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A Laboratory Comparison of Two Media for Use in the Assessment of Dermal Exposure to Pesticides

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In a laboratory study, gauze pads and Empore[1] filters were compared for their ability to assess the dermal exposure of two insecticides (chlorpyrifos and diazinon) and five herbicides (atrazine, alachlor, metolachlor, cyanazine, and 2,4-D ethylhexyl ester). The analytes, when analyzed by gas chromatography with flame ionization detection, were found to have a linear dynamic range to at least 250 θg/mL.

While a number of different solvents were examined for the desorption of the analytes, methanol was found to be the best solvent for the recovery of all the analytes from 16-ply gauze pads, while 20 percent ethyl acetate in hexane was the preferred solvent for the styrene divinylbenzene-impregnated Empore filters. Limits of detection (LODs) for the analytes were comparable for both media. For Empore filters, the LODs were 50 θg/sample for atrazine, alachlor, chlorpyrifos, diazinon, and 2,4-D ethylhexy ester, with 30 θg/sample for metolachlor, and 80 θg/sample for cyanazine. For gauze pads, the LODs were 40 θg/sample for metolachlor, 50 θg/sample for alachlor, diazinon, and 2,4-D ethylhexy ester, 60 θg/sample for atrazine and chlorpyrifos, and 80 θg/sample for cyanazine. Both gauze pads and Empore filters gave quantitative recovery for all analytes except chlorpyrifos and 2,4-D ethylhexyl ester under ambient conditions (18°C, 70% relative humidity) for up to 30 days; these analytes required refrigeration for that period to reach over 90 percent recovery.

To assess the effect of environmental conditions on the recovery of the analytes, samples of each media were spiked at about 125 θg per analyte/sample (except cyanazine which was spiked at 190 θg) and challenged for 8 hr under high (80%) and low (20%) humidity and high (40°C) and low (5°C) temperature conditions in an environmental chamber. While the Empore samples gave quantitative recovery after being challenged, recovery from the gauze pads was affected by environmental conditions, especially high temperature. Recovery from gauze pads was below 30 percent for some analytes under high temperature/high humidity conditions.

Keywords Dermal Sampling, Pesticides, Empore

Occupational exposure to insecticides and herbicides can occur during mixing or spraying operations or can occur (post-application) from inhalation of aerosolized particulate containing pesticides or contact with surfaces containing their residues. The National Institute for Occupational Safety and Health (NIOSH) investigates dermal and inhalation exposure to pesticides through research field studies and health hazard evaluations (HHEs). The National Occupational Research Agenda being developed by NIOSH and its partners identified potential health problems of agricultural workers as a major research area.(1) Therefore, studies of workers exposed to a variety of insecticides and herbicides as well as investigations of work practices in various industries where they are used were initiated. This work was an outgrowth of the need for dermal exposure assessments for organophosphorou s pesticides (chlorpyrifos and diazinon), triazine herbicides (atrazine and cyanazine), acetamide herbicides (alachlor and metolachlor), and phenoxy acid herbicides (2,4-D ethylhexyl ester).

While methods have been developed to assess airborne concentrations of these pesticides in occupational settings,(2,3) additional effort was needed for the development of dermal exposure assessment methods. Dermal exposure methods have employed exposure patches, patches from worker clothing, skin swabs, and hand washes for direct measurement of deposited analytes.(4,5) Assessments of residential exposure have been made with hand press sampling and through the use of polyurethane foam rollers.(6) Investigators have also employed fluorescent tracers mixed with the pesticide application and imaged with UV lamps to estimate exposure to pesticides.(7,8) Cotton has been used extensively as a collection media for pesticide exposure studies, either as a glove(9,10) or as a patch.(11) Charcoal cloth has been

[1]Mention of company names or products does not constitute endorsement by NIOSH or the Centers for Disease Control and Prevention.

investigated for use in the determination of fumigants, but the media is very fragile and its capacity is significantly compromised at higher relative humidity levels.[12] Hand wash procedures have also been used for assessment of dermal exposure for some pesticides; however, some pesticides have been shown to not be completely removed due to being absorbed through or absorbed onto the skin.[13]

The need for methods that employed rugged and consistent media that could be used for the collection of a variety of pesticides required the examination of new materials for collection. A newly commercialized product (Empore) containing styrene-divinyl benzene resin beads (XAD-2) enmeshed in a polytetrafluoroethylene (PTFE) matrix was viewed as promising. The material was developed for solid phase extraction of organics from aqueous samples and has been used for the determination of pesticides from surface water samples.[14,15] Since the NIOSH methods for airborne pesticides [2,3] employ XAD-2 resin in an OVS-2 sampler tube, the media was viewed as a promising candidate for the collection and quantitative recovery of pesticides and one which would not be affected by ambient moisture that could deactivate other media. This article examines the limits of detection and stability of pesticides on this media.

