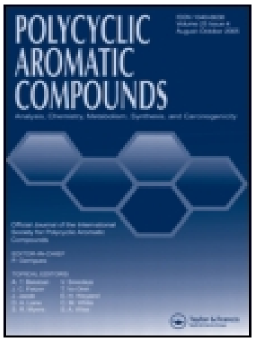

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Development of a 5-Layer Passive Organic Dermal (POD) Sampler

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A 5-layer passive organic dermal sampler was developed to allow the collection, retention, and recovery of a variety of organic compound classes simultaneously. The 5-layers, from outside in, consisted of polypropylene, polyurethane foam, C-18 solid-phase extraction disk, ethylene tetrafluoroethylene, and activated carbon cloth. The layers were enclosed in aluminum foil and placed in a muslin envelope that had a 40.0 mm diameter opening.

Ten samplers were spiked separately with three levels of diesel oil, a 50/50 diesel oil/asphalt mixture, and asphalt binder. For the diesel oil spikes, recoveries were 69.9, 71.3, 88.8, and 95.4% for 10, 10, 50, and 100 mg of diesel oil. For the 50/50 mixture, recoveries were 105.4, 92.8, and 92.0% for 10, 50, and 100 mg of the 50/50 mixture. For the asphalt binder spikes, recoveries were 104.7, 100.2, and 100.1% for 10, 50, and 100 mg of asphalt binder. For repeatability assessment, 7 samplers were spiked with 50 mg of the 50/50 mixture and recoveries averaged 92.6% (standard deviation 8.6).

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Samplers tested on asphalt paving workers proved functional, comfortable, flexible, and durable.

Key Words: asphalt paving, bitumen, dermal monitoring, method development, passive sampling, polycyclic aromatic compounds

INTRODUCTION

In 2000, the National Institute for Occupational Safety and Health (NIOSH) published an extensive literature review on the health effects of occupational exposure to asphalt (1). Over the years, a number of asphalt worker exposure studies have been conducted. Although asphalt workers are exposed by both inhalation and dermal routes, most studies have concentrated on inhalation exposure, with only a few studies also assessing dermal exposure. However, these studies were not very informative because of the sampling and analytical methods used. These studies may have focused on inhalation exposure because air sampling was common practice, with a number of accepted methods from which to choose. In addition, many researchers believe that when both inhalation and dermal exposure routes are present, the inhalation exposure poses the greater risk because the surface area of the lungs greatly exceeds that of the skin. However, unlike many indoor worker inhalation exposures, which have a relatively homogeneous chemical composition and continuous concentration range that is not highly variable, asphalt work is often performed outdoors with considerable air movement (speed and direction). For this reason and because of differing job tasks and work practices, asphalt workers' inhalation exposures can be highly variable. For many asphalt workers, their dermal exposure forms a relatively uniform coating of asphalt emission components on the skin, clothing, personal protective equipment (PPE), paving equipment, and tools. Unlike the highly variable inhalation exposure, the dermal exposure remains with the worker until the coating is washed away, and their contaminated PPE and clothing are removed. The coating consists mostly of long-chained aliphatic hydrocarbons (oils) with some aromatic compounds, including polycyclic aromatic compounds (PACs). Because of the chemical composition of the coating, it will act like a sorbent slowly concentrating asphalt emission components and will slowly saturate the workers' clothing and PPE with asphalt emission components. If the articles of clothing and PPE worn each workday are not changed or washed between usages, they will continue to saturate leading to possible breakthrough and contact with the skin, thus, potentially increasing a workers' dermal exposure. The asphalt workers' physical activity and potentially hot working environment will cause volatile components to emit from the coating, thereby, concentrating less volatile components, e.g., higher molecular weight PACs. In addition, there will be an exchange of dermal exposure components with the equipment and tools that the worker uses or touches. Hence, an asphalt workers' dermal exposure is not only chemically complex but is influenced by a number of physical factors. Not to mention, there is the potential for exposure from other sources of organic compounds, e.g., diesel oil, biodiesel, fuels, gasoline and diesel exhaust, tobacco-containing products and smoke, other combustion by-products, used and unused motor oil, lube oils, both light-weight and higher, personal hygiene products, and lotions to protect against the sun and wind. Asphalt workers' exposures are further complicated by mixed exposures, i.e., chemical, sunlight, heat, and physical exertion.

Among the conclusions reached in the NIOSH Hazard Review on asphalt (1) was that the existing data were insufficient to quantify the acute and chronic health risks of exposure and a number of research gaps were identified. NIOSH also made a recommendation to "prevent dermal exposure." Over the past 15 years, interest in studying asphalt and asphalt emissions and their health effects on workers has grown. More recent studies have often addressed research gaps identified by NIOSH (1) and during a 2006 International Health Symposium in Dresden, Germany (2). Research gaps on dermal absorption and relevant biomarkers of exposure were emphasized by some researchers at the symposium. While related research has occurred, the studies have yielded inconclusive results (3–5). Walter and Knecht (3), Cirla et al. (4), and McClean et al. (5) concluded that exposures for asphalt workers were about equal, 3-fold higher, or 8-times greater through dermal exposure than through inhalation exposure, respectively.

One possible reason for these inconsistent results is that there is almost no standardization of the dermal monitoring techniques used by researchers (6). For asphalt workers, a variety of dermal techniques were used. Väänänen et al. (7) used hand wipes with sunflower oil and polypropylene dermal pads, and McClean et al. (5) used polypropylene filters attached to an exposure pad.

Dermal monitoring techniques can be broken down into three classes: removal techniques (e.g., wipes, tape strips, washing), fluorescent tracer techniques, and surrogate skin or interception techniques (8, 9). However, not all asphalt emission components are fluorescent and removal techniques only collect what remains on the surface of the skin at the time of collection. Therefore, it was concluded that an interception technique was most appropriate. Because of limitations in the range of compounds collected, retained, and recovered from existing surrogate skin samplers, a novel 5-layer passive organic dermal (POD) sampler was developed.

