Comparison of Wipe Materials and Wetting Agents for Pesticide Residue Collection from Hard Surfaces

Nicole C. Deziel[a], Susan M. Viet*[a], John W. Rogers[a], David E. Camann[b], David A. Marker[a], Maire S. A. Heikkinen[a], Alice Y. Yau[b], Daniel M. Stout II[c], and Michael Dellarco[d]

[a]Westat, 1600 Research Blvd, Rockville, Maryland 20850
[b]Southwest Research Institute, 6220 Culebra Road, San Antonio, TX 78228-0510
[c]National Exposure Research Laboratory, U.S. Environmental Protection Agency, 109 T.W. Alexander Dr., Research Triangle Park, North Carolina 27711
[d]*Eunice Kennedy Shriver* National Institute of Child Health and Human Development, The National Children's Study, 6100 Executive Boulevard, Suite 3A01, Bethesda, MD 20892-7510
*Corresponding Author: Westat, 1600 Research Blvd, Rockville, Maryland 20850, Email: susanviet@westat.com, Phone: 301.610.5514, Fax: 301.610.4900

Short title: Comparison of pesticide surface wipe methods

ABSTRACT

Different wipe materials and wetting agents have been used to collect pesticide residues from surfaces, but little is known about their comparability. To inform the selection of a wipe for the National Children's Study, the analytical feasibility, collection efficiency, and precision of Ghost Wipes (GW), Twillwipes wetted with water (TW), and Twillwipes wetted with isopropanol (TI) were evaluated. Wipe samples were collected from stainless steel surfaces spiked with high and low concentrations of 27 insecticides, including organochlorines, organophosphates, and pyrethroids. Samples were analyzed by GC/MS/SIM. No analytical interferences were observed for any of the wipes. The mean percent collection efficiencies across all pesticides for the TI, GW, and TW were 69.3%, 31.1%, and 10.3% at the high concentration, respectively, and 55.6%, 22.5%, and 6.9% at the low concentration, respectively. The collection efficiencies of the TI were significantly greater than that of GW or TW ($p<0.0001$). Collection efficiency also differed significantly by pesticide ($p<0.0001$) and spike concentration ($p<0.0001$). The pooled coefficients of variation (CVs) of the collections efficiencies for the TI, GW, and TW at high concentration were 0.08, 0.17, 0.24, respectively. The pooled CV of the collection efficiencies for the TI, GW, and TW at low concentration were 0.15, 0.19, and 0.36, respectively. The TI had significantly lower CVs than either of the other two wipes ($p=0.0008$). Though the TI was superior in terms of both accuracy and precision, it requires multiple preparation steps, which could lead to operational challenges in a large-scale study.

Keywords: validation; collection efficiency; precision; pesticide; wipe; National Children's Study

1. Introduction

The National Children's Study (NCS) is a Congressionally mandated, multicomponent, multiyear, prospective study that will examine many effects of environmental influences on the health and development of 100,000 children from before birth until age 21. The study will investigate the impact of broadly defined chemical, biological, physical, and psychosocial environmental exposures on children's health, with the ultimate goal of improving the health, development, and well being of children. Included among the numerous environmental exposure metrics for chemicals in the Vanguard Study are home pesticide levels obtained from wipes from hard surfaces. Pesticides targeted for analysis include residential use pyrethroids, organophosphates, and organochlorines.

A variety of wipe materials were considered for inclusion in the NCS. Wipe materials employed in previous studies to collect pesticides include commercially available media such as cotton or rayon/polyester microfiber dressing sponges (Stout et al., 2009), cotton gauze and cotton balls (Cohen Hubal et al., 2006; Fenske et al., 1990; Geno et al., 1996; Gordon et al., 1999; Tulve et al., 2008; Tulve et al., 2006), analytical grade filter paper (Lioy et al., 2000; Lioy et al., 1993; Lu and Fenske, 1999; Lu et al., 2000; McCauley et al., 2001; Mohan and Weisel, 2009; Sexton et al., 2003), and polyurethane foam (Lewis et al., 1994; Lu and Fenske, 1999).

Reliance on commercially available media not produced for environmental sampling raises the possibility of changes in production parameters, discontinuation of branded media, and potential analytical interferences that may result in variability in performance over time and a general lack of standardization. Based on these considerations, the Twillwipe and the Ghost Wipe were included as candidates for the NCS. The Twillwipe is a tightly woven cotton wipe that has the advantages of general availability, standardization by the textile industry, ruggedness

of the fiber for use in wiping different surface textures, and ability to withstand aggressive pre-cleaning procedures. The Ghost Wipe, a pre-wetted polyvinyl alcohol wipe, is designed to collect metals and offers the advantages of being pre-wetted, individually packaged, ready to use, and commercially available in bulk.

Several types of wetting agents have been used previously, depending on the study objective. Studies attempting to simulate skin moisture to obtain surface to skin transferability data or hand-to-mouth transfer information have often used aqueous-based wetting agents. In contrast, studies aiming to determine surface concentrations to establish potential human exposures have often selected organic solvents. The wide range of wetting agents reported in the literature include isopropanol (Bernard et al., 2008; Cohen Hubal et al., 2006; Julien et al., 2008; Lioy et al., 2000; McCauley et al., 2001; Tulve et al., 2006), water (Fenske et al., 1990; Lu and Fenske, 1999; Mohan and Weisel, 2009), sweat simulant (70:30 phosphate buffer:acetonitrile) (Nishioka et al., 1999), methanol (Gurunathan et al., 1998), and hexane (Gurunathan et al., 1998; Lioy et al., 2002). Concerns have been raised about the use of some wetting agents in residential settings, such as isopropanol, methanol, and hexane, due to the potential to damage some surface finishes (Bernard et al., 2008; Lioy et al., 2002). In addition, participant perception of solvent odors and potential flammability issues, particularly during shipping, are also potential drawbacks for alcohols and hexane. A potential limitation of using water as the wetting agent is lower collection efficiency compared to organic solvents (Hoppin et al., 2006; Mohan and Weisel, 2009).

