

Article

Water Quality and the First-Flush Effect in Roof-Based Rainwater Harvesting, Part II: First Flush

Jessica J. Lay¹, Jason R. Vogel^{2,*}, Jason B. Belden³ , Glenn O. Brown¹  and Daniel E. Storm¹

¹ Department of Biosystems and Agricultural Engineering, Oklahoma State University, Stillwater, OK 74078, USA

² School of Civil Engineering and Environmental Science, University of Oklahoma, Norman, OK 73019, USA

³ Department of Integrative Biology, Oklahoma State University, Stillwater, OK 74078, USA

* Correspondence: jason.vogel@ou.edu

Abstract: Rainwater runoff samples from a range of roofing materials were temporally collected from 19 small-scale roof structures and two commercial buildings through simulated and actual storm events, and the concentrations of polycyclic aromatic hydrocarbons (PAHs), phosphorus flame retardants (PFLs), and pyrethroid insecticides and other water quality parameters were analyzed. In Part I of this research, the concentrations of these contaminants in roof runoff and soils receiving runoff from a range of roofing materials were evaluated. In Part II, recommendations have been developed for a first-flush exclusion to improve the quality of water harvesting for nonpotable uses. Recommendations focus on a first-flush diversion based on mass removals of total suspended solids (TSS) and PAHs linked to conductivity measurements throughout a storm event. Additionally, an upper-confidence limit (UCL) was constructed to determine the minimum diversion required to obtain 50, 75, 90, and 95% mass removal of TSS and PAH contaminants. The majority of TSS were produced during the initial 1.2 mm of runoff. Likewise, the majority of PAHs were removed during the initial 1.2 mm of runoff, except for the asphalt shingle roofs, where high PAHs were observed after 6 mm of runoff. The Texas Water Development Board (TWDB)-recommended first-flush diversion of one gallon for every 100 square feet of rooftop was not always adequate for removing 50% of TSS and PAHs from the roofs. Rainwater runoff conductivity decreased drastically between 1.2 to 2.4 mm of rainwater runoff. Diverting the first flush based on conductivity has the potential to also divert the majority of TSS and PAHs in roof runoff.

Keywords: rainwater harvesting; first flush; roof runoff; polycyclic aromatic hydrocarbons; total suspended solids; conductivity



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1. Introduction

Rainwater harvesting involves the capture, diversion, and storage of rainwater. Roof-based rainwater harvesting is implemented in both developed and developing countries for nonpotable and potable use. The majority of a rooftop's dust and debris are believed to be washed away during the initial periods of a rainfall event, a phenomenon known as the "first flush" [1,2]. In order to improve the overall water quality of harvested rainwater, many researchers have called for the diversion of the first flush to be included in a rainwater harvesting collection system [1,3–11]. The idea of a first flush originated in urban stormwater and sewage research but has since been applied to rainwater harvesting [4,10,12]. From studies based on stormwater discharges, Schriewer et al. summarized that some researchers claim the first flush occurs when at least 80% of the pollution load is transferred in the first 30% of runoff volume, whereas others suggest it occurs when most of the total pollution load is in the first 25% of runoff [13]. The first flush can be defined based on either a concentration or on a mass basis [9].

There is no universal consensus on what exactly constitutes a first flush for roof-based rainwater harvesting [1,7,9]. This is due to the many variables that play a role in the water

quality of roof runoff [8]. Roofing material, catchment parameters, precipitation events, antecedent dry period, local weather, chemical properties of the pollutants, abundance of wildlife, and the geographical location of the rainwater harvesting system all need to be taken into consideration when designing a first-flush device [4,5,10,12]. It is important to note that while diverting the first flush is important, care must be taken not to divert too much and waste clean water [4]. Research has shown varied conclusions for how much runoff should be diverted in the first flush in order to have satisfactory water quality in the rainwater harvesting system. Yaziz et al. suggested diverting 0.33 mm for galvanized iron and concrete tile roofs [14]. Martinson and Thomas proposed that contamination will be halved for each mm of rainfall that is diverted from the rainwater harvesting system [1]. The Texas Water Development Board (TWDB) recommends diverting 38 L for every 93 m² of catchment area (0.41 mm) [15]. Mendez et al. observed significantly higher concentrations of conductivity, total coliform, fecal coliform, turbidity, total suspended solids (TSS), nitrate, nitrite, and metal concentrations within a first-flush diversion of 0.41 mm compared with water harvested after the first flush [3]. For a site-specific diversion in Bisate, Rwanda, it was observed that diverting the first 1 mm of runoff would lower *Escherichia coli* concentrations to 10 colony-forming units/100 mL and reduce turbidity from 100 NTU to less than 40 NTU [4]. Kumpel et al. concluded that the first-flush diversion of rainwater harvesting systems should account for local precipitation patterns, storm intensity, and canopy conditions [5].

Studies have shown that the majority of pollutants in urban runoff are in particulate form [2,15,16]. In a watershed study, a first-flush effect was observed in the occurrence of polycyclic aromatic hydrocarbons (PAHs), where 30 to 60% of the total PAH load was discharged in the first 20% of the storm volume [17]. PAHs are ubiquitous, hydrophobic compounds that can sorb onto particulates and be transported by water on suspended sediment or through the air on dust particles [18]. PAHs are of environmental concern due to their detrimental biological effects, toxicity, mutagenicity, carcinogenicity, and their bioaccumulation potential [19,20]. Rule et al. observed a first-flush effect for PAHs in urban water catchments and contributed it to a long antecedent dry period [21]. PAHs have also been observed in rooftop runoff, as has been demonstrated in the literature and in the companion paper [3,6,21–23].

Many health concerns arise when using untreated harvested rainwater as drinking water due to possible microbial and chemical contamination [8,24–26]. In the developing world, rainwater harvesting is used for both potable and nonpotable purposes [11,26–28]. With the widespread practice of open burning in these countries, numerous contaminants, including PAHs, are released into the atmosphere that can, in turn, be atmospherically deposited onto rooftops [29–31]. PAHs have a tendency to adhere to particles and have been observed to have strong affiliations with TSS in stormwater runoff [32]. Therefore, first-flush diversions based on TSS removal can also potentially remove PAHs found in roof runoff. In the companion paper, positive correlations between PAHs, TSS, and conductivity in roof runoff were observed in roof runoff samples; therefore, recommending a first-flush diversion based on TSS or conductivity has the potential to greatly reduce PAH concentrations in harvested roof runoff [23].

