For submission to *Analytica Chimica Acta*, 2011

Development of a simultaneous extraction and cleanup method for pyrethroid pesticides from indoor house dust samples[¶]

Jeanette M. Van Emon [1*] and Jane C. Chuang [2]

[1]National Exposure Research Laboratory, U.S. Environmental Protection Agency, Las Vegas, Nevada 89193-3478, USA (vanemon.jeanette@epa.gov)

[2]Battelle (retired), Columbus, Ohio, 43201-2693, USA (ccjane20@hotmail.com)

[*]Corresponding author:

Jeanette M. Van Emon, National Exposure Research Laboratory, U.S. Environmental Protection Agency, Las Vegas, Nevada 89193-3478, USA (vanemon.jeanette@epamail.epa.gov)

Abstract An efficient and reliable analytical method was developed for the sensitive and selective quantification of pyrethroid pesticides (PYRs) in house dust samples. The method is based on selective pressurized liquid extraction (SPLE) of the dust-bound PYRs into dichloromethane (DCM) with analysis by gas chromatography/ mass spectrometry. Various adsorbents and combinations of extraction solvents and temperatures were evaluated to achieve a high-throughput sample preparation that eliminates the post-extraction cleanup step. The final method used sulfuric acid-impregnated silica (acid silica) and neutral silica together in the extraction cell with the dust sample to provide both extraction and cleanup simultaneously. The optimal ratio of dust/acid silica/silica was 1:0.8:8. The extraction was performed at 2000 psi, at 100ºC with DCM for 5 min. in three cycles. Method precision and accuracy were evaluated by the analysis of triplicate aliquots of the dust samples and the samples fortified with the target PYRs. The accuracy measured as the recoveries of the PYRs in the fortified samples ranged from 85 to 120%. The precision measured as the relative standard deviation of replicate samples was within ±25%. The SPLE method was applied to 20 house dust samples collected from households that participated in two field studies regarding exposures to pesticides and other pollutants. Similar concentrations of target PYRs were obtained for the SPLE and a stepwise extraction/cleanup procedure. The on-line SPLE procedure reduces organic solvent consumption and increases the sample throughput when compared with a traditional stepwise extraction and cleanup procedure. This study demonstrates that the SPLE procedure can be applied to complex dust matrices for analysis of PYRs for large scale exposure or environmental monitoring studies.

Key words: pyrethroid pesticides, selective pressurized liquid extraction, SPLE, GC/MS, indoor sampling, dust.

1. Introduction

Pyrethroid pesticides (PYRs) are synthetic analogues of the natural insecticide pyrethrum (a mixture of pyrethrins and cinerins) found in chrysanthemum flowers. The natural pyrethrins and cinerins have high insecticidal activity, but are easily degraded in sunlight. PYRs are the result of modifying the chemical structures of the natural compounds to impart more stability while retaining similar insecticidal activity [1]. PYRs are neurotoxins with rapid paralysis or quick knock-down effect on target pests. PYRs are frequently used for agricultural, veterinary, and indoor/outdoor domestic pest control, partly due to their effectiveness at low dosages against a broad range of insect pests. There is an increasing trend in the use of PYRs indoors, as a result of the federally mandated phase-out of most residential uses of organophosphate (OP) pesticides, particularly chlorpyrifos and diazinon [2-3]. Although PYRs exhibit relatively lower mammalian toxicity than the OP pesticides, some studies have identified PYRs as potential human neurotoxicants that may cause developmental neurotoxic and immunotoxic effects [4-6]. One of the commonly used PYRs, permethrin, is reported to have weak endocrine disrupting properties [7]. The FQPA requires the U.S. EPA to consider the cumulative effects of exposures to pesticides having the same or similar mode of action [8]. It has been suggested that the PYRs have a common mechanism of toxicity indicating that their cumulative risk effects must be investigated. Furthermore, the effects on human exposures resulting from the widespread and accelerating indoor use of PYRs are not well established suggesting prudent environmental monitoring of PYRs for assessment of exposures and cumulative risk is warranted [8,9].

House dust is a complex sample matrix generally composed of track-in soil, settled particulate matter, human and/or animal dander, insect parts, and other debris. House dust acts as an indoor sink and repository for a variety of organic pollutants, especially those with low volatility, which tend to adsorb onto materials such as carpets, or fabrics. Studies have shown [10-15] that organic pollutants such as polycyclic aromatic hydrocarbons (PAHs), OP pesticides, and PYRs are more prevalent in house dust compared to outdoor soil in residential settings. Exposure to pollutants adsorbed onto house dust may occur through inhalation of dust particles, ingestion of the dust itself or via food, as well as dermal absorption. Thus, the levels of pollutants found in house dust could be used as an indicator of indoor exposures. The National Children‘s Study, a longitudinal epidemiologic study of children’s health, includes the collection and analysis of indoor dust [16-17]. Analysis of PYRs from house dust (a complex matrix) generally involves exhaustive extraction techniques such as Soxhlet extraction or ultrasonic extraction, using a solvent or solvent mixture to remove the target compounds from the dust matrix. This is followed by solvent exchanging the resulting sample extract into a non-polar solvent for a cleanup step by open-column adsorption chromatography or solid-phase extraction (SPE) using either silica, alumina or Florisil as the column support [15, 18-21]. However, these methods are tedious and costly, especially when many samples need to be analyzed. Alternative high-throughput sample preparation methods that are low cost and efficient are desirable for large-scale exposure and environmental monitoring studies.

Pressurized liquid extraction (PLE) is an automated, fast and efficient sample extraction technique utilizing elevated temperatures and high pressures to achieve effective removal of adsorbed organic pollutants from solid matrices [22]. PLE has been successfully used for

extracting organic pollutants including pesticides, dioxins, furans, and PAHs from complex sample media (e.g., sediment, soil, food, tissue) [23-25]. PLE is an exhaustive extraction procedure removing compounds of interest as well as co-extractive interference materials from various sample matrices during a short time period (typically less than 30 min.). Thus, the resulting sample extracts usually require post-extraction cleanup to remove non-target co-extracted materials that could cause interferences for instrumental analysis. Selective PLE (SPLE) incorporates various cleanup adsorbents with the sample in the extraction cell for simultaneous sample extraction and cleanup. This technique has recently been reported as a streamlined sample preparation/cleanup strategy to simultaneously extract and cleanup pesticides, dioxins, furans, and polychlorinated biphenyls (PCB) from complex sample matrices [26-30]. To our knowledge, SPLE has not been used for simultaneous extraction and cleanup of PYRs in house dust.