Few studies have validated collection techniques and as a result, relatively little is known about the reliability, validity, and comparability of pesticide measurements collected with these different wipe materials and wetting agents (Bernard et al., 2008; Lioy et al., 2002). This

laboratory-based, experimental study compares the analytical feasibility, mean collection efficiency, and precision of three selected wipe materials and wetting agent combinations to inform the selection of a surface wipe for the NCS.

2. Materials and Methods

2.1. Study Design

Three wipes were selected for evaluation: 1) pre-cleaned cleanroom Twillwipe (4.5 in x 4.5 in, M. G. Chemicals, Toronto, Ontario, Canada) wetted with 2 mL of deionized water (TW); 2) pre-cleaned cleanroom Twillwipe (4.5 in x 4.5 in), wetted with 2 mL of isopropanol (TI); and 3) Ghost Wipe (6 in x 6 in, Environmental Express, Mt. Pleasant, SC), an individually packaged polyvinyl alcohol wipe pre-wetted with deionized water (GW).

The three wipes (TW, TI, GW) were compared at two (high and low) analyte spike concentrations to determine which had the highest mean collection efficiency and the greatest precision (characterized by the lowest coefficient of variation or CV). Twenty-six replicates of each wipe (13 at high concentration, 13 at low concentration) were required to ensure an 80% power to detect a two-fold difference in CVs and a 20% difference in collection efficiencies between wipes, based on data from two prior studies (Bernard et al., 2008; Julien et al., 2008).

2.2. Wipe Pre-cleaning

The Twillwipes (9 in x 9 in) were sectioned into four pieces (4.5 in x 4.5 in). To remove potential interfering compounds, the Twillwipe pieces were Soxhlet extracted in 1.5 L of superclean water at a cycle rate of 2 to 3 turnovers per hour for 24 hours. Twillwipes were dried in a vacuum oven at elevated temperatures for approximately eight hours until solvent odors

were not detectable. The extraction and drying procedures were repeated using isopropanol and then n-hexane (both pesticide grade or better). The cleaned and dried Twillwipes were stored in a certifiably cleaned 3 L amber glass jar with a PTFE-lined cap until use. The Ghost Wipes did not undergo any pre-cleaning.

2.3. Pesticide Application to Test Surface

Thirteen surfaces were prepared by mounting stainless steel tool wrap 309SS (Grainger Industrial Supply, 5XE78) on each of 13 plywood sheets (46 in x 22 in x 0.5 in) with double-sided foam adhesive. Stainless steel was selected over more commonly encountered household surfaces to minimize potential interferences and bias due to surface porosity and treatments. Prior to use, each wipe surface was cleaned with laboratory-grade absorbent wipes wetted with acetone and allowed to air dry. Three disposable templates constructed from card-stock paper with interior sampling area of 1 ft^2 (929 cm^2) were placed side-by-side on each stainless steel surface and secured with masking tape, without contacting the area inside each template (Fig. 1).

Two spiking solutions (one low and one high concentration) of 27 pesticides, selected for analysis in the NCS, were prepared in ethyl acetate. The low and high concentrations corresponded to approximately 8 and 80 times the estimated detection limit for each target chemical, respectively (Table 1). For pyrethrins, concentrations were elevated due to the relative concentration available in the commercially available product. Nine 10 µL drops (total volume of 90 µL) were placed onto the stainless steel surface within the confines of each of the three templates following a 3 in x 3 in grid pattern (drop separation distance of approximately 3 in). The spiking solution was allowed to air dry, a process which took approximately 90 seconds. After one set of experiments at low spike concentration, the stainless steel was removed and

replaced with new stainless steel tool wrap, mounted to create 13 additional wipe surfaces for the high spike concentration experiment.

2.4. Wipe Preparation and Sample Collection

Ghost Wipes are pre-wetted with 4 mL of deionized water by the manufacturer and therefore required no preparation. Just prior to sample collection, the Twillwipes were either wetted with deionized water (ASTM Type I reagent water) or isopropanol (Acros Organics, Geel, Belgium, 99.8+ % purity) by placing a wipe in a solvent rinsed Pyrex pie plate and pipetting 2 mL of water or isopropanol in an S-shape over it. A 2 mL aliquot was determined to be the maximum volume that could be completely absorbed in the Twillwipe without leaving large droplets of liquid on the test surface following the wiping procedures.

Each of the three wipes (TW, TI, or GW) was used to collect a single sample from within a template on each prepared surface. The area within the template was wiped in accordance with the NCS Standard Operating Procedure for Collection of Pyrethroid Wipes (NICHD, 2009). Using S-shaped, slightly overlapping motions, the wipe samples were collected first by wiping from left to right. The wipe was folded in half and used to wipe the same area in an up-and-down direction. The wipe was folded in half again and used to wipe the area around the perimeter of the sampling area. The wipe was folded in half again and placed in a straight-sided 60 mL amber glass jar. The jar was sealed with a PTFE lined lid and stored under darkened conditions at -20 °C until extraction.

2.5. Analytical Method

Wipes were extracted and analyzed using a variation of multi-residue method implemented in the American Healthy Homes Survey (Stout et al., 2009). Each wipe sample was

Soxhlet-extracted for 16 hours with 200 mL of acetone:hexane (1:1 v:v). Prior to extraction, samples were spiked with extraction surrogates composed of 0.3 μg diazinon-d_{10}, 0.3 μg of tetrachloro-m-xylene and 0.5 μg of decachlorobiphenyl. Each extract was concentrated and brought up to a final volume of 1.0 mL in 10% acetone in hexane prior to GC/MS analysis. Calibration standards and sample extracts were analyzed using an Agilent 6890 gas chromatograph (GC) coupled to an HP 5973 benchtop quadrupole mass selective detector (MSD) operated in selected ion monitoring (SIM) mode with electron ionization. The capillary GC column was a TR-35MS column (30 m x 0.25 mm i.d., 0.25 μm film thickness; Thermo Scientific, Waltham, MA, USA) and the carrier gas was helium set at a flow rate of 1.2 mL/min. Injections by Agilent 7683 autosampler (2 μL) were made in pulsed splitless mode with an injection temperature of 300°C and a pulsed pressure of 345 kPa, which was held for 0.7 min. The GC/MS interface transfer line was held at 340°C. Following injection, the column was held at 100 °C for 1 min, increased at 25°C/min to 225 °C, and increased at 5 °C/min to 320 °C. Two or three ions for each target analyte and extraction surrogate were monitored during the analysis. 4,4'-dibromobiphenyl was used as the GC/MS internal standard.

