Comparison of Wipe Materials and Wetting Agents for Pesticide Residue Collection

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Background

- Various wipe methods have been used for sampling surface pesticide residues
- Wipe materials employed
  - Cotton or rayon/polyester dressing sponges
  - Cotton gauze or cotton balls
  - Filter paper
  - Polyurethane foam

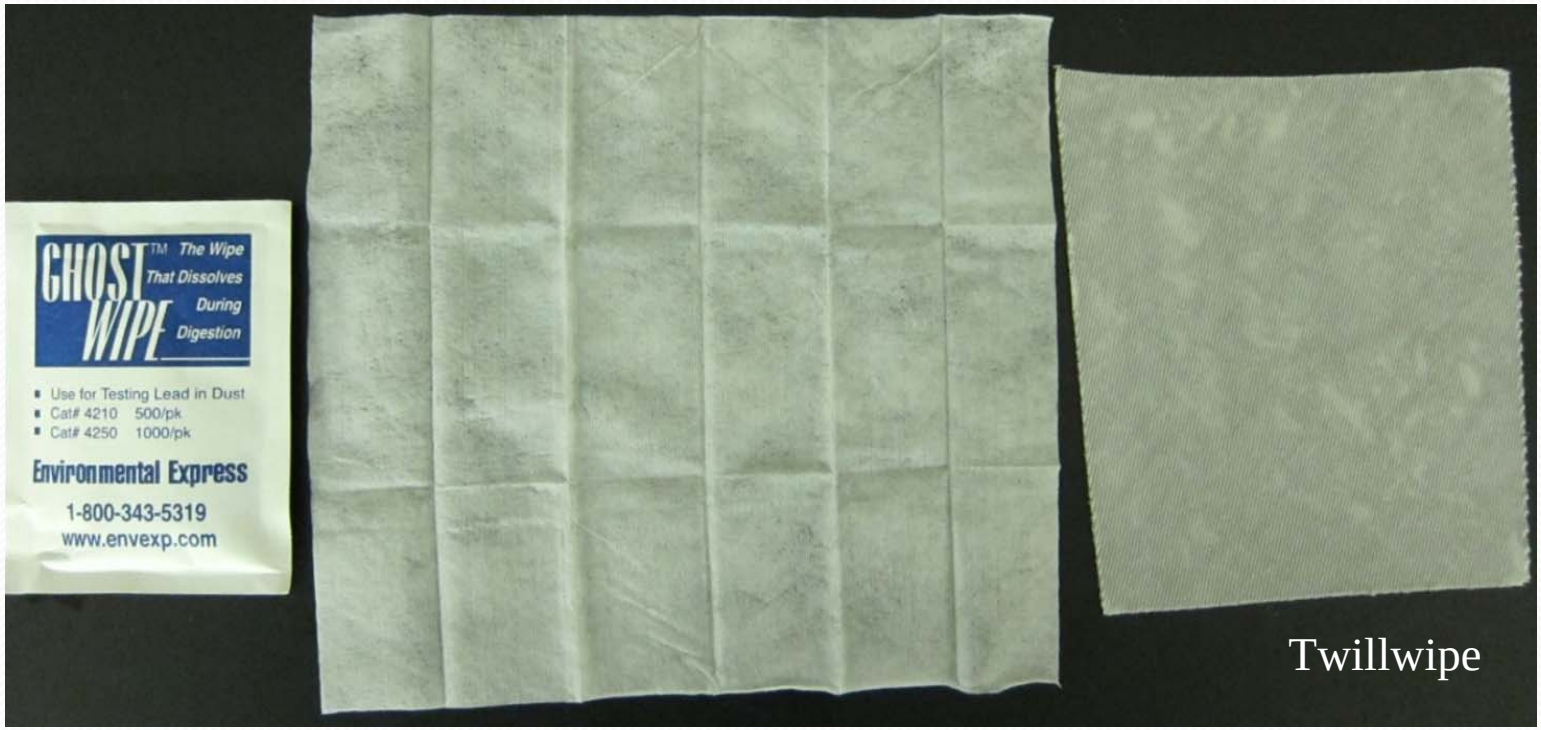
- Possibility of changes in production, discontinuation of branded media, potential analytical interferences

