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Detection of Semivolatile Organic Compounds in Permeable Pavement Infiltrate

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Abstract

The U.S. Environmental Protection Agency's Edison Environmental Center (EEC) has a research and demonstration permeable parking lot comprised of three different permeable systems: permeable asphalt, pervious concrete, and permeable interlocking concrete pavers. Water quality and quantity analysis has been ongoing since January 2010. This paper describes analysis of semivolatile organic compounds (SVOCs) to determine if hydrocarbons were in water that infiltrated through the permeable surfaces. SVOCs were analyzed in samples collected from 11 dates over a 3-year period, from February 8, 2010 to April 1, 2013. Results are broadly divided into three categories: 42 chemicals were never detected; 12 chemicals (11 chemical test) were detected at a rate of less than 10% or less; and 22 chemicals were detected at a frequency of 10% or greater (ranging from 10 to 66.5% detections). Fundamental and exploratory statistical analyses were performed on the 22 most observed chemicals. The statistical analyses were limited due to low frequency of detections and dilutions of samples, which impacted detection limits. The infiltrate data through three permeable surfaces were analyzed as nonparametric data by the Kaplan-Meier estimation method for fundamental statistics; there were some statistically observable differences in median concentration between pavement types when using Tarone-Ware comparison hypothesis test. A result was that three groups could be identified based on whether observed porous asphalt infiltrate concentration were greater than, similar to, or less than permeable interlocking concrete pavers infiltrate concentration. Identifying these three groups allowed one-way analysis on chemical attributes; the octanol water partitioning ($\log K_{OW}$), number of benzene rings, and molecular complexity were all significant. These 22 most observed chemicals in the infiltrate were further tested by Spearman rank order nonparametric for correlations between frequency of detection and chemical attributes; significant correlations were observed for porous asphalt frequency of detection and molecular weight (MW), Henry's constant, $\log K_{OW}$ and molecular complexity, while both permeable concretes did not have any significant correlations between frequency of detection and chemical parameters. Conclusions from the statistical analyses on the 22 most frequently observed SVOCs in the infiltrate indicate that porous asphalt acts as a source for chemicals with low $\log K_{OW}$ and MW and a sink for chemicals with

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high log K_{OW} and MW, while no significant pattern was observed in the SVOC infiltrate concentrations of the two types of concrete.

Introduction

In 2008, the U.S. Environmental Protection Agency (EPA) began construction at the Edison Environmental Center (EEC) on a research and demonstration permeable pavement parking lot with the long-term intent to monitor water quality of infiltrate that passes through the permeable surface and into the ground. Three commonly installed permeable surfaces of equal surface area and similar watershed area were tested: porous asphalt (PA), pervious concrete (PC), and permeable interlocking concrete pavers (PICP). The parking lot was officially opened for employee and visitor parking in November 2009, and water quality sampling began in January 2010. The efficacy of the in situ monitoring system for the site was demonstrated in Stander et al. (2013), while the ability of the permeable pavements to infiltrate stormwater was demonstrated in Brown and Borst (2013). The hydrologic performance metrics of surface infiltration rate (Brown and Borst 2014) and annual evaporation (Brown and Borst 2015a) show variation by permeable pavement surface type, with porous concrete having significantly larger infiltration rates and annual evaporation than the other two surface types.

From the perspective of water quality analysis, the purposes of monitoring the permeable parking lot are to discern if permeable surfaces had different concentrations of infiltrating pollutants. Pollutant measurements and observed statistical differences between infiltrate concentrations of the three surfaces were detailed for chloride (Borst and Brown 2014), and/or nitrogen, orthophosphate, total organic carbon, and pH (Brown and Borst 2015b), and have been presented for suspended sediment concentration (SSC) (Borst and O'Connor 2016).

Vehicles and their use are known sources of hydrocarbons and oils, as is the breakdown of vehicle components (e.g., tires) (Novotny and Olem 1994). The purpose of this study was to discern whether hydrocarbons, many of which are EPA regulated priority pollutants (USEPA 2015), were in the infiltrating water of the three different permeable pavements through the analysis of semivolatile organic compounds (SVOCs).

In a recent state-of-the-art review of several permeable pavement studies, Drake et al. (2013) indicated “hydrocarbons are not a significant pollutant in permeable pavement effluent”; however, one of the most recent studies they cited (TRCA 2008) monitored infiltrating water 1.5 m below the permeable pavement installation into native clay loam soils that had low infiltration rates. The EEC permeable pavement parking lot has sections that are unlined and infiltrate into the soil, but also has lined sections that capture infiltrate in the storage gallery at a common depth for all three permeable surfaces. It is from these lined sections that water quality samples are derived. The transfer of stormwater-derived hydrocarbons through permeable pavement to the subsurface may be of concern particularly in areas of permeable (sandy) subsurfaces, high groundwater, and where groundwater is a source to drinking water or supplies adjacent receiving waters. Also, not all permeable pavement systems only discharge to the underlying soils, with some discharging directly to stormwater conveyance

systems while others with smaller-sized storage galleries below the permeable pavement systems having overflow discharge for larger events.

Drake et al. (2013) in their state-of-the-art review went on to conclude that “Analysis on impacts on water quality must become more sophisticated and extend beyond event mean concentrations to include total load reduction, censored data (i.e., concentrations below detection levels) and frequency analysis.” Knowledge of frequency of detection and an assessment of mean and median concentration (left censored data at or below detection limits as presented here) of potentially harmful hydrocarbons (as measured by SVOC analysis) in permeable pavement infiltrate would be a benefit in circumstances of near-surface groundwater, permeable native soils, or discharge from the permeable pavement storage gallery to the stormwater conveyance system.