The development of the POD was part of a multiphase study of hot-mix asphalt (HMA) paving workers (10). Major objectives were to investigate the chemical composition and the other sources of exposures using air and dermal monitoring, and to determine the relative contribution of inhalation and dermal exposures to dose by comparing air and dermal monitoring results to biomonitoring results of urinary PAC metabolites. In addition, the potential impact of three exposure scenarios relative to routine paving operations were assessed: an inhalation control (powered air purifier respirator), dermal controls (gloves, neck cloth, clean pants and long sleeved shirts), and a clean-up control of equipment and tools by substitution of the diesel oil with a biodiesel.

In this article, the focus is on the POD designed to quantitatively collect and retain the total asphalt emissions along with all other organic sources of dermal exposure that an asphalt worker may experience, and an assessment of the quantitative recovery of all relevant compounds. In addition, the methods and data used to validate the POD and results of a field evaluation are presented.

SAMPLER DESIGN

Five sorbent layers were incorporated in the development of the POD. The unique design of the POD gives it a high capacity and makes it useful for collecting total organic compounds, i.e., both aliphatic and aromatic compounds in the solid, liquid and gas phases, simultaneously. Initially, the idea was to use an outer layer that acts not only as a barrier similar to human skin but also mimics the diffusion rates of selected organic compounds through human skin, as the outer layer of the "biologically relevant dermal sampler" does for volatile organic compounds (16). However, because the material (a polyamide membrane filter) used as the outer layer in this sampler was no longer commercially available, it was decided the outer layer need only to act as a barrier and have good chemical selectivity for organic compounds in general. The sorbent layers that were selected would provide good chemical selectivity for organic compounds in general and were stacked such that as organic compounds migrated deeper into the POD each successive sorbent layer would provide stronger interactions between the sorbent and organic compounds. In addition, because these interactions (e.g., energies of adsorption) have to be overcome during the extraction process, the sorbent layers needed to have sufficient sampling capacity and chemical selectivity to retain a given organic compound or class of organic compounds sufficiently to prevent migration to a lower layer from which they would not be recoverable.

A schematic diagram of the POD is provided in Figure 1. The top or outer polypropylene (PP) layer of the POD provides a protective barrier, much as human skin does, to keep out asphalt binder and other solid contaminants. The remaining layers are needed to collect the complex chemical mixture present in asphalt emissions and diesel oil, and to provide sufficient sampling capacity for collecting the potentially high exposure levels when diesel oil is used for cleaning. Beneath the PP layer, the order of layers is polyurethane foam (PUF), a C-18 solid-phase extraction (SPE) disk, an ethylene tetrafluoroethylene (ETFE) filter, and a 100% activated carbon cloth (ACC). The design strategy was as asphalt emissions or similar constituents permeate through the PP layer, the

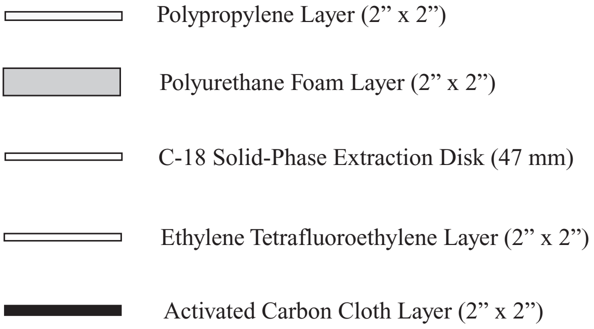

Figure 1: Schematic diagram of the 5-layer passive organic dermal (POD) sampler assembly. Polypropylene is the top or outer layer of the sampler; the other layers are shown in the order in which the layers are assembled beneath the polypropylene layer. The dimensions of each layer is listed next to each respective layer.

semi-volatile compounds would be preferentially retained on the PUF and SPE layers, and volatile compounds would be retained by the ACC. The ETFE layer served to isolate the SPE disk from the ACC. The combination of PUF and C-18 SPE layers was needed, because either layer by itself was considered inadequate for our needs. While PUF has a large sampling capacity, it may not retain the organic compounds strongly enough to prevent excessive migration to the lowest layer. While the C-18 SPE layer would more strongly retain the organic compounds than PUF, the C-18 SPE layer has a much smaller sampling capacity than PUF. However, the PUF/C-18 SPE combination does have the desired sampling capacity, chemical selectivity and retention characteristics that we were seeking.

Because of the design, the POD should be useful over a wide range of humidity and temperatures and have a large dynamic sampling range. The POD should be useful for assessing exposures to a single organic compound or multiple organic compounds simultaneously, including chemically complex mixtures such as asphalt emissions and fossil fuels.

The POD can be fastened to any surface or to a workers’ clothing with tape or a safety pin. The POD may also be attached to a Velcro mount on an arm-, leg- or headband that can be conveniently adjusted to the required fit for each worker and flexes with movement. The POD can comfortably be worn over or under clothing, including next to bare skin.

EXPERIMENTAL

Final Materials, POD Sampler Assembly, and Usage

Except for the SPE disks, all layers were cut to approximately 2″ × 2″ squares, triple rinsed in dichloromethane (HPLC Grade OmniSolv® High

Purity; EMD, Cat. No. DX0831-1; Gibbstown, NJ), and placed on Kimwipes® in a chemical fume hood to dry at ambient temperature. To facilitate rapid drying and to reduce the possibility of volatiles in the lab atmosphere from being collected on the sorbent layers, a gentle stream of ultra high purity nitrogen was directed at the sorbent layers. Dichloromethane pre-rinsed glass beakers and tweezers were used during the rinse and drying process. Once dried, these materials were stored in a clean humidistat chamber.