Calibration of the target analytes and surrogates was established by injecting six calibration standards ranging from 5 to 250 times the detection limit. The calibration curve was generated using the theoretical analyte concentration vs. the relative area (analyte area/internal standard area). The coefficient of determination (r^2) of the curves was greater than 0.99 for each of the target analytes using either a first or second order equation. Initial GC/MS analysis of the low concentration wipe samples was performed over a three-day period using an Agilent 6890/5973 instrument. To improve sensitivity, the analysis of deltamethrin, esfenvalerate, cyfluthrin, and cypermethrin in the low concentration wipe samples was repeated using an

Agilent 7890/5975 instrument. The GC/MS analysis of the high concentration level wipe samples was performed during a separate three-day period and encountered no significant analytical difficulties. If the target analyte was observed at the proper retention time and the identifying criteria were met, the measured value was reported. If no signal was detected in the retention window, the concentration was reported as not detected.

2.6. Quality Control Samples

Blanks of each wipe type (TW, TI, GW) were obtained before collection of both the low-level and high-level replicates by wiping the cleaned foil surface (unspiked). One solvent blank per 21 to 24 samples was used to assess any analyte contamination or analytical interferences introduced during extraction. Spiked media was obtained by fortifying one of each wipe with nine drops of the high-level multi-pesticide solution (Table 1) following the collection of the high-level replicates.

2.7. Statistical Analysis

Collection efficiencies were calculated as the ratio of the amount of the pesticide measured on the wipe sample to the known amount spiked onto the sampling surface. Arithmetic means and 95% confidence intervals were calculated for descriptive purposes. All other statistical analyses were performed using the natural logarithm of the collection efficiency measurements. The log transformation was used to facilitate estimation of the CVs and to ensure that all predicted concentrations were greater than zero. Using the log-transformed data, mean collection efficiencies across pesticides were calculated for each combination of replicate, wipe and spike level. Variances in collection efficiencies across replicates for each combination of

pesticide, wipe, and spike level were averaged across pesticides to calculate pooled variances by wipe and spike level. For presentation, means and variances of log-transformed collection efficiencies were converted to geometric means and CVs of collection efficiencies. Variance (σ^2) was converted to CV assuming the log-transformed values had a normal distribution, using Eq. 1. The pooled variances were converted to CVs using Eq. 1 and are referred to as "pooled CVs." For each replicate, wipe and spike level, the "overall collection efficiency" was calculated as the geometric mean of the collection efficiencies across pesticides.

$$CV = \sqrt{e^{\sigma^2} - 1} \qquad (1)$$

A linear mixed model was used to assess collection efficiency differences among wipes using the SAS MIXED procedure. The model combined a three-way analysis of variance model for the mean log-transformed collection efficiency with a variance model with several components of variance. The analysis of variance model included all main effects and interactions of three factors: wipe, spike concentration, and pesticide. The variance model included components for differences among wipe surfaces within spike concentration, differences among wipe samples within type of wipe (TW, TI, and GW), and laboratory measurement error of pesticide concentrations in each wipe sample. Pesticide measurements on the wipe samples of the same type were treated as repeated observations and the among wipe variance was assumed to differ by the type of wipe.

To assess precision differences among wipes using the overall collection efficiency measure, Levene's test, adapted for these data, was implemented as follows using the SAS GLM procedure: the log-transformed overall collection efficiency was predicted by the interaction of wipe material and spike level, and Levene's test was applied to the residuals using a model with

only wipe material as the independent predictor. CVs for the different variance components were calculated from the mixed model variance component estimates using Equation 1.

3. Results

3.1. Analytical Feasibility

Analysis of blanks and samples revealed no component interference or background amount of any target pesticide from the matrix. The mean recovery across the three field spike matrices was between 80% and 105% for 19 of the target pesticides, but lower (70 to 79%) for diazinon, malathion, pyrethrin I, imiprothrin, and deltamethrin, and poorer (51 to 68%) for esfenvalerate, fipronil, and pyrethrin II. The mean recoveries of the three extraction surrogates for all three types of wipes ranged between 75% to 102% over the 13 replicates and were within acceptable QC parameters (70% to 130%). The more volatile tetrachloro-m-xylene surrogate in some replicates of the high concentration-level GW wipes showed recoveries of 56% to 69%. The extraction surrogate recoveries suggest that all wipe replicate extractions performed well, except for slightly less efficient extraction of some of the more volatile pesticides, such as heptachlor, diazinon, malathion, and chlorpyrifos, in some of the high-level GW wipes.

3.2. Collection Efficiency

All but two pesticides were detectable in all measurements at both high and low spike concentration. Eleven of the thirteen replicates of the TW wipe for cyfluthrin and cypermethrin at the low spike concentration level were undetectable. Due to these high rates of non-detection, data for cyfluthrin and cypermethrin for all three wipes were excluded from the figures, the statistical analysis, and the calculation of the overall collection efficiency. Excluding only cyfluthrin and cypermethrin measurements in TW had only a minimal effect on the statistical

estimates and would not have changed the conclusions. It was determined to be more prudent to exclude these analytes from all further analyses.

