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

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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 Twillwipes wetted with isopropanol (TI), Ghost Wipes (GW), and Twillwipes wetted with water (TW), and 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 collection efficiencies for the TI, GW, and TW at high concentration were 0.08, 0.17, and 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

collection efficiency; precision; pesticide; wipe; National Children's Study

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1. Introduction

The National Children's Study (NCS) is a Congressionally mandated, multicomponent, multiyear, prospective study that will examine the impact of broadly defined chemical, biological, physical, and psychosocial environmental exposures on the health and development of 100,000 children from before birth until age 21. Included among the numerous potential environmental exposure metrics under consideration are home pesticide levels obtained from wipes from hard surfaces. Pesticides targeted for analysis include past and current residential-use pyrethroids, organophosphates, and organochlorines.

A variety of wipe materials were considered for surface sampling in the NCS based on prior performance, product availability over the study period, and ease of implementation in a large-scale study. Wipe materials used previously to collect pesticides include 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; Stout and Leidy, 2000; Tulve et al., 2008; Tulve et al., 2006; Bernard et al., 2008), 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). Commercially available wipe materials targeted for general consumer use (e.g., cotton gauze and surgical sponges) may be susceptible to changes in production parameters, such as thickness, texture, and chemical additives that may result in variability in performance, introduce chemical interferences, and result in a general lack of standardization. Wipe media produced specifically for environmental sampling or requiring adherence to industry-based specifications may be less likely to undergo frequent product changes. For example, the Twillwipe, a tightly woven, rugged, cotton wipe, was considered for inclusion within NCS, because it is widely available and standardized by the textile industry and capable of withstanding intensive cleaning processes involving a range of solvents. The Ghost Wipe, a pre-wetted polyvinyl alcohol wipe, meets ASTM specifications for lead collection and is commercially available in bulk. The Ghost Wipe is also pre-wetted, individually packaged, and ready to use, making it relatively easy to implement in a large-scale study.

Wetting agents were considered for the NCS based on past performance and minimizing potential damage to residential surfaces. 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 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 (Stout et al., 1995; 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). 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). Participant perception of solvent odors and potential flammability issues associated with transport and shipping are also potential concerns for alcohols and hexane. However, use of water as a wetting agent could result in lower collection efficiencies compared to organic solvents (Hoppin et al., 2006; Mohan and Weisel, 2009).

Relatively little is known about the reliability, accuracy, and comparability of pesticide measurements collected with these different wipe materials and wetting agents (Bernard et al., 2008; Liroy et al., 2002). This laboratory-based, experimental study compares the analytical feasibility, mean collection efficiency, and precision of three wipe material 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 (9 in $\times$ 9 in M. G. Chemicals, Toronto, Ontario, Canada) wetted with 2 mL of deionized water (TW); 2) pre-cleaned cleanroom Twillwipe wetted with 2 mL of isopropanol (TI); and 3) Ghost Wipe (6 in $\times$ 6 in, Environmental Express, Mt. Pleasant, SC, USA), an individually packaged polyvinyl alcohol wipe pre-wetted with 4 mL deionized water (GW). The three wipes (TW, TI, GW) were compared at two analyte spike concentrations to determine the mean collection efficiency and the 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

Twillwipes were pre-cleaned to remove contamination with pesticides as well as other chemicals associated with the textile manufacturing process that might interfere with the chemical analysis. The Twillwipes (9 in $\times$ 9 in) were sectioned into four pieces (4.5 in $\times$ 4.5 in) Soxhlet extracted in 1.5 L of superclean water at a cycle rate of 2 to 3 turnovers per hr for 24 hr. Twillwipes were dried in a vacuum oven at elevated temperatures for 8 hr at 50°C. The extraction and drying procedures were repeated using isopropanol and then n-hexane (both analytical grade, EMD Chemicals, Gibbstown, NJ, USA). 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, being pre-packaged and pre-wetted, did not undergo any pre-cleaning.

2.3. Pesticide Application to Test Surface

Thirteen surfaces were prepared by mounting stainless steel tool wrap 309SS (Part number: 5XE78, Grainger Industrial Supply, USA) on each of 13 plywood sheets (46 in $\times$ 22 in $\times$ 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. Prior to use, each wipe surface was cleaned with laboratory-grade absorbent wipes (Kimwipes, Kimberly-Clark, Dallas, TX, USA) wetted with acetone (>95.5% purity, Thermo Fisher Scientific, Waltham, MA, USA) and allowed to air dry. Three disposable templates constructed from card-stock paper with an interior sampling area of 1 ft² (929 cm²) were placed side-by-side on each stainless steel surface and secured in position with masking tape (Fig. 1).

