Potential for 6PPD-Q Removal from Tire-Derived Aggregate Leachate by Passive Soil Media Filtration

August 2025

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Prepared as part of contract number DRR 21023.

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Executive Summary

Tire-Derived Aggregate (TDA), a recycled material made from shredded tires, is utilized in engineering applications due to its advantageous physical properties, such as being lightweight and highly permeable. Despite its benefits, environmental concerns have surfaced regarding the leaching of 6PPD-quinone (6PPD-Q), a toxic transformation product of a common tire antioxidant. This compound has been identified as acutely toxic to aquatic species, specifically coho salmon, prompting a closer examination of its potential release from TDA installations that are exposed to water infiltration.

This study explores whether passive filtration through soil or sand media could effectively remove 6PPD-Q from TDA leachate, thereby mitigating its environmental impact. The project began with the development of a method to reliably produce leachate containing elevated concentrations of 6PPD-Q. Materials used to produce the 6PPD-Q leachate included TDA type A (TDA-A), uncolored rubber mulch, and crumb rubber.

A series of filtration experiments were conducted to assess the efficacy of various soil and sand media in removing 6PPD-Q from the leachate. The findings were promising. Soil-based filters with depths as shallow as nine inches consistently removed more than 95% of the toxic compound and in most tested scenarios resulted in effluent concentrations below the Lethal Concentration 50 (LC_{50}) of 6PPD-Q for coho salmon. Surprisingly, sand filters, including beach and river sands, demonstrated equal or superior performance, achieving removals of up to 99.8%. These results challenge previous assumptions that sand would be ineffective due to its lack of organic matter and rapid flow-through characteristics.

However, the study also revealed substantial challenges in accurately measuring 6PPD-Q concentrations. Laboratory analyses were frequently affected by matrix interference, and inconsistencies between labs underscored the urgent need for standardized methods in sampling, processing, and analysis. With only a limited number of laboratories currently able to perform 6PPD-Q testing, the high costs and long turnaround times further constrain the development of sound regulatory guidance.

Despite these analytical limitations, the overall results support the conclusion that passive filtration through soil or sand layers beneath TDA fills can significantly reduce the risk posed by 6PPD-Q leachate. These findings have implications not only for the continued use of TDA in stormwater-influenced environments but also for broader applications in stormwater treatment systems adjacent to sensitive aquatic habitats.

To build on this work and inform future design practices, further research is recommended to explore the long-term behavior of 6PPD-Q in environmental settings, the mechanisms driving its removal in different media, and the practical lifetime of such filtration systems. Field verification of laboratory findings will be essential, as will exploring how similar filtration approaches could be adapted for managing roadway runoff that poses a risk to nearby surface waters.

Background and Study Objectives

In many engineering applications, tire-derived aggregate (TDA) is a superior product compared to more traditional rock aggregate. In some applications, such as retaining wall backfill, TDA may be subject to occasional wetting from groundwater seepage or from surface infiltration of precipitation. In other applications, such as stormwater infiltration and treatment galleries, TDA fill is frequently saturated with surface runoff. In nearly all cases, leachate from the TDA is ultimately reintroduced into the groundwater or surface water environment.

The potential negative impact of TDA leachate on surface and groundwater systems has been studied extensively for over 30 years, focusing on a wide range of water quality constituents of concern under actual use conditions. As summarized in Finney and Maeda (2016), previous studies have found the leachate to have little to no measurable impact. In the case of TDA-filled infiltration galleries, the effluent quality is often better for common metals, organics and nutrients than the quality of stormwater entering the system (Maeda and Finney, 2018). However, in 2021, a compound associated with tires known as 6PPD-quinone (6PPD-Q) was discovered to be extremely toxic to coho salmon. 6PPD-Q is an ozonation product of the parent antioxidation compound 6PPD, commonly used in tire rubber. Recently published studies have determined the median Lethal Concentration 50 (LC_{50}) of 6PPD-Q to be 95 ng/l for 1+ year-old coho salmon and 41 ng/l for juvenile coho (Tian et al., 2022, Lo et al. 2023).

Prior to encouraging continued use of TDA in engineering applications where the material may be subject to wetting and subsequent runoff to the environment, determining the potential contribution of 6PPD-Q from the material should be investigated. If there is a risk of release of leachate at near-lethal concentrations of the compound, design modifications for future TDA applications and post-treatment for existing systems may be necessary.