The objective of this study was to develop a robust and high sample-throughput SPLE method for gas chromatography/mass spectrometry (GC/MS) analysis to determine PYRs in house dust. Various combinations of cleanup adsorbents, extraction temperatures, and solvents were evaluated to determine the optimal SPLE procedure. Aliquots of twenty bulk dust samples from two field observational studies [19, 31] were analyzed by the SPLE-GC/MS for method validation. The overall method precision, based on percent standard deviation (%RSD) of replicate dust samples, and method accuracy, based on the percent recovery of fortified dust samples were established. The performance of the SPLE procedure was evaluated in terms of method precision, accuracy, detection limit, sample throughput, and estimated cost in comparison to a conventional stepwise extraction and cleanup method.

2. Materials and Methods

2.1. Chemicals and reagents

All solvents including acetonitrile, dichloromethane (DCM), hexane, acetone, methanol, and diethyl ether were of analytical or distilled-in-glass grade purchased from VWR (West Chester, PA, USA). Allethrin, tetramethrin, bifenthrin, lambda-cyhalothrin, *cis*- and *trans*-permethrin, cyfluthrin, cypermethrin, esfenvalerate, and deltamethrin, and phenanthrene-d_{10} were obtained from ChemService (West Chester, PA, USA). Cellulose fiber filters for the PLE were from Dionex (Sunnyvale, CA). Silica (100-200 mesh, grade 60A or equivalent) was purchased from Fisher Scientific (Fair Lawn, NJ, USA). Alumina, Florisil (60-100 mesh), sulfuric acid, C_{18} SPE, aminopropyl SPE, and Florisil SPE cartridges (1g) were obtained from Sigma (St. Louis, MO, USA).

2.2. Dust samples

The SPLE method development and evaluation were based on real world house dust samples obtained from the Children's Total Exposure to Persistent Pesticides and Other Persistent Organic Pollutants (CTEPP) study and the Pesticide Exposures of Preschool Children Over Time (PEPCOT) study [19, 31]. CTEPP samples were taken from vacuum cleaner bags collected during normal household vacuuming. PEPCOT samples were indoor floor house dust collected with a High Volume Small Surface Sampler (HVS3; Cascade Stack Sampling Systems Inc., Bend OR, USA) following an ASTM standard procedure [32]. All dust samples were separated into coarse and fine (<150 μm) fractions. Literature reports indicate that only the fine fraction of

house dust contains significant quantities of organic pollutants [11]. Additionally the fine fraction is most likely to adhere and remain on human skin [33-34]. Only the fine dust fraction was analyzed.

2.3. SPLE development

2.3.1. Optimization of SPLE

The SPLE was performed using a Dionex Accelerated Solvent Extraction (ASE) 200 system (Sunnyvale, CA, USA). The SPLE conditions were optimized using dust samples and fortified dust samples (prepared by adding 50 or 200 µL of a 1 ng μL^{-1} PYR standard solution to a sample aliquot). Table 1 summarizes a series of experiments performed during method development. Different ratios of adsorbent to sample were packed into the extraction cells. The cell was fitted with a cellulose filter to avoid clogging of the metal frit at the outlet of the cell. A known amount (0.5 -1 g) of dust was then added to the extraction cell. Finally, the cell was filled to the top with muffled sand. All extractions were performed at 2000 psi with a flush volume of 100% and a purge time of 60s. Two or three static cycles of 5 min. each were used for each extraction solvent (hexane, 50% hexane in acetone, or DCM) and temperature (100° or 120°C). The resulting extracts were concentrated and analyzed by GC/MS for the target PYRs.

2.3.2. Multi-step extraction and cleanup

All dust samples were extracted as described elsewhere [19, 31] with DCM using sonication. Two different post-extraction procedures were employed. In method one, the sample extract was solvent exchanged into acetonitrile and cleaned by passing them through a SPE system consisting of a C_{18} cartridge on top of an aminopropyl cartridge [19]. In method two, the sample extract was solvent exchanged into hexane and cleaned by a Florisil SPE cartridge [31]. After the SPE cleanup, the target fraction was concentrated and analyzed by GC/MS.

2.3.3. SPLE Procedure Validation

Twenty house dust samples from the two observational studies [19, 31] were prepared by the optimized SPLE condition. A known amount of dust sample (0.5 g), acid silica (0.4 g), and neutral silica (4 g), were packed in an extraction cell as shown in Figure 1. Whenever sufficient sample was available, a 1-g aliquot of dust was used maintaining the same ratio of sample to adsorbents (1: 0.8 : 8). The void space of the extraction cell was filled with clean sand. The extraction was performed with DCM at 2000 psi and 100ºC for 3 cycles of 5 min. The purge time was 60 s with 100% flush volume. The DCM extract was concentrated and spiked with the internal standard (IS), phenanthrene-d_{10}, for GC/MS analysis.

2.4. GC/MS analysis

Analyses of the standard solutions and sample extracts were performed on a Hewlett-Packard GC/MS, operated at 70 eV electron impact (EI), in the selected ion monitoring (SIM) mode. Data acquisition and processing were performed with a ChemStation data system. The GC column

was a DB 5 fused silica capillary (60m x 0.32 mm, 0.25 µm film thickness). Helium was used as the GC carrier gas. Samples were injected in the pulsed splitless mode at an injection temperature of 280°C. Following injection, the GC column was held at 70°C for 2 min., temperature programmed to 200°C at 15°C/min. then to 290°C at 6°C/min., and held at 290°C for 15 min. Ion peaks including one for quantitation and one to two for qualification were monitored for each target PYR [19]. Identification of the target PYRs was based on their GC retention times relative to the IS and the relative abundances of the monitored ions. Quantification was based on comparisons of the integrated ion current responses of the target ions to that of the IS. A calibration curve of each target PYR was generated from the analyses of standard solutions (5-1000 ng mL^{-1}) using a regression analysis where the correlation coefficient (r) value was 0.99 or greater.

