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Polyurethane foam (PUF) passive samplers for monitoring phenanthrene in stormwater†

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Pollution from highway stormwater runoff has been an increasing area of concern. Many structural Best Management Practices (BMPs) have been implemented for stormwater treatment and management. One challenge for these BMPs is to sample stormwater and monitor BMP performance. The main objective of this study was to evaluate the feasibility of using polyurethane foam (PUF) passive samplers (PSs) for sampling phenanthrene (PHE) in highway stormwater runoff and BMPs. Tests were conducted using batch reactors, glass-tube columns, and laboratory-scale BMPs (bioretention cells). Results indicate that sorption for PHE by PUF is mainly linearly relative to time, and the high sorption capacity allows the PUF passive sampler to monitor stormwater events for months or years. The PUF passive samplers could be embedded in BMPs for monitoring influent and effluent PHE concentrations. Models developed to link the results of batch and column tests proved to be useful for determining removal or sorption parameters and performance of the PUF-PSs. The predicted removal efficiencies of BMPs were close to the real values obtained from the control columns with errors ranging between -8.46 and 1.52% . This research showed that it is possible to use PUF passive samplers for sampling stormwater and monitoring the performance of stormwater BMPs, which warrants the field-scale feasibility studies in the future.

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Considerable research has been conducted on passive samplers for monitoring environmental pollution, but no systematic work has been done for developing passive samplers for stormwater sampling and structural Best Management Practices (BMP) monitoring. This study evaluate the feasibility of using polyurethane foam (PUF) passive samplers (PSs) for sampling phenanthrene (PHE) in highway stormwater runoff. Tests results indicate that PUF can sorb PHE quickly with a high sorption capacity, and PUF-PS can be used for long-term monitoring of BMP performance. Models were developed for determining parameters and performance of the PUF-PSs. Potential users will find guidance to use PUF-PSs for sampling SVOCs in stormwater runoff and for BMP performance evaluation.

1. Introduction

Pollution from highway stormwater runoff has been an increasing area of concern within the environmental field.^{1,2} To respond to the need for reduced contamination within highway runoff, many structural Best Management Practices (BMPs) have been implemented. Challenges for BMPs include monitoring their effectiveness and determining effluent concentrations. The current methods for stormwater sampling include

sending technicians to the field or installing auto-samplers to collect either grab or composite samples. These methods become costly, cumbersome and, in many cases, infeasible due to the potentially large number of BMPs across a region and the irregularity and difficulty of predicting storms. Passive samplers have been proven to be reliable and cost-effective for monitoring groundwater, seawater and air pollution,^{3,4} but a greater understanding is needed for using them for monitoring stormwater and BMP performance.

Passive samplers are systems that are able to acquire a sample from a discrete location without the active media transport induced by pumping (*e.g.*, in an auto-sampler) or purge techniques.^{3,4} Broadly speaking, based on sampler mechanisms and nature of the collected sample, passive samplers can be classified as three types: *i.e.*, type 1 recovers a grab water sample; type 2 relies on diffusion of the analytes to reach and maintain equilibrium with the sampled medium in the sampler; and type 3 relies on diffusion and sorption to accumulate analytes in the sampler.^{3,5-7} Types 2 and 3 passive

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samplers have been used for sampling air, surface water, groundwater/wells, and sediment pore water. For stormwater sampling and BMP monitoring, only type 1 passive samplers have been developed; examples include: (1) gravity flow samplers; (2) siphon flow samplers; (3) rotational flow samplers; (4) flow splitting samplers; and (5) direct sieving samplers.^{3–5} Essentially, these type 1 passive samplers are designed to catch a small portion of stormwater runoff to characterize the Event Mean Concentration (EMC) of a storm event. Information is lacking on using passive samplers (particularly types 2 and 3) for sampling/monitoring of BMPs both on an episodic basis and in a long-term period.

We conducted a preliminary feasibility study on development of a new stormwater passive sampler that uses polyurethane foam (PUF) as a sorbent for sampling polycyclic aromatic hydrocarbons (PAHs) in highway stormwater runoff. PAHs are a group of organic compounds that are commonly found in highway runoff, and they are usually present at trace (*i.e.*, $\mu\text{g L}^{-1}$) or ultra-trace (*i.e.*, ng L^{-1}) levels in stormwater. Such low concentrations require extraction from 10 to 100 liters of runoff sample for routine analytical methods.⁸ These analytical challenges provide the incentive to develop type 2 or 3 passive sampler for sampling PAHs. In this study, we selected PUF because of its low-cost and efficiency for sorption of different organic compounds. PUF has been used commonly as a passive air sampler for semi-volatile organic compounds (SVOCs), such as PAHs and polychlorinated biphenyls (PCBs).^{9–12} However, to our knowledge, PUF has not been used as an absorbent in passive samplers for monitoring PAHs in stormwater runoff.

The objectives of this study were to investigate the feasibility of developing PUF passive samplers for (1) sampling PAHs in stormwater and (2) monitoring the performance of BMPs for treatment of phenanthrene (PHE), one of common PAHs in highway stormwater runoff.^{8,13} As a preliminary feasibility study, we tested the passive samplers developed *via* kinetic and sorption studies in batch reactors, glass-tube columns, and laboratory-scale BMPs (bioretention cells) to preliminarily characterize the PUF passive samplers for PHE sampling and to evaluate the performance of BMPs for PHE removal on an episodic basis and in a long-term period.