Two spiking solutions (one low and one high concentration) consisting of 27 pesticides (Sigma Aldrich, St. Louis, MO, USA or Chem Service, West Chester, PA, USA) were prepared in ethyl acetate (>99.9% purity, Thermo Fisher Scientific, Waltham, MA, USA). The low and high concentrations corresponded to approximately 8 and 80 times the estimated detection limit for each target chemical, respectively (Table 1). A volume of 90 μ L of the low concentration spiking solution, which contained the low spike amounts given in Table 1 of the 27 pesticides, was drawn into a 100 μ L syringe. Nine 10 μ L drops (a 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 $\times$ 3 in grid pattern (droplet separation distance of approximately 3 in). The droplets dried by solvent evaporation after approximately 90 seconds. Wipe samples were collected 7 to 10 minutes after spiking of the stainless steel surface. Subsequently, the stainless steel was removed and replaced with new stainless steel tool wrap and mounted to create 13 additional wipe surfaces for the high concentration experiment.

2.4. Wipe Preparation and Sample Collection

Ghost Wipes are pre-wetted with 4 mL of deionized water by the manufacturer and required no preparation. Prior to sample collection, the Twillwipes were either wetted with deionized water (Direct-Q 5 system, Millipore, Bedford, MA, USA) or isopropanol (99.8 % purity, Acros Organics, Geel, Belgium) by placing a wipe in a solvent rinsed Pyrex pie plate and pipetting 2 mL of deionized water or isopropanol in an S-shape onto the media. 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 the confines of a template placed on each prepared surface. The area within the template was wiped in accordance with the NCS Standard Operating Procedure for Collection of Pyrethroid Wipes (NICHHD, 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 wiped around 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 $-20\text{ }^{\circ}\text{C}$ until extraction.

2.5. Analytical Method

Wipes were extracted and analyzed using a variation of a multi-residue method implemented in the American Healthy Homes Survey (Stout et al., 2009). Prior to extraction, samples were spiked with surrogate standards composed of 0.3 μg diazinon- d_{10} (C/D/N Isotopes, Pointe-Claire, Quebec, Canada), 0.3 μg of tetrachloro-m-xylene (Restek, Bellefonte, PA, USA), and 0.5 μg of decachlorobiphenyl (Restek, Bellefonte, PA). Each wipe sample was Soxhlet-extracted for 16 hours with 200 mL of acetone:hexanes (1:1) (Thermo Fisher Scientific, Waltham, MA; purity of hexanes $\geq 99.9\%$; purity of acetone $\geq 99.5\%$). Each extract was concentrated and brought up to a final volume of 1.0 mL in 10% acetone in hexanes prior to GC/MS analysis. Calibration standards and sample extracts were analyzed using an Agilent (Santa Clara, CA, USA) 6890 gas chromatograph (GC) coupled to an Agilent 5973 benchtop quadrupole mass selective detector (MSD) operated in selected ion monitoring mode with electron ionization. The capillary GC column was a TR-35MS column (30 m $\times$ 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 $300\text{ }^{\circ}\text{C}$ and a pulsed pressure of 345 kPa, which was held for 0.7 min. The GC/MS interface transfer line was held at $340\text{ }^{\circ}\text{C}$. Following injection, the column was held at $100\text{ }^{\circ}\text{C}$ for 1 min, increased at $25\text{ }^{\circ}\text{C}/\text{min}$ to $225\text{ }^{\circ}\text{C}$, and increased at $5\text{ }^{\circ}\text{C}/\text{min}$ to $320\text{ }^{\circ}\text{C}$. Two or three ions for each target analyte and extraction surrogate were monitored during the analysis. 4,4'-dibromobiphenyl (Restek, Bellefonte, PA) was used as the internal standard to monitor the performance of the GC/MS system and to determine the relative area in the calibration process.

Calibration of the target analytes and surrogates was established by injecting 6 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 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 and high concentration 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 were obtained by fortifying the blank media with aliquots of the standard solution at the concentrations shown in Table 1.

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. For each replicate surface, wipe type, and spike level, the “overall collection efficiency” was calculated as the geometric mean of the collection efficiencies across pesticides. Variances in collection efficiencies across replicates for each combination of pesticide, wipe type, and spike concentration were averaged across pesticides to calculate pooled variances by wipe and spike concentration. 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.”