Reynolds Wrap® heavy-duty aluminum foil was pre-rinsed in dichloromethane, dried, cut into pieces of approximately 7″ × 9″ and used to hold the 5-layers of the POD sampler together. In the center of each, a 40-mm diameter opening (12.6 cm^2 sampling area) was punched. For assembly, a piece of aluminum foil was laid flat on a clean dry surface, and a pre-cut PP (90-mm membrane filter, 10-μm pore size; Pall Life Sciences, Cat. No. 60139; VWR; Bridgeport, NJ) layer was weighed and then centered over the opening in the aluminum foil. On two opposite sides, the aluminum foil was folded over the edge of the PP layer and back such that it would hold the layer in place and not obstruct the opening in the aluminum foil. A pre-cut PUF (SKC, Inc., special order item; Eighty Four, PA) layer was laid over the PP layer; as before, the aluminum foil was folded over the PUF layer and back. A 47-mm C-18 SPE (oil/grease extraction disk; Fisher Scientific, Cat. No. 14-638-30A; Pittsburgh, PA) disk was laid over the PUF layer; then, in this order, pre-cut layers of ETFE (200-μm thickness and 150 μm mesh; SKC, Inc., special order item; Eighty Four, PA) and ACC (100%; University Products, Cat. No. 9-066-3936; Holyoke, MA) were laid over the PUF layer, and the aluminum foil was folded over the ACC layer. The resulting rectangular piece of aluminum foil was folded from the opposite ends such that a square was formed that locked the previous folds and the 5-layers in place; the excess aluminum foil was cut away. The aluminum foil also restricted sampling to the opening of the POD and not through the walls of the sampler and served as a heat barrier for the POD.

These aluminum foil packets containing the 5-layers were inserted into a muslin envelope (3.75” × 5” herbal tea bag; Starwest Botanicals, Cat. No. 481020; Rancho Cordova, CA) that was sealed on three edges with a 40-mm diameter opening punched through the center of one side of the envelope. However, before the aluminum foil packet was inserted into a muslin envelope, the 40-mm diameter opening in the muslin envelope was reinforced with a 2″ × 2″ piece of Reynolds Wrap® super heavy-duty aluminum foil that was pre-rinsed in dichloromethane, dried and had a 40-mm diameter opening punched through the center of the foil. The 40-mm diameter openings in the super heavy-duty aluminum foil and a muslin envelope were aligned and heat-sealed together using an impulse sealer (Technopack Corporation, Cat. No. MMS-205; Miami, FL). An aluminum foil packet containing the 5-layers was inserted into the reinforced muslin envelope so that the 40-mm diameter openings were

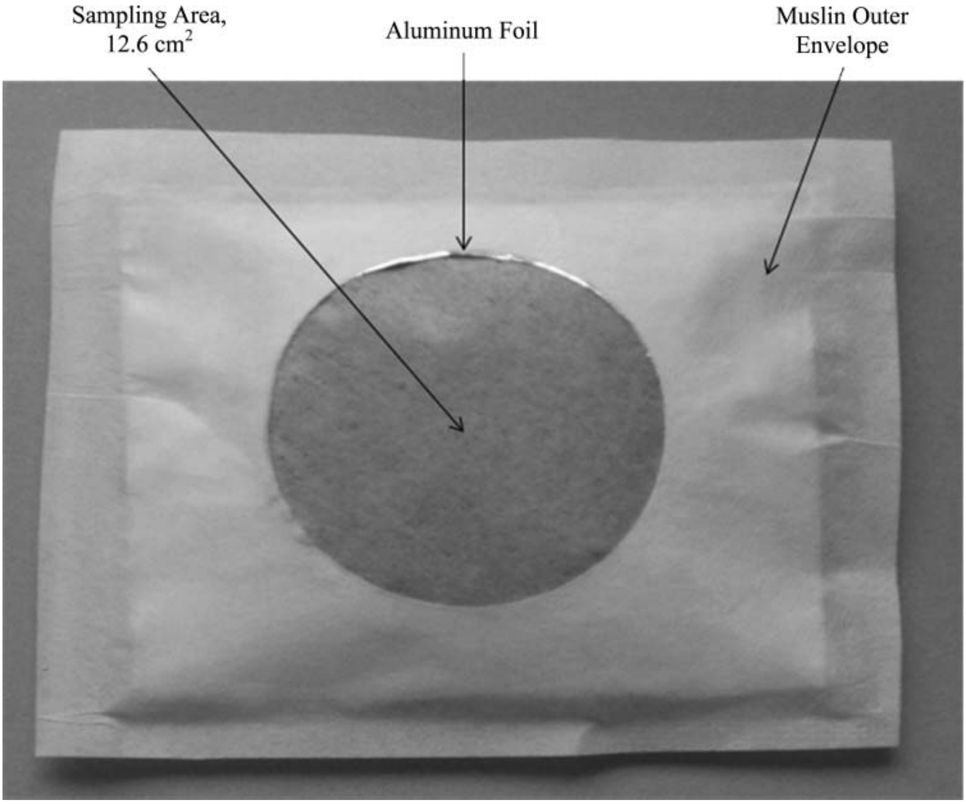

Figure 2: Photograph of an unused 5-layer passive organic dermal (POD sampler. Aluminum foil is used to restrict sampling to just the opening in the sampler, to hold the 5-layers together, to serve as a heat barrier for the sampler, and to prevent the layers from coming out the opening in the sampler. The aluminum foil and the 5-layers are inserted into a muslin envelope that is heat sealable to hold everything in place and yet be comfortable against a worker's skin. Aluminum foil also is used to reinforce the opening in the muslin envelope. The openings through the aluminum foil and muslin envelope is 40.0 mm in diameter, resulting in a sampling area of 12.6 cm^2.

aligned and all edges were heat-sealed to hold the 5-layers in place. Excess muslin fabric was trimmed off, and the outside of each assembled muslin envelope was numbered. Next, the backing on one side of a piece of carpet tape approximately 2″ wide was removed, and the carpet tape was adhered to the back of the assembled muslin envelope forming the 5-layer POD sampler; see Figure 2. For storage, each POD was inserted into a 8″ × 12″ Mylar® bag (dual track zip-seal and a tamper evident seal; IMPAK Sorbent Systems, Cat. No. 08MFS12TEZ; Los Angeles, CA), and the opening was heat-sealed.