3. Results and discussion

The objective of the study was to develop a streamlined and robust analytical method (i.e., SPLE-GC/MS) that provides effective extraction of PYRs from dust matrix and eliminates the post-extraction step for the quantitative determination of PYRs. Method development and validation results are discussed below.

3.1. Method development

Initially, the SPLE conditions (alumina, 10% $AgNO_3$ in silica, and acid silica as co-extracted adsorbents) previously developed for dioxins and furans in soil and sediment were evaluated for

the PYRs [29]. However, quantitative recoveries of target PYRs from the dust matrix could not be obtained (Table 1, experiment 1). PYRs contain a common chemical structure of an acid moiety, a center ester bond and an alcohol moiety. The main pathway for degradation of PYRs is hydrolysis of the central ester linkage and subsequent oxidation of both the acid and alcohol moieties. The low recoveries of PYRs could be partly due to the degradation of the PYRs by co-extracted adsorbents. Subsequent experiments (Table 1, experiments 2-14) were carried out to achieve effective removal of PYRs adsorbed on dust, reduce the co-extracted materials, and minimize the potential PYR degradation. Since the extraction pressure generally does not have a significant effect on the extraction yield, the pressure was kept at 2000 psi in all experiments. Table 1 summarizes the SPLE parameters studied including: (1) co-extracted adsorbents (silica, Florisil, alumina or acid silica), (2) extraction solvents (15% DCM in hexane, 50% hexane in acetone, or DCM), and (3) extraction temperature (100° or 120° C).

A series of SPLE conditions were evaluated using single adsorbents (silica, Florisil, alumina), with DCM at 100° or 120°C. All the resulting sample extracts from the single adsorbent experiments had a yellow to greenish color, and some were cloudy. The GC chromatographic profiles of these sample extracts indicated that a post-extraction cleanup step was needed to remove the rising background and the interference components that eluted closely to the retention time of permethrin, cyfluthrin, and cypermethrin. After applying the post-extraction cleanup step to these sample extracts, satisfactory GC chromatograms were obtained. Figure 2 summarizes the recoveries of the fortified PYR from different adsorbents (dust: adsorbent ratio = 1:10). Note that some of the PYRs contain two or three asymmetric carbons or chiral centers and resulted in several stereoisomers in the standards used. The standards contain four well-resolved

GC peaks each for cyfluthrin (I, II, III, IV) and cypermethrin (I, II, III, IV), and two peaks each for esfenvalerate and tetramethrin while permethrin standards were isomer specific (*cis*- and *trans*-permethrin). Average recoveries of these PYR isomers are shown in Figures 2 and 3. Consistent recoveries of each PYR isomers were obtained under each SPLE condition. The percent relative standard deviation (%RSD) values of the recoveries for these isomers ranged from 0 to 30% with higher %RSD values (20-30%) observed for the target PYRs with less than 30% average recoveries.

Quantitative recoveries (52-130%) of all target PYRs were obtained when silica was used. Recoveries of tetramethrin were only 2% and 18%, respectively, when Florisil and alumina were used and only 52% when silica was used. The relatively low recoveries of tetramethrin could be from the ester bond cleavage or oxidation by the co-extracted adsorbent. Recoveries of bifenthrin, permethrin, cyfluthrin, and fenvalerate were greater than 70%, but recoveries for the later-eluted cypermethrin, esfenvalerate, and deltamethrin were 41-51% when Florisil was used. Satisfactory recoveries (>70%) were obtained for bifenthrin and permethrin when alumina was used. Among the three adsorbents tested, silica provided the best recovery results. Similar PYR recoveries were obtained for both extraction temperatures. Therefore, the lower temperature (100°C) was used for the subsequent dual-adsorbent experiments, to minimize the presence of co-extractable interferences. Among the three solvents tested, 50% hexane in acetone yielded the highest amounts of extractable organic materials; the amounts from the other two solvents were lower. The extraction solvent used for the later dual-adsorbent experiments was DCM because of its better overall recoveries.

Additional experiments were performed using dual adsorbents (silica and acid silica) since acid silica could provide cleaner or colorless extracts as demonstrated in our previous study [29], and silica performed the best of any single adsorbent tested. Various ratios of dust to these two adsorbents were tested (Table 1). The sample extracts generated from the dual-adsorbent experiments were mostly clear; some had a light yellow color. The resulting SPLE extracts exhibited lower extractable organic materials compared with those from single adsorbent experiments and could be analyzed by GC/MS without any post-extraction cleanup. The GC chromatograms of the dust samples exhibited well-resolved symmetrical peaks, with no rising background or co-eluting interferences.

Figure 3 shows the recoveries of target PYRs under different dust to adsorbent ratios. Quantitative recoveries, typically less than 60% of PYRs could not be obtained with ratios of 1:2:8 and 1:2.5:25 for the dust: acid silica: silica. Quantitative recoveries (>90%) of all fortified PYRs with the exception of tetramethrin were achieved when the sample to adsorbent ratio was 1:0.8:8 (dust: acid silica: silica). As stated before, the loss of tetramethrin was probably due to its reactivity. Thus, the SPLE approach is not suitable for this particular PYR, and tetramethrin was not included in the method performance experiments described below.

In summary, a streamlined analytical method was developed to determine selected PYRs in dust samples. The method consisted of extracting dust samples with silica and acid silica with a ratio of 1:0.8:8 using DCM under 2000 psi, at 100ºC for 5 min. in three cycles and analyzing the concentrated sample extracts by GC/MS.