Background - continued

- Wetting agents employed
  - Isopropanol
  - Water
  - Sweat simulant (70:30 phosphate buffer:acetonitrile)
  - Methanol
  - Hexanes
- Potential damage to surfaces, perception of odor, variable collection efficiency
- Relatively little known about reliability, validity, and comparability of different methods

Study Design

- 3 wipes selected for study:
  - Pre-cleaned Twillwipe (4.5 in x 4.5 in, M. G. Chemicals) wetted with 2 mL of deionized water (TW)
  - Pre-cleaned Twillwipe (4.5 in x 4.5 in), M. G. Chemicals) wetted with 2 mL of isopropanol (TI)
  - Ghost Wipe (pre-packaged, 6 in x 6 in, Environmental Express), wetted with 4 mL deionized water



Study Design - continued

- 3 x 2 factorial design – 3 wipes at high and low pesticide concentrations

- Sample size selected to ensure 80% power to detect a 20% difference in mean collection efficiency and a two-fold difference in CVs between wipes
  - 26 replicates per wipe - 13 replicates at high analyte concentrations and 13 at low analyte concentrations

Wipe Preparation

- Precleaning of Twillwipe (for TW, TI)
  - 9 x 9 inch wipes cut into 4 sections of 4.5 x 4.5 inch
  - Up to 50 pieces placed in 5L Soxhlet extractor
  - Extracted in 1.5L water, 2-3 turnovers/hour for 24 hours
  - Dried in vacuum oven 8 hours
  - Procedure repeated with isopropanol and n-hexane

- GW – Prepackaged, no precleaning

27 Pesticides Tested

Organochlorines

α-Chlordane
γ-Chlordane
4,4'-DDE
4,4'-DDT
Heptachlor

Organophosphates

Chlorpyrifos
Diazinon
Malathion

Pyrethroids

Allethrin
Bifenthrin
Cyfluthrin
λ-Cyhalothrin
Cypermethrin
Deltamethrin
Esfenvalerate
Fenpropathrin
Imiprothrin
cis-Permethrin
trans-Permethrin
Prallethrin
Pyrethrin I
Pyrethrin II
Resmethrin
Sumithrin
Tetramethrin