Details for using the POD during Phase II of the project are discussed elsewhere (10). The procedure consisted of removing a POD from the Mylar® bag, removing the backing from the carpet tape, and adhering the POD to the center of the plastic armband that was modified to fit the forearm instead of the upper arm. After use, the POD was photographed, detached from the armband, wrapped in a 12″ × 12″ piece of pre-rinsed aluminum foil, and placed back into the same Mylar® bag from which it was removed and resealed.

The select sorbents, the dimensions for the 5-layers and attachment of the POD to the HMA paving worker differed for the spiking experiments and field tests. These differences were described in later subsections.

Sampler Capacity

In preliminary experiments, to determine the dimensions of the five sorbent layers needed to provide adequate sampling capacity for the proposed study, two stacks of five different sorbent layers of either 47-mm or 90-mm diameter were evaluated. The PUF, ETFE, and ACC sorbent materials were not pre-cut into 2″ × 2″ squares as previously described but were pre-cut to form a 47-mm and 90-mm diameter layer for each. An uncut 90-mm PP filter and a 47-mm C-18 SPE disk described previously were used. In addition, the following sorbent materials were used: a 47-mm PP membrane filter (10-μm pore size; Pall Life Sciences, Cat. No. 61757; VWR; Bridgeport, NJ) and a 90-mm C-18 SPE disk (oil/grease extraction disk; Fisher Scientific, Cat. No. 14-638-30B; Pittsburgh, PA). Except as noted here, all sorbent layers were pre-treated and stacked in the same order as previously described to form a 47-mm or 90-mm sampler. The aluminum foil used to hold the 47-mm or 90-mm sorbent layers together was not folded over and back as described previously to better hold the layers in place. The 40-mm and 90-mm pre-cut openings in muslin envelopes were not reinforced with aluminum foil as previously described.

These samplers were spiked with No. 2 diesel oil containing red dye (Off-road diesel; Indiana Department of Revenue; Heritage Research Group ID #: A798584; Indianapolis, IN) using a syringe, in a manner to prevent saturation and soaking through the PP layer. The mass spiked on the 47-mm and 90-mm sampler was 228.8 mg or 208.3 mg, respectively.

After sitting for 2 h at ambient temperature, the spiked samplers were disassembled and extracted as follows. The PP, PUF/SPE, and ETFE/ACC layer(s) were placed in separate vials, dichloromethane was added (for volume added to each vial see Table 1), vials were vortexed for 1 min, and then sonicated for 20 min. After additional sample preparation, an aliquot from the prepared extract was analyzed using a gas chromatograph with a flame ionization detector (GC/FID) for total organic matter (TOM); the sample preparation procedure, and instrumental and experimental conditions were described elsewhere (10).

Materials and Methodology used to Spike POD Samplers to Determine Recoveries

The outer layer of nine 47-mm POD samplers, assembled as described in the “Sampler Capacity” subsection, were separately spiked with 10 mg, 50 mg,

Table 1: Volume of dichloromethane used to extract sorbent layer(s) and aluminum foil from the spiked 47-mm and 90-mm samplers used to evaluate capacity

	Volume of Dichloromethane (mL)	
Layer(s)	90-mm Sampler	47-mm Sampler
PP	5	3
PUF/SPE	35	20
ETFE/ACC	10	5
Aluminum Foil	3	3

PP = Polypropylene; PUF/SPE = Polyurethane Foam/C-18 Solid-phase Extraction Disk; ETFE/ACC = Ethylene Tetrafluoroethylene/100% Activated Carbon Cloth.

or 100 mg of diesel oil, a 50/50 diesel oil/asphalt mix, or asphalt binder (PG 64-22; BP; Whiting, IN), respectively. Although part of a preliminary spiking investigation and probably containing a PP layer from a different lot, results for a tenth POD spiked with 10 mg diesel oil were available. The 50/50 diesel oil/asphalt mix was prepared gravimetrically by combining 5.0198 g of asphalt binder with 5.0234 g diesel oil. The diesel oil and 50/50 diesel oil/asphalt mix were applied to the outer layer of a POD sampler using a syringe. The asphalt binder was heated on a hot plate until it softened sufficiently so that when the tip of a disposable pipet touched the surface of the asphalt binder some of it adhered and was then transferred to the outer layer of a POD in small amounts until the desired mass was achieved.

Except as noted here, these spiked POD samplers were processed and analyzed as described in the last paragraph of the preceding subsection. Each PP layer was reweighed before extraction. The volume of dichloromethane was 3, 20, and 3 mL for the PP, PUF/SPE, and ETFE/ACC layer(s), respectively.

Materials and Methodology used to Determine Repeatability of the POD Sampler

The outer layer of seven 47-mm POD samplers, assembled as described in the “Sampler Capacity” subsection, were separately spiked with 50 mg of a 50/50 diesel oil/asphalt mix using a syringe. These spiked POD samplers were processed and analyzed as described in the last paragraph of the “Sampler Capacity” subsection along with the exceptions noted in the last paragraph of the preceding subsection.

Other Sorbent Materials Evaluated during Study to Determine Repeatability

Two additional samplers with different sorbent materials substituted for the C-18 SPE extraction layer were spiked as described in the preceding subsection. These samplers were processed and analyzed as described in the last paragraph of the “Sampler Capacity” subsection along with the exceptions noted in the last paragraph of the “Materials and Methodology used to Spike POD Samplers to Determine Recoveries” subsection. One sampler contained a specially prepared muslin envelope with XAD-2 (pre-cleaned Supelpak-2 resin, styrene divinylbenzene copolymer, 20–60 mesh size; Supelco, Cat. No. 2-0279; Bellefonte, PA) heat-sealed into small islands so that the material was held somewhat stationary within the muslin envelope. The other sampler contained a 47-mm XAD-2 SPE disk (glass fiber disks embedded with XAD-2; Restek, Cat. No. 26023; Bellefonte, PA).