3.2. Method performance

The accuracy and precision of the new SPLE-GC/MS method were evaluated with three dust samples fortified with target PYRs at a level at least twice the ambient PYR amount as determined in the samples (Table 2). The accuracy was evaluated based on the recoveries obtained from the fortified samples, and the precision was based on the %RSD of the recoveries of the triplicate aliquots of each fortified dust sample. As shown in Table 3, quantitative recoveries were obtained in the fortified dust samples ranging from 85 to 120% and the %RSD was less than 25%, ranging from 1.4 to 23%. The overall method accuracy of the SPLE-GC/MS method was greater than 80%, with the precision within ±25%. Method blanks consisting of clean sand and the adsorbents were analyzed using the same procedure. None of the target PYRs were detected in the method blanks suggesting that there was no contamination during the SPLE. The estimated detection limit for the PYRs tested ranged from 1 to 10 ng g^{-1} based on the standard solution with the lowest concentration and a sample size of 1 g dust.

3.3. Method comparison

Twenty dust samples from two observational studies [19, 31] were analyzed using the SPLE method to demonstrate its suitability for routine analysis. The data obtained from the SPLE-GC/MS method were compared with the results obtained from the previous studies that used different sample preparation procedures (i.e., stepwise extraction and SPE cleanup), but the same detection technique (i.e., GC/MS). Summary statistics (sample size, arithmetic and geometric means, standard deviation, minimum concentration, 25th percentile, 50th percentile, 75th

percentile, and maximum concentration) for these two data sets are shown in Table 3. The SPLE-GC/MS results were generally in good agreement with those obtained from the stepwise extraction/cleanup-GC/MS. Permethrin was detected in all the samples while deltamethrin was not found in any of the dust samples. The Pearson correlation coefficient for the permethrin (sum of the *cis*- and *trans*-permethrin) concentrations from the two sets of data was r=0.9814, which was statistically significant ($p<0.0001$). There is a strong statistical evidence of a linear association present in the permethrin concentrations between the two sets of data. The linear regression equation between data set A (SPLE-GC/MS) and data set B (stepwise extraction/cleanup-GC/MS) is $A = 1.0525 \times B - 1.9722$ with the square of the correlation coefficient, R^2 of 0.9632. Figure 4 displays the relationship between the two sets of data on permethrin concentrations. The estimated sample throughput by the SPLE procedure is about 50% higher than the step-wise extraction/cleanup procedure, since the cleanup step is not required for the SPLE. The higher sample throughput achieved with the SPLE procedure translates to the reduction in overall analytical costs due to lower material and labor requirement. Similar overall method precision, accuracy, and detection limits were obtained from both sample preparation procedures. These findings demonstrated that the SPLE-GC/MS method is robust and can be considered for routine laboratory analysis for large numbers of samples generated from future large-scale exposure and monitoring studies.

4. Conclusion

An SPLE procedure was developed to effectively extract PYRs from a complex dust matrix without post-extraction cleanup prior to GC/MS analysis. Quantitative recoveries (85-120%) were achieved with fortified dust samples, with an overall method precision within ±25% and an

estimated detection limit of 1-10 ng g^{-1}. The SPLE-GC/MS method facilitates sample throughput and reduces the workload for routine laboratory analysis, cutting overall costs. PYR concentrations derived from the SPLE-GC/MS were in a good agreement with those from the analytical procedures using the lengthy stepwise extraction/cleanup approach for the 20 dust samples.

5. Acknowledgements

We would like to thank James Starr of the United States Environmental Protection Agency, National Exposure Research Laboratory for providing us with the vacuum bag house dust samples. We thank Margaret Tefft and Eiko Weller of Battelle for sample preparation and analysis. The United States Environmental Protection Agency through its Office of Research and Development funded and collaborated in the research described here under Contract #EP-W-09-024. It has been subjected to Agency review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

6. References

[1] J.E. Casida. Pyrethrum flowers and pyrethroid insecticides. Environ. Health Perspect. 1980, 34, 189-202.

[2] Federal Register, Volume 65, Number 235, pp 76233-76240, December 6, 2000.

[3] Federal Register, Volume 66, Number 7, pp 1977-1981, January 10, 2001.

[4] P. Ericksson, U. Talts. Neonatal exposure to neurotoxic pesticides increases adult susceptibility A review of current findings. Neurotoxicology 2000, 21, 37-47.

[5] T.J. Shafer, D.A. Meyer, K.M. Crofton. Developmental neuro-toxicity of pyrethroid insecticides: critical review and future research needs. Environ. Health Perspect. 2005, 113, 123-136.

[6] N. Grosman, F. Diel. Influence of pyrethroids and piperonyl butoxide on the Ca2+-ATPase activity of rat brain synaptosomes and leukocyte membranes. Int. Immunopharmacol. 2005, 5, 263-270.

[7] S.S. Kim, R.D. Lee, K.J. Lim, S.J. Kwack, G.S. Rhee, J.H. Seok. Potential estrogenic and antiandrogenic effects of permethrin in rats. J. Reprod. Deviations, 2004, 51, 201-210.

[8] Food Quality Protection Act (FQPA), http://www.epa.gov/agriculture/lqpa.html.

[9] D.M. Soderlund, J.M. Clark, L.P. Sheets, L.S. Mullin, V.J. Piccirillo, D. Sargent, J.T. Stevens, M.L.Weiner. Mechanisms of pyrethroid neurotoxicity: implications for cumulative risk assessment. Toxicology 2002, 171, 3-59.

[10] J.C. Chuang, P.J. Callahan, R.G. Menton, S.M. Gordon, R.G. Lewis, N.K.Wilson. Monitoring methods for polycyclic aromatic hydrocarbons and their distribution in house dust and track-in soil. Environ. Sci and Technol 1995, 29, 494-500.

[11] R. G. Lewis, C.R. Fortune, R.D. Willis, D.E. Camann, J.T. Antlet. Distribution of pesticides and polycyclic aromatic hydrocarbons in house dust as a function of particle size. Environ. Health Perspect. 1999, 107, 721-726.

[12] J.C. Chuang, P.J. Callahan, C.W. Lyu, N.K. Wilson. Polycyclic aromatic hydrocarbon exposures of children in low-income families. J. Expo. Anal. and Environ. Epidemiol. 1999, 2, 85–98.

[13] N.K. Wilson, J.C. Chuang, C.W. Lyu. Levels of persistent organic pollutants in several child day care centers. J. Expo. Anal. Environ. Epidemiol. 2001, 11, 449–458.