Methods

There were 11 rainfall events monitored for SVOCs over a 3-year period from February 8, 2010 until April 1, 2013. There were up to four sampling locations for each permeable surface, two duplicates and a field blank for an individual event, resulting in 153 samples. Impermeable driving lanes constructed of hot-mix asphalt were the watershed areas for the permeable parking areas comprised of lined and unlined areas. Fig. 1 (adapted from plans) shows the schematics of the permeable pavements and lined sections with buried drainage pipes to the sample collection tanks. Individual surface locations are denoted by abbreviations to surface type, i.e., PA, PC, and PICP, and lined areas (denoted 1 through 4 from west to east in Fig. 1) that collected infiltrate from permeable surfaces and drain to collection tanks (also numbered 1 through 4 in Fig. 1). The liners are 0.4 m below each permeable surface. Each permeable surface was laid on AASHTO No. 2 size aggregate though thickness of each surface varied depending on structural needs of the particular application. The PA is 0.08 m thick and PC is 0.15 m thick. The 0.09-m-thick impermeable pavers were placed on a 0.05-m layer of AASHTO No. 8 aggregate, which also served to fill spaces between pavers; an additional 0.10-m layer of AASHTO No. 57 aggregate separated the No. 8 and No. 2 aggregate. SVOC samples were taken from the sample collection tanks prior to mixing procedures that were used for other water quality parameters. A more detailed description of the liners, permeable surfaces, and drainage piping is provided in Brown and Borst (2014), while details of the water quality sampling effort are described in Borst and Brown (2014).

All SVOC samples were analyzed by USEPA (1996) method 8270C Semivolatile Organic Compounds by gas chromatography/mass spectrometry (GC/MS) with selected ion monitoring (SIM) to achieve the lower detection limits for the base/neutrals and acids (BNA) fraction. There were 43 samples analyzed for both PA and PICP and only 36 analyzed for PC. Due to loadings in the samples, certain fractions, particularly the BNA fraction, of the samples required dilutions to facilitate the instrumental analysis; this increased the detection limits on certain analytes in those fractions. There were also minor variations in detection limits over the course of the 11 rainfall events. While this does not directly affect the reported value, it did limit the statistical analyses that could be performed on the results.

The SVOC sampling effort was part of a water quality larger sampling effort of the permeable pavement parking lot, which is described in further detail in Borst and Brown (2014). Concentrations of suspended sediment concentration (SSC) (ASTM 2013) and total organic carbon (TOC) [EPA 415.3 (Potter et al. 2005)] in the infiltrate of each permeable surface and the potential relationship to observed SVOC concentrations are also discussed herein.

Statistical Methods

Due to the large number of nondetects (ND) in the data set and changes in detection limits (DL) (due in part to dilutions), the Kaplan-Meier (KM) estimation method, a nonparametric statistical approach, was used as recommended in the ProUCL technical manual (USEPA 2013). The KM estimation method uses a distribution function estimate and adjusts for NDs.

For two-sample comparative hypothesis testing, analysis by the Tarone-Ware (TW) comparison hypothesis test was conducted (USEPA 2013) to test for differences in median infiltrate concentrations of the three permeable surfaces. This nonparametric test analyzes the differences between the distributions of two data sets even when there are multiple NDs with different detection limits and ND values that exceed detected values, as was the case with this SVOC data set. The TW test assumes comparable distribution shapes and variability. The TW test is meant for left-censored data sets (USEPA 2013).

The TW test was performed at a pp-value of 0.05 (all statistical test were conducted at a pp-value of 0.05). In making three two-sample comparisons for each of the 22 chemicals, 66 hypothesis tests were performed. This creates a multiple comparison issue, as the probability of a Type I (incorrectly concluding a significant difference when there is not) is 5% for each individual test. In doing 66 tests, it was estimated that three to four Type I errors may occur simply by chance.

The use of *ProUCL* (USEPA 2013) for analysis was limited to SVOCs infiltrate concentrations that had at least 10% detections at or above the DL for all permeable surfaces. The EPA guidance (USEPA 2000) suggests that analysis of proportions of detections are appropriate for less than 50% and down to 10% detections. However, results for several chemicals for two of the permeable surfaces were observed to fall below this 10% threshold; these data were included in the analyses presented as at least three infiltrating concentrations were observed above DL per chemical per permeable surface and claims are not being made about these data independently, but how these data interacted with the data set of detected values of infiltrate of all three surfaces as a whole.

Most statistical analysis on individual datum points were performed in *ProUCL 5.0* (USEPA 2013). However, calculations and analysis were also made in *Excel* and *Statistica 10* (StatSoft). Medians and means of the DL were calculated in *Excel*. Correlation analysis (to determine if there was a significant difference from zero), Shapiro-Wilk histogram analyses (test for normality), and categorical one-way analysis of variance (ANOVA) were performed in *Statistica 10* (StatSoft).

A single mean value was calculated in *Excel* for locations with duplicate samples to be used in analysis. When one sample was below the DL and the other above, the sample below DL was assigned a value of $\frac{1}{2}$ DL to compute the mean value. Over the 11 sampling dates, 21 duplicates were collected. Of the 22 chemicals detected at a rate greater than 10% of the infiltrate samples, 55.6% duplicates were both ND, 23.4% both had detection values, and 21.0% had one value that was detected and the other ND (which resulted in use of $\frac{1}{2}$ DL). These percentages varied between chemicals (e.g., diethyl phthalate had the most pairs of ND at 18, phenanthrene had the most pairs of detections at 13, while di-n-butyl phthalate had the most mixed pairings of detections and ND at 8).