Table 1 presents the percent arithmetic mean collection efficiencies and 95% confidence intervals for each pesticide, wipe, and spike concentration. There were clear differences between wipes with the overall mean collection efficiencies of the TI, GW, and TW wipes at the low spike concentration of 55.6%, 22.5%, and 6.9%, respectively. The overall mean collection efficiencies of the TI, GW, and TW wipes at the high spike concentration were 69.3%, 31.1%, and 10.3%. For each spike concentration and pesticide, the associated confidence intervals do not overlap, demonstrating that the TI had statistically significant higher collection efficiency than the GW, which in turn was statistically significantly higher than TW. Fig. 2 presents the distributions of the arithmetic mean collection efficiencies by wipe and spike concentration. A comparison of the medians and inter-quartile ranges demonstrates that the collection efficiency with the TI is superior to the GW or the TW.

Results of the 3-way analysis of variance mixed model are presented in Table 2. Wipe, pesticide, and spike concentration were all statistically significant predictors of collection efficiency ($p<0.0001$). The interactions involving pesticides were all significant, indicating that not only was the observed collection efficiency different among pesticides, but in addition, those differences depended on the combination of pesticide, wipe, and spike concentration.

3.3. Precision

The collection efficiencies using the TI were more precise (lower CV) than those using the GW, which were more precise than those using the TW (Figure 3). The pooled CVs for the TI (0.08), GW (0.17), and TW (0.24) wipes at high spike concentrations were less than the

pooled CVs for the TI (0.15), GW (0.19), and TW (0.36) wipes at low spike concentrations. Levene's test found the overall precision differences among wipes to be statistically significant ($p<0.0008$).

The variance component estimates from the mixed model, expressed as CVs in Table 3, provide additional information on the possible sources of the variation. The measurement error CV is smallest for the TI wipe and largest for the TW wipe, and smaller for the high spike concentration compared to the low spike concentration. The among-wipe variance components are similar in magnitude to the measurement error variance components. A relatively small additional variability was associated with differences among the 13 wipe surfaces. Based on the combined effect of the measurement error and among wipe variance components, measurements using the TI wipe are more precise than measurements using the GW wipe, which are more precise than measurements using the TW wipe.

4. Discussion

Despite its importance, little work has been done to compare the performance of commonly used wipe materials and wetting agents for pesticide residue collection. This study found that samples collected with the Twillwipe wetted with isopropanol had significantly greater accuracy and precision compared to the Twillwipe wetted with water or the Ghost Wipe. However, some of the operational issues associated with the field use of these sampling media must be considered when selecting a wipe for a study.

The Twillwipe with isopropanol yielded an overall collection efficiency of 69.3% at high spike concentration and 55.6% at low spike concentration. Bernard et al. (2008) conducted a

validation study in a subset of the pesticides examined in the current study at two concentrations for two wipe collection methods, including surface wipes with isopropanol, observed collection efficiencies of 84% to 97% using a cotton gauze wipe wetted with isopropanol for select pesticides (Bernard et al., 2008). The observed higher collection efficiencies in the Bernard study may be due to differences in the experimental design. Bernard et al. used spike concentrations that were one to three orders of magnitude greater than the current study. In addition, they used two wipes (an isopropanol-wetted wipe followed by a dry wipe) and had a longer contact times with the test surface (2 or 10 minutes).

As expected, collection with isopropanol yielded higher collection efficiencies compared to water. Most of the pesticides in the analytical suite exhibit low water solubility. Therefore, it would be expected that isopropanol would be an overall more efficient solution for solvating a residue. Our finding that collection efficiencies were higher when isopropanol was used as the wetting agent compared to water was consistent with a study by Mohan and Weisel (2009). Using the "Lioy-Weisel-Wainman" press sampler to collect an unspecified formulation of permethrin from a hard surface, they observed a higher collection efficiency when using isopropanol (90%) as a wetting agent compared to water (46%). They attributed this reduction to the water not fully wetting the sampling medium. Modifications to their design yielded a dramatically improved 74% to 90% collection efficiency with water, but it is unclear if solvation of surface residues or the mechanical action of the wipe matrix abrading over the surface were the primary factors contributing to the increased efficiency.

The increased collection efficiency and higher precision exhibited by the GW as compared to the TW could be due to the presence of monomers from the polyvinyl alcohol wipe material. An alcohol scent was observed when Ghost wipe packages were opened. Possibly the

addition of an organic component to the water could be responsible for the greater collection efficiency of the GW wipe as compared to the TW wipe, which is wetted purely with water. If true, this observation suggests the use of co-solvents could have the advantages of reducing odor, minimizing flammability, or increasing collection efficiency in future studies, and warrants further exploration.

Certain pesticides were not collected with great efficiency or precision by any of the methods evaluated. Pyrethrin II, fipronil, and diazinon were collected with less than 60% efficiency with all wipes at both high and low concentrations. The instability of natural pyrethrins (oxidation in air and photodecomposition) likely contributed to their relatively lower collection efficiencies. In addition, pyrethrins and their analogs (such as allethrin, resmethrin or prallethrin) are thermally labile and can be difficult to determine by GC analysis. Consequently, further optimization of the analytical method, including analysis by LC, might yield more reliable results.

In terms of precision, the TI was significantly more precise than the GW, which in turn was more precise than the TW. Because field measurements are generally more variable than controlled laboratory experiments, the pooled CV provides a lower bound estimate for the error variance when assessing similar levels of pesticides in the field. NIOSH gives a general guidance of 25% as an acceptable CV (NIOSH, 2003) and it is generally accepted that a sampling method with CV of less than 10% has high precision. At high concentrations, the pooled CV for all wipes met the NIOSH criterion of 25%. At low concentrations, the pooled CVs for the TI (15%) and GW (19%) met the NIOSH criteria, but the pooled CV for the TW (36%) exceeded it. Only the high concentration TI exhibited a CV of less than 10%. Greater precision at high

concentrations is a common finding, as measurements tend to be more variable at concentrations closer to the limit of detection.