Other

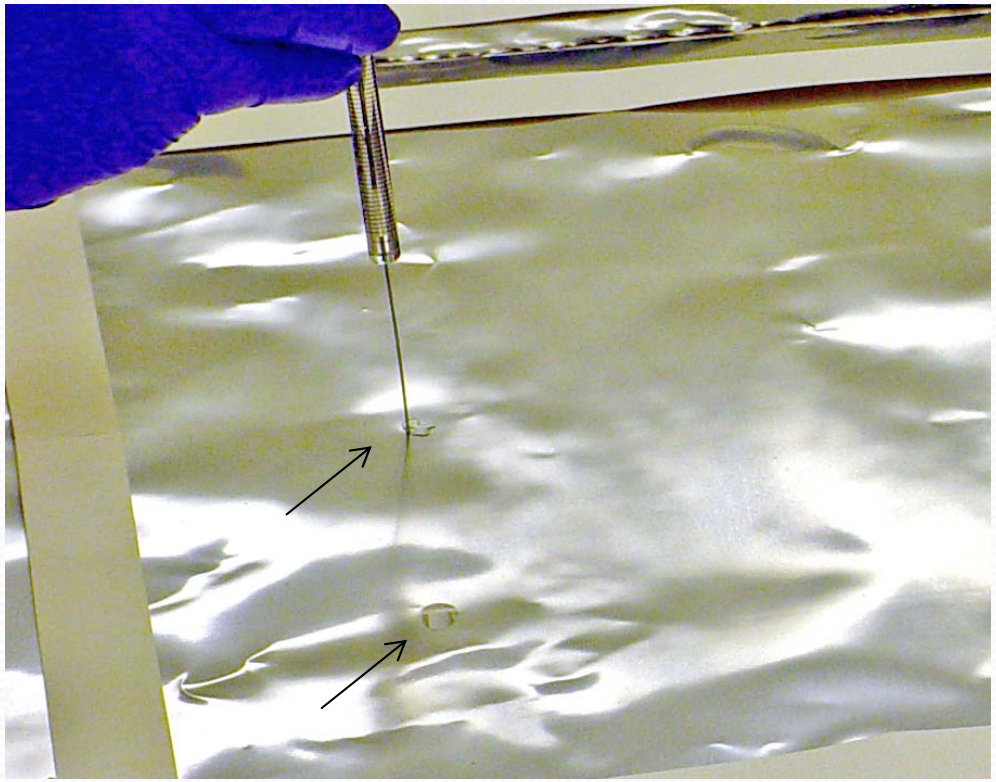
Fipronil
Piperonyl butoxide

Test Surface Preparation

- Stainless steel tool wrap 309SS mounted on plywood with double-sided foam adhesive
- Surface cleaned with acetone and allowed to dry
- 13 disposable sets of triplicate templates (interior sampling area = 1 sq. ft.) secured with masking tape

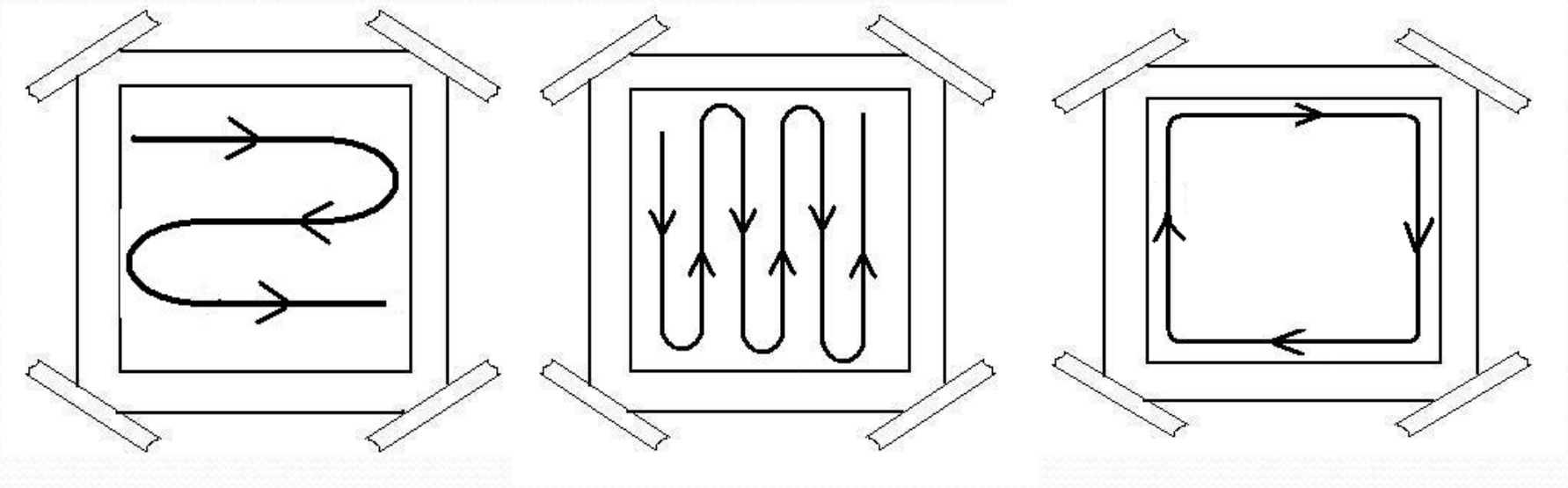
Test Surface Preparation – cont'd

- Spiking solutions prepared in ethyl acetate
  - 27 pesticides in each solution
  - Low spiking solution corresponded to ~ 8 x DL
  - High spiking solution corresponded to ~ 80 x DL
  - Concentrations of some pyrethroids were elevated
- Nine 10-µL drops (90 µL) placed within wiping each area, allowed to air dry