Results

Table 1 lists the 42 SVOCs that were never detected over the span of the sampling period. Table 1 also provides number of detections for chemicals for each surface with less than 10% detections in numerical/alphabetical order; of these 12 chemicals, six are considered EPA priority pollutants (USEPA 2015).

A list of the 22 chemicals observed in this study at a rate of greater than 10% detections is presented in Table 2 in alphabetical order. The KM mean of the chemicals along with frequency of detection, calculated coefficient of variation (COV), medians, and information regarding DL for each permeable surface are provided. Of these 22 chemicals, 21 are classified as EPA priority pollutants (USEPA 2015), while only 2-methylnaphthalene is not so classified.

As shown at the end of Table 2, the KM means are greater than or equal to the mean of the DL 62% (41/66) of the time for all surfaces and median infiltrate concentration are always greater than or equal to the mean DL. PICP infiltrate concentrations had the largest number of KM means greater than the mean DL at 50% (11/22), while PA median infiltrate concentrations exceeded the median DL at 55% (12/22). Of note, none of the chemicals with detections below 10% for a particular infiltrating surface are considered to have calculated KM means that exceed the DL mean and only benzo(a)pyrene had a calculated KM mean concentration for PA infiltrate (four detections) at the DL.

For each of the 22 chemicals, a TW test was used to test for significant differences in median concentrations between each permeable surface. There are three possible pairs of results (e.g., the median concentration of 2-methylnaphthalene in PA infiltrate, 0.03 ug/L, is larger than that from PC infiltrate, 0.0175 ug/L, and PICP infiltrate, 0.02 ug/L and these difference are significantly different by the TW test whereas the difference between PC and PICP is not statistically different). These results were grouped according to similar testing results. For nine chemicals, infiltrate concentration through PA is greater than both PC and PICP infiltrate concentration, for seven chemicals there is no significant difference infiltrate concentration between the three pairs of infiltrate, and for three chemicals PA infiltrate concentration is considered less than both PC and PICP infiltrate concentration; for the three remaining chemicals, there was no mutually observed pattern.

Only two chemicals were observed to be subject to Type 1 error (inequality of $p < 0.05$ or equality of $p > 0.5$) and this only affected comparison testing of PA and PC; pentachlorophenol had a result of $PA > PC$ (0.037) but also satisfied the hypothesis of $PA = PC$ (0.074), while benzo(k)fluoranthene had a result of $PA < PC$ (0.031) but also satisfied the hypothesis of $PA = PC$ (0.062).

For the most part, the TW comparison testing of the PC infiltrate concentration yields results similar to PICP infiltrate concentration though the distinction between PC and PA results may not be as strong as that between PICP and PA. If the comparison of PA to PICP infiltrate is only considered, three distinct groups of SVOCs emerge, i.e., group 1, $PA > PICP$; group 2, $PA = PICP$; and group 3 $PA < PICP$. This is presented in Table 3 with associated percentages of frequency of detection for each surface. A Shapiro-Wilk histogram analysis of the frequency of detection indicated that both PC (mean = 38) and PICP (mean = 34) overall mean frequency of detections for these 22 SVOCs are normally distributed, while PA frequency of detection was not normally distributed. Fig. 2, a box and whisker plot with means of frequency of detection posted for each group (StatSoft), demonstrates that the means for group 1 PA exceed group 2 PA which in turn exceed group 3 PA, while the means for PC and PICP are similar across the three groups.

The number of calculated KM means and medians above the DL mean and median are shown in Table 4 and reflect a similar pattern of distribution of the box plots in Fig. 2, which is an analysis of frequency of detection. The KM mean PA infiltrate concentration is only greater than the DL mean 46% of the time, though 90% of these occurrences are associated with Group 1 ($PA > PICP$), with one observation (10%) for Group 2 ($PA = PICP$), and none (0%) for Group 3 ($PA < PICP$). On the other hand, PICP mean and median infiltration concentrations are more evenly spread across the three groupings; of the three surfaces, only PICP infiltrate concentrations had two means and a median greater than the DL in Group 3 ($PA < PICP$).

Table 4 also shows the number of times the calculated KM COV was below 1, which provides greater confidence in the statistical results. This happened most frequently for the PA infiltrate (11 times) and particularly within Group 1 ($PA > PICP$) (seven times). The PICP infiltrate had 10 occurrences of $COV < 1$, though it was fairly well distributed through the three groups, while PC infiltrate only had seven occurrences with the majority (five) coming in Group 2 and none for Group 3. This further supports grouping by comparison of PA to PICP as calculated through TW analysis as the PC results have greater variance. This becomes more evident when one matches times that both the KM mean exceeds DL and KM $COV < 1$. This occurred exclusively six times in Group 1 for PA (anthracene, fluoranthene, fluorene, phenanthrene pyrene, and acenaphthene) and corresponded to the highest (top four) frequency of detections. For PICP this occurs five times, twice in Group 1 (fluorene and phenanthrene), once in group 2 (diethyl phthalate) and twice in Group 3 [benzo(a)pyrene and benzo(g,h,i)perylene], while for PC it occurs once in Group 1 (pyrene) and twice in Group 2 (di-n-butylphthalate and diethyl phthalate).