[14] N.K. Wilson, J.C. Chuang, C.W. Lyu, R. Menton, M.R. Morgan. Aggregate exposures of nine preschool children to persistent organic pollutants at day care and at home. J. Expo. Anal. Environ. Epidemiol. 2003, 13, 187–202.

[15] M. Morgan, L. Sheldon, C. Croghan, P. Jones, J.C. Chuang, N.K. Wilson. An observational study of 127 preschool children at their homes and daycare centers in Ohio: Environmental pathways to cis- and trans-permethrin exposure. Environ. Res. 2007, 104, 266-274.

[16] A. Bradman and R.M. Whyatt. Characterizing exposures to nonpersistent pesticides during pregnancy and early childhood in the National Children's Study: A review of monitoring and measurement methodologies. Environ. Health Perspect. 2005, 58, 1377-1383.

[17] L.L. Needham, H. Ozkaynak, R.M. Whyatt, D.B. Barr, R.y. Wang, L. Neaher, G. Akland, T. Bahadori, A. Bradman, R. Fortman, L.J.S. Liu, M. Morandi, M.K. O'Rourke, K. Thomas, J. Quackenboss, P.B. Ryan, V. Zartarian. Exposure assessment in the National Children's Study: Introduction. Environ. Health Perspect. 2005, 113, 1076-1082.

[18] M. Yasin, P.J. Baugh, G.A. Bonwick, D.H. Davies, P. Hancock, M. Leinoudi. Analytical method development for the determination of synthetic pyrethroid insecticides in soil by gas chromatography-mass spectrometry operated in negative-ion chemical-ionization mode. J, of Chromatogr. A, 1996, 754 (1-2), 235-243.

[19] J. Starr, S. Graham, D. Stout, K. Andrews, M. Nishioka. Pyrethroid pesticides and their metabolites in vacuum cleaner dust collected from homes and day-care centers. Environ. Res. 2008,108, 271-279.

[20] R.Julien, G. Adamkiewicz, J.I. Levy, D. Bennett, M. Nishioka, J.D. Spengler. Pesticide loadings of select organophosphate and pyrethroid pesticides in urban public housing. J. Expo. Sci. Environ. Epidemiol. 2008, 18, 167-174.

[21] M.E. Harnly, A. Bradman, M. Nishioka, T.E. Mckone, D. Smith, R. Mclaughlin, G. Kavanagh-Baird, R. Castorina, B. Eskenazi. Pesticides in dust from homes in an agricultural area. Environ. Sci. Technol. 2009, 43, 8767-8774.

[22] B.E. Richter, B.A. Jones, J.L. Ezzell, N.L.Porter. Accelerated solvent extraction: a new technique for sample preparation. Anal. Chem. 1996, 68, 1033-1039.

[23] M. Misita, M. Schrock, K. Tracy, J. Tabor. Simultaneous extraction of PCDD/PCDF and PCBs using accelerated solvent extraction for sediment, tissue, and sludge matrices. Organohalogen Compounds, 2003, 60, 37-40.

[24] K. Saito, A. Sjodin, C.D. Sandau, M.D. Davis, H. Nakazawa, Y. Matsuki, D.G. Patterson Jr. Development of a accelerated solvent extraction and gel permeation chromatography analytical method for measuring persistent organohalogen compounds in adipose and organ tissue analysis. Chemosphere, 2004, 57, 373-381.

[25] P. Wang, Q. Zhang, Y. Wang, T. Wang, X. Li, L. Ding, G. Jiang. Evaluation of Soxhlet extraction, accelerated solvent extraction, and microwave-assisted extraction for the determination of polychlorinated biphenyls and polybrominated diphenyl ethers in soil and fish samples. Analytica Chimica Acta, 2010, 663, 43-48.

[26] E. Bjorklund, S. Sporring, K.Wiberg, P. Haglund, C. von Holst. New strategies for extraction and clean-up of persistent organic pollutants from food and feed samples using selective pressurized liquid extraction. Trends in Anal. Chem. 2006, 25(4), 318-325.

[27] P.Haglund, S. Sporring, K. Wiberg, E. Bjorklund. Shape-selective extraction of PCBs and dioxins from fish and fish oil using in-cell carbon fractionation pressurized liquid extraction. Anal. Chem. 2007, 79, 2945-2951.

[28] M. Fernandez-Alvarez, M. Llompart, J.P. lamas, M. Lores, C. Garcia-jares, M. Garcia-Chao, T. Dagnac. Simultaneous extraction and cleanup method based on pressurized solvent extraction for multiresidue analysis of pesticides in complex feed samples. J. Agric. Food Chem. 2009, 57, 3963-3973.

[29] J.C. Chuang, J.M. Van Emon, M.E. Schrock. High-throughput screening of dioxins in sediment and soil using selective pressurized liquid extraction with immunochemical detection. Chemosphere 2009, 77, 1217–1223.

[30] Z. Zhang, E. Ohiozebau, S.M. Rhind. Simultaneous extraction and cleanup of polybrominated diphenylethers and polychlorinated biphenyls from sheep liver tissue by selective pressurized liquid extraction and analysis by gas chromatography-mass spectrometry. J. of Chromatogr. A 2011, 1218, 1203-1209.

[31] N.K. Wilson, J.C. Chuang, W.J. Strauss, C. Lyu, N. Iroz-Elardo, T. Pivetz. Pesticide exposures of preschool children over time. Final report to NCER, STAR Grant R829363, 2008.

[32] ASTM, Standard practice for collection of floor dust for chemical analysis. D5438-94, Annual Book of ASTM standards, Vol. 11.03. American Society for Testing and Materials, West Conshohocken, PA. 1997, 517-523.

[33] S.S. Que Hee, B. Peace, C.S. Clark, J.R. Boyel, R.L. Bornschein, P.B. Hammond. Evaluation of efficient methods to sample lead sources, such as house dust and hand dust, in the homes of children. Environ. Res. 1985, 38, 77-95.

[34] M.J. Duggan, M.J. Inskip, S.A. Rudle, J.S. Moorcroft. Lead in playground dust and on the hands of school children. Sci. Total Environ. 1985, 44, 65-79.