2. Material and methods

2.1. Chemicals and analysis

PUF sheet (100 pore-per-inch, density of 0.03 g cm^{-3}) was purchased from ITW Inc. ¹⁴C-labeled PHE (phenanthrene-9-¹⁴C, specific activity = 0.1 mCi mL^{-1}) was purchased from American Radiolabeled Chemicals Inc. PHE standard solution ($200 \mu\text{g mL}^{-1}$ in methylene chloride, analytical standard) was purchased from Supelco Inc. ACS grade methanol and HPLC grade methylene chloride were purchased from Fisher Scientific. The Millipore Simplicity System was used to produce the deionized (DI) water (electrical conductivity = $18 \text{ M}\Omega \text{ cm}$).

Unlabeled PHE stock solution was prepared by adding PHE standard solution into DI water to obtain a stock solution of $1000 \mu\text{g L}^{-1}$, which then was diluted sequentially to a series of

concentrations ($0.03\text{--}1000 \mu\text{g L}^{-1}$). The PHE solutions were spiked with the ¹⁴C-labeled PHE solution and then were used in different tests. The ¹⁴C-labeled PHE solution was made by adding $20 \mu\text{L}$ of high activity ($=100 \mu\text{Ci mL}^{-1}$) stock solution of ¹⁴C-labeled PHE to 100 mL DI water. The ¹⁴C concentration in the liquid phase was measured with a Packard A2500 liquid scintillation counter (LSC). The ¹⁴C sorbed onto PUF was eluted first (see ESI†) and then analyzed with LSC.

To eliminate PHE that may have accumulated in the PUF prior to any tests, the PUF was soaked in methanol for 12 h in a beaker, then rinsed with DI water three times, and finally oven dried for 12 h at $70 \text{ }^\circ\text{C}$.

2.2. Experimental design

Four different sets of tests were conducted: (1) sorption kinetic tests; (2) sorption isotherm tests; (3) glass-tube column sorption tests; and (4) BMP tests (*i.e.*, with PUF passive samplers embedded in lab-scale BMPs). Details of the design of these tests follow.

2.2.1. Sorption kinetic tests. Kinetic studies were conducted in batch reactors (Fig. 1) stirred with a magnetic stirrer at a speed of $\sim 150 \text{ rpm}$. The batch reactor was filled with $\sim 0.1 \text{ g}$ PUF/beaker (about 30 pieces of PUF, each with a size of $0.5 \text{ cm} \times 0.5 \text{ cm} \times 0.76 \text{ cm}$) and 40 mL ¹⁴C-spiked PHE solution (concentrations = $0.03, 0.3, 2.0, \text{ and } 10 \mu\text{g L}^{-1}$). The bulk solution was sampled at 5, 10, 15, 35, 60, 180, and 720 min.

Sampling rate of passive sampler was affected by water flow velocity.¹⁴ It was reported that sorption of an organic contaminant in a PUF air sampler is closely related to the wind speed.¹⁵ Therefore, we assumed that in the initial period, PHE sorption onto PUF and PHE removal in bulk solution follows first-order kinetics:

$$\frac{dc}{dt} = -k_B C \quad (1)$$

$$M = V(C_0 - C) = VC_0(1 - e^{-k_B t}) \quad (2)$$

where M is the PHE mass sorbed by the sampler until time t [M]; k_B is a first-order rate constant (obtained from batch tests) [T^{-1}]; C_0 and C is PHE concentration in bulk solution (stormwater runoff) at $t = 0$ and $t = t$ [M L^{-3}], respectively; t is contacting time [T] in the batch reactor; and V is the batch reactor volume.

2.2.2. Sorption isotherm tests. Three groups of tests were conducted with batch reactors (Fig. 1) for determining PHE sorption isotherms. The first group used six PHE concentrations ($0.03, 0.3, 2.0, 5.0, 10, \text{ and } 15 \mu\text{g L}^{-1}$) to mimic the range of PAH concentration in stormwater.⁸ The second and third groups were designed based on the solubility of PHE in water, $0.99\text{--}1.29 \text{ mg L}^{-1}$ at $25 \text{ }^\circ\text{C}$,¹⁶ and eight PHE concentrations ($1.0, 10, 50, 100, 200, 400, 700, \text{ and } 1000 \mu\text{g L}^{-1}$) were utilized. PUF pieces ($\sim 0.05 \text{ g}$ for the first and second, and $\sim 0.009 \text{ g}$ for the third group tests) were put into a beaker with 50 mL ¹⁴C-spiked PHE solution. Based on results of the kinetic test, the equilibrium time was set to be 120 min. Sorption isotherm curves were fit with either the Freundlich or Langmuir model:

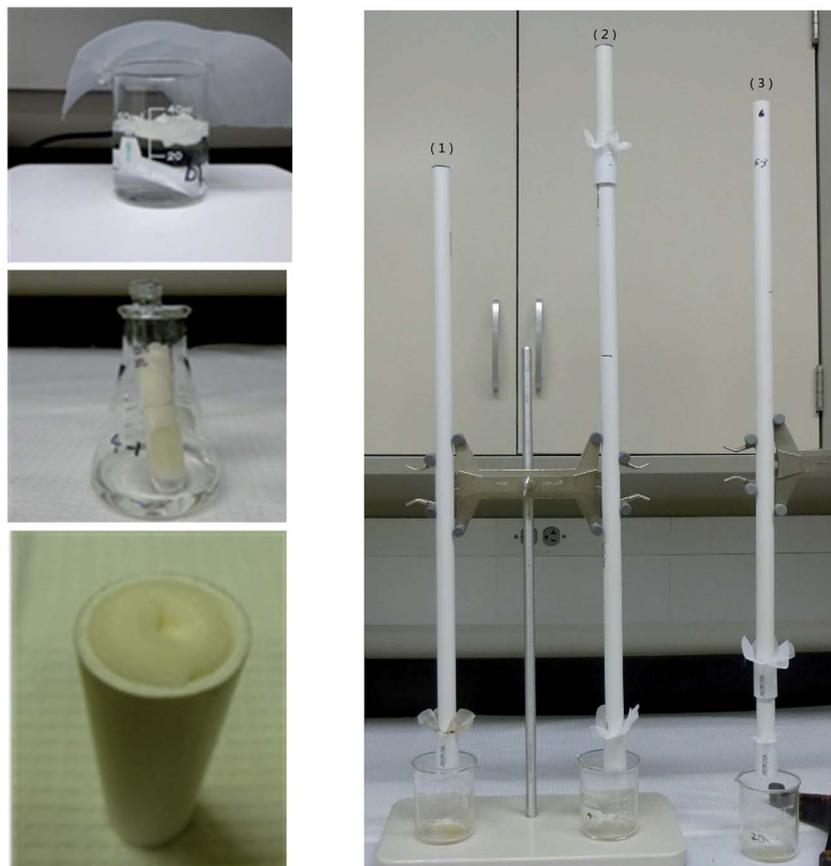


Fig. 1 Batch and column reactors used. (Left top) Beaker tests for evaluating sorption kinetics and isotherm tests. (Left middle) Glass-tube columns filled with a PUF passive sampler with two possible PUF sizes. (Left bottom) Top view of a PUF passive sampler ($\phi = 1.91$ cm, height = 7.62 cm) used in (right) lab-scale BMPs (column bioretention cells), where column (1) is the control (no PUF sampler) and a PUF sampler is placed on top (2) and at bottom (3) of the BMPs for measuring influent and effluent.

$$q_e = K_f C_e^n \text{ or } q_e = \frac{b q_{e,m} C_e}{1 + b C_e} \quad (3)$$

where q_e is the solid-phase concentration of PHE [M of PHE on solid phase per M of sorbent]; K_f is Freundlich capacity factor [M M⁻¹]/[L³ M⁻¹]⁻ⁿ; n is Freundlich intensity parameter; b is Langmuir equilibrium constant [L³ M⁻¹]; $q_{e,m}$ is the maximum q_e [M M⁻¹] and C_e is the aqueous-phase concentration of PHE at equilibrium [M L⁻³].

2.2.3. Glass-tube column sorption tests. The objective of these tests was to evaluate the performance of the PUF passive sampler for PHE sorption during storm events without the influence of BMPs. The PUF passive sampler was made by rolling the PUF sheet into a plug and squeezing the plug into the lower part of a glass-tube column (with an inner diameter $\phi = 1.27$ cm and the length = 11.43 cm) (Fig. 1). Two PUF plug sizes, 3.81 cm (~0.8 g) and 6.35 cm (~1.3 g) in length were tested. There was 5.08–7.62 cm space above the PUF plug in the glass-tube column, which allowed water head (pressure) to build when adding the synthetic stormwater (Table 1). The glass-tube column has an open end for collecting the effluent of the stormwater in an Erlenmeyer flask (Fig. 1).

Studies show the initial runoff of stormwater contains the majority of pollutant,^{1,17,18} and most treatment BMPs are designed to treat the first 1.27 cm (half inch) of runoff, which is

Table 1 Chemical composition of synthetic stormwater for lab-scale column tests²⁰

| Constituent | Concentration (mg L ⁻¹) |
|--|-------------------------------------|
| Pond sediment ^a | 500 |
| Pb(NO ₃) ₂ | 0.16 |
| Cu(NO ₃) ₂ ·H ₂ O | 0.11 |
| Zn(NO ₃) ₂ ·6H ₂ O | 0.91 |
| Na ₂ CO ₃ | 0.9 |
| NaCl | 200 |
| Kaolin | 40 |
| Phenanthrene | 0.03–10 µg L ⁻¹ |

^a The portion used was passed through the 250 micrometer (mess # 60) sieve of the sediment collected from a local highway stormwater outfall (e.g., the I-80 detention basin near 108th Street in Omaha). The characterization (µg g⁻¹) of the dry sediment is: Cr = 12.148; Fe = 3054.209; Ni = 7.255; Cu = 28.076; Zn = 113.842; Ag = 31.982; Cd = < detection limit (= 1.228 µg L⁻¹); Sb = < detection limit (= 8.404 µg L⁻¹); Pb = 19.076; and NO₃⁻ = 185. The pH and conductivity of the synthetic stormwater were not adjusted.

also called the water quality volume (WQV).¹⁸ The WQV for a bioretention cell can be calculated as:

$$\text{WQV} = \frac{A_F [K(H_f + d_f)t_f]}{d_f} \quad (4)$$

where WQV is water quality volume (mL); A_F is surface area of ponding area (cm²); d_f is filter medium depth (cm); K is hydraulic conductivity of filter media (cm per day); H_f is average height of water above filter bed (cm) (typically 7.6–11.4 cm); and t_f is filter bed drain time (days). Given $\Phi = 1.27$ cm, $d_f = 45.72$ cm, $K = 280.4$ cm per day (measured value for PUF-PRF), $H_f = 7.62$ cm and $t_f = 1$ day,¹⁸ we found the $A_F = 1.266$ cm² ($=3.14 \times (1.27/2)^2$) and WQV of 414 mL ($=1.266 \times 280.4 \times (7.62 + 45.72) \times 1/45.72$) to be the amount of runoff to be contacted by the glass-tube column (as it was used to simulate the BMP columns shown in Fig. 1).