Table 5 ranks the 22 most frequently observed SVOCs by molecular weight (MW); other chemical properties included in Table 5 are Henry's constant, solubility, octanol-water

partitioning coefficient (K_{OW}), number of rings with subset of benzene rings, and molecular complexity (a calculated estimate based on number and variety of bond connections and diversity of atoms contained in molecule) (Hendrickson et al. 1987). A series of Spearman rank order nonparametric correlations (StatSoft) between the detection frequency of each of the three surfaces and the chemical parameters listed in Table 5 were performed. Significant correlations were observed between PA frequency of detection and MW (−0.53), Henry's constant (−0.69), log K_{OW} (−0.43), and molecular complexity (−0.67), while both PC and PICP detection frequency did not have any significant correlations with these chemical parameters.

One-way analysis of ANOVA (StatSoft) were performed on log K_{OW} , number of benzene rings, and molecular complexity as these chemical parameters satisfied the assumption of normality for each group through Shapiro-Wilk histogram analyses. All ANOVA were significant ($p < 0.05$), though molecular complexity had the lowest pp-value at 0.000003 and highest $F(2, 19) = 27.395$. Fig. 3 shows results of this one-way ANOVA for molecular complexity.

Also included in Table 5 are the maximum contaminant levels for drinking water (USEPA 2009). Pentachlorophenol had two observations at 3.3 ug/L that were higher than action levels for drinking water (1 ug/L) for PA infiltrate. Benzo(a)pyrene had two observations, 0.26 ug/L for PA and 0.255 ug/L for PC, above the action level of 0.2 ug/L. All three surfaces had infiltrate observations of bis(2-ethylhexyl)phthalate above the action level of 6 ug/L with 7 for PA (highest 26.9 ug/L), 3 for PC (22.3 ug/L), and 4 for PICP (33.5 ug/L).

Discussion

As shown in Fig. 2, the mean of detection frequency for PICP and PC infiltrate does not significantly vary across the three defined groups, while PA does change, i.e., $PA > PICP$ in group 1, $PA = PICP$ in Group 2 and $PA < PICP$ in Group 3. Results for PA infiltrate concentration are robust for Group 1 as six of the chemicals are above the detection limit and have $COV < 1$. One conclusion that can be derived from this data set is that the PA itself is a source for some SVOCs in the PA infiltrate, as represented by Group 1 ($PA > PICP$), which have correspondingly low molecular weight (LMW), and a sink for other SVOCs, as represented by Group 3 ($PA < PICP$), which have correspondingly high molecular weight (HMW). Infiltrating SVOCs with higher log K_{OW} , MW and molecular complexity were mostly likely being sorbed by the PA.

These results of this SVOC analyses add better understanding to previously reported TOC measurements; the infiltrate TOC concentrations in the PA was statistically larger than both PC and PICP, while PC and PICP were statistically similar (Brown and Borst 2015b). As these experimental watershed areas are similarly comprised of runoff from the asphalt driving lanes, the additional TOC is most likely leachate from the PA. The binding agent of PA contains hydrocarbons, while the other surfaces are not made from hydrocarbon-containing materials. Organic carbon, and in this study, SVOCs, i.e., with lower log K_{OW} , MW, and molecular complexity but greater frequency of detection (Table 3), were leaching from the PA. As TOC analysis is not chemical specific, the combined results of this SVOC

and previous TOC analysis would indicate that the porous asphalt is most likely leaching lower MW organic compounds, even compounds that are not specifically tested for using method 8270C of the USEPA (1996). The sources for the SVOCs in the infiltrate of PC and PICP are most likely the aforementioned hydrocarbons and oils from vehicle use.

Concurrent SSC monitoring, i.e., from January 26, 2010 through June 4, 2013, indicated that SSC of the PICP infiltrate was statistically larger than the other two infiltrates. SSC was 52.7 mg/L for PICP, 21.3 mg/L for PA, and 7.6 mg/L for PC and a one-way ANOVA results and post hoc test using Fisher's least-significant difference test (total $p=0.0001$) to determine difference between means of the SSC in the infiltrate for each permeable surface indicated that $\text{PICP} > \text{PC}$ ($p < 0.0001$), $\text{PICP} > \text{PA}$ ($p < 0.0036$), and $\text{PC} = \text{PA}$ ($p = 0.20$) (Borst and O'Connor 2016). As the PICP infiltrate was the only infiltrate to have estimated KM SVOC means greater than the DL and four of five chemicals with $\text{COV} < 1$ for Group 3 ($\text{PA} < \text{PICP}$) as shown in Table 4, there is the possibility that the higher SSC observed in the PICP infiltrate is associated with the greater frequency of detection, medians, KM means, and KM COV for Group 3 ($\text{PA} < \text{PICP}$) SVOCs in PICP infiltrate. The observation of SVOCs benzo(a)pyrene and benzo(g,h,i)perylene, which have higher $\log K_{OW}$, coincides with aforementioned identification of these two chemicals as being both above DL and $\text{COV} < 1$ for this surface; high $\log K_{OW}$ is an indicator of chemicals less likely to be dissolved and more likely to sorb to solids. Whether this was due to sorption of SVOCs to solids or greater pore spaces (due to construction and design technique of PICP, which relies on void space of AASHTO no. 8 aggregate between pavers) that allowed for these higher molecular complexity SVOCs to infiltrate through the PICP was not determined in this study.