Wipe Sample Collection

- Each 1 sq ft area wiped according to NCS Pyrethroid Wipe Protocol (parallel to ASTM Wipe Method for Lead)
  - S-shaped wipe from left to right, folded
  - S-shaped wipe up and down, folded
  - Perimeter wipe



- Placed in 60-mL amber glass jar
- Stored at -20°C until extraction

Extraction

- Wipe samples spiked with diazinon (diethyl-d_{10}), tetrachloro-m-xylene (TCMX), and decachlorobiphenyl as extraction surrogates
- Soxhlet-extraction with 250mL hexanes:acetone (1:1) for 16 hours
- Pass extract through anhydrous sodium sulfate to remove water
- Concentrate extract to 1.0mL volume in 10% acetone in hexanes

GC/MS Analysis

- GC column: Mid-polarity phase, 35% Phenyl polysilphenylene-siloxane (30m; 0.25mm id; 0.25 µm film thickness)
- Pulsed splitless injection
- 4,4’-Dibromobiphenyl as internal standard
- Six-point calibration curve covering a 50-fold range
- Mass spectrometer in selected ion monitoring (SIM) mode

Quality Control

- One sampling blank of each wipe (TW, TI, GW) before collection of low level replicates
- One sampling blank of each wipe (TW, TI, GW) before collection of high level replicates
- One spike of high level spike solution (90 µL) directly onto each wipe (TW, TI, GW) after collection of high level replicates
- One solvent blank with each extraction batch of 21 – 24 samples

Statistical Analysis

- Collection efficiency = ratio of measured to known spiked amount of each pesticide
- Used measured amount when below DL
- Used log-transformed collection efficiency
- Linear mixed model (SAS MIXED procedure) used to assess differences among wipes
- Precision based on coefficient of variation (CV) of collection efficiency

Results – Analytical Feasibility

- No component interference or background of target pesticides in any wipe
- Mean recovery across three field spikes:
  - 80-105% for 19 pesticides
  - 70-79% for diazinon, malathion, pyrethrin I, imiprothrin, deltamethrin
  - Esfenvalerate (68%), fipronil (64%), pyrethrin II (51%)
- Extraction surrogate recoveries: 75-102% over the 13 replicates at each spike level
- Lower (56-69%) recovery of more volatile TCMX surrogate from GW in last 6 high-level replicates