Three rain intensities were used so that the duration for each rain event to reach the WQV was 0.5, 3, and 12 h, respectively, which correspond to (1) a 10 year 0.5 h storm, (2) a 2 year 3 h storm, and (3) a 1 year 12 h storm if a curve number of 85 is used (see ESI[†]). To reduce the use of radioactive material (¹⁴C-labeled PHE), we only applied 50 mL of ¹⁴C-spiked PHE solution to the glass-tube column for a duration of 3.6, 21.7, and 87.0 min, respectively. By doing so, we kept the hydraulic loading rate of the column to be the same as that loaded with 404 mL solution for 0.5, 3, and 12 h, respectively. In addition, for each rain event, four ¹⁴C-spiked PHE solutions (0.03, 0.3, 2.0, 5.0, and 10 $\mu\text{g L}^{-1}$) were used in the synthetic stormwater to mimic different PAH concentrations in stormwater runoff. After the glass-tube column sorption test, the PUF passive sampler was eluted for analyzing the sorbed mass of PHE on the PUF (called M), which can be used to calculate the PHE concentration in synthetic stormwater used in the test (see eqn (7) below).

2.2.4. Linking batch kinetic tests with column tests. The plug flow reactor model (eqn (5)) with first-order kinetics ($r = -k_p C$) was used to simulate the sampler in the glass-tube column tests:

$$C = C_w \exp(-k_p t_p) \quad (5)$$

where C_w and C are PHE concentrations in stormwater as influent and effluent of the sampler [M L^{-3}], respectively; k_p is the first-order rate constant [T^{-1}]; and t_p is the contact time between stormwater and PUF sampler [T] (=hydraulic retention time of sampler). According to the literature,^{4,6} eqn (6) was used to determine the PHE uptake rate by the PUF sampler:

$$\frac{dm}{dt} = Qk_o \left(C_w - \frac{C_s}{K_{\text{SW}}} \right) \quad (6)$$

where m is mass sorbed onto the PUF [M]; C_w is defined in eqn (5); Q is stormwater flow through the sampler [$\text{L}^3 \text{T}^{-1}$]; k_o is the general mass distribution coefficient of PHE between the PUF sampler and stormwater runoff ($=M/(C_w \text{WQV})$ with C_w being the PHE concentration in synthetic stormwater used in the test) [–]; C_s is PHE concentration in PUF [M of PHE per M of PUF] at time t ; and K_{SW} is sampler–water partition coefficient at equilibrium [$\text{L}^3 \text{M}^{-1}$ of PUF]. For short exposure times, C_s is much

smaller than its equilibrium value (*i.e.*, $C_s \ll K_{\text{SW}}C_w$). Thus, eqn (6) becomes $dm/dt = Qk_o C_w$, and its integration becomes:

$$M = Qk_o C_{\text{avg}} t = (\text{WQV})k_o C_{\text{avg}} \quad (7)$$

where M is the sorbed mass of PHE onto PUF [M]; and C_{avg} is the time-weighted average concentration in stormwater [M L^{-3}]. From eqn (5) and (6), we can derive eqn (8):

$$M = (Q_t)k_o C_{\text{avg}} = (Q_t)C_{\text{avg}}[1 - \exp(-k_p t_p)], \text{ i.e., } k_o = 1 - e^{-k_p t_p} \quad (8)$$

Eqn (8) links k_o with k_p , and therefore, k_B if $t_p = t_B$, (the reaction time of a batch reactor). Therefore, it is possible to use a batch reactor to obtain k_o of a PUF passive sampler.

2.2.5. BMP tests. These tests were to determine if the PUF passive samplers could (i) monitor the PAHs in influent and effluent of the BMPs, and (ii) be used to estimate the removal efficiency of the BMPs under the influence of single or multiple storm events. The PUF passive sampler and the lab-scale columns used are shown in Fig. 1. The columns were made of PVC pipe ($\Phi = 1.91$ cm) and filled with 45.72 cm of media (50% compost and 50% sand).^{19,20} To conduct the column test under the same condition, three columns were used (Fig. 1). The WQV was 937 mL ($=2.864 \times 280.4 \times (7.62 + 45.72) \times 1/45.72$) calculated by eqn (4). Here, we used the k (hydraulic conductivity) of PUF for calculating WQV. In the field BMPs, the k values are between 15.2–60.1 cm per day, which may allow longer contacting time between the passive sampler and stormwater, which would result in a more reliable result. Again, we only loaded 50 mL of ¹⁴C-labeled PHE solution to the test columns for 1.6, 9.6, 38.4 min to provide the same hydraulic loading rate as the half-inch WQV from the 0.5-, 3-, 12 h storm event, respectively. The column tests included tests for single-storm and multi-storm events (below).

For single storm tests, 3 initial PHE concentrations (0.03, 2 and 10 $\mu\text{g L}^{-1}$) were used for each of the three storm events (*i.e.*, duration = 0.5, 3, 12 h). ¹⁴C in influent and effluent samples were analyzed for calculation of the BMP removal efficiency of PHE. The PUF passive sampler at the top and bottom of the columns were collected for eluting and then analyzing the sorbed mass of PHE (M), which then was used to calculate the PHE concentrations in the stormwater (*i.e.*, the influent and effluent of the BMP) with eqn (7). The claimed removal efficiency of PHE by the PUF passive sampler and the removal efficiency of the control are calculated with:

$$E_{\text{CS}} = [(C_{\text{CS,inf}} - C_{\text{CS,eff}})/C_{\text{CS,inf}}] \times 100\% \quad (9)$$

$$E_{\text{CON}} = [(C_{\text{inf}} - C_{\text{eff}})/C_{\text{inf}}] \times 100\% \quad (10)$$

where E_{CS} is the sampler's claimed removal efficiency, $C_{\text{CS,inf}}$ and $C_{\text{CS,eff}}$ are the claimed (predicted) PHE concentration by sampler in the influent and effluent, respectively (both can be calculated with eqn (7)); E_{CON} is the control column removal efficiency, C_{inf} and C_{eff} is the influent and effluent concentration of PHE of the control BMP. The feasibility of using the PUF passive sampler to predict PHE removal in the BMPs can be evaluated by comparing the two removal efficiencies.