Since the discovery of the link between 6PPD-Q and coho salmon deaths in urban streams, most research has focused on confirming these findings, investigating its toxicity to other aquatic organisms, and improving laboratory testing methods. However, there has been less focus on exploring ways to mitigate the impact of 6PPD-Q leachate from tire rubber on the aquatic environment. Prior to identifying 6PPD-Q's role, Spromberg et al. (2016) found that bioretention facilities could reduce the impact of stormwater on coho salmon mortality. Later, Rodgers et al. (2023) observed that when stormwater leachate containing 6PPD-Q was filtered through a soil column, the resulting effluent did not exhibit toxic effects on coho. The objective of this study is to determine whether soil mantle treatment of leachate from TDA can effectively reduce the concentration of 6PPD-Q below values currently considered a threat to the aquatic environment.

Tasks and Procedures

The project was divided into two tasks. The preliminary task was to determine a procedure to prepare water samples containing 6PPD-Q that could be used for the influent to soil media filters. Ideally, the leachate containing 6PPD-Q would meet four criteria:

1. Be easy and inexpensive to prepare,
2. Use tire rubber materials so that other constituents resemble those in a field setting with TDA leachate,
3. Minimize the presence of contaminants that might interfere with the analysis of 6PPD-Q concentrations, and
4. Reliably produce 6PPD-Q concentrations exceeding typical stormwater concentrations.

Soaking and/or sprinkling the end-of-life tire materials—TDA type A (TDA-A), uncolored rubber mulch, and crumb rubber (Figure 1, Figure 2, Figure 3)—with dechlorinated potable water satisfies criteria 1 and 2. TDA-A is a coarse, shredded tire material ranging from 3 to 4 inches in size, often containing embedded steel wire, and commonly used in civil engineering applications. Since rubber mulch and crumb rubber do not contain embedded wire, leachate from these materials also satisfies criterion 3. The first task of this investigation will determine whether soaking and/or sprinkling these materials produces leachate with a sufficiently high concentration of 6PPD-Q to satisfy criterion 4.

While published data is not available, 6PPD-Q concentrations in direct TDA leachate would likely be higher than those encountered in stormwater runoff. For this testing program, TDA soaking is used to produce influent water with 6PPD-Q concentrations representative of typical stormwater applications, not the elevated concentrations expected from direct TDA contact. As summarized by Hua (2023), concentrations as high as 2,430 ng/L have been measured in urban stormwater runoff dominated by tire wear particles. To reliably produce 6PPD-Q concentrations exceeding typical stormwater concentrations for robust filter testing, a target concentration greater than 2,500 ng/L in the influent water is assumed to represent the upper range likely encountered in stormwater practice.

Figure 1. Source materials used for producing leachate containing 6PPD-Q: from left TDA-A, tire rubber mulch, tire crumb.

Figure 2. Soaking TDA-A (left) and tire rubber crumb (right).

Figure 3. Preparing to sprinkle water over TDA-A.

The second and primary project task was to test the characteristics of an engineered soil layer in reducing the concentration of 6PPD-Q in TDA leachate through four filtration experiments (Table 1).

Soil media filtration columns were used to simulate the soil layer below a TDA fill. The soil media was contained in 20-gallon HDPE vertical tanks (24 inches tall and 12 inches in diameter) with a side drain near the bottom (Figure 4). While some 6PPD-Q uptake into the walls of the tanks may have occurred, Clark and Ahearn (2024) and Herrera (2024) found that there was negligible loss of 6PPD-Q when using HDPE sample containers. The bottoms of the columns were filled with clean gravel up to one inch above the bottom of the side drain. The configuration of the side drain and gravel fill allowed for up to 18 inches of soil media, which corresponds to the depth of soil determined by Finney and Maeda (2016) to be sufficient for the removal of organic and inorganic compounds of concern in leachate from a TDA-filled stormwater infiltration gallery. The testing scenarios involved determining the impact of different soil types and different soil depths in removing 6PPD-Q from the influent water source.