Conclusions

For the majority of the SVOCs analyzed, there were either no detections (42) or detections at a rate below 10% for infiltrate concentration (12). Twenty-two SVOCs had detections at rate over 10%, which allowed for statistical analysis. The calculated KM mean infiltrate concentration for most of these 22 chemicals were equal to ($=$) or above ($>$) the DL for each surface and 21 of these 22 SVOCs were classified as EPA priority pollutants (USEPA 2015).

Through statistical analysis of concentrations and frequency of detections of the permeable infiltrate for these 22 SVOCs, it appears that the porous asphalt acts as a source for SVOCs with chemical parameters of lower MW and smaller values of $\log K_{OW}$ and molecular complexity, but a sink for SVOC with higher MW and greater $\log K_{OW}$ and molecular complexity. The 22 SVOC frequency of detections observed in the infiltrate of both permeable concrete surfaces were more evenly distributed through the identified groupings, i.e., normally distributed around a single mean, than the PA, and did not have statistically significance correlation analysis associated with chemical parameters, as did PA infiltrate; however, PICP appears to potentially infiltrate higher molecular complexity compounds at a rate that even exceeds PC.

Additional, future measurements should be taken to determine whether the observed trends described are continuing. If higher $\log K_{OW}$ SVOCs were actually sorbed to the PA, there is the potential expectation that breakthrough may occur at some point, and some of these

SVOCs may begin to be detected at higher frequency at a later date. Further testing at and below the native soil interface below the parking lot would inform whether SVOCs in the permeable parking infiltrate may be migrating to groundwater through unlined areas.

Changes or lack of changes in the concrete permeable surfaces are also of interest, especially, continued analysis of PICP to see if there is a change in the higher log K_{OW} SVOCS observed in the infiltrate concentrations or frequency of detection as higher log K_{OW} SVOCS were associated with USEPA (2009) maximum contaminant level thresholds for drinking water (Table 5). Though there were relatively few observations at or above drinking water contaminant levels (USEPA 2009) in the permeable infiltrate, bis(2-ethylhexyl)phthalate stands out as exceeding contaminant levels the most frequently of this subset of SVOC. It was observed exceeding the drinking water contaminant level of 6 ug/L for all three permeable pavements and had a calculated KM mean of approximately 3 ug/L for PA and PICP and 2 for PC.

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Fig. 1.
Detailed plan of permeable surfaces and lined sections with drainage to collection tanks

Fig. 2.
 Box and whisker plot of frequency of detection of permeable pavements according to group

Fig. 3.

Plot of one-way ANOVA for molecular complexity according to group

Table 1.

Chemicals with Limited (<10%) or Zero Detection Frequency

Chemicals	Detections per event	Surface type
1,2,4-trichlorobenzene ^a , 1,2-dichlorobenzene ^a , 1,3-diphenylhydrazine ^a , 1,4-dichlorobenzene ^a , 2,4,5-trichlorophenol, 2,4,6-trichlorophenol ^a , 2,4-dichlorophenol ^a , 2,4-dinitrophenol ^a , 2,4-dinitrotoluene ^a , 2,6-dinitrotoluene ^a , 2-chloronaphthalene ^a , 2-chlorophenol, 2-nitrophenol ^a , 3-chlorobenzidine ^a , 3-nitroaniline, 4,6-dinitro-2-methylphenol, 4-bromophenyl phenyl ether ^a , 4-chloroaniline, 4-chlorophenyl phenyl ether ^a , 4-nitroaniline, aniline, benzidine ^a , Bis(2-chloroethoxy)methane ^a , bis(2-chloroethyl)ether ^a , Bis(2-chloroisopropyl)ether ^a , carbazole, dibenzofuran, dimethyl phthalate ^a , hexachlorocyclopentadiene ^a , hexachloroethane ^a , isophorone ^a , nitrobenzene ^a , N-nitrosodimethylamine ^a , N-nitrosodimethylamine ^a , N-nitrosodiphenylamine, 2,3,4,6-tetrachlorophenol ^a , acetophenone, atrazine, biphenyl, parathion	No detections	N/A
2,4-dimethylphenol ^a	2	PA
2-methylphenol	2	PA
3-methylphenol and 4-methylphenol ^b	2, 2	PA
4-chloro-3-methylphenol	1	PICP
4-nitrophenol ^a	1, 1	PC
Benzoic acid	3	PA
Benzyl alcohol	1	PC
	1, 1	PA
	1	PA
	2	PC
	3	PICP
Butyl benzyl phthalate ^a	1	PICP
	1	PC
Di-n-octylphthalate ^a	1	PC
Hexachlorobenzene ^a	1, 3	PICP
	2	PA
	3, 1	PC
Hexachlorobutadiene ^a	1, 3	PICP
	2	PA
	2, 1	PC

^a EPA priority pollutant (USEPA 2015).^b Individual chemicals cannot be discerned.

Table 2.
Nonparametric Results of Kaplan-Meier (KM) Estimation Method for 22 Most Frequently Detected Chemicals