Bernard et al. (2008) observed CVs of less than 25% at the high concentration for the 14 pesticides analyzed, and less than 27% at low concentrations for 13 different pesticides and 32% for deltamethrin. This was for both hard and carpeted surfaces with 8 replicates. Again, this greater precision may be because these experiments were conducted at concentrations one to three orders of magnitude greater than in the current study.

Our mixed model allowed us to explore the components of the variability in the collection efficiency measurements. The lower measurement precision associated with TW and low spike concentrations is related, at least partially, to lower precision for measurements closer to the detection limit. There are additional differences in collection efficiency among wipes of the same type, perhaps reflecting, in part, variation in how the technician wiped the test surfaces using the different wipes. The variance component reflecting variation in collection efficiency among the test surfaces is likely to be larger when collecting wipe samples in the field than this laboratory setting, due to greater variability in the types and properties of the wide range of surfaces in residences.

On a study of the magnitude of NCS, emphasis is put on the operational characteristics of the sampling media, such as cost, packaging, ease of use, durability, stability of media and collected analytes during long term storage, minimal and/or well-characterized interferences, and availability of sampling media for procurement for the entire study duration. The three wipes employed in this study were durable and easy to use. The Ghost Wipe had some favorable qualities. It yielded acceptable CVs, is commercially available, and because it is ASTM certified for metal collection, it likely has established production standards and a continuous supply. Due

to its larger dimension, the GW was observed to be easier to manipulate and wipe within the confines of template. The Ghost Wipe has the distinct advantage of convenience by being pre-wetted, individually packaged, and ready to use when opened.

An advantage of the Twillwipe is that cotton fabric is produced under standards as specified by the textile industry. Consequently, material can be procured following defined standards in terms of thread count, weave, finishing and ruggedness. Another benefit of the Twillwipe is that it can be rigorously pre-cleaned using custom conditions as required for the analytes of interest. However, such pre-cleaning increases costs. Twillwipes or cotton media are versatile in that they can be wetted using a range of solvents based on the solubility of the target compounds and study demands. The Twillwipes, prepared for this study, were cut from the manufacturers stock to smaller dimension than the GW, and found to be harder to use for wiping. TW and TI were found to leave less solvent on the stainless steel surface following wiping than with the GW which may be associated with the more sorbent qualities of the cotton fabric or the customized volume of the wetting agents. It was noted that the Twillwipe was difficult to fold due to its tight weave and had to be placed in a wide container (Pyrex pie plate) to be wetted with water or isopropanol. Wetting a Twillwipe in a home setting might pose difficulties due to space limitations, the presence of an isopropanol odor, and the potential for media contamination. These issues could be overcome by pre-wetting the wipe prior to site visits while employing rigorous field quality control procedures to identify field contamination issues. The effects of evaporation of wetting agents and potential for media contamination require additional evaluation if wipes were wetted in advance. Also, additional time required by technicians to prepare the wipe media is a drawback in a large scale field study where multiple sample types are collected.

Some concerns regarding wetting agents, particularly isopropanol, have been raised due the potential to damage surface finishes (Bernard et al., 2008; Lioy et al., 2002). However, the American Healthy Homes Survey, a study which sampled floors with hard surfaces in 500 homes using an isopropanol wetted wipe material reported no resulting damage of flooring surfaces or finishes (Pinzer, E., personal communication, 10/30/2009).

5. Conclusion

The need for progress towards standardization of a method for sampling surfaces for the pesticide residues in residential environment is exemplified in the numerous methods available in the literature. Too often the methods deployed have lacked validation and have practical or analytical deficiencies resulting in poor between-study comparability. This study represents an important step towards producing systematically validated evaluations of wipe media for field collection of pesticide residues. The final question is which methodological approach for collecting these pesticides from hard surfaces is supported by these findings and might be recommended to researchers interested in sampling these particular pesticides. Because of its superior accuracy and precision, use of the Twillwipe wetted with isopropanol in the NCS and other epidemiological studies has the potential to reduce exposure misclassification, in particular where pesticide levels on environmental surfaces are low. However, it requires lengthy preparation steps, such as pre-cleaning and wetting in the field. These steps can become a significant use of resources in a large-scale study such as the NCS but must be weighed against the value of a standardized approach capable of efficiently collecting a sufficient mass for the purposes of generating survey results and model inputs for risk assessments and relationships to health outcomes.

This study illustrates the tradeoffs that can be encountered with the selection of available commercial materials for surface wipe sampling in longitudinal cohort studies. In this case the Ghost Wipe is easy to use, its pre-packing affords minimal preparation requirements for field use, and provides adequate reproducibility when deployed. In contrast, the Twillwipe with isopropanol gives greater accuracy and reproducibility, but requires additional preparation for field use to achieve its superior characteristics, and may be more cumbersome to deploy in the field. The additional preparation required for field use may result in instances of increased variability. Consequently, there are limitations associated with each media that must be considered depending on the nature and scope of the study. Moreover, the lack of commercially available prepackaged wipe materials with different wetting agents highlights the need in the marketplace for a better selection of environmental sample collection materials.

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Fig.1. Three side-by-side templates on the stainless steel sampling surface for one replicate set. One wipe type (GW, TI, TW) was used within one template.