It was anticipated that organic compounds in the soil may be an important factor for 6PPD-Q removal. Therefore, filtration test 1 investigated three different soil materials with a range of organic content: all compost, a 50-50 mix by volume of topsoil and compost, and all topsoil (Figure 5). The topsoil was sourced from a local garden, and the compost used was the widely available Gardner & Bloome Organics Purely Compost. A detailed chemical and nutrient balance for these products was not available. The columns were filled with the soil media by hand without compaction, but repeated flushing with water prior to use resulted in sufficient settling to fill any significant voids. There was some concern that using an 18-inch media depth might result in non-detects for the effluent 6PPD-Q concentration of all three media. Therefore, a media depth of 9 inches was used for each column to hopefully provide sufficient contact depth and yet result in measurable concentrations of effluent 6PPD-Q.

Filtration test 2 examined the impact of soil media depth on 6PPD-Q removal using compost media at depths of 6, 12, and 18 inches. Finally, filtration tests 3 and 4 evaluated the performance of common construction fill materials such as soil fill, beach sand, and river sand, at a media depth of 18 inches (Figure 6). In many cases, a TDA fill would be subject to wetting on an intermittent basis, and the filtration media might be relatively dry, resulting in poor constituent removal in the first flush of leachate. Therefore, in filtration test 3, the potential impact of this first-flush condition was also investigated.

In each of the filtration experiments, the filters were initially flushed with dechlorinated potable water to consolidate the media and then allowed to gravity drain. To minimize the impact of a dilution effect from the initial potable water flush, the media was then flushed with the same water that was used in the filtration run and again allowed to gravity drain. Finally, the filters were loaded with typically 2 to 3 liters of influent water containing 6PPD-Q. The influent volume varied depending on the effluent sampling requirements and the relatively low percolation rate of the soil media. Influent samples were taken after completely mixing the source container. All the effluent was collected from a filter and mixed prior to taking a sample to determine the effluent concentration of 6PPD-Q.

As a cost-saving measure, only one leachate sample was initially collected when determining the procedure to prepare water samples containing 6PPD-Q to be used as influent for the soil media filters. Later, to increase confidence in the results, replicate samples of the leachate were collected. Replicate samples were always taken for both the filter influent and effluent in the filtration experiments.

At the time of this investigation, only two commercial labs located in California were available to perform the analysis of water samples for 6PPD-Q. Both labs used liquid chromatography coupled with mass spectrometry (LC-MS) to determine 6PPD-Q concentrations, generally following the draft EPA Method 1634 (EPA, 2024). The method used by the two labs only differed from each other in the techniques used during the sample preparation stage. Lab 1 used solid phase extraction (SPE) during sample preparation, while Lab 2 did not.

Table 1. Summary of objectives and conditions for the filtration experiments.

Filtration Experiment Number	Objective	Column 1 Media Type, Depth (inches)	Column 2 Media Type, Depth (inches)	Column 3 Media Type, Depth (inches)
1	Determine whether the fraction of organic material in the filtration media impacts 6PPD-Q removal	Topsoil, 9	Topsoil/ compost mix (50/50), 9	Compost, 9
2	Determine the impact of the filtration media depth on 6PPD-Q removal	Compost, 6	Compost, 12	Compost, 18
3	Determine the 6PPD-Q removal characteristics of different construction fill materials and whether there is a significant "first flush" effect	High-clay content fill soil, 18	Beach sand, 18	Not used
4	Determine the 6PPD-Q removal characteristics of different construction fill materials at different media depths	High-clay content fill soil, effective depths of 18 and 36	Beach sand, 18	River sand, 18

Figure 4. 12-inch diameter HDPE filtration columns.

Figure 5. Filtration media (with nonvolatile portion in the dish for comparison) for 9-inch depth test; from left topsoil, topsoil/compost mix, compost.

Figure 6. Construction fill media used for filtration; from left high-clay fill soil, river sand, beach sand.

Results and Discussion

Initial efforts to create a suitable influent feedwater for the filtration experiments, with a 6PPD-Q concentration greater than 2,500 ng/l, involved soaking TDA-A and tire crumb rubber in dechlorinated potable water for 7 and 14 days. Both soaking periods produced leachate with sufficient 6PPD-Q concentrations. However, oxidation of the wire in the TDA resulted in considerable added solids and color to the leachate, which might interfere with accurately determining the concentration of 6PPD-Q (Table 2). The additional 7 days of soaking for the 14-day sample did not yield a significantly higher concentration of 6PPD-Q, making the extended soak time unwarranted.