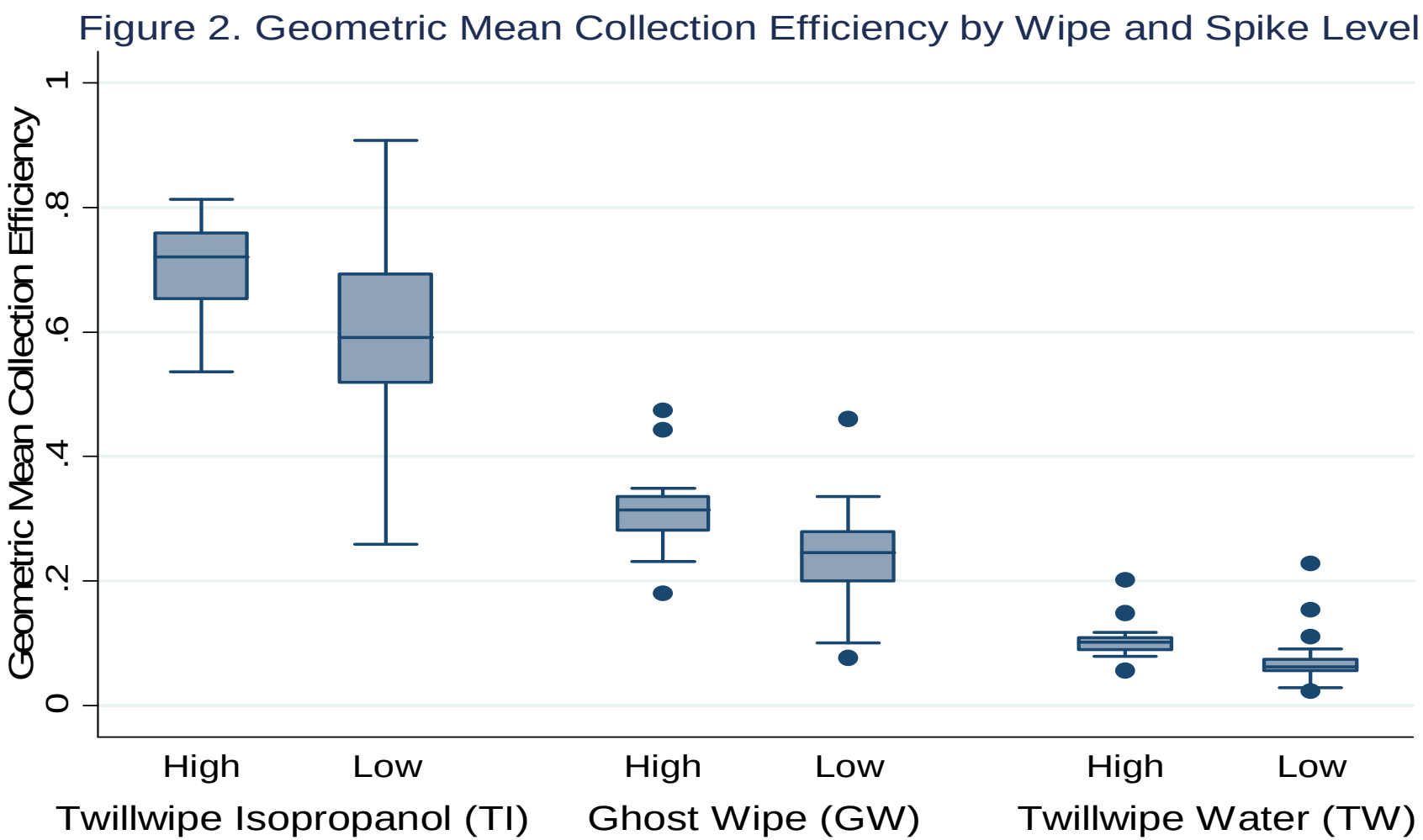
Results – Collection Efficiency over 27 Pesticides