For multi-storm events, five storm tests were deployed to mimic multiple storm events occurring in series (but with dry days between the events) during a period of 34 days. This test was conducted with two concentrations (2.0 and 10.0 $\mu\text{g L}^{-1}$) with the same storm event duration arrangement. After the 5 storm events, the PHE in different samplers was analyzed, and the data were interpreted in the same way as for single storm events. The claimed runoff concentrations are average values calculated as:

$$M = \sum_{i=1}^n k_{oi} C_i Q_i \quad (11)$$

$$C_{\text{avg,ms}} = \frac{M}{k_{o,\text{avg}} \sum_{i=1}^n Q_i} \quad (12)$$

where $k_{o,\text{avg}}$ is the average k_o value determined in glass-tube column tests ($k_{o,\text{ave}} = (k_o(0.5 \text{ h}) + k_o(3 \text{ h}) + k_o(12 \text{ h}))/3$); $C_{\text{avg,ms}}$ is the average PHE concentration of synthetic stormwater (influent of the passive sampler during multiple storm

events); i is the i^{th} storm event ($i = 1$ to 5). The other parameters are defined before. The claimed and real BMP removal efficiency were calculated by eqn (9) and (10), respectively.

3. Results

3.1. Sorption kinetic and isotherm tests

Sorption of PHE by PUF is very fast (Fig. 2). Within the first 15 min, about 83.8–95.5% of the PHE was sorbed, and the PHE concentration in bulk solution follows first-order removal with an average k_B being 0.355 min^{-1} ($= (0.387 + 0.481 + 0.265 + 0.286)/4$). Fig. 3 shows that the Freundlich model fits the data of the three isotherm tests well. From the third isotherm test (Fig. 3D), we found the maximum sorption capacity of PUF for PHE is $5967 \mu\text{g g}^{-1}$. For the PHE concentration in the range of 0.03 – $15 \mu\text{g L}^{-1}$ (a field PHE range), the PHE sorbed onto the PUF was in the range of 88.8–94.9% after reaching sorption equilibrium (Fig. 3A).

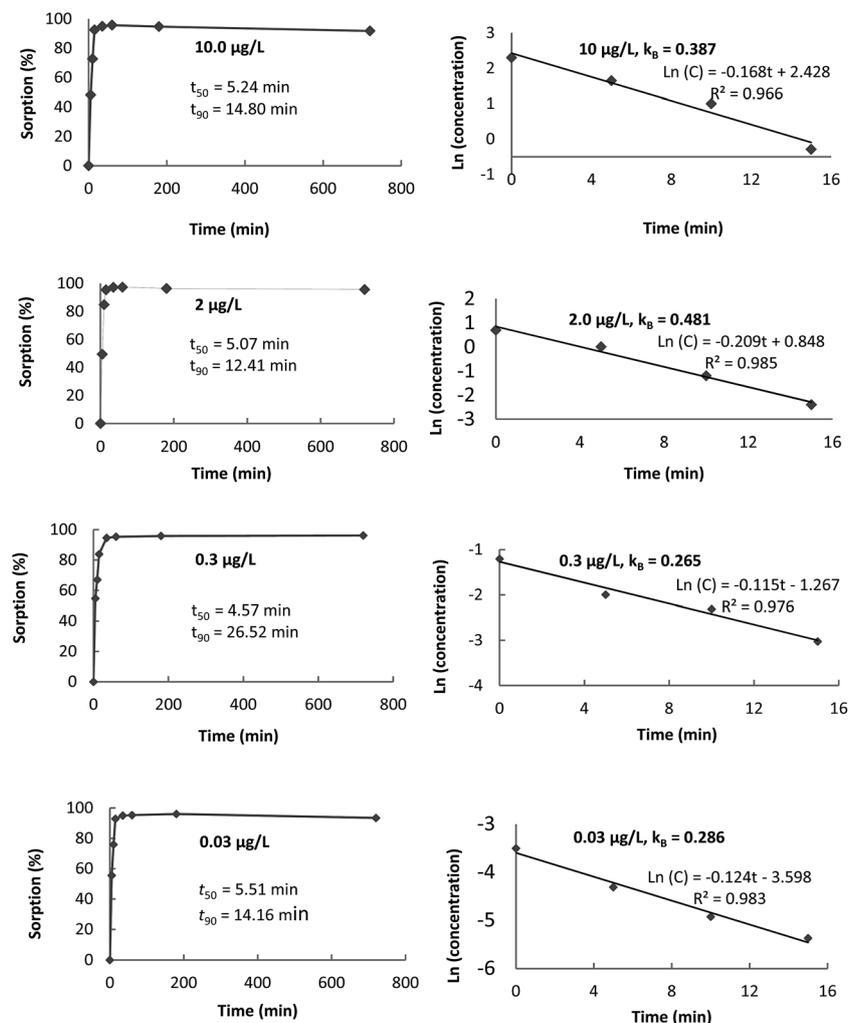


Fig. 2 Time courses of sorption percentage for PHE under different initial PHE concentrations in batch tests (left) and the PHE concentration in bulk solution decreases with first-order decay in the first 15 min (right). t_{50} and t_{90} are the times when the sorption percentage reaches 50% and 90%. The average $k_B = 0.355 \text{ min}^{-1}$.