Since the leaching of 6PPD-Q from the tire rubber is a surface phenomenon, tire crumb rubber was expected to produce higher concentrations of the constituent compared to TDA, given the much higher surface area to volume ratio. In addition, since it does not contain wire, using crumb rubber would avoid potential contamination issues with the oxidized steel wire in TDA. Unfortunately, in what was a recurring issue throughout this project, the analytical laboratory that performed the analysis reported 6PPD-Q concentration results for the samples that were clearly in error. In this case, while the concentration of 6PPD-Q for the 7-day tire crumb soak sample seemed reasonable at 6,200 ng/l, the 14-day soak value of 46 ng/l was unreasonably low (Table 2). When asked to review the results for the crumb rubber, the lab eventually confirmed that the results were in error and should not be used. The errors in the results were believed to be primarily due to matrix interference, where the term “matrix” refers to constituents in the sample other than the constituent of interest. In this case, those other constituents were interfering with one or more of the procedures in the analytical method for 6PPD-Q, masking the true concentration of the compound.

Table 2. 6PPD-Q from soaking TDA and crumb rubber.

Soak time (days)	6PPD-Q concentration from TDA-A (ng/l)	6PPD-Q concentration from tire crumb (ng/l)
7	5,300	6,200*
14	6,800	46*

*Lab decided these values were in error (biased low).

Since the transformation of 6PPD to 6PPD-Q is an oxidative process, the impact of aeration while soaking TDA and crumb rubber was explored. Unfortunately, the 6PPD-Q concentrations reported by the lab were much lower than expected. Ultimately, the lab admitted that the reported values were likely in error and should not be used (Table 3).

Table 3. 6PPD-Q from soaking and aerating TDA and crumb rubber.

Aerated soak time (hours)	6PPD-Q concentration from TDA-A (ng/l)	6PPD-Q concentration from tire crumb (ng/l)
0.5	17*	110*
23	300*	130*

*Lab decided these values were in error (biased low).

To simulate rainfall runoff from a pile of TDA and to explore a simple method for preparing influent water for the filtration experiments, dechlorinated potable water was sprinkled over TDA-A and crumb rubber held in a stainless-steel colander. Two samples were collected from each medium. Composite samples from the runoff of the initial sprinkling process were denoted as Pass 1. For TDA, a portion of the Pass 1 sample was sprinkled over the TDA a second time, and the runoff was labeled as Pass 2. For crumb rubber, the Pass 2 sample was the runoff from a second sprinkling of fresh dechlorinated water, not the effluent from Pass 1.

The results for TDA were inconsistent with other results, with a higher 6PPD-Q concentration in the Pass 1 sample than the Pass 2 sample (5,200 ng/l vs. 3,700 ng/l) (Table 4). Since the Pass 1 effluent water was reused as the influent water for Pass 2, the concentration of 6PPD-Q in Pass 2 was expected to increase. This result further diminished confidence in the results reported by the lab. The results reported by the lab from the crumb rubber samples were also unreasonably low (40 ng/l for Pass 1 and 42 ng/l for Pass 2) (Table 4). Upon review, the lab verified that the concentrations were in error and should not be used.

Table 4. 6PPD-Q from sprinkling water over TDA and crumb rubber.

Sprinkled over media	6PPD-Q concentration from TDA-A (ng/l)	6PPD-Q concentration from tire crumb (ng/l)
Pass 1	5,200	40[1]
Pass 2	3,700[2]	42[1]

[1] Lab decided these values were in error (biased low).
[2] Recycled effluent for Pass 2 with TDA, not with tire crumb.

While the high surface area and the absence of wire in the crumb rubber were positive features, the small particle size made it challenging to handle. Therefore, the use of a third end-of-life tire material, uncolored rubber mulch, was explored. This material is wire-free and has a higher surface area to volume ratio than TDA-A. Rubber mulch was soaked for 5 minutes to produce a leachate containing 6PPD-Q.