The objective of this research was to evaluate the water quality of roof runoff from different roofing materials, determine the occurrence of PAHs, phosphorus flame retardants, and pyrethroid insecticides in roof runoff and soils receiving roof runoff, and quantify a first-flush recommendation. This article is Part II of a two-part journal article, and it is focused on the first-flush results and recommendations, specifically (1) quantifying a first-flush diversion based on mass removals of TSS and PAHs and (2) evaluating a first-flush occurrence in roof runoff based on continuous conductivity measurements throughout a storm event. Results from the water quality study, along with a study on the accumulation of PAHs in soils receiving roof runoff, are presented in the companion paper [23].

2. Materials and Methods

2.1. Roof-Runoff Sampling

Runoff samples were collected from eighteen roof structures representing asphalt shingle, metal, and clay tile roofs, under three separate simulated rainfall events, and roof runoff from field samples was collected during actual storm events from two commercial-sized buildings (metal and a tar and gravel roof) and one asphalt shingle roof built on site for this study. All samples from this study were analyzed for the following: pH, conductivity, TSS, turbidity, nitrate-nitrogen, boron, sodium-adsorption ratio, and dissolved iron, copper, zinc, and manganese. Some samples from the field sampling events were also analyzed for the presence of total coliforms and *Escherichia coli*. Water samples were also analyzed for the presence of seventeen PAHs (Σ PAHs: naphthalene, 2-methyl naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, ideno(1,2,3-cd)pyrene, dibenz(a,h)anthracene, and benzo(g,h,i)perylene); phosphorus flame retardants (PFRs) tris(2-chloroethyl) phosphate (TCEP), tris(1,3-dichloro-2-propyl) phosphate (TDCPP); and pyrethroid insecticides bifenthrin, cypermethrin, and lambda-cyhalothrin using solid-phase extraction coupled with gas chromatography-mass spectrometry following EPA Method 525.3. Detailed information regarding the methods references, simulation, and field sampling studies, as well as the water quality results, can be found in the companion paper and Lay [23,33].

2.2. Percent Mass Removals

Water quality results for TSS and PAHs (Σ PAHs, Σ Carcinogenic PAHs, fluoranthene, and benzo(a)pyrene) detected in samples from the rainfall simulations were used to calculate the percent mass removals of the pollutants based on runoff depths 0–1.2, 1.2–2.4, 2.4–3.6, and >6.0 mm for each set of six samples collected from each roof for each simulation event. The Σ PAHs include all PAHs observed in a given sample that were measured from the list of 17 PAHs described in Section 2.1. The Σ Carcinogenic PAHs include known and probable carcinogens benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, ideno(1,2,3-cd)pyrene, dibenz(a,h)anthracene. Runoff depths of 3.6–6.0 mm were not evaluated, as these samples were not analyzed for PAHs, PFRs, or pyrethroid insecticides. The sixth sample from each roof falls into the >6.0 mm runoff depth; runoff volumes for the sixth sample varied based on the roofing material and rainfall intensity, as described in the companion paper [23]. For the calculations, it was presumed that all of the particulates and pollutants were washed from each roof during each simulated rainfall event. Results from the field samples were not used in these calculations, as only portions of the runoff were sampled throughout a storm event, compared with the rainfall simulations in which all runoff was collected from each roof.

2.3. First-Flush Diversions Based on Upper-Confidence Limit

The runoff depths required to divert 50, 75, 90, and 95% of the pollutants on a mass basis were calculated by interpolating the results from the percent mass removals for each set of samples based on runoff depth and determining what runoff depth would provide the given percent removal. After determining what runoff depth was required, an upper-confidence limit (UCL) was constructed to determine the minimum diversion required for a specified percentage of samples to obtain a 50, 75, 90, and 95% mass removal of TSS and PAH contaminants. Following procedures outlined by Bender et al., these data were ranked from the smallest to largest diversion in order to obtain a distribution-free UCL for a desired percentile [34]. Next, binomial probability was used to determine the UCL. The binomial probability density function, B , “calculates the probability that no more than n minus u values from a total of n observations exceed the $(100p)$ th percentile of the sampled population, where p is the probability (p -value) of interest” as is given by,

$$B_{n,p}(u) = \binom{n}{u} p^u (1-p)^{n-u} \quad (1)$$

$$\binom{n}{u} = \frac{n!}{u!(n-u)!} \quad (2)$$

$$B(u-1, n, p) \geq 1 - \alpha \quad (3)$$

where u is the ranking of the smallest integer and α is the significance level. The measured value corresponding to u is the final first-flush diversion value recommended for the given roof type at the UCL based on the given percent mass removal. When computing the UCL, an $\alpha = 0.1$ was used and indicates that there is a 10% chance that a Type I error will occur, meaning that the null hypothesis would be rejected when it is true.

2.4. Continuous Conductivity Monitoring

Conductivity is considered a leading parameter in assessing roof runoff quality [13,22]. Hydrolab MS5 Water Quality Multiprobes (sondes) (Hach®, Loveland, CO, USA) were used to record continuous data on the conductivity, turbidity, and temperature of the roof runoff passing through the downspouts at the field sampling site. A single downspout on both the tar and gravel and metal roofs was replaced and modified with a polyvinyl chloride (PVC) pipe configuration in order to allow for continuous water quality readings and sampling, while a smaller yet identical PVC downspout configuration was placed on the asphalt shingle roof (Figure 1). The new downspout was designed to (1) store water in between storm events to keep a water quality sonde wet and (2) allow for sampling of roof runoff. The sondes were installed in the extension of a 45° PVC wye in the downspouts. The sondes were calibrated in the field before each event using a two-point calibration curve for turbidity readings with 100 NTU and 1000 NTU standards and calibrated for EC using a 1413 $\mu\text{S}/\text{cm}$ standard. Only conductivity results were deemed usable at the end of the study; the turbidity readings had numerous interferences with readings due to air bubbles created when runoff entered the downspouts or from large debris occasionally blocking the sensor.



Figure 1. Modified downspout configuration for the metal roof (left), tar and gravel roof (middle), and asphalt shingle roof (right).