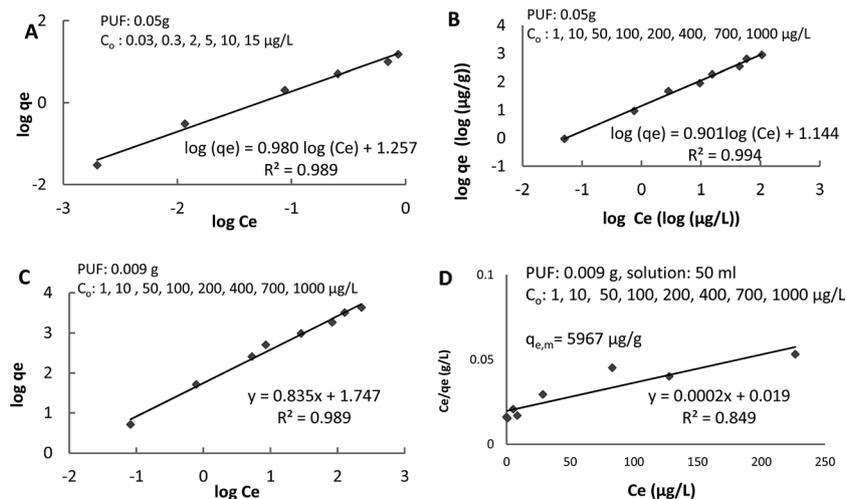


Fig. 3 Sorption isotherm curves in the concentration range of 0.03–15 $\mu\text{g L}^{-1}$ (A) and 1.0–1000 $\mu\text{g L}^{-1}$ (B–D) using 0.05 g (A, B) and 0.009 g (C and D) PUF at $22 \pm 1^\circ\text{C}$ and their fitting with the Freundlich (A–C) and Langmuir model (D).

3.2. Glass-tube column sorption tests

At different PHE concentrations (0.03, 0.3, 2.0, and 10 $\mu\text{g L}^{-1}$), about 34.9–46.3% of the PHE was sorbed onto the 3.81 cm PUF (glass-tube) plug samplers, and 75.0–95.2% onto the 6.35 cm PUF (glass-tube) plug samplers after the stormwater passed through glass-tube columns. For the 6.35 cm PUF samplers, the k_o values are 0.84, 0.92 and 0.92 under rainfall intensity of 0.5, 3.0, and 12 h duration, respectively (Fig. 4a–d line A). The corresponding k_o values calculated with eqn (8) with $k_B = 0.355 \text{ min}^{-1}$ and the flow through time of 3.6, 21.7, 87.06 min providing equivalent hydraulic loading rates for the storms of a 0.5-, 3.0-, and 12 h duration are 0.73, 0.99 and 1.00,

respectively (Fig. 4d, line B). It is interesting to notice that if the actual flow through time (6.3 min) for the 0.5 h storm is used, the k_o equals 0.89 (line C in Fig. 4d). Fig. 4d indicates that the partition of PHE from stormwater to PUF increases when the rainfall intensity decreases (*i.e.*, runoff flow decreases), but would be stable after the rainfall intensity decreases to a certain degree (*e.g.*, 1.27 cm runoff generated over 3 h). It should be noted that k_o obtained from batch tests and eqn (8) (line B in Fig. 4d) are higher than that obtained from the glass-tube column test (line A in Fig. 4d). This is because in batch tests, PUF were cut into smaller pieces that had a better contact with the test solution, while in glass-tube column tests, there were

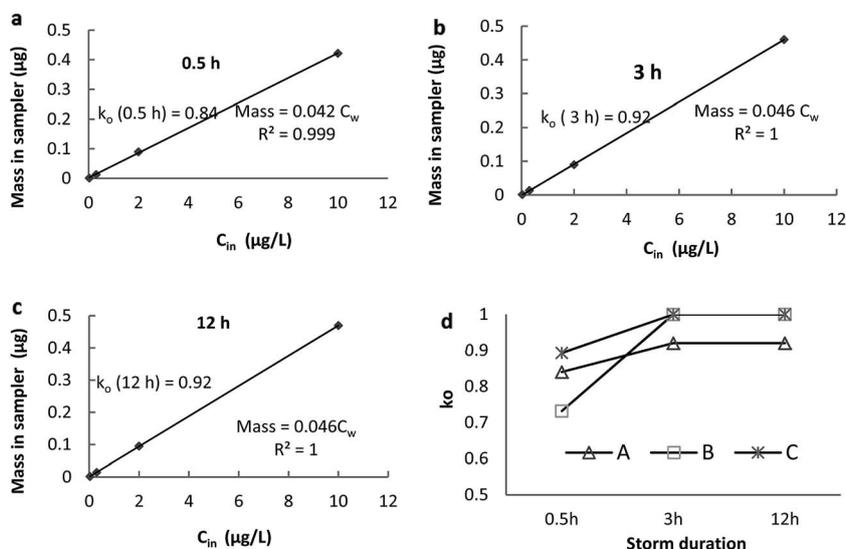


Fig. 4 (a–c) Sorbed PHE mass (M) by PUF passive sampler as a function of influent synthetic stormwater concentrations (C_w) and rainfall intensities (0.5, 3.0, 12.0 h duration) in glass-tube column tests. M was obtained by analyzing the concentration of PHE eluted from the PUF passive sampler. k_o was calculated with eqn (7). (d) Comparison of k_o obtained from glass-tube column tests (line A *i.e.*, the test results) and from batch tests and eqn (8) (with $k_B = 0.355 \text{ min}^{-1}$ from Fig. 2): line B with the flow through time $t = 3.71, 22.27, 89.06$ min and line C with $t = 6.30, 24.81, 90.00$ min for the storm of a 0.5-, 3.0-, and 12 h duration, respectively.