EXPERIMENTAL

Materials

All chemicals were reagent grade or better and used as received. Insecticides (chlorpyrifos and diazinon) and herbicides (alachlor, metolachlor, atrazine, cyanazine, and 2,4-D ethylhexyl ester) used were analytical grade (ChemService, West Chester, PA). Stock solutions of pesticides were prepared in ethyl acetate at 500 μg/mL. Calibration standards (0.01 μg/mL to 250 μg/mL) were prepared by serial dilution. Dermal media consisted of 16 ply, U.S.P. Type VII cotton gauze (Cat. No. 052124, Abco Dealers, Inc., LaVergne, TN) cut into 2-inch × 2-inch sections and 47-mm disks of poly(styrenedivinylbenzene) resin beads embedded in a PTFE matrix (Cat. No. 98-0503-0022-1, 3M Corp., St. Paul, MN). Samples were stored in amber 8- or 12-oz wide-mouth bottles with PTFE-lined caps under either ambient or refrigerated conditions.

Analysis of the pesticides was by an HP 5890 GC (Hewlett Packard, Palo Alto, CA) with flame ionization detector using a 15-m, 0.53-mm ID, 0.5 μm film SPB-5 column (Supelco, Bellefonte, PA) and helium flow of 1.3 cm^3/min with quantitation by AI-450 software (Dionex, Sunnyvale, CA).

Post-sampling stability studies were performed in a modified refrigeration unit (Model FT1W-TRGBOL, Jorden, Philadelphia, PA), equipped with a heater unit, in which air (either dry or humified by aspiration through a trap containing deionized water) could circulate.

Procedures

The linearity of response for the compounds was examined by analysis of solutions at concentrations from 1.0 μg/mL to 500 μg/mL. Candidate desorption solvents were screened by fortifying ("spiking") with a mixture of the analytes samples of the media which had been placed into individual, amber, 12-oz wide-mouth bottles. The solvent was allowed to evaporate from the samples, which were then capped with PTFE-lined lids. The samples were desorbed the next day with 10 mL of the candidate solvent. Candidate desorbing solutions, identified from examination of previous work, were: methanol, ethyl acetate, 1:1 diethyl ether in hexane, and 20 percent ethyl acetate in hexane. The Plackett-Burman design,[16] with 12 samples per solvent/media tested, included the factors: desorption time (2 hr or 30 minutes), sonication (yes, no) or placement on a shaker, pre-sampling humidity (80% RH, ambient), and analyte concentration (high: 625 μg/sample and low: 250 μg/sample). The NIOSH acceptance criteria for estimated recovery from the primary collection medium should be greater than or equal to 75 percent,[17] so the acceptance of the design, which was replicated for each solvent, required average recoveries of at least 75 percent for all analytes at both concentrations. The optimum desorption solvent for each media was then employed for the rest of the study.

The limit of detection[17] for the analytes was determined by spiking 15 samples of each medium, which had been placed in individual, amber, 12-oz wide-mouth bottles, with from 25 μg/sample to 125 μg/sample of each analyte and desorbing with 10 mL of solvent under the optimal conditions as determined above. Storage stability of the analytes on the media was determined by spiking, at 500 μg analyte/sample, 21 samples of each medium. The samples, which had been placed in individual, amber, 8- or 12-oz wide-mouth bottles, were capped with PTFE-lined caps (after the solvent had evaporated) and left in a cool, dark site until ready for desorption. Samples were desorbed and recoveries of the analytes compared on days 1, 7, 14, and 30 (n = 9, 3, 3, and 3, respectively). In addition, recoveries for other samples (n = 3 each) kept either under refrigeration or stored in clear glass containers and exposed to ambient light, were examined at day 30.