Arithmetic Mean

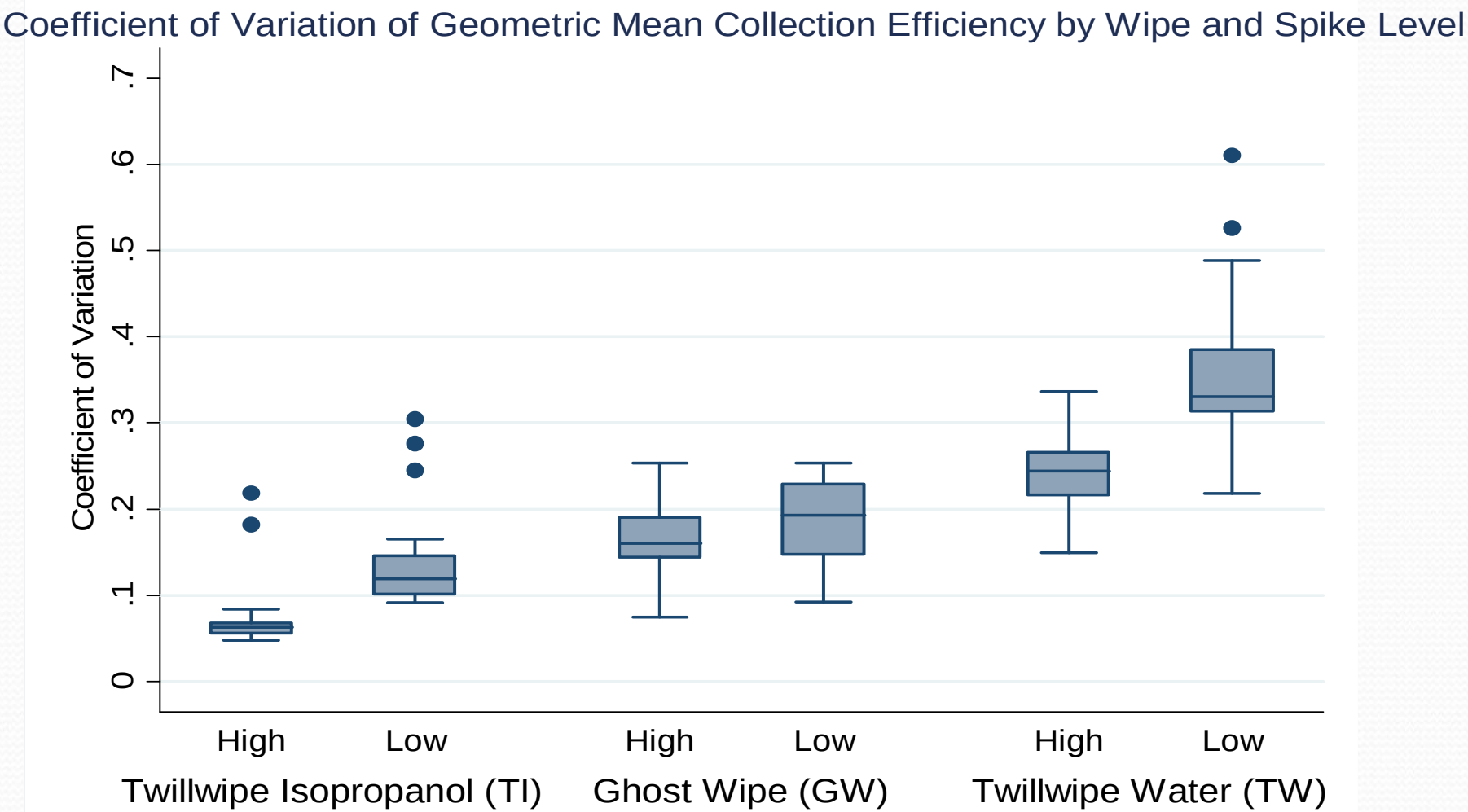
(95% Confidence Interval)

Pesticide Concentration	TI	GW	TW
Low	57.1% (53.3, 61.2)	22.9% (20.9, 25.0)	6.6% (5.6, 7.8)
High	69.8% (67.1, 72.6)	3o.8% (28.2, 33.8)	10.2% (8.9, 11.6)

Results - Collection Efficiency



Results - Precision



Results – Operational Issues

- Twillwipe with Isopropanol (TI)
  - Defined threadcount, weave, finishing, ruggedness
  - Can be rigorously precleaned
  - Can be wetted with optimal liquid volume
  - Requires pre-wetting in field
  - Difficult to fold during wiping
  - Isopropanol can damage some surfaces, strong odor
- Ghost Wipe (GW)
  - Standardized manufacture – could be customized
  - Pre-packaged
  - Same wipes as used for metals, same procedure
  - Mild odor

Conclusions

- Demonstrated a valid methodology for comparison of wipe methods
- Showed clear and significant differences between collection efficiency and precision of 3 wipes at both concentration levels
- Allows comparison of analytical results across wipe methods

Conclusions - continued

- Allows selection of wipe appropriate to study needs:
  - If low detection limits are required, select wipe with highest collection efficiency – Twillwipe wetted with isopropanol
  - If ease of use in field is desired and participant concerns are issues, e.g., large multi-center epidemiology study like the National Children's Study – consider Ghost Wipe (possibly customized)

Questions?

- Contactncs@mail.nih.gov

- Study conducted as formative research in the National Children's Study.