Table 2 Result of single storm event^a

| Test conc. & data category | Storm event duration (h) | | |
|--|--------------------------|---------|---------|
| | 0.5 | 3 | 12 |
| Initial concentration (C_{inf}): 0.03 $\mu\text{g L}^{-1}$ | | | |
| C_{eff} ($\mu\text{g L}^{-1}$) | 0.00684 | 0.00542 | 0.00558 |
| $C_{\text{CS,inf}}$ ($\mu\text{g L}^{-1}$) | 0.0315 | 0.0304 | 0.0279 |
| $C_{\text{CS,eff}}$ ($\mu\text{g L}^{-1}$) | 0.0078 | 0.00748 | 0.00474 |
| E_{CS} | 77.2% | 81.93% | 81.47% |
| E_{CON} | 75.24% | 75.46% | 82.99% |
| Initial concentration (C_{inf}): 2.0 $\mu\text{g L}^{-1}$ | | | |
| C_{eff} ($\mu\text{g L}^{-1}$) | 0.143 | 0.0538 | 0 |
| $C_{\text{CS,inf}}$ ($\mu\text{g L}^{-1}$) | 2.16 | 2.28 | 2.10 |
| $C_{\text{CS,eff}}$ ($\mu\text{g L}^{-1}$) | 0.156 | 0.0564 | 0 |
| E_{CS} | 92.85% | 97.31% | 100% |
| E_{CON} | 92.78% | 97.53% | 100% |
| Initial concentration (C_{inf}): 10.0 $\mu\text{g L}^{-1}$ | | | |
| C_{eff} ($\mu\text{g L}^{-1}$) | 0.753 | 0 | 0.710 |
| $C_{\text{CS,inf}}$ ($\mu\text{g L}^{-1}$) | 8.91 | 9.26 | 9.63 |
| $C_{\text{CS,eff}}$ ($\mu\text{g L}^{-1}$) | 0.854 | 0.758 | 1.08 |
| E_{CS} | 92.47% | 100% | 90.9% |
| E_{CON} | 90.42% | 91.52% | 88.79% |

^a C_{inf} and C_{eff} is the influent and effluent concentration of PHE of the control BMP; $C_{\text{CS,inf}}$ and $C_{\text{CS,eff}}$ are the claimed (predicted) PHE by the samplers in the influent and effluent, respectively (both can be calculated with eqn (7)); E_{CS} is the sampler's claimed removal efficiency (eqn (9)); and E_{CON} is the control column removal efficiency (eqn (10)).

some parts of the PUF that were not in good contact with the test solution for the 0.5 h storm. Because real storms would have a longer contacting time than we used (e.g., about 8 times longer than 3.6 min used for 0.5 h storm), it is reasonable to use a batch reactor to evaluate $k_{\text{B}} (=k_{\text{p}})$ and then k_{o} via eqn (8). The results of Fig. 2 and 4 indicate that under dynamic conditions, a sorption time of ~ 20 min should be enough for the PUF passive sampler to sorb most (e.g., $>95\%$) of the PHE in stormwater that is in contact with the sampler, similar to PHE removal in a batch reactor with the same reaction period.

3.3. BMP tests

3.3.1. Single storm events. The calculated concentrations and BMP treatment efficiencies are summarized in Table 2. The claimed concentration by the PUF passive samplers ($C_{\text{CS,inf}}$ and $C_{\text{CS,eff}}$) was calculated by eqn (7), with k_{o} being 0.84, 0.92, and 0.92 for the storm events of 0.5, 3.0, and 12 h, respectively, that were obtained from Fig. 4 (glass-tube column tests). In general, the claimed treatment efficiencies of the BMPs were very similar to the treatment efficiency of the control with the errors ranging between -6.47% and 1.52% (as per data shown in Table 2). For the influent sampler, the claimed concentration was slightly higher than the actual influent concentration during the low and moderate concentration tests (0.3 and $2.0 \mu\text{g L}^{-1}$), while for the high concentration tests the claimed concentration was always a bit lower than the actual influent concentration (Table 2).

Table 3 Results of multiple storm events with synthetic stormwater of 2.0 and 10.0 $\mu\text{g L}^{-1a}$

| Date & rainfall intensity | Inf. conc. ($\mu\text{g L}^{-1}$) | Eff. conc. ($\mu\text{g L}^{-1}$) | BMP treatment efficiency (%) |
|--|-------------------------------------|-------------------------------------|------------------------------|
| Initial concentration (C_{inf}): 2.0 $\mu\text{g L}^{-1}$ | | | |
| Nov. 11 (0.5 h) | 2.0 | 0 | 100 |
| Nov. 18 (3 h) | 2.0 | 0.053 | 97.35 |
| Nov. 19 (3 h) | 2.0 | 0.339 | 83.05 |
| Nov. 30 (0.5 h) | 2.0 | 0.0365 | 98.18 |
| Dec. 15 (12 h) | 2.0 | 0.154 | 92.30 |
| Average value | 2.0 | 0.116 | 94.18 |
| Claimed average value ^a | 1.83 | 0.140 | 92.35 |
| Error (%) | -8.58 | 20.69 | -1.83 |
| Initial concentration (C_{inf}): 10.0 $\mu\text{g L}^{-1}$ | | | |
| Nov. 11, (0.5 h) | 10.0 | 1.047 | 89.53 |
| Nov. 18, (3 h) | 10.0 | 0.998 | 90.12 |
| Nov. 19, (3 h) | 10.0 | 1.76 | 82.4 |
| Nov. 30, (0.5 h) | 10.0 | 0.303 | 96.97 |
| Dec. 15, (12 h) | 10.0 | 0.335 | 96.65 |
| Average conc. | 10.0 | 0.887 | 91.13 |
| Claimed average value ^a | 8.805 | 0.667 | 92.42 |
| Error (%) | -11.95 | -24.80 | 1.29 |