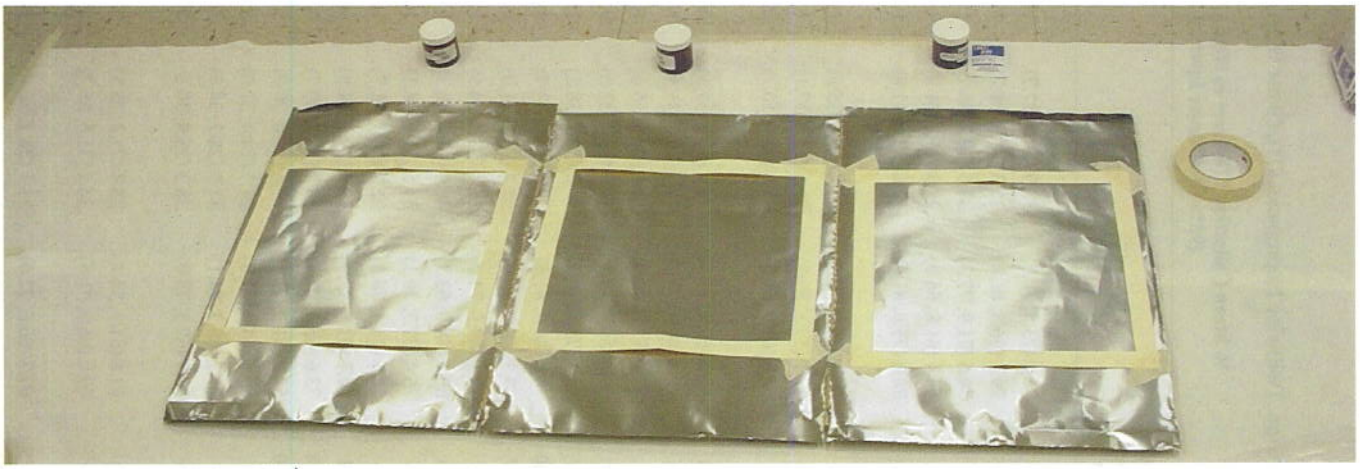

Table 1
Arithmetic mean collection efficiency (%) for each target pesticide at low and high spike concentrations for each wipe: Twillwipe Isopropanol (TI), Ghost Wipe (GW), and Twillwipe Water (TW).

			% Mean Collection Efficiency at Low Concentration (95% Confidence Interval)				% Mean Collection Efficiency at High Concentration (95% Confidence Interval)		
Analyte	**Detection Limit (ng)**	**Low Spike Amount (ng)**	**TI**	**GW**	**TW**	**High Spike Amount (ng)**	**TI**	**GW**	**TW**
Organochlorines									
α-chlordane	5	40	69.7 (66.0, 73.4)	26.6 (24.4, 28.8)	7.3 (5.9, 8.7)	400	76.0 (73.5, 78.5)	33.9 (30.5, 37.2)	11.2 (9.5, 12.9)
γ-chlordane	5	40	73.5 (69.4, 77.5)	27.6 (25.3, 29.9)	7.6 (6.2, 9.1)	400	79.1 (76.5, 81.8)	35.3 (31.9, 38.7)	11.7 (9.9, 13.5)
4,4-DDE	2	16.2	69.6 (65.7, 73.4)	26.6 (24.3, 29.0)	7.3 (6.0, 8.7)	162	74.6 (71.9, 77.3)	33.5 (30.2, 36.7)	11.0 (7.9, 10.7)
4,4-DDT	2	15.8	54.2 (49.4, 59.1)	22.8 (19.9, 25.8)	9.2 (8.0, 10.5)	158	64.4 (61.8, 66.9)	28.2 (25.2, 31.3)	9.3 (7.9, 10.7)
heptachlor	10	81	44.0 (39.6, 48.4)	15.4 (13.6, 17.2)	5.3 (4.1, 6.6)	810	78.0 (75.0, 81.0)	28.6 (25.4, 31.8)	10.6 (9.0, 12.1)
Organophosphates									
chlorpyrifos	10	81	71.0 (66.9, 75.2)	24.9 (22.8, 26.9)	7.7 (6.3, 9.2)	810	77.1 (74.7, 79.5)	32.8 (29.6, 35.9)	11.6 (9.9, 13.2)
diazinon	5	40	49.9 (47.0, 52.8)	33.4 (31.6, 35.2)	11.2 (9.9, 12.6)	400	57.1 (55.3, 59.0)	34.6 (32.1, 37.1)	11.8 (10.8, 12.9)
malathion	5	40	60.2 (56.6, 63.8)	46.4 (42.9, 49.9)	23.8 (20.0, 27.6)	400	62.8 (61.0, 64.6)	47.6 (45.0, 50.2)	20.3 (18.5, 22.1)
Pyrethroids									
allethrin	100	800.4	54.1 (50.6, 57.6)	19.7 (18.3, 21.1)	6.3 (5.1, 7.6)	8004	72.8 (69.9, 75.7)	31.7 (29.1, 34.3)	10.6 (9.1, 12.1)
bifenthrin	2	15.8	65.3 (60.9, 69.6)	28.3 (25.0, 31.6)	7.7 (6.0, 9.5)	158	72.2 (69.9, 74.4)	32.4 (29.3, 35.5)	10.3 (8.7, 12.0)
cyfluthrin	10	79.8	91.6 (84.2, 99.0)	34.1 (30.5, 37.7)	<14.0[a]	798	75.9 (73.0, 78.9)	31.2 (27.5, 35.0)	10.5 (8.8, 12.3)
λ-cyhalothrin	10	79.9	53.4 (49.2, 57.6)	19.8 (17.3, 22.3)	4.8 (3.6, 6.0)	799	68.2 (65.9, 70.5)	28.7 (25.4, 32.0)	9.2 (7.6, 10.7)
cypermethrin	20	159.7	84.2 (79.2, 89.2)	30.3 (27.4, 33.2)	<12.8[a]	1597	81.4 (78.5, 84.3)	34.2 (30.1, 38.2)	11.9 (10.0, 13.8)
deltamethrin	200	1600	68.7 (64.3, 73.0)	21.2 (18.2, 23.9)	5.7 (4.6, 6.8)	16000	78.2 (74.9, 81.5)	29.9 (26.0, 33.7)	9.3 (7.6, 11.0)
esfenvalerate	100	799.7	80.0 (74.9, 85.2)	25.1 (21.9, 28.2)	6.4 (5.1, 7.7)	7997	67.3 (64.7, 70.0)	27.2 (23.4, 31.0)	8.7 (7.2, 10.2)
fenpropathrin	10	79.9	59.6 (55.1, 64.0)	21.5 (19.0, 24.0)	5.7 (4.4, 7.1)	799	72.1 (69.5, 74.7)	31.4 (28.4, 34.5)	10.0 (8.3, 11.6)
imiprothrin	100	799.6	43.8 (40.7, 47.0)	32.1 (29.7, 34.6)	16.0 (13.1, 19.0)	7996	60.6 (58.0, 63.3)	44.4 (42.4, 46.3)	15.0 (13.6, 16.3)
cis-permethrin	5	39.6	64.6 (59.7 69.4)	27.3 (23.8, 30.8)	6.0 (4.5, 7.6)	396	76.4 (73.7, 79.1)	34.5 (31.0, 38.1)	10.7 (8.9, 12.6)
trans-permethrin	5	40.2	62.9 (57.8, 67.9)	23.1 (20.3, 25.8)	6.3 (5.2, 7.5)	402	74.1 (71.4, 76.8)	32.2 (28.7, 35.7)	10.4 (8.7, 12.2)
prallethrin	100	956.4	52.2 (48.7, 55.7)	20.2 (18.6, 21.8)	6.5 (5.3, 7.6)	9564	70.7 (67.5, 73.9)	32.3 (29.7, 34.8)	10.5 (9.1, 12.0)
pyrethrin I	172	3235	35.0 (30.4, 39.6)	10.2 (9.0, 11.4)	3.1 (2.4, 3.8)	32350	73.6 (66.3, 80.8)	28.2 (25.8, 30.7)	8.3 (6.6, 9.9)
pyrethrin II	128	2411	26.7 (22.7, 30.7)	7.8 (6.7, 8.9)	2.4 (1.8, 3.0)	24110	57.2 (51.2, 63.1)	18.5 (16.0, 20.9)	5.9 (4.7, 7.1)
resmethrin	5	40	53.9 (50.9, 57.0)	21.1 (19.1, 23.1)	5.8 (4.7, 6.8)	400	65.4 (63.1, 67.8)	27.7 (24.4, 31.0)	8.8 (7.4, 10.2)
sumithrin	5	39.9	59.8 (55.1, 64.5)	25.1 (22.0, 28.2)	7.9 (6.3, 9.5)	399	71.7 (69.3, 74.1)	31.5 (28.2, 34.7)	10.2 (8.6, 11.8)
tetramethrin	2	16	61.0 (48.6, 73.4)	22.4 (19.2, 25.6)	6.9 (4.6, 9.2)	160	70.3 (67.5, 73.0)	28.3 (25.9, 30.6)	10.2 (8.6, 11.8)
Other									
fipronil	5	40.2	41.7 (38.7, 44.7)	18.8 (17.1, 20.4)	7.3 (6.1, 8.5)	402	53.8 (51.1, 56.4)	23.4 (21.3, 25.5)	9.0 (8.1, 10.0)
piperonyl butoxide	2	16	57.9 (54.7, 61.2)	30.7 (28.6, 32.8)	9.3 (8.0, 10.7)	160	69.0 (66.3, 71.6)	34.2 (31.6, 36.7)	11.1 (9.6, 12.5)
Overall									
overall[a]			55.6 (52.0, 59.2)	22.5 (20.6, 24.3)	6.9 (5.7, 8.0)		69.3 (66.6, 72.0)	31.1 (28.3, 33.8)	10.3 (8.9, 11.8)