Chemical	2-methylnaphthalene			Acenaphthene			Acenaphthylene			Anthracene		
	Surface			Surface			Surface			Surface		
	PA	PC	PICP	PA	PC	PICP	PA	PC	PICP	PA	PC	PICP
DL minimum (ug/L)	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
DL maximum (ug/L)	0.1	0.1	0.06	0.1	0.1	0.06	0.1	0.1	0.06	0.1	0.05	0.03
DL mean (ug/L)	0.03	0.02	0.02	0.03	0.02	0.02	0.03	0.02	0.02	0.02	0.02	0.01
DL median (ug/L)	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.01
Minimum detected (ug/L)	0.01	0.0075	0.0075	0.01	0.0075	0.01	0.01	0.01	0.015	0.01	0.01	0.01
Maximum detected (ug/L)	0.1	0.42	0.08	0.25	0.1	0.08	0.04	0.1	0.09	0.15	0.15	0.09
Detection frequency (%)	62	25	28	84	42	23	30	42	35	86	56	46
KM mean (ug/L)	0.03	0.03	0.01	0.06	0.02	0.02	0.02	0.02	0.02	0.03	0.02	0.02
Median (50% quant) (ug/L)	0.03	0.0175	0.02	0.06	0.02	0.02	0.02	0.02	0.02	0.03	0.01	0.01
KM coefficient of variation (COV)	0.8	2.6	1.1	0.8	1.2	1.0	0.5	0.9	0.9	0.8	1.1	1.0
KM mean <, > or = DL mean	=	>	<	>	=	=	<	=	=	>	=	>
Median <, > or = DL median	>	>	>	>	>	>	=	=	=	>	=	=
Chemical	Benzo(a)anthracene			Benzo(a)pyrene			Benzo(b)fluoranthene			Benzo(g,h,i)perylene		
	PA	PC	PICP	PA	PC	PICP	PA	PC	PICP	PA	PC	PICP
DL minimum (ug/L)	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02	0.02
DL maximum (ug/L)	0.1	0.1	0.06	0.1	0.05	0.03	0.15	0.15	0.09	0.1	0.1	0.06
DL mean (ug/L)	0.03	0.03	0.02	0.02	0.03	0.02	0.05	0.04	0.03	0.04	0.03	0.02
DL median (ug/L)	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Minimum detected (ug/L)	0.01	0.0075	0.01	0.02	0.0075	0.015	0.02	0.015	0.015	0.03	0.015	0.015
Maximum detected (ug/L)	0.22	0.06	0.12	0.26	0.255	0.15	0.29	0.255	0.15	0.17	0.255	0.09
Detection frequency (%)	40	50	46	9.3	56	35	9.3	39	35	7.0	22	35
KM mean (ug/L)	0.02	0.01	0.02	0.02	0.02	0.03	0.03	0.03	0.03	0.02	0.02	0.03
Median (50% quant) (ug/L)	0.02	0.0175	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
KM coefficient of variation (COV)	1.8	0.8	1.2	1.5	1.5	0.8	1.5	1.6	0.8	0.9	1.7	0.8
KM mean <, > or = DL mean	<	<	=	=	<	>	<	<	=	<	<	>
Median <, > or = DL median	>	>	>	=	=	=	=	=	=	=	=	=

Chemical	2-methylnaphthalene			Acenaphthene			Surface			Acenaphthylene			Anthracene		
	Benzo(k)fluoranthene			Bis(2-ethylhexyl)phthalate			Surface			Chrysene			Dibenz(a,h)anthracene		
	PA	PC	PICP	PA	PC	PICP	PA	PC	PICP	PA	PC	PICP	PA	PC	PICP
DL minimum (ug/L)	0.01	0.01	0.01	0.78	0.78	0.78	0.78	0.78	0.78	0.01	0.01	0.01	0.02	0.01	0.01
DL maximum (ug/L)	0.1	0.1	0.06	1.42	1.42	1.42	1.42	1.42	1.42	0.15	0.15	0.09	0.15	0.15	0.09
DL mean (ug/L)	0.03	0.03	0.02	1.27	1.24	1.27	1.27	1.27	1.27	0.04	0.03	0.02	0.04	0.04	0.03
DL median (ug/L)	0.02	0.02	0.02	1.42	1.42	1.42	1.42	1.42	1.42	0.01	0.01	0.01	0.02	0.02	0.02
Minimum detected (ug/L)	0.01	0.01	0.01	0.79	0.86	1.00	1.00	0.01	0.0075	0.01	0.0075	0.01	0.01	0.015	0.015
Maximum detected (ug/L)	0.36	0.255	0.15	21.9	22.3	33.5	33.5	0.25	0.03	0.12	0.23	0.255	0.12	0.255	0.12
Detection frequency (%)	12	46	35	35	25	30	37	39	47	9.3	14	23			
KM mean (ug/L)	0.02	0.02	0.02	2.91	2.46	2.88	2.88	0.02	0.01	0.03	0.02	0.02	0.02	0.02	0.02
Median (50% quant) (ug/L)	0.02	0.02	0.02	1.42	1.42	1.42	1.42	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
KM coefficient of variation (COV)	1.8	1.6	0.8	1.58	1.78	2.07	1.8	0.5	1.0	2.1	1.9	1.1			
KM mean <, > or = DL mean	<	<	=	>	>	>	>	<	<	<	<	<	<	<	<
Median <, > or = DL median	=	=	=	=	=	=	=	>	>	>	=	=	=	=	=
Chemical	Diethyl phthalate			Di-n-butylphthalate			Surface			Fluoranthene			Fluorene		
	PA			PC			PICP			PA			PC		
	PA	PC	PICP	PA	PC	PICP	PA	PC	PICP	PA	PC	PICP	PA	PC	PICP
DL minimum (ug/L)	0.66	0.66	0.66	0.84	0.84	0.84	0.84	0.84	0.84	0.02	0.02	0.01	0.01	0.01	0.01
DL maximum (ug/L)	0.77	0.77	0.77	1.71	1.71	1.71	1.71	1.71	1.71	0.1	0.1	0.1	0.1	0.1	0.06
DL mean (ug/L)	0.71	0.71	0.71	1.38	1.39	1.38	1.38	0.04	0.03	0.02	0.03	0.03	0.03	0.03	0.02
DL median (ug/L)	0.67	0.67	0.67	1.70	1.70	1.70	1.70	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Minimum detected (ug/L)	0.76	0.748	0.84	0.80	0.99	0.725	0.725	0.02	0.015	0.015	0.01	0.0075	0.01		
Maximum detected (ug/L)	1.26	2.01	2.47	4.72	4.04	4.95	4.95	0.35	0.12	0.17	0.23	0.19	0.24		
Detection frequency (%)	9.3	14	16	26	39	30	81	47	44	77	33	21			
KM mean (ug/L)	0.70	0.73	0.77	1.22	1.50	1.27	1.27	0.06	0.03	0.03	0.05	0.02	0.03		
Median (ug/L)	0.76	0.76	0.76	1.70	1.70	1.70	1.70	0.06	0.02	0.02	0.05	0.02	0.02		
KM coefficient of variation (COV)	0.18	0.32	0.43	0.70	0.56	0.79	0.8	0.8	1.1	0.8	1.3	0.7			
KM mean <, > or = DL mean	<	>	>	<	>	<	<	>	=	=	>	<	>	>	>
Median <, > or = DL median	>	>	>	=	=	=	=	>	=	=	>	=	=	=	=