In order to account for mixing between the stored downspout water and incoming rainfall runoff, a rhodamine tracer study was conducted on the larger downspout configurations prior to the field study. A known rhodamine dye concentration mixture was constantly injected into the downspout using a peristaltic pump. Samples were taken every 30 s in order to see how long it took the water in the downspout to become completely mixed with the incoming mixture. Three flow rates were tested, and the following best-fit regression equation ($R^2 = 0.90$) was developed from the measured data using Microsoft Excel based on measured values of cumulative flow into the system (used to calculate proportion) and rhodamine concentration:

$$X = \left(\frac{EC_d}{102.71} \right)^{\frac{1}{0.1508}} \quad (4)$$

where X is the fraction of the downspout water with the given conductivity and EC_d ($\mu\text{S}/\text{cm}$) is the conductivity of the water in the downspout. Using the fraction calculated

from the regression equation, the conductivity of the incoming rainwater was determined based on its mixing with the downspout water that was present before the storm. The conductivity of the rainfall runoff was calculated by

$$EC_{rain} = \frac{EC_d - X(EC_{di})}{(1 - X)} \quad (5)$$

where EC_{rain} ($\mu\text{S}/\text{cm}$) is the conductivity of the rain. This equation was used only when there was a fraction of the nonrainwater in the downspout (i.e., $X > 0$). Otherwise, the recorded values were reported from the sonde for the conductivity of the rainwater.

3. Results and Discussion

3.1. Percent Mass Removals

Tukey–Kramer results from the companion paper show significant differences ($\alpha = 0.05$) between TSS concentrations and each of the six runoff depths from the simulated rainfall events [23]. The percent mass removal of TSS based on runoff depths was between 35 and 90% during the first 1.2 mm of runoff depth between the three roof types (Figure 2), representing 6–11% of the total runoff for each roof. Turbidity can serve as a surrogate for TSS [35], creating the potential for first-flush diverters to be designed to include sensors that measure the turbidity of the runoff. The diverters could be programmed to divert the runoff until a desired turbidity value is measured [36–38]. However, difficulties were experienced in this study when attempting to continuously measure turbidity throughout a storm event. The turbidity sensors had interference in readings due to air bubbles in the runoff, even though attempts were made to reduce bubbles forming when the runoff entered the downspout. An improved downspout design is needed in order to accurately measure the turbidity of the roof runoff.

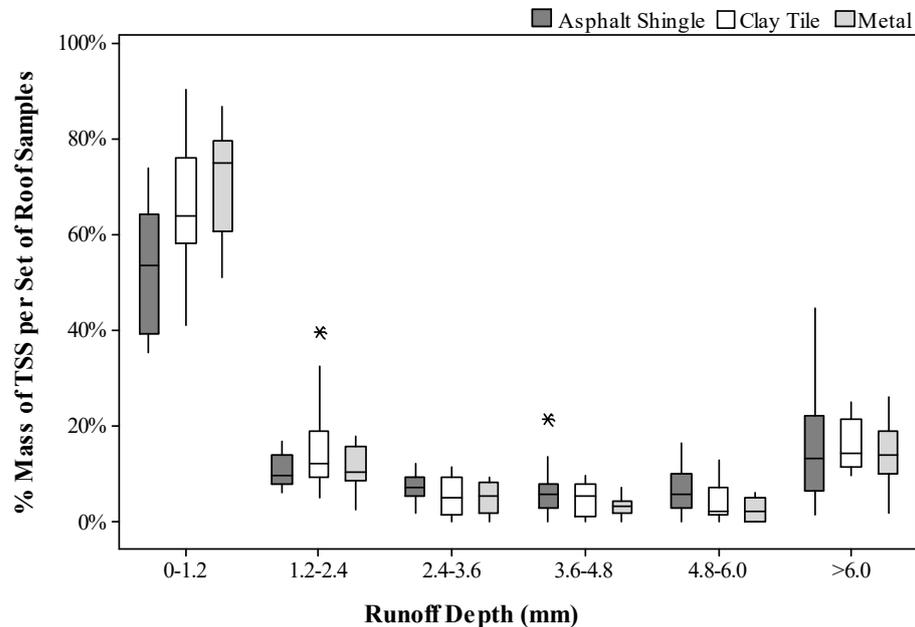


Figure 2. Percent mass of TSS removed based on runoff depth per set of roof samples. The * symbols indicate outlier values in that data set.

On a percent mass basis, the majority of PAHs observed in the roof runoff samples were removed during the initial 1.2 mm of runoff with the exception of the asphalt shingle roofs for Σ Carcinogenic PAHs, fluoranthene, and benzo(a)pyrene, as is shown in Figures 3–6. Van Metre and Mahler observed no evidence that asphalt shingles were a source of PAHs in urban runoff, indicating that the PAHs observed in the roof runoff most likely originated from atmospheric deposition [18]. The texture of roofing materials has an impact on

retention, runoff behavior, and weathering processes [16]. The longer retention times of Σ Carcinogenic PAHs, fluoranthene, and benzo(a)pyrene observed in the asphalt shingle runoff compared with the other roofs can be attributed to the rougher surface texture of the asphalt shingles. The asphalt shingle roofs also had higher concentrations of PAHs in runoff compared with the metal and clay tile roofs [23]. Fluoranthene was observed to have a longer retention time in the roof runoff than benzo(a)pyrene, which could be due to the fact that fluoranthene has a higher solubility in water than benzo(a)pyrene. This observation agrees with research that has also suggested that lower molecular weight PAHs can be observed more frequently and at the highest concentrations in urban runoff [20].

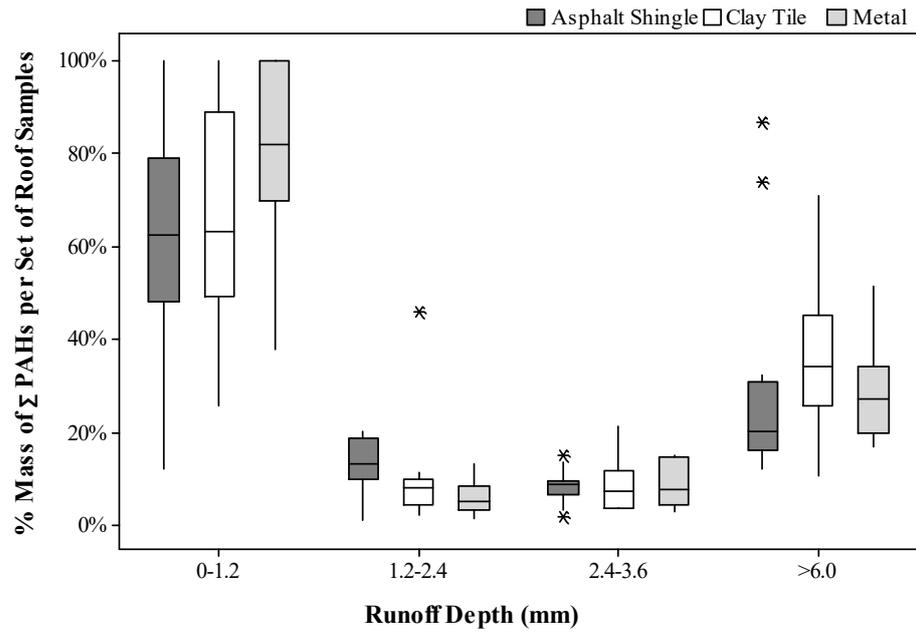


Figure 3. Percent mass of PAHs removed based on runoff depth per set of samples. The * symbols indicate outlier values in that data set.