The post-sampling stability of the analytes on the media was investigated by carefully spiking the analytes on the media at 125 μg/sample with an Eppendorf pipet, allowing the solvent to evaporate, and then exposing the spiked media to an array of temperature and humidity conditions in a two-level factorial design.[16] Twelve samples (six of each medium randomly placed into the chamber) were subjected to eight hours at either 5°C and 19 percent RH, 40°C and 19 percent RH, 5°C and 84–95 percent RH, or 40°C and 58–64 percent RH. The samples were removed from the chamber, placed into amber bottles with PTFE lids, and desorbed and analyzed the next day.

RESULTS AND DISCUSSION

A temperature program of 80°C (1 min hold), 80°C–150°C at 4°C/min (5 min hold), 150°C–250°C at 12°C/min (15 min hold), was found to give baseline resolution of all analytes. All of the insecticides and herbicides exhibited a linear response to at least 250 μg/mL (Table I). The results of the screening experiments

TABLE I
Linear dynamic range and limits of detection for pesticides from dermal media

	Alachlor	Atrazine	Chlorpyrifos	Cyanazine	Diazinon	2,4-D ethylhexyl ester	Metolachlor
Linear dynamic range (μg/mL)	2.5–500	2.5–500	5–250	3.7–750	2.5–500	4.8–480	2.8–500
LOD—Gauze (μg/sample)	50	60	60	80	50	50	40
LOD—Empore (μg/sample)	50	50	50	80	50	50	30

indicated that methanol was the best solvent for recovery of the analytes from gauze, while 20 percent ethyl acetate in hexane was found to be optimal for recovery of the analytes from the Empore material. While sonication was not required for quantitative recovery, the use of a shaker with a 2 hr desorption was required for best results at both concentration levels. The limits of detection for the analytes were comparable for each medium and ranged from 30–80 μg/sample (Table I). For some analytes such as chlorpyrifos, use of an electron capture (ECD) detector rather than the flame ionization detector could have lowered the detection limit, but this was not investigated.

The analytes were found to be quantitatively recovered from both media over the 30-day period studied (Table II). Recoveries from gauze were quantitative (99–110%) for day 1 samples and remained above 88 percent for all analytes during the 30 days. Refrigeration of the samples improved the recovery of some analytes on the media. Recoveries from the Empore medium were also quantitative (97–110%) for day 1 samples and were only slightly lower (down to 81%) than gauze over the 30 days. Refrigeration of these samples resulted in a slight improvement in recoveries (to above 92%) of the analytes. In neither case were samples significantly affected by exposure to light, possibly because the samples were only exposed to subdued laboratory lighting rather than direct sunlight. While long-term stability of the analytes in the desorbing solution was not investigated, samples reanalyzed one to two days after initial analysis showed no differences from the initial values for any analyte.

A number of factors, including environmental conditions, can have an effect on the stability of pesticides and herbicides on media. For this examination, which involved no mechanical agitation during the weathering of the fortified media, the mechanism of loss would be expected to be either evaporative loss or degradation of the analyte. While quantitative recoveries (95–116%) were obtained for all analytes on the Empore filter disks under all combinations of temperature and humidity (Table III), this was not the case for the analytes on the gauze pads. While quantitative recoveries (93–121%) from gauze were observed for the analytes under low temperature conditions, significant losses (recoveries to as low as 13%) could be observed for diazinon, alachlor, metolachlor, and cyanazine at higher temperatures. With vapor pressures (at 20°C) of 1.4×10^{-7}, 1.3×10^{-5}, and 1.0×10^{-8} torr [18] for diazinon, metolachlor, and cyanazine, respectively, evaporative loss would not be expected to be a major contributor to their loss. Diazinon, alachlor, atrazine, and chlorpyrifos are all reported to be sensitive to heat, [18] but only diazinon and alachlor show significant losses, with chlorpyrifos being unaffected, over the 8-hour weathering under high temperature conditions. However, thermal degradation alone cannot account for the losses on the gauze pads under high temperature conditions or concomitant losses would have been expected for the same analytes on the Empore medium. That even higher losses are observed under high humidity conditions leads to the possibility of hydrolysis of the analytes on the media. The Empore media, being largely hydrophobic (because of its PTFE