Chemical	2-methylnaphthalene			Acenaphthene			Surface			Acenaphthylene			Anthracene		
	Indeno(1,2,3-cd)pyrene			Naphthalene			Surface			Pentachlorophenol			Phenanthrene		
	PA	PC	PICP	PA	PC	PICP	PA	PC	PICP	PA	PC	PICP	PA	PC	PICP
DL minimum (ug/L)	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.03	0.01	0.03	0.03
DL maximum (ug/L)	0.15	0.15	0.09	0.1	0.1	0.06	0.15	0.03	0.03	0.03	0.15	0.03	0.15	0.15	0.09
DL mean (ug/L)	0.04	0.04	0.03	0.03	0.02	0.02	0.04	0.03	0.02	0.04	0.03	0.02	0.04	0.03	0.02
DL median (ug/L)	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.01	0.01	0.01
Minimum detected (ug/L)	0.01	0.02	0.02	0.01	0.0075	0.01	0.02	0.01	0.0075	0.01	0.02	0.02	0.02	0.0075	0.0075
Maximum detected (ug/L)	0.21	0.26	0.12	0.23	0.14	0.07	3.30	0.09	0.45	0.20	0.21	0.11			
Detection frequency (%)	9.3	14	30	70	33	26	74	58	51	70	75	65			
KM mean (ug/L)	0.02	0.02	0.02	0.04	0.01	0.02	0.33	0.14	0.07	0.06	0.03	0.03			
Median (50% quant) (ug/L)	0.02	0.02	0.03	0.04	0.02	0.02	0.12	0.03	0.03	0.05	0.03	0.03			
KM coefficient of variation (COV)	1.9	1.9	1.1	1.0	1.5	0.9	2.1	1.35	1.4	0.8	1.1	0.9			
KM mean <, > or = DL mean	<	<	<	>	<	=	>	>	>	>	=	>	>	=	>
Median <, > or = DL median	=	=	>	>	>	>	>	>	>	>	>	>	>	>	>
Total 22 chemicals															
Chemical	Phenol			Pyrene			Surface			PA			PC		
	PA	PC	PICP	PA	PC	PICP	PA	PC	PICP	PA	PC	PICP	PA	PC	PICP
	PA	PC	PICP	PA	PC	PICP	PA	PC	PICP	PA	PC	PICP	PA	PC	PICP
DL minimum (ug/L)	0.39	0.39	0.39	0.02	0.02	0.02	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01
DL maximum (ug/L)	0.78	0.78	1.23	0.15	0.15	0.09	1.71	0.09	1.71	0.09	1.71	2.37	2.37	2.37	2.37
DL mean (ug/L)	0.68	0.66	0.68	0.05	0.03	0.03	—	0.03	—	—	—	—	—	—	—
DL median (ug/L)	0.78	0.78	0.78	0.02	0.02	0.02	—	0.02	—	—	—	—	—	—	—
Minimum detected (ug/L)	0.97	0.90	1.24	0.02	0.015	0.015	0.01	0.015	0.01	0.0075	0.0075	0.0075	0.0075	0.0075	0.0075
Maximum detected (ug/L)	10.7	3.55	6.44	0.20	0.12	0.14	21.9	0.14	21.9	22.3	33.5	33.5	33.5	33.5	33.5
Detection frequency (%)	26	17	7	74	47	40	43	40	43	37	34	38	38	38	38
KM mean (ug/L)	1.35	0.69	0.59	0.07	0.04	0.05	—	0.05	—	—	—	—	—	—	—
Median (50% quant) (ug/L)	0.78	0.78	0.78	0.08	0.03	0.025	—	0.025	—	—	—	—	—	—	—
KM coefficient of variation (COV)	1.74	1.18	1.60	0.55	0.80	1.00	12 ^a	1.00	12 ^a	7	14	33	33	33	33
KM mean <, > or = DL mean	>	>	<	>	>	>	>	>	>	>	>	>	>	>	>
Median <, > or = DL median	=	=	=	>	>	>	22	>	22	22	22	22	22	22	66

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^a Number less than or equal to 1.
^b Number greater than ($>$) or equal to ($\geq$) detection limit mean or median.

Table 3.