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

A linear mixed model was used to assess collection efficiency differences among wipes using the SAS MIXED procedure (SAS 9.2, SAS Institute Corporation, Inc., Cary, NC). 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 type, 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 concentration, 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 Eq. 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 concentration 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, the 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 did not change 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 type, and spike concentration. There were clear differences between wipe types 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%, respectively. 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 type 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 type, 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 those differences depended on the combination of pesticide, wipe type, 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 observed that samples collected with the TI had significantly greater accuracy and precision compared to the TW or the GW. 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 mean collection efficiencies of the TI in the current study were lower than those reported with cotton wipes wetted with isopropanol in Bernard et al. (2008), likely due to differences in experimental design. The range of the mean collection efficiencies for seven pesticides included in both studies (chlorpyrifos, malathion, fipronil, permethrin, cyfluthrin, cypermethrin, and deltamethrin) were 42–92% and 54–81% at low and high concentrations, respectively, in the current study compared to 84–97% and 96–100% at low and high concentrations, respectively, in Bernard et al. Similarly, Bernard et al. used cotton wipes wetted with isopropanol, but applied concentrations that were one to three orders of magnitude greater than the current study. Furthermore, they used a larger volume of wetting agent (10 mL) than in the current study (2 mL) and two wipes (a wetted wipe followed by a dry wipe).

Our selection of wetting agent volume was a balance between optimizing collection efficiency while utilizing a single wipe. In order to minimize the potential to damage some finished surfaces as small a volume of wetting agent as practical was used. Because wipes collect via the mechanical wiping action and the solvation of the surface, use of a greater wetting volume (e.g., 5 mL or 10 mL) would be expected to increase the collection efficiency of the TI or TW. However, our initial testing demonstrated that volumes greater than 2 mL left substantial liquid on the test surface, requiring following the wetted wipe with a dry wipe thereby increasing the potential for damage to floor surfaces and requiring additional wipe media. Because our objective was a direct comparison of a single TW and single TI with a single GW, and because the use of a second dry GW was unnecessary, use of a second dry Twillwipe would have biased the comparison of TW and TI with GW.

The collection with isopropanol yielded higher collection efficiencies compared to water, likely because most pesticides in the analytical suite exhibit low water solubility and would therefore more readily solubilize in isopropanol than water. This finding was consistent with a study by Mohan and Weisel (2009), who using the “Lioy-Weisel-Wainman” press sampler to collect an unspecified formulation of permethrin from a hard surface, 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 have been due to the presence of monomers from the polyvinyl alcohol wipe material. An alcohol scent was observed when Ghost wipe packages were opened, suggesting that some of the polyvinyl alcohol monomers from the wipe material could have been released into the deionized 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 low and high concentrations. Pyrethrins are relatively unstable and sensitive to decomposition by oxidative, thermolytic and photolytic processes which 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. Fipronil was shown in the American Healthy Home Survey (Stout et al., 2009) to exhibit similarly poor recoveries suggesting the compound may exhibit losses during the extractions process, particularly at such low concentrations. Diazinon is among the more volatile compounds included in the analytical suite and might have partly volatilized during the drying process following spiking the stainless steel surface. Consequently, further examination of methodological procedures and the optimization of the analytical method, including analysis by LC for the more unstable compounds, might yield more reliable results for these compounds.

Because a stainless steel surface was used to compare wipe performance, the collection efficiencies presented in the current study are likely higher than what would be found in the field. Because these collection efficiencies were not developed for the purposes of correction, use of the reported collection efficiencies to adjust measured field concentrations would have to be performed cautiously. Whether concentrations of pesticides measured from wipe samples should be corrected for collection efficiency depends on the study objective. In an epidemiologic study, collection efficiency correction would not change the relative ranking of the estimated exposure of the participants. However, if one is interested in estimating aggregate exposure or using the measurements to set safe levels, then the absolute exposure and not the relative exposure is of interest, and adjustment of concentrations may be warranted.

At high concentrations, the pooled CV for all wipes met the NIOSH guidance for acceptable CVs of 25% (NIOSH, 2003). 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. 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 <25% and <32% at high and low concentrations, respectively, but this included both hard and carpeted surfaces.