^a Each of all loadings was 50 mL of synthetic stormwater. On Nov. 11, the columns were loaded with stormwater for 1.6 min to mimic the hydraulic loading rate of a 0.5 h storm; 7 d later, loaded for 9.6 min to mimic 3 h storm; 1 d later, loaded for 9.6 min to mimic a 3 h storm; 11 d later, loaded for 1.6 min to mimic a 0.5 h storm, and 15 d later, loaded 38.4 min to mimic a 12 h storm. Claimed average value: eqn (12) is used to calculate the claimed average $C_{\text{avg,ms}}$ for influent and $C_{\text{avg,ms}}$ for effluent; and claimed average BMP treatment efficiency = $[(C_{\text{avg,ms}}$ for influent - $C_{\text{avg,ms}}$ for effluent)/ $C_{\text{avg,ms}}$ for influent] $\times 100\%$.

3.3.2. Multiple storm events. The claimed $C_{\text{avg,ms}}$ by the PUF samplers were calculated by eqn (12), with $k_{\text{o,avg}}$ being 0.89 $[=(0.84 + 0.92 + 0.92)/3]$ from Fig. 4. The influent concentration obtained by eluting the PUF plug for M and then calculating $C_{\text{avg,ms}}$ was less than the actual influent concentration with an error of -8.58% in the $2.0 \mu\text{g L}^{-1}$ tests and -11.95% in the $10.0 \mu\text{g L}^{-1}$ tests (Table 3). Considering the complexity of the BMP systems, these results seem to be satisfactory. The effluent concentration values were very low due to the high removal efficiency for PHE by the BMPs. The claimed removal efficiencies were very close to the actual values (error = -1.83% for $2.0 \mu\text{g L}^{-1}$ and 1.12% for $10 \mu\text{g L}^{-1}$ as shown in Table 3).

4. Discussion

Semivolatile organic compounds (SVOCs) are a significant group of micropollutants in stormwater runoff.² Measuring the SVOC concentrations in stormwater runoff using standard analytical methods is difficult and costly because they are generally present at trace (i.e. $\mu\text{g L}^{-1}$) or ultra-trace (i.e. ng L^{-1}) levels. Therefore, development of passive samplers for sampling SVOCs in stormwater would be very beneficial.

PUF disk samplers are commonly used passive samplers for monitoring SVOCs in the atmosphere.^{9,11,12} When the equilibrium between the PUF sampler and air is achieved, the air

concentration of a SVOC can be estimated from the adsorbed chemical mass by the sampler and the sampler-air partition coefficient (K_{sw}) or from a passive sampling rate.⁵ For the first time, we have developed a type 2 PUF passive sampler for stormwater sampling. Results of our tests indicate that PUF can quickly sorb PHE even if the PHE concentration in stormwater is at the level of $\mu\text{g L}^{-1}$ and the contact time between PUF and the stormwater is very short. In addition, PUF has a large sorption capacity for PHE. Considering a PHE concentration in the stormwater to be $10 \mu\text{g L}^{-1}$, a 1.5 g PUF passive sampler ($\phi = 1.27 \text{ cm}$, length = $\sim 7.33 \text{ cm}$) can handle (in contact with) 895 L stormwater (based on the maximum adsorbing capacity, $5967 \mu\text{g g}^{-1}$, Fig. 3), which equals to 1242 cm of water for a watershed. Therefore, a PUF passive sampler can be used in the field for several years. Results of column tests indicate that it is feasible to use PUF passive samplers for BMP performance evaluation and for sampling SVOCs in stormwater runoff (e.g., the influent of BMP). A PUF passive sampler can be embedded in the field for sampling/monitoring of BMPs both on an episodic basis and in a long-term period. For example, adding PUF passive samplers at the top (inlet area) and bottom (outlet area) of a bioretention cell would allow the samplers to sample the influent and effluent of the bioretention cell.

In this study, we used k_o obtained from glass tube columns to analyze the data obtained in BMP tests. We then evaluated the feasibility of using batch tests to evaluate k_o via eqn (8). While we did it successfully, more studies are needed to evaluate how k_o is affected by test conditions, such as rainfall intensity, different targeting compounds, mass of PUF used, etc. More importantly, the column systems and test conditions used in this study are relatively simple; more consideration must be given in order to develop stormwater passive sampler techniques for real-world applications. Critical issues include: how to obtain the actual flow rate that contacts with the passive sampler; what are the effects of contacting time between the sampler and stormwater; what are the effects of possible interference of other pollutants with the passive sampler; how to evaluate the volatilization effects of SVOCs; and can the PUF samplers be used for other kind of BMPs. Therefore, future studies are needed.

5. Conclusions

According the results of this study, it can be concluded that (1) PUF can quickly sorb PHE even if the PHE concentration in stormwater is at the level of $\mu\text{g L}^{-1}$ and the contact time between PUF and the stormwater is very short; (2) the high sorption capacity allows the PUF passive sampler to monitor stormwater events for months or years; (3) it is feasible to use PUF passive samplers for sampling SVOCs in stormwater runoff and evaluating BMP performance for removal of SVOCs in stormwater runoff; and (4) the challenge is to find the actual flow rate that contacts with the passive sampler and the contacting time between the sampler and stormwater.

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