In an effort to increase the confidence of the results, three replicate samples were sent to the original lab (Lab 1) and to the only other California-based laboratory that performed 6PPD-Q analysis at the time (Lab 2). Since the samples were not from a known certified standard stock solution, evaluating the accuracy of each lab’s reported concentrations is not possible. However, given the lower variability in the reported concentrations, it can be concluded that the results from Lab 1 were more precise than those from Lab 2 (Table 5).

All samples contained small particles of tire rubber, which could continue to leach 6PPD-Q before lab analysis, resulting in potentially an overestimation of the 6PPD-Q concentration at the time of sampling. The degree of overestimation would be a function of the amount of rubber solids and the hold time between sampling and analysis. To investigate this possibility, a portion of the replicate 1 sample was filtered with a 1.0-

micron GF filter. The concentration of 6PPD-Q in the filtered replicate 1 was 23% lower than the unfiltered sample reported by Lab 1 and 32% lower than the unfiltered sample reported by Lab 2 (Table 5). This result indicates that while the majority of the 6PPD-Q in the sample was in the soluble state, explicit sampling and sample hold time protocols need to be adopted prior to developing meaningful regulatory standards for this compound. Additionally, further research is needed to determine additional properties of 6PPD-Q, such as its half-life and the nature of its transformation products.

Table 5. 6PPD-Q from soaking rubber mulch.

Sample replicate	Lab 1 6PPD-Q (ng/l)	Lab 2 6PPD-Q (ng/l)
1	2,700	4,500
1 (filtered)	2,200	3,400
2	2,600	-
3	2,600	3,600

Rubber mulch was also sprinkled with dechlorinated potable water to produce a leachate containing 6PPD-Q. Continuing the effort to increase confidence in the results, samples were sent to Lab 1 and Lab 2. Samples were collected from the runoff of the first sprinkling (Pass 1) and then after the second sprinkling (Pass 2), with a portion of the Pass 1 sample. The expectation was that the concentration of 6PPD-Q for Pass 2 would be higher than for Pass 1, since Pass 1 water was reused as the sprinkling water for Pass 2. The results reported by Lab 1 followed the expected trend, with values of 670 ng/l and 2,700 ng/l for Pass 1 and 2, respectively (Table 6). However, the values reported by Lab 2 were counterintuitive, with 1,200 ng/l reported for Pass 1 and 1,000 ng/l for Pass 2.

Table 6. 6PPD-Q from sprinkling water over rubber mulch.

Sprinkled over rubber mulch	Lab 1 6PPD-Q (ng/l)	Lab 2 6PPD-Q (ng/l)
Pass 1	670	1,200
Pass 2*	2,700	1,000

*Recycled effluent for Pass 2.

The results presented above show that a variety of procedures can produce a leachate with concentrations of 6PPD-Q greater than 2,500 ng/l, the selected target concentration for the source water in the soil media filtration experiments. Rubber mulch was chosen as the preferred material due to its ease of use and the absence of steel wire. For the filtration experiments, a combination of the soaking and sprinkling methods was used. The influent water was prepared by soaking approximately 25 kg of rubber mulch in approximately 35 liters of dechlorinated potable water for 24 hours. Subsequently, 2 to 3 liters of this leachate were sprinkled twice over 1 kg of fresh rubber mulch.

Selecting which lab to use for the analysis of samples from the filtration experiments for 6PPD-Q concentrations was difficult. The results from more than half of the samples sent to Lab 1 were subsequently determined to be erroneous and not usable (Table 2, Table 3, Table 4). However, the precision of the results from Lab 1 appeared to be improving (Table 5). While Lab 2 maintained that their findings were accurate and precise, the precision seemed low in the rubber mulch soaking experiment (Table 5), and the results were counterintuitive in the experiment where the rubber mulch was sprinkled with water (Table 6). Based on the higher precision recent results, it was decided to use Lab 1 for the filtration experiments, with replicate samples sent to provide a check on the precision of the results.

The 6PPD-Q concentration results presented in the tables below are the averages of the two replicate values from unfiltered samples. In two of the filtration experiments, some of the initial results provided by Lab 1 were questioned. After review, the lab determined that the reported concentrations were incorrect due to matrix interference in the LC-MS process. The lab then reprocessed the samples using a modified procedure to (hopefully) produce more accurate results.