[a]Mean of two detected values. Data for cyfluthrin and cypermethrin are excluded from the statistical analyses and the overall mean.

Fig. 2. Mean collection efficiency by wipe and spike concentration. Box extends from 1st to 3rd quartile; bars reflect most extreme point within 1.5 times the inter-quartile range.

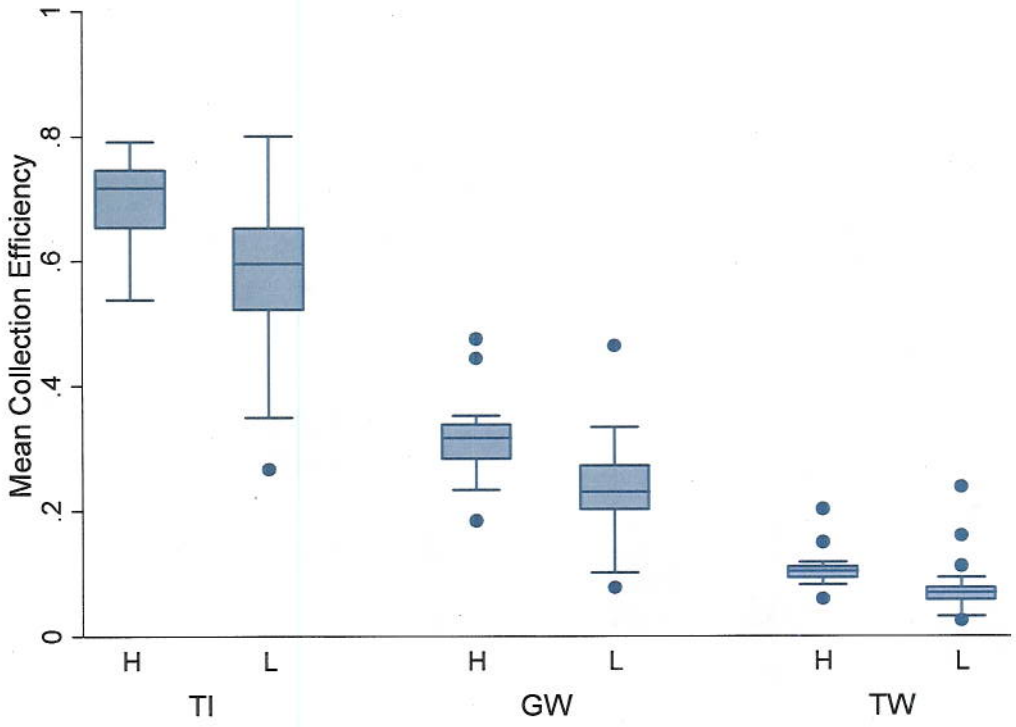

Fig. 3. Coefficient of Variation of the geometric mean collection efficiency by wipe and spike concentration. Box extends from 1st to 3rd quartile; bars reflect most extreme point within 1.5 times the inter-quartile range.