TABLE II
Percent recovery of pesticides as a function of storage time

	Empore						Gauze					
	Day 1	Day 7	Day 14	Day 30	Day 30 (refrig)	Day 30 (light)	Day 1	Day 7	Day 14	Day 30	Day 30 (refrig)	Day 30 (light)
Alachlor	99.3	92.8	83.5	94.9	102.6	103.9	101.5	98.2	93.8	102.0	115.5	92.8
Atrazine	108.4	96.2	87.1	92.3	91.1	91.1	99.4	97.5	92.9	91.7	95.8	88.1
Chlorpyrifos	109.9	96.3	92.4	81.0	92.6	87.5	99.5	97.1	95.7	88.3	100.0	98.7
Cyanazine	101.7	95.7	91.4	94.9	98.0	96.3	99.7	99.0	99.4	102.7	111.8	92.7
Diazinon	102.2	97.2	88.2	94.8	101.7	102.7	100.6	98.2	91.5	97.9	109.5	77.4
2,4-D ethylhexyl ester	98.0	97.3	87.2	86.2	95.4	92.0	104.1	98.6	90.8	92.2	101.3	99.8
Metolachlor	97.0	97.4	86.8	95.0	101.5	101.8	110.3	104.7	98.7	103.7	115.5	99.5

Average variation (1 s.d.) for Empore recovery was 3.8 percent and for gauze, 3.5 percent.

TABLE III
Percent recovery of pesticides as a function of temperature and relative humidity

	Empore				Gauze			
	5°C 19% RH	5°C 84–95% RH	40°C 19% RH	40°C 58–64% RH	5°C 19% RH	5°C 84–95% RH	40°C 19% RH	40°C 58–64% RH
Alachlor	109.8	99.8	101.6	102.6	111.8	103.6	46.1	24.1
Atrazine	114.5	116.4	108.6	120.4	103.8	111.9	98.1	80.6
Chlorpyrifos	101.6	100.1	95.2	103.0	93.2	102.8	103.8	99.4
Cyanazine	111.8	102.9	104.6	104.6	121.3	104.6	42.9	25.6
Diazinon	111.9	107.3	99.5	110.4	97.6	94.7	23.8	13.3
2,4-D ethylhexyl ester	108.4	109.7	106.8	113.1	110.9	106.3	96.1	81.0
Metolachlor	111.4	101.8	103.6	105.0	117.8	109.0	70.0	47.5

Average variation (1 s.d.) for Empore recovery was 4.1 percent and for gauze, 5.3 percent.

construction), may inhibit hydrolytic degradation. The gauze pads, however, readily absorb ambient moisture and this may expedite degradation of any sensitive compounds (such as cyanazine) under higher temperatures. That not all "sensitive" compounds degrade under these conditions indicates the need to examine their stability on the sampling media empirically under a wide range of potential environmental conditions as part of any method development validation effort.

CONCLUSIONS AND RECOMMENDATIONS

The laboratory evaluation found both media to have similar limits of detection for the analytes tested (alachlor, metolachlor, atrazine, cyanazine, diazinon, chlorpyrifos, and 2,4-D ethylhexyl ester). While each media requires a different polar solvent mixture to recover the analytes, both media required a 2 hr desorption on a shaker assembly for optimum quantitative results. When stored under ambient conditions in amber bottles with PTFE lids, recoveries from gauze were quantitative (above 88%) for all analytes over a 30-day period, while recoveries from the Empore medium were slightly lower (above 81%) over the 30 days. Refrigeration of samples resulted in an improvement in recoveries (to above 92%).

The post-sampling stability of the analytes on the media differed substantially. Whereas all the analytes tested were found to be stable on the Empore medium under even rigorous weathering conditions, the compounds diazinon, alachlor, and cyanazine suffered significant degradation on the gauze pads under high temperature conditions, especially when accompanied by high humidity. The observed losses are consistent with hydrolysis of the compounds by the occluded interstitial water and not evaporative losses or simple thermal degradation. The results of this work point to the need for examination of post-sampling stability studies of this type in method validation.

The new Empore material, although more costly than other media, appears to be very suitable for the determination of sensitive compounds and should be considered as another alternative in the arsenal of dermal collection media. Aspects relating to sample collection efficiency of, or mechanical retention of any sampled particulate on, the media were not examined and would need to be investigated. Future work in the field with this media (field stability studies and field comparisons), and with polyurethane foam (PUF) being investigated by other NIOSH researchers, will hopefully lead to improved assessments of occupational exposures to pesticides.

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