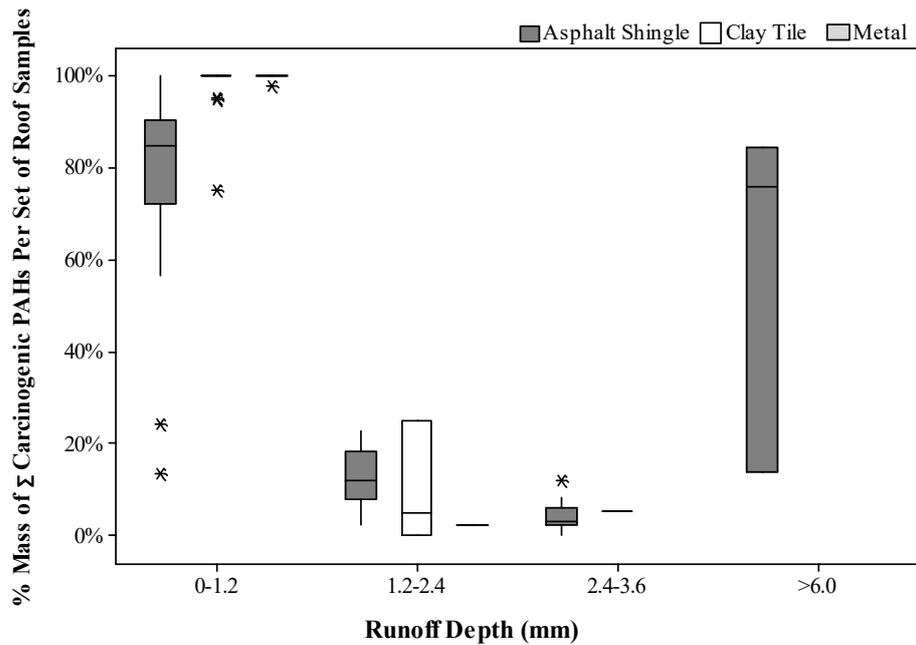


Figure 4. Percent mass of carcinogenic PAHs removed based on runoff depth per set of samples. The * symbols indicate outlier values in that data set.

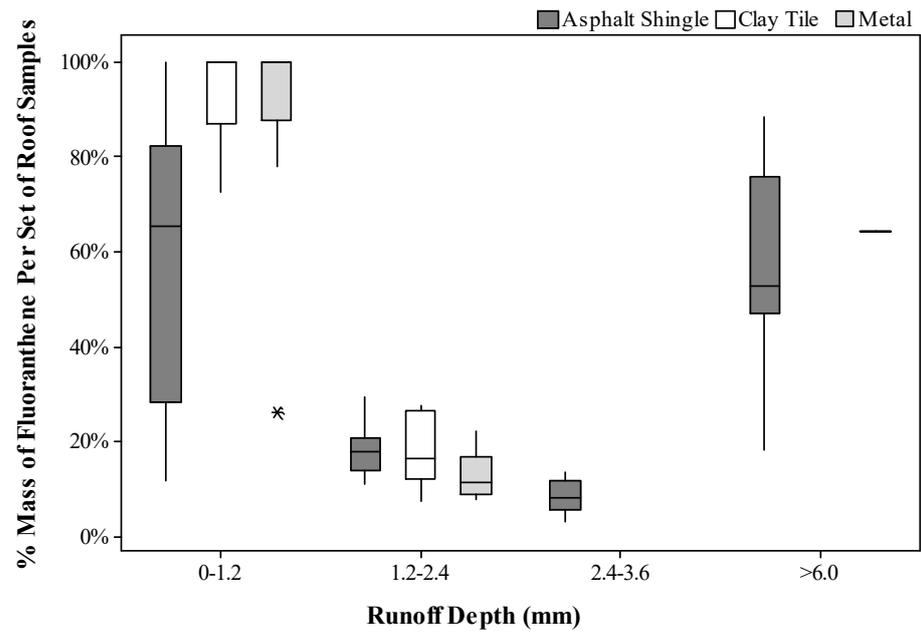


Figure 5. Percent mass of fluoranthene removed based on runoff depth per set of samples. The * symbols indicate outlier values in that data set.

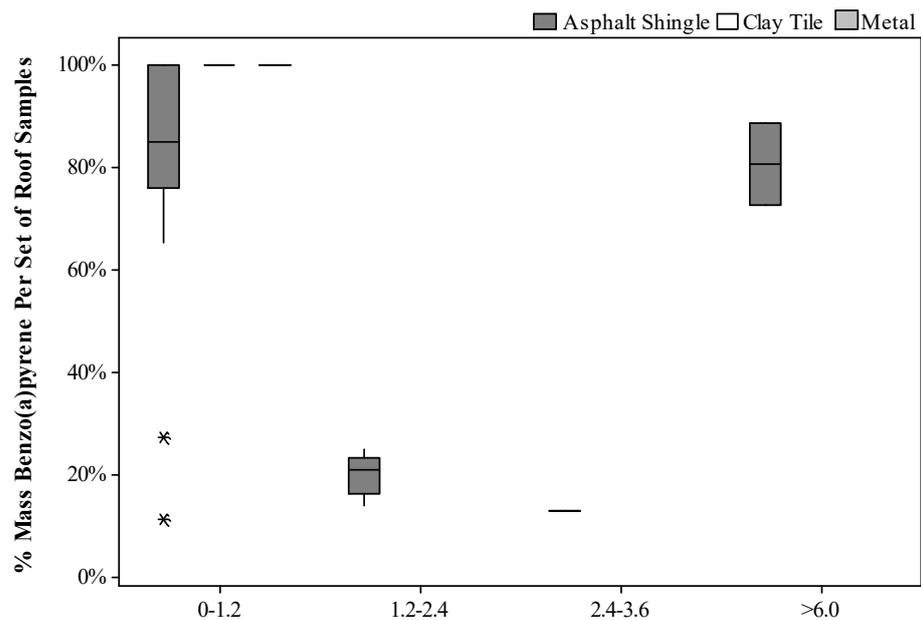


Figure 6. Percent mass removed of benzo(a)pyrene based on runoff depth per set of samples. The * symbols indicate outlier values in that data set.

