tool
- Highly trained technician needed
Other Measurements

- Analytical extraction & quantitation
- Electro-magnetic spectra
  - X-ray fluorescence
  - IR absorption
  - UV fluorescence?
  - Optical (Indicator)?
- Non-destructive chemical assays
  - Minor extraction & Colorimetry
  - ELISA?
Pesticide Estimation

• Estimation = Use of Indirect Proxy
• Bioassay
  – Caged mosquito tests = Effective concentration
• Other proxies
  – Wash count
  – Use / deployment time
  – Wear, abrasion, weight loss, etc.?
• Per-garment/net vs. population estimates
## Electromagnetic Tests

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>AM Radio</th>
<th>Short wave radio</th>
<th>Television FM radio</th>
<th>Microwaves radar</th>
<th>Millimeter waves, telemetry</th>
<th>Infrared</th>
<th>Visible light</th>
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- **Low frequency**
- **Long wavelength**
- **Low quantum energy**

- **High frequency**
- **Short wavelength**
- **High quantum energy**
X-Ray Fluorescence

- Non-destructive, fast, accurate
- Measures elements, not chemicals
- Commercial rugged field instruments exist
- Ca. $40,000
• Deltamethrin tests precise & replicable
• X-rays penetrate folded nets
• In field: 885 nets / 6 days
• Cost / unit low
X-Ray vs. Chlorine

- Air absorption of low-energy X-rays (2.62 keV)
- Other Cl sources
  - Pigments, sweat, sea, etc.
- New instruments
- New methods?
IR Absorption

- Bonds absorb for bending, bowing, etc.
- Commercial rugged field instruments exist
- Ca. $35,000 for multi-function hand-held instrument
Mid-IR Absorption of Cotton, Nylon 6 6, and Permethrin
IR Absorption

[Graph showing IR Absorption with two lines: Untreated ACU and Treated, Normalized 2]
Other electromagnetic

• UV Fluorescence
  – Electron excitation & response has typical signal for atoms.
  – Good evidence for high sensitivity in agricultural residue studies
  – Prototype development 2014?
  – Potential instrument cost $5,000?

• Indicator Dye
  – Search for color with similar fate to pesticides
Chemical Assays

- Goal: simple, inexpensive, and accurate field test to measure insecticides on the surface of the net (CDC; IVCC; etc.?)
Cyanopyrethroid Field Test Kit
Extract on Filter Paper
Standardized Colorimetry
Bioassay vs. Chemo-assay

Deltamethrin CFT values (µg/sample)

% Mosquito Mortality

- Killian et al. 2008 (n=6)
- Kroeger et al. 2004 (n=1)
- Graham et al. 2005 (n=3)
- CDC (n=9)
- Vestergaard (n=1)

Deltamethrin whole net levels (mg/m²)
CDC/Laos (Deltamethrin)

The IR-4 Project

Threshold for net failure

$\frac{t}{2} = 5.6$ months

$\frac{t}{2} = 2.4$ months

Deltamethrin proportion of new net

Months

Upper side panel (position B)

Bottom side panel (position E)
Chemo-Assay Challenges

- Specificity to alpha-cyano group?
- Standardization of extraction
- Variability of pesticide on nets
  - Net top vs. bottom
  - Surface vs. bulk
- ELISA (immunoassays)
New Chemo-Assays?

- Reagents independent of alpha-cyano group
  - Permethrin (Steve Smith; CDC)
- ELISA (immunoassays)?
Chemical Distinctions

Permethrin (4 stereoisomers)

Alpha-Cypermethrin

Deltamethrin
Fabric Polymers

Cotton Cellulose

Nomex (Kevlar)

HPDE Polyethylene

Nylon 6,6

PET Polyester
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<th>Permethrin</th>
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<th>Alpha-Cypermethrin</th>
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Performance Criteria

• Sensitive & accurate
• Effective for all fabric composition
• Field-deployable (rugged, easy to train)
• Acceptable to users
• Inexpensive
  – Individual items vs. aggregate characterization
• Applicable to all treated fabrics
  – Nets, clothing, wall hangings, shade/rain covers, blankets, etc.
### Feasibility Summary

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<th>All Materials?</th>
<th>User Acceptability</th>
<th>Cost</th>
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