Field Test

Sampling was conducted using 47-mm samplers that did not have reinforced openings on two workdays at a HMA paving worksite. Three HMA paving workers (operator, screedman, and raker) were sampled. On the last day of sampling, two control (concrete) workers were also sampled. For the HMA paving workers, the POD samplers were affixed to four distinct anatomical locations: the lower pant leg above the boot, the wrist/forearm, the center of the upper chest in the breathing zone area, and the center front of the worker’s hardhat; for the controls, the POD samplers were affixed to their wrist/forearm. The POD samplers were affixed using either tape, double-sided carpet tape, or a safety pin. In addition, three area samples were collected each sampling day using POD samplers that were affixed to or near the paving equipment, and two background samples were collected, away from the asphalt paving operations, each sampling day using POD samplers.

After sampling, each POD was wrapped in pre-rinsed aluminum foil and replaced in the same Mylar® bag from which the sampler was stored prior to sampling. The POD samplers were transported on ice and stored at −20°C until analysis. Except as noted here, the POD samplers were processed and analyzed as described in the last paragraph of the “Sampler Capacity” subsection along with the exceptions noted in the last paragraph of the “Materials and Methodology used to Spike POD Samplers to Determine Recoveries” subsection. An additional aliquot of each PP extract was analyzed for dichloromethane solubles; experimental conditions were described elsewhere (10). Except for extracts from the ETFE/ACC layers, additional aliquots of each extract were prepared and analyzed for asphalt binder by high temperature GC/FID and for select PACs by GC/mass spectroscopy (GC/MS); sample preparation procedures, and experimental and instrumental conditions were described elsewhere (10).

RESULTS

Sampler Capacity

Results indicated the 47-mm sampler retained approximately 13%, 51%, and 7% of the diesel oil spiked on the PP, PUF/SPE, and ETFE/ACC layer(s), respectively; the 90-mm sampler retained approximately 10%, 80%, and 3% of the diesel oil spiked on the PP, PUF/SPE, and ETFE/ACC layer(s), respectively. While the aluminum foil from the 90-mm sampler contained no detectable diesel oil components, the aluminum foil from the 47-mm sampler contained approximately 0.1% of the diesel oil components. Total recoveries (TOM) for the 47-mm and 90-mm samplers were approximately 72% and 93%, respectively. While the 90-mm C-18 SPE layer smelled like diesel oil, it showed no visible evidence of the red dye contained in the diesel oil; however, the red dye was clearly visible on the 47-mm C-18 SPE layer.

All remaining test results in the following subsections were obtained using the 47-mm POD samplers as described in the “EXPERIMENTAL/Sampling Capacity” subsection. The POD samplers as described in the “EXPERIMENTAL/Final Materials, POD Sampler Assembly, and Usage” subsection were not used until the next phase of the project.

Determination of Percent Recoveries for Spiked POD Samplers

A bar graph of the percent recovery for each layer(s) and percent total recovery of TOM from ten separately spiked POD samplers at three levels (10, 50, or 100 mg) with either diesel oil, a 50/50 diesel oil/asphalt mixture or asphalt binder are presented in Figure 3. Any discrepancies between the numbers in the figure and the recovery data and calculated results presented below are due to rounding of the numerical data in the figure; this statement also applies to the next two subsections.

For the diesel oil and the 50/50 diesel oil/asphalt mixture, chemical components were recovered from across all 5-sorbent layers; average recoveries were 28.9% (standard deviation (SD) = 9.6), 48.0% (SD = 19.1), and 11.0% (SD = 3.2) for the PP, PUF/C-18 SPE, and ETFE/ACC layers, respectively. For asphalt binder only, chemical components were recovered only from the PP layer.

For diesel oil, average total recovery for all spikes was 81.4% (SD = 12.7). For the 50/50 diesel oil/asphalt mixture, average total recovery for all spikes was 96.7% (SD = 7.6). For asphalt binder, average total recovery for all spikes was 101.7% (SD = 2.6). For the diesel oil and the 50/50 diesel oil/asphalt mixture, the average total recovery for all spikes was 87.9% (SD = 12.9). For all spiked POD samplers, average total recovery was 92.0% (SD = 10.4).

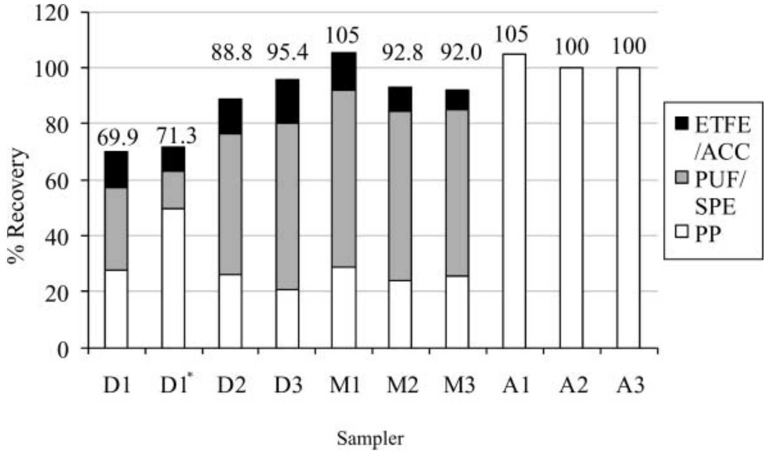

Figure 3: Percent recovery for each layer(s) and percent total recovery of ten spiked passive organic dermal (POD) samplers. The outer layer of each sampler is separately spiked, as indicated below. Percent recoveries are determined as total organic matter (TOM) utilizing a gas chromatograph with a flame ionization detector. Average total recovery is 92.1% (standard deviation = 12.5). ETFE/ACC = Ethylene Tetrafluoroethylene/100% Activated Carbon Cloth; PUF/SPE = Polyurethane Foam/C-18 Solid-phase Extraction Disk; PP = Polypropylene; D1 and D1* = 10 mg, D2 = 50 mg, D3 = 100 mg of Diesel Oil; M1 = 10 mg, M2 = 50 mg, M3 = 100 mg of a 50/50 Diesel Oil/Asphalt Mixture; A1 = 10 mg, A2 = 50 mg, A3 = 100 mg of Asphalt Binder. D1* = results for this sampler is from an earlier spiking investigation.