3.2. First-Flush Diversions Based on Upper-Confidence Limit

Table 1 provides a summary of the recommended first-flush diversions based on percent mass removals for TSS and PAHs for asphalt shingle, metal, and clay tile roofs using an $\alpha = 0.1$, utilizing the mass balance method suggested by Martinson and Thomas [1]. All of the recommended first-flush diversions in Table 1 are based on the confidence that no more than ten percent of the diversions required to obtain a 50, 75, 90, and 95% percent mass removal exceed the listed recommendation. The UCL for the TSS results was 72% and 85% for the PAHs. The differences in UCL were due to the difference in the number of recommendations evaluated ($n = 12$ for TSS and $n = 18$ for PAHs for each percent removal category). TSS were only evaluated for two rainfall simulation events.

Table 1. First-flush diversion recommendations (mm) for asphalt shingle, metal, and clay tile roofs based on percent mass removals of TSS (UCL = 72%, $\alpha = 0.1$) and PAHs (UCL = 85%, $\alpha = 0.1$).

Percent Mass Removals	TSS	Σ PAHs	Σ Carcinogenic PAHs	Fluoranthene	Benzo(a)pyrene
Asphalt Shingle					
50%	2.88	4.10	4.27	5.12	4.00
75%	7.54	7.13	7.22	12.5	7.08
90%	12.6	13.6	8.99	16.8	8.93
95%	15.4	16.7	12.3	18.3	9.55
Metal					
50%	1.13	2.31	1.47	0.77	0.60
75%	3.76	6.03	2.21	1.15	0.90
90%	8.89	14.6	2.65	1.85	1.08
95%	11.5	17.7	2.79	2.12	1.14
Clay Tile					
50%	1.04	3.35	0.63	0.81	0.60
75%	4.85	9.16	0.95	1.26	0.90
90%	8.27	11.7	1.14	1.94	1.08
95%	10.1	12.4	1.20	2.17	1.14

The asphalt shingle roofs require a much larger diversion than the metal and clay tile roofs in order to meet the same percent removal of TSS or PAHs. Therefore, asphalt shingle roofs may not be the most ideal for rainwater harvesting if metal or clay tile roofs are available instead. DiBlasi et al. found a positive correlation exists between PAHs and TSS in stormwater runoff, as was also observed in the companion paper [23,32]. Based on the results shown in Table 1, if the first-flush diversion is based on the mass removal of TSS, then there is a potential that the majority of the Σ Carcinogenic, fluoranthene, and benzo(a)pyrene PAHs will also be removed. When observing the Σ PAHs diversion recommendations, a higher diversion was required compared with TSS diversions for the same percent mass removals for all three roof types except for the 75% mass removal diversion from the asphalt shingle roof. This increase could be due to lighter-weight PAHs having a longer retention time in the roof runoff and not being mobilized as quickly, as was observed when comparing diversion results of fluoranthene (molecular weight of 202.3 g/mole) with benzo(a)pyrene (252.3 g/mole) in this study in Table 1.

When comparing the first-flush diversion recommendations in Table 1 with the 0.41–1.0 mm diversions recommended by Doyle and Shanahan, Mendez et al., Yaziz et al., the TWDB, and [3,4,14,15], the TWDB diversion is not adequate for removing at least 50% of TSS and Σ PAHs for all three roofs, or for at least 50% removal of Σ Carcinogenic PAHs for asphalt shingle and metal roofs, or 50% removal of fluoranthene and benzo(a)pyrene from asphalt shingle roofs. However, they are similar to the 2–5 mm first-flush diversion suggested by Kus et al., although their study did not include PAHs [10]. As noted in the companion paper, the concentrations of TSS observed in the runoff samples did not always meet US EPA nonpotable urban water reuse guidelines, while the PAH concentrations were observed at concentrations below Health-Based Screening Levels and USEPA Maximum Contaminant Levels (MCLs) [23]. Therefore, diverting the first flush based on TSS may be more appropriate versus diverting based on the occurrence of PAHs. However, DiBlasi suggests that TSS may be used as a proxy for PAH removal in bioretention [32]. Based on these results, using TSS as a proxy for Σ PAHs appears to underestimate the first-flush diversion requirement for PAHs.

3.3. Continuous Conductivity Monitoring

The continuous conductivity measurements provided a better understanding of conductivity concentrations throughout a storm event compared with the discrete samples

that were collected at irregular time intervals during the field sampling, as described in the companion paper [23]. The storm events did not have the same runoff volume per roof for each event and each roof did not have the same catchment area. The continuous conductivity measurements were normalized and plotted versus runoff depth for the asphalt shingle, metal, and tar and gravel roofs (Figure 7, Figure 8, and Figure 9, respectively). The maximum conductivity concentrations for each event are shown in Table 2. The maximum concentration did not always occur in the initial runoff. In the companion paper, the conductivity results were compared with USEPA irrigation water reuse recommendations. All storm events except for S11 had no degree of restriction on irrigation, while runoff from S11 from the asphalt shingle roof briefly had a “slight to moderate” restriction on irrigation (conductivity 700–3000 $\mu\text{S}/\text{cm}$), according to the recommended irrigation water reuse guidelines [23].

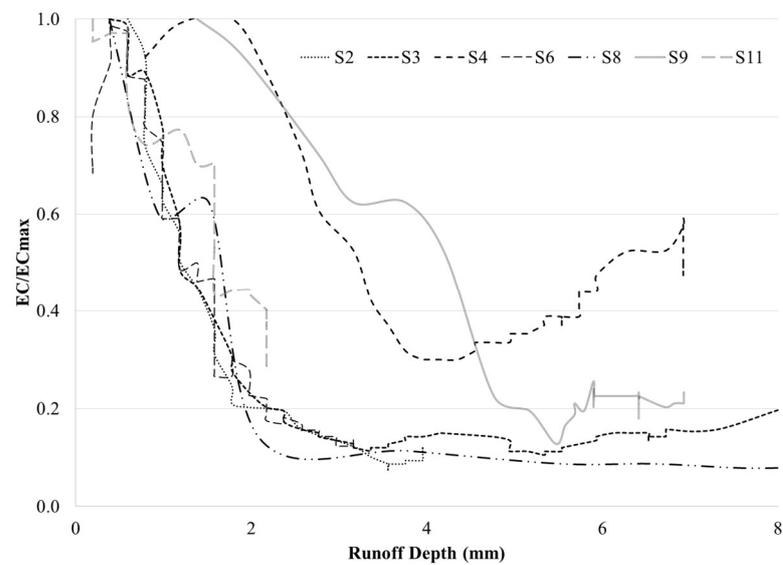


Figure 7. Normalized continuous conductivity measurements of the asphalt shingle roof runoff for a given storm event (S).