With the “recipe” for preparing influent containing a sufficiently high concentration of 6PPD-Q established, testing to determine the capability of passive soil media filtration to remove the contaminant could proceed. The first filtration experiment examined whether the fraction of organic material in the filtration media impacts 6PPD-Q removal. Previous field studies found that the toxic effect of stormwater on coho salmon was reduced after passing through vegetated wetlands (Spromberg et al., 2016), suggesting that soil-based filtration media with a high organic mass fraction may be more effective at removing 6PPD-Q than media with a lower organic mass fraction.

The filtration columns were filled to a depth of 9 inches with three different media: (1) topsoil, (2) a 50/50 mix by volume of topsoil and compost, and (3) compost. The volatile fraction of the media determined by Standard Methods 2540 G (American Public Health Association, 1995), used as a measure of organic mass fraction, ranged from 11% for the topsoil to 57% for the compost (Table 7). The laboratory reported that the influent concentrations of 6PPD-Q should be considered approximate due to adjustments made in the isotope dilution process to mitigate matrix interference, which reduced the standard accuracy of the methodology. The results were very encouraging, with over 99% removal of 6PPD-Q in only a 9-inch depth for all three media (Table 7). The impact of the higher organic mass fraction in the topsoil/compost mix and the compost compared to the topsoil alone was relatively minor, with only a 0.1% difference in 6PPD-Q removal. This experiment suggests that media with only a modest organic mass fraction can achieve a very high degree of 6PPD-Q removal.

Table 7. Effect of organic mass fraction of the filtration media on 6PPD-Q removal.

Media (9 inches deep)	Volatile Fraction (%)	Influent concentration[1] (ng/l)	Effluent concentration[1] (ng/l)	6PPD-Q removal (%)
Topsoil	11	(720)[2] 6,850[3]	36	99.5
Topsoil/Compost	24	(740)[2] 6,300[3]	26	99.6
Compost	57	(695)[2] 6,400[3]	26	99.6

[1] Concentration values are an average of two replicates.
[2] Initial values provided by lab, biased low due to matrix interference in isotope dilution.
[3] Influent values are approximate based on re-analysis of isotope dilution results to remove interference bias.

The second filtration experiment examined the impact that filtration media depth has on 6PPD-Q removal. Increasing the media depth increases the opportunity for 6PPD-Q removal mechanisms to occur. Therefore, it was expected that until a threshold was reached, increasing the filtration media depth would result in an increase in 6PPD-Q removal. The filtration columns were filled with compost to depths of 6, 12, and 18 inches. The compost was from the same commercial manufacturer as used in the first experiment. The influent concentration of 6PPD-Q was slightly lower than in the first experiment. The removal percentage of 6PPD-Q increased from 95% for 6 inches of compost, to 98% for 12 inches of compost, and over 99% for 18 inches of compost (Table 8).

Unexpectedly, the effluent concentration of 6PPD-Q from the 12-inch compost column was 500% higher than from the 9-inch compost column in the first experiment, with values of 115 ng/l vs. 26 ng/l, despite a slightly lower influent 6PPD-Q concentration (5,950 ng/l vs 6,300 ng/l). It is unknown whether this result represents random variations in the filtration performance or is due to the persistent difficulties that the analytical lab had in compensating for interference issues in their analysis.

Table 8. Effect of filtration media depth on 6PPD-Q removal.

Compost media depth (inches)	Influent concentration* (ng/l)	Effluent concentration* (ng/l)	6PPD-Q removal (%)
6	6,150	305	95.0
12	5,950	115	98.1
18	5,650	13	99.8

*Concentration values are an average of two replicates.

Given that the organic content of the media seemed to play only a minor role in the removal characteristics of 6PPD-Q in the filters, the third filtration experiment explored the 6PPD-Q removal characteristics of construction fill materials that would commonly be found below a TDA fill. One filter was filled with 18 inches of rinsed beach sand, and another filter was filled with 18 inches of high-clay road fill material. Previous research had suggested that the sand would have very poor 6PPD-Q removal capabilities due to the lack of organic content and the high hydraulic conductivity of the medium, resulting in a relatively short contact time (McIntyre and Kolodjiez, 2021).