Table 1. Evalustion of the optimal SPLE procedure

SPLE Experimental Conditions Tested[a]	**Cleanup Step**[b]	**Recovery, %**
Single adsorbent		
1. Co-extracted with 5 g silica using DCM @120°C	Yes	57-135%
2. Co-extracted with 5 g silica using DCM @100°C	Yes	60-123%
3. Co-extracted with 10 g silica using DCM @100°C	Yes	52-130%
4. Co-extracted with 10 g silica using 10% DCM in hexane @100°C	Yes	21-76%
5. Co-extracted with 10 g silica using using 50% hexane in acetone @100°C	Yes	51-92%
6. Co-extracted with 5 g Florisil using DCM @100°C	Yes	5-89%
7. Co-extracted with 10 g Florisil using DCM @100°C	Yes	2-82%
8. Co-extracted with 5 g Alumina using DCM @100°C	Yes	11-83%
9. Co-extracted with 10 g Alumina using DCM @100°C	Yes	11-79%
Duel-adsorbents		
1. Co-extracted with Acid silica (2.5 g) and silica (25 g) using DCM @100°C	No	10-59%
2. Co-extracted with Acid silica (2 g) and silica (8 g) using DCM @100°C	No	39-66%
3. Co-extracted with Acid silica (1 g) and silica (20 g) using DCM @100°C	No	27-86%
4. Co-extracted with acid silica (0.8 g) and silica (8 g) using DCM @100°C	No	59-120%

[a] A purge time of 60 s, a flush volume of 100% and an extraction time of 2 x 5 min. or 3 x 5 min. at 2000 psi were used in all experiments.

[b] Yes denotes that post-extraction cleanup of the extract was required prior to GC/MS because of interference observed in the GC/MS analysis of the extracts without the cleanup step.

Table 2. Accuracy and precision of the PYR analysis of dust samples by SPLE-GC/MS

Compound	Dust-1[a]		Dust-2 [a]		Dust-3 [a]	
	Recovery	%RSD	Recovery	%RSD	Recovery	%RSD
Bifenthrin	84.8±9.1	11	87.1±2.9	3.3	90.2±21	23
lambda-Cyhalothrin	103±13	13	111±1.8	1.6	103±10	10
cis- and trans-Permethrin[b]	103±11	11	85.8±2.4	2.8	101±13	13
Cyfluthrin (I, II, III, IV)[b]	92.3±3.0	3.3	96.9±6.0	6.2	98.5±6.1	6.2
Cypermethrin (I, II, III, IV)[b]	94.3±7.7	8.2	99.3±5.0	5.0	100±18	18
Esfenvalerate (I, II)[b]	100±5.5	5.5	102±3.6	3.5	120±10	8.3
Deltamethrin	92.5±1.3	1.4	105±14	13	98.0±16	16

[a] The optimal SPLE condition was employed by extracting 1 g of dust sample with silica and acid silica with a ratio of 1:0.8:8 using DCM under 2000 psi, at 100ºC for 5 min. in three cycles. Fortified levels were 400 ng g^{-1} for dust samples 1 and 3, and 100 ng g^{-1} for dust sample 2. Data are from triplicate fortified samples for each dust sample. Percent Recovery = (average amount in the fortified sample-amount in the non-fortified sample)/fortified amount * 100.

[b] Reported data are average recoveries of the individual isomers.

Table 3. Data summary statistics for the SPLE-GC/MS and the step-wise extraction/cleanup-GC/MS methods (ng g^{-1})

Compound	SPLE-GC/MS[a]				Step-wise extraction/cleanup-GC/MS[a]			
	Min.	50th percentile	75th percentile	Max.	Min.	50th percentile	75th percentile	Max.
Bifenthrin	<1	4.20	61.3	287	<1	5.21	38.1	219
lambda-Cyhalothrin	<1	10.9	40.5	206	<1	9.87	60	219
cis- and *trans*-Permethrin[a]	74.0	746	1216	4981	96.1	733	1125	5106
Cyfluthrin (I, II, III, IV)[a]	<5	101	398	1006	<5	114	296	1051
Cypermethrin (I, II, III, IV)[a]	<5	<5	109	1670	<5	<5	99.8	2107
Esfenvalerate (I, II)[a]	<10	<10	68.9	1036	<10	<10	78.8	943
Deltamethrin	<10	<10	<10	<10	<10	<10	<10	<10

[a] Reported data are sums of the individual isomers.

Figure Captions

Figure 1. Schematic diagram of a packed PLE cell: dust sample (0.5 or 1 g), acid silica (0.4 or 0.8 g), and neutral silica (4 or 8 g)

Figure 2. Recovery of PYRs in dust samples under different SPLE conditions with a single adsorbent, using DCM at 100°C.

Figure 3. Recovery of PYRs in dust samples under different SPLE conditions with dual adsorbents, using DCM at 100°C.

Figure 4. Comparative permethrin concentrations in dust samples using SPLE/GC/MS and a stepwise extraction and cleanup with GC/MS detection.

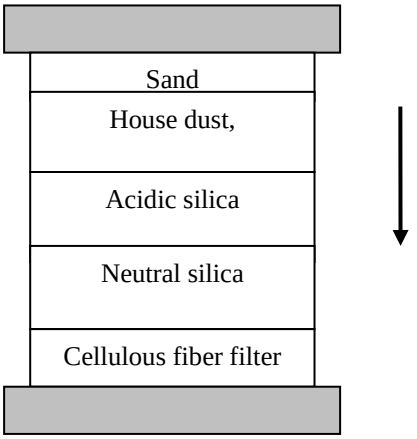
Sand
House dust,
Acidic silica
Neutral silica
Cellulous fiber filter