Determination of Repeatability using Spiked POD Samplers and Other Sorbent Results

A bar graph of the percent retained for each layer(s) and percent total recovery of TOM from seven separately spiked POD samplers at 50 mg with a 50/50 diesel oil/asphalt mixture are presented in Figure 4. Chemical components were recovered from across the 5-sorbent layers. Average recoveries were 45.6% (SD = 17.5), 36.2% (SD = 19.6), and 8.0% (SD = 1.4) for the PP, PUF/C-18 SPE, and ETFE/ACC layers, respectively; and the average total recovery was 89.1% (SD = 4.4).

For the muslin envelope containing XAD-2 that was substituted for the C-18 SPE layer in a POD that was spiked with 50 mg of the 50/50 diesel oil/asphalt mixture, the bar graph results for the percent retained for each layer(s) and percent total recovery for this sampler are presented in Figure 4. Chemical components were recovered from across the 5-sorbent layers. Average recoveries were 37.4%, 72.3%, and 1.4% for the PP, PUF/XAD-2, and ETFE/ACC layers, respectively; and the total recovery for this sampler was 111.0%.

For the XAD-2 SPE layer that was substituted for the C-18 SPE layer in a POD that was spiked with 50 mg of the 50/50 diesel oil/asphalt mixture, the bar graph results for the percent retained for each layer(s) and percent total recovery are presented in Figure 4. Chemical components were recovered from

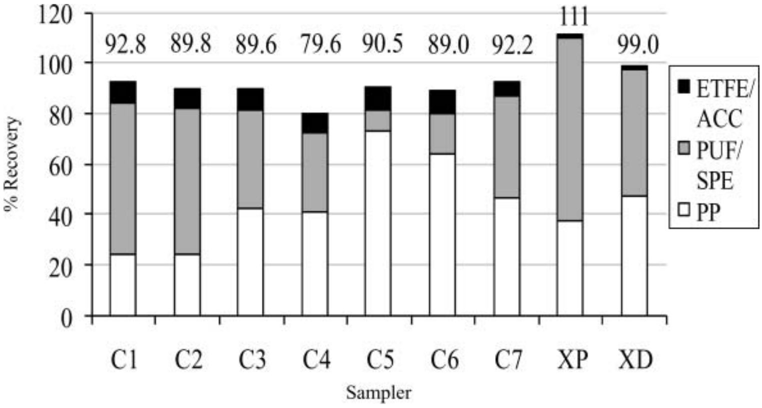

Figure 4: Percent recovery for each layer(s) and percent total recovery of nine spiked passive organic dermal (POD) samplers. Seven samplers (C1-C7) contain a C-18 solid-phase extraction (SPE) disk; the remaining samplers contain either XAD-2 powder (20–60 mesh, XP) in a muslin envelope or an XAD-2 SPE disk (XD). The outer layer of each sampler is separately spiked with 50 mg of a 50/50 diesel oil/asphalt mixture. Percent recovery is determined, as total organic matter (TOM), utilizing a gas chromatograph with a flame ionization detector. Average total recovery for all nine samplers is 92.6% (standard deviation (SD) = 8.6). Average total recovery for the seven samplers containing a C-18 SPE disk is 89.1% (SD = 4.4). ETFE/ACC = Ethylene Tetrafluoroethylene/100% Activated Carbon Cloth; PUF/SPE = Polyurethane Foam/Solid-phase Extraction Disk; PP = Polypropylene.

across the 5-sorbent layers. Average recoveries were 47.5%, 50.1%, and 1.4% for the PP, PUF/XAD-2 SPE, and ETFE/ACC layers, respectively; and the total recovery for this sampler was 99.0%.

Field Test

After sampling, many of the POD samplers showed visible evidence of staining similar to that seen when oil or grease gets on clothing. In addition, some POD samplers had dark spots and black smears that were likely evidence of exposure to higher molecular weight petroleum derived-products such as the asphalt binder; these dark spots and black smears were usually found on the POD placed on the leg of a HMA worker. Photographs of each POD were taken to preserve this visible evidence.

Because the TOM and asphalt binder concentrations were minimal for the HMA operator, these results were not useful for deciding placement of the POD samplers on HMA workers in the next phase of the project and therefore were not included. In addition, because the dichloromethane solubles and asphalt binder concentrations and the results for the concrete workers, as well as, area and background POD samplers were not useful for deciding placement of the POD samplers on HMA workers in the next phase of the project, these results were not included. However, any observations made regarding the POD samplers usefulness, feasibility for sampling HMA workers, durability and related

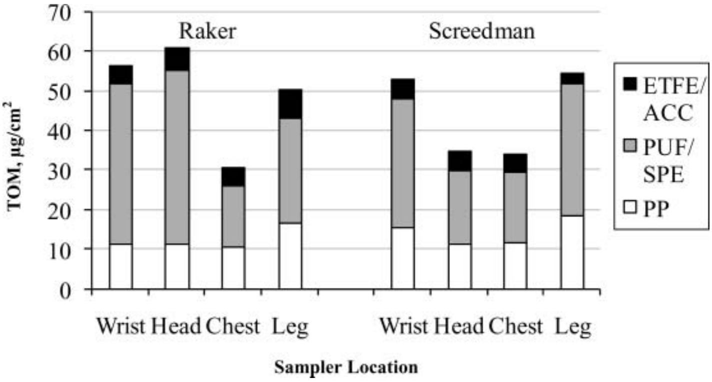

Figure 5: Determination of total organic matter (TOM) for each layer(s) of passive organic dermal (POD) samplers attached at four Locations on two hot-mix asphalt Paving workers. Samplers are attached to the lower pant leg above the boot, wrist/forearm, center of the upper chest in breathing zone, and center front of the worker's hardhat of a raker and a screedman. TOM is determined utilizing a gas chromatograph with a flame ionization detector. ETFE/ACC = Ethylene Tetrafluoroethylene/100% Activated Carbon Cloth; PUF/SPE = Polyurethane Foam/C-18 Solid-phase Extraction Disk; PP = Polypropylene.

logistical issues were taken into consideration in later sections and for deciding on the final POD assembly. These data were also taken into consideration in another paper on the pilot phase of the project (11).