Contrary to expectations, both filters demonstrated 6PPD-Q removal rates exceeding 99%, with effluent concentrations below 30 ng/l (Table 9). Surprisingly, the beach sand filter had an effluent 6PPD-Q concentration of 11 ng/l and a removal rate of 99.8%, outperforming both the road fill and the previously tested compost filters, which also utilized 18 inches of media.

This experiment also explored whether there was lower removal performance during the "first flush" of influent by comparing the concentrations of 6PPD-Q in the first, second, and third 500 ml samples of filter effluent from the influent volume of 2,000 ml in the road fill filter. The effluent concentration of 6PPD-Q decreased for each successive sample, from 27 ng/l in the first 500 ml of effluent, to 21 ng/l in the second, and 14 ng/l in the third (Table 9). The initial filtrate likely traveled shorter pathways through the medium, resulting in less contact time compared to subsequent filtrate. These results support the observation from the second experiment that longer detention times associated with deeper media improve 6PPD-Q removal (Table 8). However, the removal rate for the first flush of effluent was still excellent (99.6%), with a 6PPD-Q effluent concentration of 27 ng/l, which is below the LC_{50} of 41 ng/l for juvenile coho for this constituent.

Table 9. 6PPD-Q removal using construction fill filtration media.

Media (18 inches deep)	Sample	Influent concentration[1] (ng/l)	Effluent concentration[1] (ng/l)	6PPD-Q removal (%)
Beach Sand	-	(1,005[2]) 6,700	(ND[2]) 11	99.8
High-clay road fill	1st 500 ml	(985[2]) 6,050	27	99.6
High-clay road fill	2nd 500 ml	-	21	99.7
High-clay road fill	3rd 500 ml	-	14	99.8

[1] Concentration values are an average of two replicates.
[2] Initial value provided by lab that were changed following new extraction.

The final filtration experiment attempted to confirm the 6PPD-Q removal results for construction fill materials (beach sand and high-clay road fill) observed in the previous experiment. This experiment also explored the potential for additional removal capacity of road fill by further increasing the media depth. Effluent from the high-clay road fill media filter (denoted as Pass 1) was collected and reloaded into the filter, resulting in the final effluent (Pass 2) having been exposed to an effective media depth of 36 inches. To test the sensitivity of the removal rate to the influent 6PPD-Q concentration, the influent concentration was reduced by diluting the original solution with 1 liter of dechlorinated potable water for every 3 liters of influent water prepared using the methods and materials from the previous filtration experiments.

Unfortunately, instead of the expected reduction of approximately 25%, the influent 6PPD-Q concentrations observed in the previous experiments, the lab reported nearly an order of magnitude reduction. Influent 6PPD-Q concentrations, previously in the 5,000 ng/l to 7,000 ng/l range, were expected to decrease to the 4,000 ng/l to 5,000 ng/l range but instead were reported as 790 ng/l to 800 ng/l (Table 10). Interestingly, the initially reported influent values for Filtration Experiments 1 and 3 were similar in magnitude to the lower influent 6PPD-Q concentrations. However, these values were later revised by the lab to nearly an order of magnitude higher following a reanalysis (Table 7 and Table 9). When asked to review the unexpectedly low influent concentrations of 6PPD-Q, the lab reported that the samples exhibited the least matrix interference of any influent samples previously submitted. Barring an unlikely dilution error by their technicians, they expressed confidence that the results were accurate. Left unresolved is the accuracy of the "corrected" influent 6PPD-Q concentrations reported in the previous filtration experiments, given the samples were subject to greater matrix interference.

The 6PPD-Q removal performance for the high-clay road fill media was surprisingly poor, with an 18-inch media depth (Pass 1) effluent concentration of 190 ng/l (76% removal), compared to 27 ng/l (99.6% removal) for the first 500 ml effluent sample in the previous experiment using the same filter configuration (Table 10). After an additional pass through the filter, yielding an effective media depth of 36 inches (Pass 2), the effluent 6PPD-Q concentration was only reduced to 58 ng/l (69% removal).