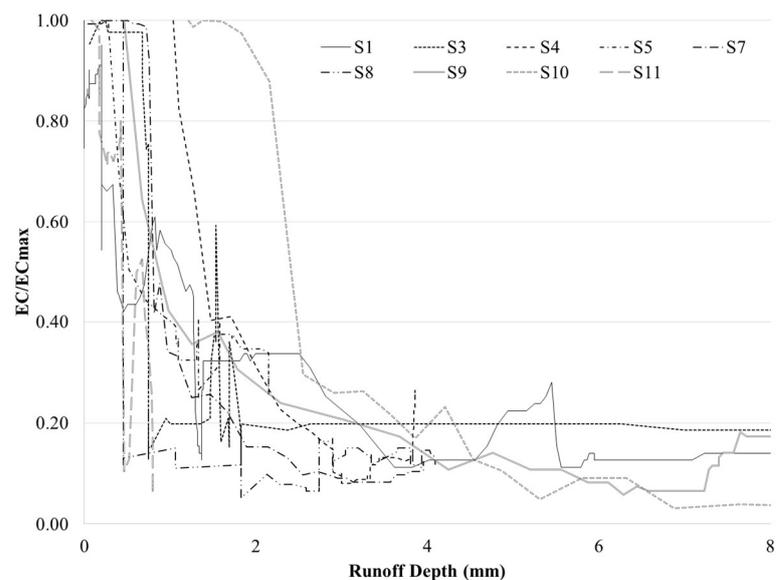


Figure 8. Normalized continuous conductivity measurements of the metal roof runoff for a given storm event (S).

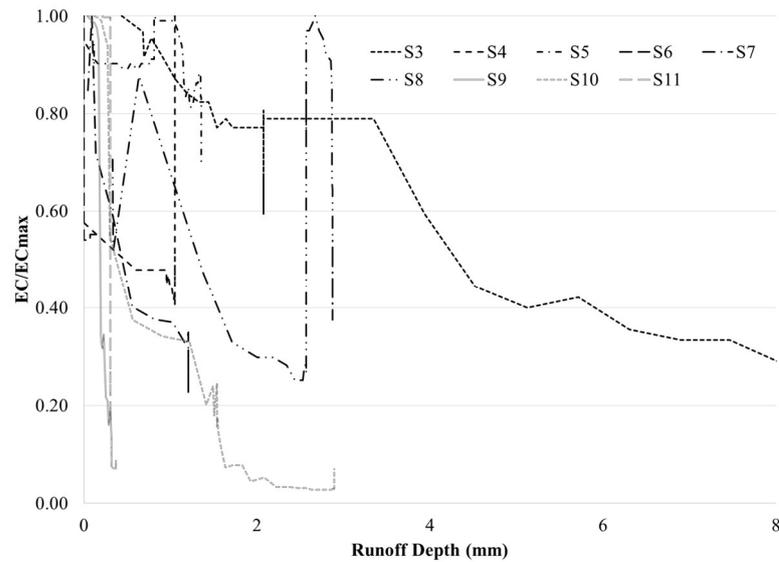


Figure 9. Normalized continuous conductivity measurements of the tar and gravel roof runoff for a given storm event (S).

Table 2. Maximum conductivity concentrations ($\mu\text{S}/\text{cm}$) from continuous measurements of roof runoff during storm events.

Date	Storm Event	Asphalt Shingle	Metal	Tar and Gravel
3 April	S1	-	71	-
11 April	S2	138	86	-
13 April	S3	133	-	45
19 April	S4	57	136	82
28 April	S5	-	136	102
11 May	S6	154	-	87
20 May	S7	-	144	191
29 May	S8	115	153	64
6 June	S9	133	121	493
15 June	S10	-	636	357
9 July	S11	752	766	751

Continuous conductivity measurements revealed an overall decreasing trend in concentrations throughout a storm event, indicating the presence of a first flush [8]. During some storm events, the conductivity was observed to increase again after the initial drop in conductivity. As the storm events for the field sampling were not simulated and were of varying intensities throughout a single storm event, the increase in conductivity could be due to an increase in rainfall intensity as the storm continued, thereby washing away more dust and debris from the roofs.

The conductivity of runoff from the asphalt shingle roof decreased by 23–51% from the highest conductivity measurements within the first 1.2 mm of runoff and by 80–89% within 2.4 mm of runoff when excluding storm events S4 and S9. Storm event S4 did not follow this same trend, perhaps due to the highest conductivity reading occurring later in the runoff depth compared with the other storm events. During S9, the asphalt shingle downspout was empty of water prior to the start of the storm event, and the sonde was unable to begin recording until 1.4 mm of runoff had occurred. The metal roof runoff conductivities decreased by 17–89% within the first 1.2 mm of runoff and by 66–92% by 2.4 mm of runoff when excluding storm event S10. S10 required 2.6 mm of runoff depth to notice a significant decrease in conductivities, where a 70% decrease was observed between 2.2 and 2.6 mm of runoff depth. Due to the flatness and poor catchment efficiency of the tar and gravel roof, the runoff depth measured was generally much less than the asphalt shingle and metal roofs. Storm events S3, S5, S6, S7, S8, S9, and S10 had runoff depths

of at least 1.2 mm and had a decrease in conductivity of 16–68%. Only storm events S3, S8, and S10 had runoff depths of at least 2.4 mm and had a decrease in conductivity of 21–97%. However, the conductivity from S8 increased again at 2.6 mm of runoff to reach its maximum conductivity observed during the storm event.

Conductivity was shown to be positively correlated ($\alpha = 0.05$) to TSS, turbidity, and the presence of PAHs in roof runoff in both the simulated rainfall events and field sampling results [23]. As was observed in the percent mass removals of TSS and PAHs in Section 3.1, a large percentage of the pollutants (on a mass basis) can be diverted within the first 1.2–2.4 mm of runoff depth. The continuous conductivity data from the field sampling sites show that the conductivity can greatly decrease from its original concentration within the first 2.4 mm of runoff depth. There is potential for designing automated first-flush diverters to divert runoff based on conductivity measurements that can, in turn, significantly divert contaminants like TSS and PAHs from storage tanks. Research and development on first-flush diverters equipped with automated control via sensors was also proposed by Förster [39]. Further research is needed in this area.