A bar graph of the concentration of TOM determined from each layer(s) and total concentration of TOM from POD samplers located at the four locations on the bodies of a HMA raker and screedman are presented in Figure 5. The average TOM concentrations for both workers were 13.0 (SD = 2.9), 28.8 (SD = 10.6), and 4.9 (SD = 1.1) μg/cm^2 on the PP, PUF/C-18 SPE, and ETFE/ACC layers, respectively. The average total TOM concentration for both workers was 46.6 (SD = 11.5) μg/cm^2. The average total TOM concentration on POD samplers located on the wrist/forearm was 54.5 (SD = 3.4) μg/cm^2, on the head was 47.5 (SD = 17.7) μg/cm^2, on the chest was 32.0 (SD = 3.4) μg/cm^2, and on the leg 52.0 (SD = 2.8) μg/cm^2.

Chromatograms of the TOM obtained from an air sample and from the PP, PUF/C-18 SPE, and ETFE/ACC layers that were in the POD samplers attached at four locations (lower pant leg above the boot, wrist/forearm, center of the upper chest in breathing zone, and center front of the worker's hardhat) on a HMA worker are shown in Figure 6. The air sample and the POD samples were collected on the same HMA raker on the same day. Each chromatogram showed a different elution profile indicating that each sample and sample layer(s) contained differing chemical components of the asphalt emissions and other organic sources to which the HMA raker was being exposed on this workday.

Although the POD samplers were analyzed for select PACs and the results were summed to obtain the total PAC concentrations, the results indicated

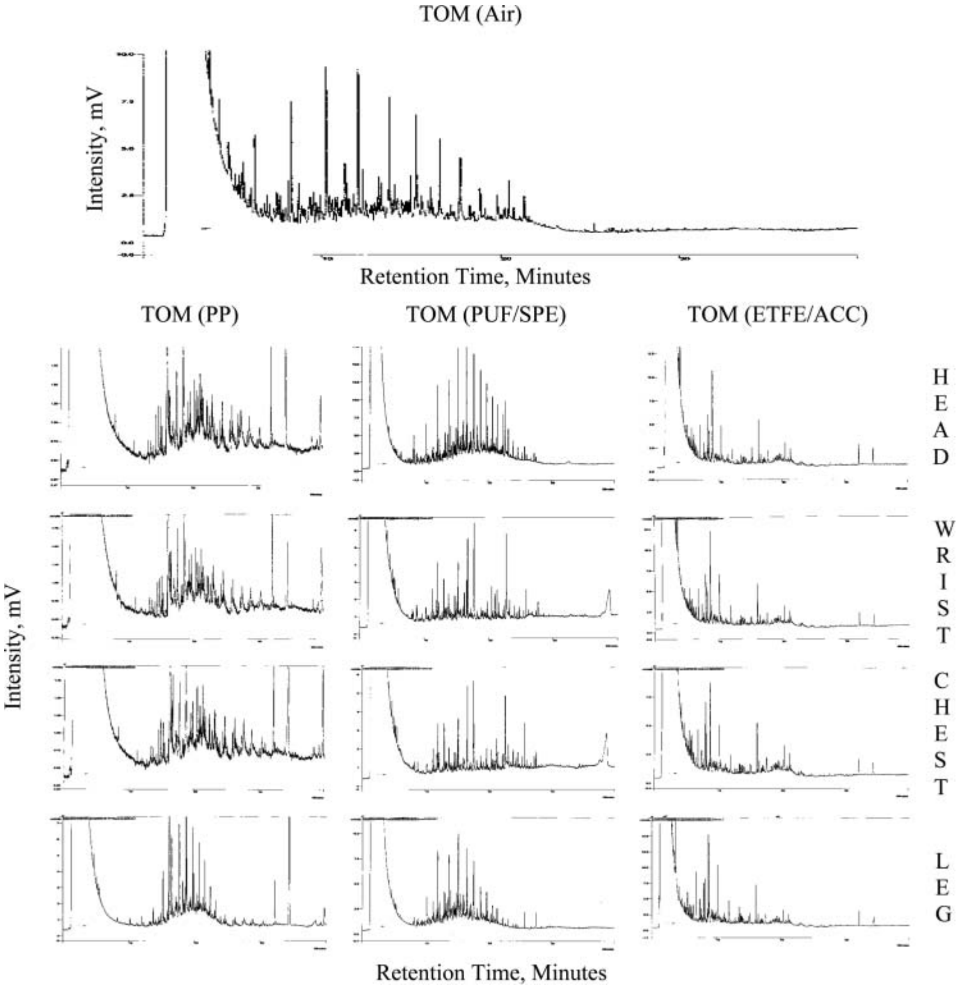

Figure 6: Total organic matter (TOM) chromatograms. Top chromatogram is obtained from an air sample collected in a raker's personal-breathing zone. Remaining chromatograms are obtained from dermal samplers attached at four locations (lower pant leg above the boot, wrist/forearm, center of the upper chest in breathing zone, and center front of the worker's hardhat) on a raker; chromatograms show the results collected on different layer(s) of the passive organic dermal (POD) sampler. Chromatograms are collected utilizing a gas chromatograph with a flame ionization detector. PP = Polypropylene; PUF/SPE = Polyurethane Foam/C-18 Solid-phase Extraction Disk; ETFE/ACC = Ethylene Tetrafluoroethylene/100% Activated Carbon Cloth.

that a variety of PACs was collected; however, the results also indicated a wide variation in the distributions of the PACs across the 5-sorbent layers for both job task and for POD location. Although these data were not useful for deciding on placement of the POD samplers on HMA workers in the next phase of the project, the POD was shown to be useful for collecting PAC exposures of HMA paving workers. For these reasons and because this phase of the investigation was not intended to be a definitive exposure assessment study, the PAC data and results were not included but were taken into consideration in paper on the pilot study (11).