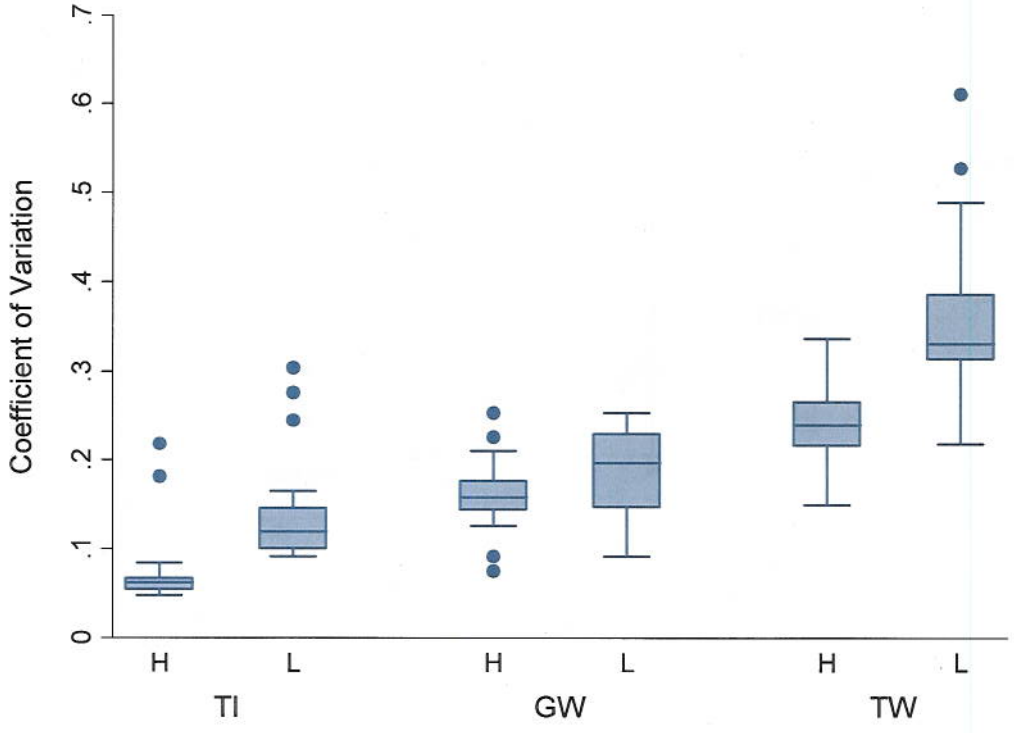

Table 2. Fixed effects in linear mixed model predicting geometric mean collection efficiency.

Fixed Effects	Degrees of Freedom		F-Value	P-value
	Numerator	Denominator		
Spike concentration	1	24	58.85	<0.0001
Wipe	2	48	1148.74	<0.0001
Spike concentration*wipe	2	48	3.07	0.0557
Pesticide	24	1728	309.93	<0.0001
Pesticide*spike concentration	24	1728	74.99	<0.0001
Pesticide*wipe	48	1728	75.76	<0.0001
Pesticide*spike concentration*wipe	48	1728	7.10	<0.0001

Table 3. Coefficients of variation (CV) associated with variance components, derived from mixed model.

Wipe	Spike Concentration	Measurement Error CV	Among Wipe CV	Among Surface CV[a]
Twillwipe Isopropanol	High	0.048	0.075	
	Low	0.089		
Ghost Wipe	High	0.074	0.127	0.055
	Low	0.112		
Twillwipe Water	High	0.081	0.235	
	Low	0.205		

[a]Among Surface CV applies to all wipes and spike concentrations.

Abbreviations: ASTM, American Society for Testing and Materials; CV, coefficient of variation; GW, Ghost Wipe; NCS, National Children's Study; TI, Twillwipe wetted with isopropanol; TW, Twillwipe wetted with water

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Supplemental Information: Run parameters and target ions for the analytes

Column Flow Rate: 1.2 mL/min Helium
Injection Port Temperature: 300°C
Injection Volume: 2 µL pulsed splitless for 0.75 min
Oven Temperature Program: 100°C for 0.5 min; 100-225 °C @ 25°C/min, 225-320°C@ 5°C/min, hold at 320°C for 5 min
Transfer Line Temperature: 285°C
MS Zone Temperatures: MS Quad – 150°C / MS Source – 230°C

Compound	Primary Ion	Secondary Ions (Q1, Q2)
GC/MS Internal Standard(s)		
4,4'-Dibromobiphenyl	312	314
Organophosphorus pesticides		
Chlorpyrifos	314	316, 197
Diazinon	304	276, 179
Malathion	173	256, 125
Organochlorine pesticides		
Chlordane (α & γ)	373	375, 377
p,p'-DDE	318	316, 246
p,p'-DDT	235	237, 165
Heptachlor	272	274, 270
Pyrethrins and Pyrethroids		
Allethrin	302	136, 123
Bifenthrin	181	165, 166
Cyfluthrin	206	226, 163
Cypermethrin	163	181, 165
Deltamethrin/Tralomethrin	251	253, 255
Esfenvalerate	167	225, 419
Fenpropathrin	181	97, 265
Imiprothrin	318	123
lambda-Cyhalothrin	197	208, 181
cis-Permethrin	183	163, 165
trans-Permethrin	183	163, 165
Prallethrin	134	123, 300
Pyrethrin I	133	123, 161
Pyrethrin II	161	160, 133
Tetramethrin	164	165
Sumithrin	183	184, 123
Resmethrin	171	123