4. Conclusions

This comprehensive study of utilizing the mass removal of TSS and PAHs to estimate first-flush diversion has overall demonstrated that many diversion recommendations may be too small to remove a large percentage of these pollutants for these three roof types (asphalt shingle, metal, and clay tile). A summary of the major findings is as follows:

- The majority of TSS (on a mass basis) were removed during the initial 1.2 mm of runoff for the asphalt shingle, metal, and clay tile roofs. Based on water quality results in the companion paper, diverting the first flush based on TSS may be more appropriate versus diverting based on the occurrence of PAHs.
- On a percent mass basis, the majority of PAHs observed in the roof runoff samples were removed during the initial 1.2 mm of runoff with the exception of the asphalt shingle roofs for Σ Carcinogenic PAHs, fluoranthene, and benzo(a)pyrene, where a high percentage of PAHs were also observed after 6 mm of runoff had occurred. The longer retention of PAHs on asphalt shingle roofs compared with the metal and clay tile roofs may be attributed to the rougher surface of the asphalt shingle roofs.
- When observing the first-flush diversion recommendations based on 50, 75, 90, and 95% removal of pollutants, the asphalt shingle roofs require a much larger diversion than the metal and clay tile roofs in order to meet the same percent removal of TSS or PAHs.
- Higher first-flush diversions were required for the removal of Σ PAHs compared with TSS diversions for the same percent mass removals for all three roof types, except for the 75% mass removal diversion from the asphalt shingle roof. This increase could be due to lighter-weight PAHs having a longer retention time in the roof runoff and not being mobilized as quickly.
- There is potential that the majority of the Σ Carcinogenic, fluoranthene, and benzo(a)pyrene PAHs will be removed if the first-flush diversion is based on the mass removal of TSS, although the correlation may underestimate the removal of the PAHs and should perhaps be applied with a factor of safety.
- The TWDB recommended first-flush diversion was not adequate for removing at least 50% of TSS and Σ PAHs for all three roofs, or for at least 50% removal of Σ Carcinogenic PAHs for asphalt shingle and metal roofs, or 50% removal of fluoranthene and benzo(a)pyrene from asphalt shingle roofs in this study.
- When continuously measuring the conductivity throughout a storm event, it was observed that the conductivity can decrease drastically within the first 1.2 to 2.4 mm of runoff. There is potential for designing automated first-flush diverters to divert runoff based on conductivity measurements that can, in turn, significantly divert contaminants like TSS and PAHs from storage tanks.

- Further research is needed on the use of continuously monitored specific conductance or other parameters to estimate first-flush diversion volume.

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References

1. Martinson, D.B.; Thomas, T. Quantifying the first-flush phenomenon. In Proceedings of the 12th International Rainwater Catchment Systems Conference, New Delhi, India, 15–18 November 2005.
2. Zhang, M.; Chen, H.; Wang, J.; Pan, G. Rainwater utilization and storm pollution control based on urban runoff characterization. *J. Environ. Sci.* **2010**, *22*, 40–46. [CrossRef]
3. Mendez, C.B.; Klenzendorf, J.B.; Afshar, B.R.; Simmons, M.T.; Barrett, M.E.; Kinney, K.A.; Kirisits, M.J. The effect of roofing material on the quality of harvested rainwater. *Water Res.* **2011**, *45*, 2049–2059. [CrossRef] [PubMed]
4. Doyle, K.C.; Shanahan, P. Effect of first flush on storage-reliability-yield of rainwater harvesting. *J. Water Sanit. Hyg. Dev.* **2012**, *2*, 1–9. [CrossRef]
5. Kumpel, E.; Charlebois, B.; Wittbold, P.; Reckhow, D. Effective first flush volumes in experimental household-scale rainwater catchment systems. *AQUA-Water Infrastruct. Ecosyst. Soc.* **2023**, *72*, 814–826.
6. Förster, J. Variability of roof runoff quality. *Water Sci. Technol.* **1999**, *39*, 137–144. [CrossRef]
7. Mamun, A.A.; Shams, S.; Nuruzzaman, M. Review on uncertainty of the first-flush phenomenon in diffuse pollution control. *Appl. Water Sci.* **2020**, *10*, 53. [CrossRef]
8. Gikas, G.D.; Tsihrintzis, V.A. Assessment of water quality of first-flush roof runoff and harvested rainwater. *J. Hydrol.* **2012**, *466*, 115–126. [CrossRef]
9. Lye, D.J. Rooftop runoff as a source of contamination: A review. *Sci. Total Environ.* **2009**, *407*, 5429–5434. [CrossRef]
10. Kus, B.; Kandasamy, J.; Vigneswaran, S.; Shon, H. Analysis of first flush to improve the water quality in rainwater tanks. *Water Sci. Technol.* **2010**, *61*, 421–428. [CrossRef]
11. Meera, V.; Ahammed, M.M. Water Quality of Rooftop Rainwater Harvesting Systems: A Review. *J. Water Supply Res Technol.-Aqua* **2006**, *55*, 257–268. [CrossRef]
12. Sansalone, J.; Cristina, C. First Flush Concepts for Suspended and Dissolved Solids in Small Impervious Watersheds. *J. Environ. Eng.* **2004**, *130*, 1301–1314. [CrossRef]
13. Schriewer, A.; Horn, H.; Helmreich, B. Time focused measurements of roof runoff quality. *Corros. Sci.* **2008**, *50*, 384–391. [CrossRef]
14. Yaziz, M.I.; Gunting, H.; Sapari, N.; Ghazali, A.W. Variations in rainwater quality from roof catchments. *Water Res.* **1989**, *23*, 761–765. [CrossRef]
15. TWDB. *The Texas Manual on Rainwater Harvesting*; Texas Water Development Board: Austin, TX, USA, 2005.
16. De Buyck, P.J.; Van Hulle, S.W.H.; Dumoulin, A. Roof runoff contamination: A review on pollutant nature, material leaching and deposition. *Rev. Environ. Sci. Biotechnol.* **2021**, *20*, 549–606. [CrossRef]
17. Göbel, P.; Dierkes, C.; Coldewey, W.G. Storm water runoff concentration matrix for urban areas. *J. Contam. Hydrol.* **2007**, *91*, 26–42. [CrossRef] [PubMed]