One POD affixed using tape and a safety pin was lost during the field test. Other POD samplers affixed with tape or safety pins had to be adjusted throughout the workday to ensure the POD samplers did not become detached. POD samplers affixed to the clothing of workers using carpet tape was too inflexible and interfered with range of motion, hence, worker performance; also, when it was time to remove and store some of these POD samplers, the muslin envelopes were torn because the carpet tape adhered to the POD too strongly. Probably the biggest problem observed during the field test was that as the workers moved about performing their tasks, the layers of some the POD sampler started to come through the opening in the sampler, and the layers had to be manually pushed back into place. Consequently, the final POD assembly utilized a reinforced opening and the aluminum foil used to hold the layers together was also used to hold the layers in place; because of these final modifications, this problem was not observed in the next phase of the project, data are not reported herein.

DISCUSSION

For the capacity study, the object was only to determine whether a 47-mm or 90-mm samplers were needed for the next phase of the study; therefore, only one sampler each was used. A mass of approximately 200 mg was considered representative of a worst case exposure scenario; this was based on the preliminary field investigation where the highest TOM exposure found on a pair of cotton gloves was 0.52 mg/cm^2 (11). The mass spiked on the 47-mm and 90-mm sampler was approximately 35 and 20 times greater than that of the equivalent mass on the cotton gloves, respectively. For subsequent spiking experiments, 100 mg (approximately 17.5 times the equivalent mass on the cotton gloves) was used to determine recoveries and repeatability.

Although the recovery from the 47-mm sampler during the capacity study was only 72%, the experiment was not repeated because the vial used for extraction was too small for an efficient extraction. This conclusion was supported by the subsequent validation experiments. In addition, the recovery from the 90-mm sampler was approximately 93%.

Overall, results of the capacity study indicated that the sampler design performed as expected. Diesel oil components on the ETFE/ACC layers consisted of the lighter or more volatile components; therefore, only the most volatile diesel oil components migrated to the deepest sorbent layer, the ACC layer. Because most of the diesel oil components were retained on the PUF/C18 SPE layers and for the 90-mm sampler no red dye was visible on the C-18 SPE layer, it was concluded that the PUF layer comprised most of the sampling capacity of the sampler. Because no diesel oil components were found on the aluminum foil from the 90-mm sampler and only a trace amount from the 47-mm sampler, breakthrough does not appear to be a cause for concern except possibly in the worst exposure environments. The 47-mm sampler should have sufficient sampling capacity for collecting most exposures that a HMA paving worker would experience. Based on these results, the five sorbent layers selected should prove appropriate for sampling asphalt and other organic emissions at a HMA paving worksite.

The results of the spiking experiments using the asphalt binder showed that the PP layer acted as a barrier much like human skin does in that all of the asphalt binder was found only this layer. In addition, the results indicated the asphalt binder was quantitatively recovered from the PP layer. Furthermore, the spiking experiments showed that both diesel oil and the 50/50 diesel oil/asphalt mixture breakthrough the PP layer and were quantitatively retained on the PUF/C-18 SPE and ETFE/ACC layers. More importantly, the results also indicated the components in the diesel oil and the 50/50 diesel oil/asphalt mixture were 88% recoverable with reasonable variability for all spiking levels. The recovery and variability results improved if the results for the lowest spiking level (10 mg) were not included in the statistical analysis; this is an expected outcome because sampling efficiency decreases at the lower end of the sampling range for any sampler. The 10 mg spike was selected because 7 mg was the minimum concentration of TOM found on the gloves during the pilot study (11).

Although the percent total recoveries were better for the samplers that substituted XAD-2 for the C18 SPE disk, the samplers would be impractical. Too much time would be required to assemble enough samplers for most projects. The XAD-2 SPE disks were too friable for most sampler applications, thereby, causing results to be irreproducible.

The four locations for POD placement on a HMA paving worker were selected because those locations were considered to have the greatest potential for dermal exposure. However, because POD samplers placed on the lower pant leg just above the boot often became contaminated with asphalt binder and because the TOM results for the POD samplers affixed to the center front of the hardhat of the HMA paving worker were variable (SDs were at least 6.8 times that of the other locations sampled), these two locations were deemed unacceptable for the next phase of the project. For the remaining two locations, the POD samplers affixed to the wrist/forearm collected 70% more TOM compared to POD samplers placed on the center of the upper chest in the breathing zone. Furthermore, the TOM results for POD samplers affixed to the wrist/forearm were 33% less variable than POD samplers placed in the chest region. For these reasons, it was decided that POD samplers would be affixed only to the wrist/forearm of HMA paving workers in the next phase of the project. For the next phase of the project, it was decided that the POD samplers would be attached to adjustable wristbands using double-sided carpet tape. This decision was made to increase worker comfort, to decrease the likelihood of POD samplers becoming detached and lost, and to reduce sampler flexibility thereby minimizing or possibly eliminating the need to manually push the sampler media back into place throughout the day.

CONCLUSIONS AND FUTURE WORK

The method development and results described in this article indicate that the POD is a useful sampler for conducting routine dermal monitoring to assess the exposures of HMA paving workers to chemically complex mixtures such as asphalt emissions and diesel oil. The POD can be used to collect, retain, and recover a wide variety of organic compounds simultaneously or a single organic analyte.

In the next phase of the project, the POD was used to assess dermal exposures among HMA pavers, and the results were compared to a hand-washing technique using sunflower oil; results will be presented elsewhere. The POD also will be used in future projects to evaluate dermal exposures during an exposure control study using warm-mix asphalt and to evaluate dermal exposures for aircraft fuel handlers. The POD may also be used to evaluate exposures for fire fighters as part of another project. However, before these future studies can take place another source of the polypropylene outer layer must be identified.

In addition, in future work it would be interesting to investigate materials other than polypropylene as an outer layer. The use of a polyimide membrane filter or membrane filters with disulfide or sulfone chemical bonds should be investigated because these materials would more closely mimic the chemical composition and structure of human skin; the stratum corneum, which is the outer layer, is our primary protective barrier for blocking chemicals from entering the body by way of the dermal route of exposure.

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