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 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, 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, 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 GW yielded acceptable CVs and collection efficiencies, is commercially available, likely has established production standards and a continuous supply, and is the easiest to implement in a large-scale study. Due to its larger dimension, the GW was observed to be easier to manipulate and wipe within the confines of template. The TI showed improved performance relative to the other wipes. Additionally, it is produced under standards as specified by the textile industry and can be readily procured while maintaining consistency by using industry standards such as thread count, weave, finishing and ruggedness. However, the TI requires precleaning and prewetting, drawbacks in a large-scale field study where multiple sample types are collected. Pre-cleaning is important for removal of potential analytical interferences as well as pesticide contamination, particularly when analyzing pesticides at trace levels. Past experience demonstrates that wipe media can contain interfering compounds (Stout et al., 2009). Given the challenges in measuring trace levels of pesticides in homes as well as the statistical challenges posed by prevalence of non-detected values in epidemiologic studies (Lubin et al., 2004), pre-cleaning can serve to maximize the probability of obtaining high quality measurements and improve detection frequencies. A benefit of the Twillwipe is that it can be rigorously pre-cleaned using custom conditions as required for the analytes of interest. Furthermore, it is versatile in that it 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. Conversely, the wipe is sufficiently versatile that it could easily be modified to accommodate user specified dimensions. 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.

5. Conclusion

The need for standardization of methods for sampling surfaces for the pesticide residues in residential environment is exemplified by the numerous and varied methods described in the literature. Too often these methods have lacked validation and have practical or analytical deficiencies resulting in poor between-study comparability. This study represents an

important step towards producing systematic evaluations of wipe media for the 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 the pesticides examined here. Because of its superior collection efficiency, accuracy and precision, broad availability and versatility, use of the Twillwipe wetted with isopropanol would be generally recommended. The media might be particularly suited for studies where field staff can be trained to efficiently perform the sampling procedure and minimize potential field contamination and where laboratory equipment for pre-cleaning is readily available. The Ghost Wipe is appealing for a large-scale study where the prepackaged convenience is highly desired to minimize technician as well as occupant burden or where target compounds are predominantly water soluble.

This study illustrates the tradeoffs that can be encountered with the selection of available commercial materials for surface wipe sampling in longitudinal cohort studies. There are limitations associated with each material 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.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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HIGHLIGHTS

We compared accuracy and precision of three wipes used for collecting pesticide residues in homes.

Twillwipes wetted with isopropanol had significantly greater accuracy and precision than Ghost Wipes or Twillwipes wetted with water.

Though superior, the Twillwipes with isopropanol require multiple preparation steps, a limitation for a large-scale study.

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.

Fig. 2.

Mean collection efficiency by wipe type and spike concentration.^{a,b}

^aTI, Twillwipe isopropanol; GW, Ghost Wipe; TW, Twillwipe Water; H, high concentration; L, low concentration.

^bBox 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 type and spike concentration.^{a,b}

^aTI, Twillwipe isopropanol; GW, Ghost Wipe; TW, Twillwipe Water; H, high concentration; L, low concentration.

^bBox extends from 1st to 3rd quartile; bars reflect most extreme point within 1.5 times the inter-quartile range.

Table 1

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

Analyte	Detection Limit (ng)	Low Spike		% Mean Collection Efficiency at Low Concentration (95% Confidence Interval)			High Spike Amount ^a (ng)	% Mean Collection Efficiency at High Concentration (95% Confidence Interval)		
		Amount ^a (ng)	TI	GW	TW	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 ^b	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 ^b	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)	

Analyte	Detection Limit (ng)	Low Spike		% Mean Collection Efficiency at Low Concentration (95% Confidence Interval)				High Spike		% Mean Collection Efficiency at High Concentration (95% Confidence Interval)			
		Amount ^d (ng)		TI	GW	TW		Amount ^d (ng)		TI	GW	TW	
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 ^b				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)	

^aThe low and high spike amounts correspond to approximately 8 and 80 times the estimated detection limit for each target chemical, respectively.

^bMean of two detected values. Data for cyfluthrin and cypermethrin are excluded from the statistical analyses and the overall mean.

Table 2

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

Fixed Effects	<u>Degrees of Freedom</u>		F- Value	P-value
	Numerator	Denominator		
Spike concentration	1	24	58.85	<0.0001
Wipe type	2	48	1148.74	<0.0001
Spike concentration*wipe type	2	48	3.07	0.0557
Pesticide	24	1728	309.93	<0.0001
Pesticide*spike concentration	24	1728	74.99	<0.0001
Pesticide*wipe type	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 Type	Spike Concentration	Measurement Error CV	Among Wipe CV	Among Surface CV ^a
Twillwipe Isopropanol	High	0.048	0.075	0.055
	Low	0.089		
Ghost Wipe	High	0.074	0.127	
	Low	0.112		
Twillwipe Water	High	0.081	0.235	
	Low	0.205		

^a Among Surface CV applies to all wipe types 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