Comparative Grouping of Porous Asphalt and Porous Concrete Based on Results of Tarone-Ware Comparison Hypothesis Test of Medians for Permeable Surfaces Infiltrate Concentrations with Detection Frequency

Group	Chemical	Detection frequency (%)		
		PA	PICP	PC
Group 1 (PA > PICP)	2-methylnaphthalene	62	28	25
	Acenaphthene	84	23	42
	Anthracene	86	46	56
	Fluoranthene	81	44	47
	Fluorene	77	21	33
	Naphthalene	70	26	33
	Pentachlorophenol	74	51	58
	Phenanthrene	70	65	75
	Phenol	26	7	17
	Pyrene	74	40	47
Group 2 (PA = PICP)	Acenaphthylene	30	35	42
	Benzo(a)anthracene	40	46	50
	Bis(2-ethylhexyl)phthalate	35	30	25
	Chrysene	37	47	39
	Dibenz(a,h)anthracene	9.3	23	14
	Diethyl phthalate	9.3	16	14
	Di-n-butylphthalate	26	30	39
	Benzo(a)pyrene	9.3	35	56
	Benzo(b)fluoranthene	9.3	35	39
	Benzo(g,h,i)perylene	7	35	22
Group 3 (PA < PICP)	Benzo(k)fluoranthene	12	35	46
	Indeno(1,2,3-cd)pyrene	9.3	30	14

Table 4.

Number and Percentages of KM Mean and Median Concentration Greater Than Detection Limit per Group

Group	Chemicals	Number KM mean > LOD (percentage of groupings)			Number median > LOD (percentage of groupings)		
		PA	PICP	PC	PA	PICP	PC
All groups	22	10 (46%) [11]	11 (50%) [10]	7 (32%) [7]	12 (55%)	10 (45%)	9 (41%)
Group 1 (PA > PICP)	10	9 (90%) [7]	6 (60%) [3]	4 (40%) [2]	9 (90%)	6 (60%)	6 (60%)
Group 2 (PA = PICP)	7	1 (14%) [3]	3 (43%) [3]	3 (43%) [5]	3 (43%)	3 (43%)	3 (43%)
Group 3 (PA < PICP)	5	0 (0%) [1]	2 (40%) [4]	0 (0%) [0]	0 (0%)	1 (20%)	0 (0%)

Table 5.

Frequently Detected Chemicals in Order of Molecular Weight

Name and CAS number	MW (g/mol) ¹	Henry's Constant (mol/Pa·m ³ @ 20 – 25°C) ²	Solubility (mg/L) ¹	Log <i>K</i> _{OW} ^{1,4}	Number of Rings ^{1,3}	Molecular Complexity ¹	Maximum Contaminant Level (MCL) (ug/L) ⁵
Phenol (108952)	94.11124	28	82800	1.5	1 (1)	46.1	
Naphthalene (91203)	128.17052	2.1×10 ⁻²	31	3.3	2 (2)	80.6	
2-methylnaphthalene (91576)	142.1971	1.8×10 ⁻²	24.6	3.9	2 (2)	128	
Acenaphthylene (208968)	152.19192	8.2×10 ⁻²	10	3.7	3 (2)	184	
Acenaphthene (83329)	154.2078	7.2×10 ⁻²	4×10 ⁻¹	3.9	3 (2)	155	
Fluorene (86737)	166.2185	1.1×10 ⁻¹	Insoluble	4.2	3 (2)	165	
Phenanthrene (85018)	178.2292	2.3×10 ⁻¹	1.15	4.5	3 (3)	174	
Anthracene (120127)	178.2292	2.0×10 ⁻¹	4.34×10 ⁻²	4.4	3 (3)	154	
Fluoranthene (206440)	202.2506	6.9×10 ⁻¹	2.3×10 ⁻¹	5.2	4 (3)	243	
Pyrene (129000)	202.2506	7.5×10 ⁻¹	1.35×10 ⁻¹	4.9	4 (4)	217	
Diethyl phthalate	222.23716	22	1080	2.5	1 (1)	223	
Benzo(a)anthracene (56553)	228.28788	1.4	9.4×10 ⁻³	5.8	4 (4)	294	
Chrysene (218019)	228.28788	2.3	1.89×10 ⁻³	5.7	4 (4)	264	
Benzo(b)fluoranthene (205992)	252.30928	15	1.5×10 ⁻³	6.4	5 (4)	372	
Benzo(k)fluoranthene (207089)	252.30928	17	8.0×10 ⁻⁴	6.4	5 (4)	338	
Benzo(a)pyrene (50328)	252.30928	20	1.62×10 ⁻³	6.0	5 (5)	372	
Pentachlorophenol (87865)	266.33654	41	14	5.1	1 (1)	150	
Indeno(1,2,3-cd)pyrene (193395)	276.33068	29	6.2×10 ⁻³	7.0	6 (5)	453	
Benzo(g,h,i)perylene (191242)	276.33068	30	2.6×10 ⁻⁴	6.6	6 (6)	411	
Di-n-butyl phthalate (84742)	278.34348	9.3	11.2	4.7	1 (1)	271	
Dibenz(a,h)anthracene (53703)	278.34656	180	2.49×10 ⁻³	6.5	5 (5)	361	1.8×
Bis(2-ethylhexyl) phthalate (117817)	390.55612	5.8×10 ⁻¹	0.27	7.4	1 (1)	394	

¹Kim et al. (2016).²Sander (2014).³Number of rings with total number of benzene rings in parentheses.⁴*K*_{OW} = octanol-water partitioning coefficient (calculated).⁵EPA (2009).