18. Stein, E.D.; Tiefenthaler, L.L.; Schiff, K. Watershed-based sources of polycyclic aromatic hydrocarbons in urban storm water. *Environ. Toxicol. Chem.* **2006**, *25*, 373–385. [[CrossRef](#)]
19. Van Metre, P.C.; Mahler, B.J.; Furlong, E.T. Urban Sprawl Leaves Its PAH Signature. *Environ. Sci. Technol.* **2000**, *34*, 4064–4070. [[CrossRef](#)]
20. Haritash, A.K.; Kaushik, C.P. Biodegradation aspects of Polycyclic Aromatic Hydrocarbons (PAHs): A review. *J. Hazard. Mater.* **2009**, *169*, 1–15. [[CrossRef](#)]
21. Rule, K.; Comber, S.; Ross, D.; Thornton, A.; Makropoulos, C.; Rautiu, R. Sources of priority substances entering an urban wastewater catchment—Trace organic chemicals. *Chemosphere* **2006**, *63*, 581–591. [[CrossRef](#)]
22. Dao, D.A.; Tran, S.H.; Dang, H.T.; Nguyen, V.A.; Nguyen, V.A.; Do, C.V.; Han, M. Assessment of rainwater harvesting and maintenance practice for better drinking water quality in rural areas. *J. Water Supply Res. Technol.-Aqua* **2021**, *70*, 202–216. [[CrossRef](#)]
23. Lay, J.J.; Vogel, J.R.; Belden, J.B.; Brown, G.O.; Storm, D.E. Water Quality and the First-Flush Effect in Roof-Based Rainwater Harvesting, Part I: Water Quality and Soil Accumulation. *Water* **2024**, *16*, 1402. [[CrossRef](#)]
24. Van Metre, P.C.; Mahler, B.J. The contribution of particles washed from rooftops to contaminant loading to urban streams. *Chemosphere* **2003**, *52*, 1727–1741. [[CrossRef](#)] [[PubMed](#)]
25. Morgado, M.E.; Hudson, C.L.; Chattopadhyay, S.; Ta, K.; East, C.; Purser, N.; Allard, S.; Ferrier, M.D.; Sapkota, A.R.; Sharma, M.; et al. The effect of a first flush rainwater harvesting and subsurface irrigation system on E. coli and pathogen concentrations in irrigation water, soil, and produce. *Sci. Total Environ.* **2022**, *843*, 156976. [[CrossRef](#)]
26. Rocher, V.; Azimi, S.; Gasperi, J.; Beuvin, L.; Muller, M.; Moillon, R.; Chebbo, G. Hydrocarbons and Metals in Atmospheric Deposition and Roof Runoff in Central Paris. *Water Air Soil Pollut.* **2004**, *159*, 67–86. [[CrossRef](#)]
27. GrmaGrmasha, R.A.; Abdulameer, M.H.; Stenger-Kovács, C.; Al-Sareji, O.J.; Al-Gazali, Z.; Al-Juboori, R.A.; Meiczinger, M.; Hashim, K.S. Polycyclic aromatic hydrocarbons in the surface water and sediment along Euphrates River system: Occurrence, sources, ecological and health risk assessment. *Mar. Pollut. Bull.* **2023**, *187*, 114568. [[CrossRef](#)]
28. De Kwaadsteniet, M.; Dobrowsky, P.H.; van Deventer, A.; Khan, W.; Cloete, T.E. Domestic Rainwater Harvesting: Microbial and Chemical Water Quality and Point-of-Use Treatment Systems. *Water Air Soil Pollut.* **2013**, *224*, 19. [[CrossRef](#)]
29. Estrellan, C.R.; Iino, F. Toxic emissions from open burning. *Chemosphere* **2010**, *80*, 193–207. [[CrossRef](#)]
30. Gogra, A.B.; Yao, J.; Kabba, V.T.S.; Sandy, E.H.; Zaray, G.; Gbaniea, S.P.; Bandagbad, T.S. A situational analysis of waste management in Freetown, Sierra Leone. *J. Am. Sci.* **2010**, *6*, 124–135.
31. Zhang, T.; Fiedler, H.; Yu, G.; Ochoa, G.S.; Carroll, W.F., Jr.; Gullett, B.K.; Marklund, S.; Touati, A. Emissions of unintentional persistent organic pollutants from open burning of municipal solid waste from developing countries. *Chemosphere* **2011**, *84*, 994–1001. [[CrossRef](#)]
32. DiBlasi, C.J.; Li, H.; Davis, A.P.; Ghosh, U. Removal and Fate of Polycyclic Aromatic Hydrocarbon Pollutants in an Urban Stormwater Bioretention Facility. *Environ. Sci. Technol.* **2008**, *43*, 494–502. [[CrossRef](#)]
33. Lay, J.J. Water Quality and the First-flush Effect in Roof-based Rainwater Harvesting. Master's Thesis, Oklahoma State University, Stillwater, OK, USA, 2014. Available online: <https://shareok.org/handle/11244/14959> (accessed on 1 March 2024).
34. Bender, D.A.; Zogorski, J.S.; Mueller, D.K.; Rose, D.L.; Martin, J.D.; Brenner, C.K. *Quality of Volatile Organic Compound Data from Groundwater and Surface Water for the National Water-Quality Assessment Program, October 1996–December 2008*; US Geological Survey Scientific Investigations Report 2011-5204; USGS: Rapid City, SD, USA, 2011; 128p. Available online: <http://pubs.usgs.gov/sir/2011/5204/> (accessed on 1 March 2024).
35. Miguntanna, N.S.; Egodawatta, P.; Kokot, S.; Goonetilleke, A. Determination of a set of surrogate parameters to assess urban stormwater quality. *Sci. Total Environ.* **2010**, *408*, 6251–6259. [[CrossRef](#)] [[PubMed](#)]
36. Farreny, R.; Morales-Pinzon, T.; Guisasola, A.; Taya, C.; Rieradevall, J.; Gabarrell, X. Roof selection for rainwater harvesting: Quantity and quality assessments in Spain. *Water Res.* **2011**, *45*, 3245–3254. [[CrossRef](#)] [[PubMed](#)]
37. Christensen, V.G.; Ziegler, A.C.; Jian, X. In Continuous turbidity monitoring and regression analysis to estimate total suspended solids and fecal coliform bacteria loads in real time. In Proceedings of the Seventh Federal Interagency Sedimentation Conference, Reno, NV, USA, 25–29 March 2001; pp. III-94–III-101.
38. Jones, A.S.; Stevens, D.K.; Horsburgh, J.S.; Mesner, N.O. Surrogate Measures for Providing High Frequency Estimates of Total Suspended Solids and Total Phosphorus Concentrations. *JAWRA J. Am. Water Resour. Assoc.* **2011**, *47*, 239–253. [[CrossRef](#)]
39. Förster, J. Patterns of Roof Runoff Contamination and Their Potential Implications on Practice and Regulation of Treatment and Local Infiltration. *Water Sci. Technol.* **1996**, *33*, 39–48. [[CrossRef](#)]

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