Figure 1

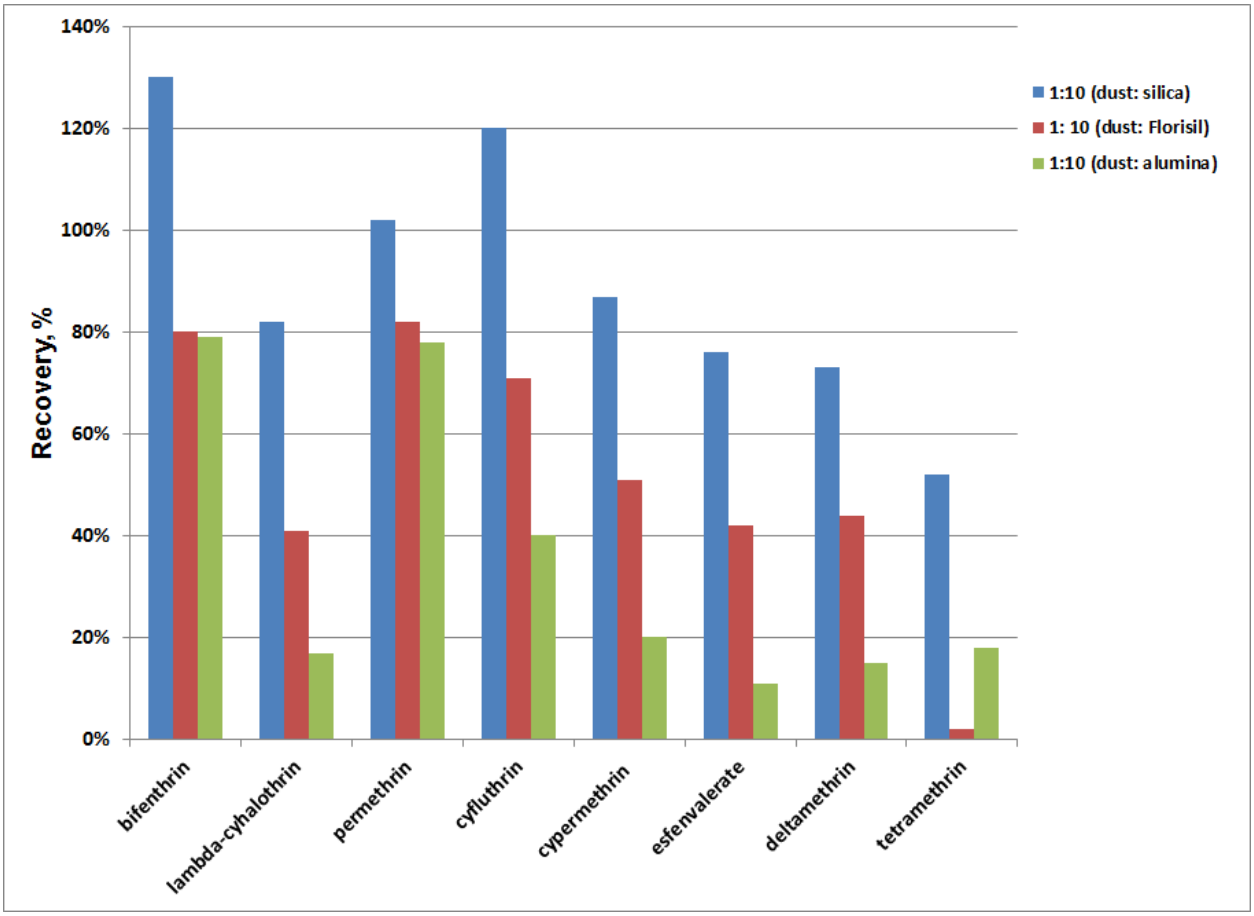
140%
120%
100%
80%
60%
40%
20%
0%
Recovery, %
1:10 (dust: silica)
1: 10 (dust: Florisil)
1:10 (dust: alumina)
bifenthrin
lambda-cyhalothrin
permethrin
cyfluthrin
cypermethrin
esfenvalerate
deltamethrin
tetramethrin

Figure 2

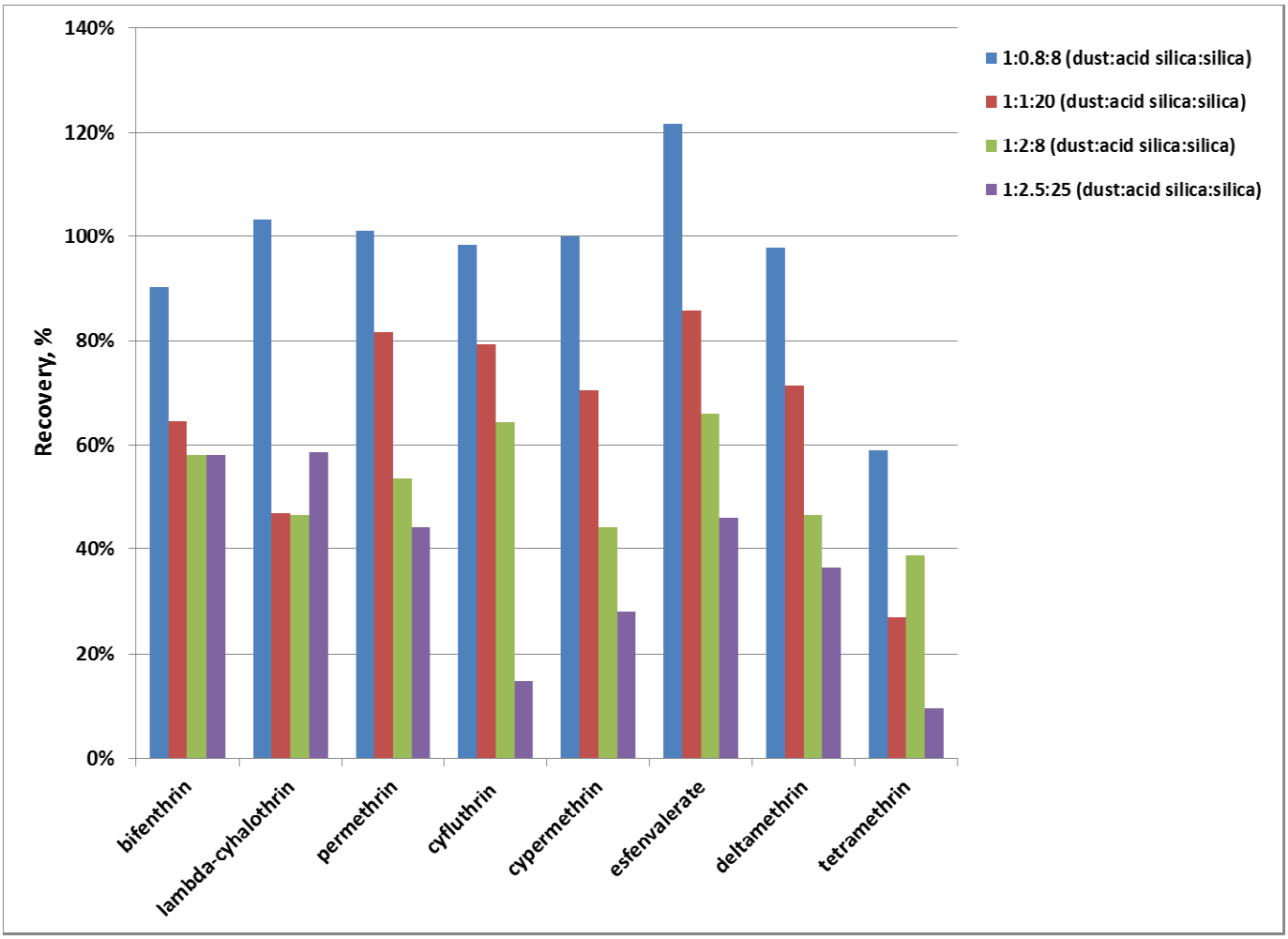
140%
120%
100%
80%
60%
40%
20%
0%
Recovery, %
1:0.8:8 (dust:acid silica:silica)
1:1:20 (dust:acid silica:silica)
1:2:8 (dust:acid silica:silica)
1:2.5:25 (dust:acid silica:silica)
bifenthrin
lambda-cyhalothrin
permethrin
cyfluthrin
cypermethrin
esfenvalerate
deltamethrin
tetramethrin

Figure 3

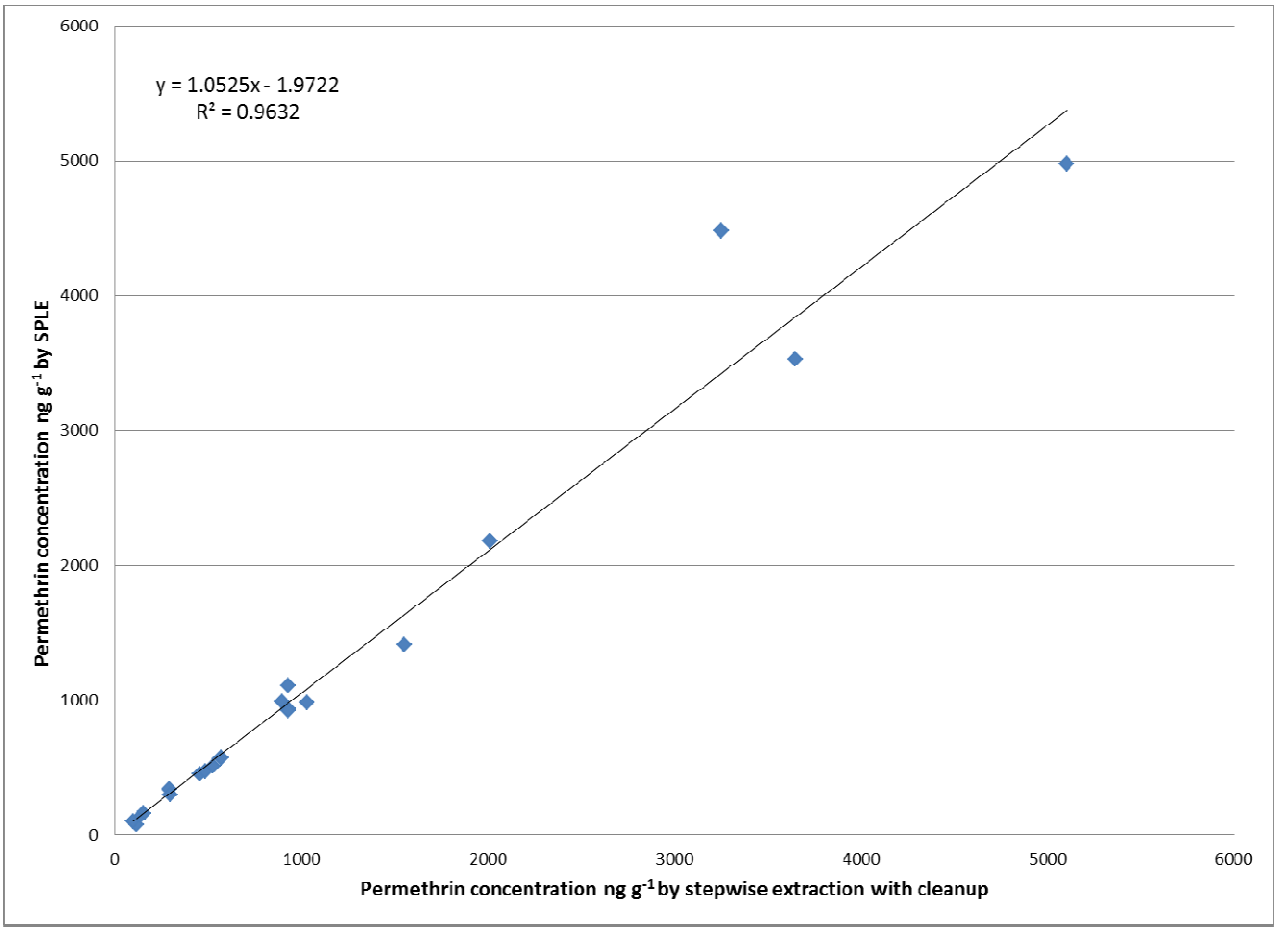
y = 1.0525x - 1.9722
R² = 0.9632
Permethrin concentration ng g-1 by SPLE
Permethrin concentration ng g-1 by stepwise extraction with cleanup
0
1000
2000
3000
4000
5000
6000

Figure 4