While the 6PPD-Q removal performance for the high-clay road fill media filter was much worse than expected, the sand filter media removal performance again exceeded expectations. The experiment utilized the same beach sand media filter and an additional filter containing 18 inches of river sand. For both sand media filters, the effluent 6PPD-Q concentration was reported as a non-detect (ND), with a method detection limit of 15 ng/l (Table 10). These results suggest that sand media filters may be at least as effective, if not more effective, than soil for the removal of 6PPD-Q. This finding is surprising, given that sand filtration without chemical addition is generally associated with the physical removal of particulate constituents, whereas the 6PPD-Q in these experiments was primarily in the soluble state, as shown in Table 5.

Table 10. Additional testing of the 6PPD-Q removal characteristics of sand and construction fill filtration media.

Media (18 inches deep)	Influent concentration[1] (ng/l)	Effluent concentration[1] (ng/l)	6PPD-Q removal (%)
High-clay road fill (Pass 1)	800	190	76
High-clay road fill (Pass 2[2])	190	58	69
Beach sand	790	ND	100
River sand	790	ND	100

[1] Concentration values an average of two replicates.
[2] Effective media depth for Pass 2 is 36 inches.

Conclusions and Recommendations

The results of this investigation indicate that passive filtration through compost, soil, compost/soil blend, or sand layer below a TDA fill can serve as an effective treatment technology for removing 6PPD-Q from TDA leachate. Specific conclusions based on the results include:

1. Analytical Challenges: The analytical method used to determine the concentration of 6PPD-Q is highly susceptible to matrix interference, which compromises the accuracy and precision of the results. Given that this problem occurred with relatively clean samples, obtaining reliable results from field samples containing dissolved constituents from an assortment of other sources besides tire rubber may prove challenging.
2. Sensitivity and Sampling Standards: The concentration of 6PPD-Q that is toxic to certain aquatic organisms is close enough to the analytical method detection limit, that well-defined protocols for sample collection, storage, and processing are needed to avoid biasing the results. Current practices seem haphazard, and no specific standards exist that would ensure that samples sent to two different laboratories would result in comparable 6PPD-Q concentrations.
3. Limited Laboratory Availability: Since 6PPD-Q was only recently identified as a contaminant of concern, there are few qualified laboratories available to perform the analysis. This results in long turnaround times (3 to 4 weeks) and high costs ($450 per sample), which hinders research and regulatory gathering of information.
4. Filtration Efficiency: With the exception of one experiment, greater than 95% removal of 6PPD-Q was observed with as little as 9 inches of soil media filtration.
5. Effect of Media Depth: Increasing the filtration media depth increased the 6PPD-Q removal rate, reaching up to 99.8% with 18 inches of media.
6. Media Type and Removal Efficiency: For soil-based filtration media, the removal rate of 6PPD-Q increased slightly with an increase in the organic mass fraction of the media. However, two different types of sand media were as effective in removing 6PPD-Q as any soil-based media tested. This result was unexpected, as previous research had found that sand filtration provided little 6PPD-Q removal (McIntyre and Kolodjiez, 2021).

Given that the results suggest a soil or sand layer can effectively remove 6PPD-Q from TDA leachate, it is recommended that a long-term university-led laboratory and field study be conducted to inform design practices for TDA fills. The study should investigate the following topics:

- The half-life of 6PPD-Q in the surface and subsurface water environments.
- The mechanisms responsible for 6PPD-Q removal in the media filters.
- The removal capacity (“lifetime”) of various soil and sand filtration media.
- Field observations of 6PPD-Q concentrations below existing TDA fills to verify the laboratory findings in this investigation.
- The adaptation of soil and sand media filtration for localized filters to remove 6PPD-Q from roadway stormwater runoff directly adjacent to surface water resources.

Abbreviation and Acronyms

6PPD – N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine

6PPD-Q – 6PPD-Quinone

GF Filter – Glass Fiber Filter

HDPE – High-Density Polyethylene

LC_{50} – Lethal Concentration 50

LC-MS – Liquid Chromatography-Mass Spectrometry

ND – Non-Detect

ng/l – Nanograms per Liter

SPE – Solid Phase Extraction

TDA – Tire Derived Aggregate

TDA-A – Tire Derived Aggregate Type A

Glossary of Terms

6PPD (N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine): A chemical antioxidant widely used in tire rubber to prevent degradation and cracking from ozone and oxygen exposure.

6PPD-Q (6PPD-Quinone): A transformation product of 6PPD resulting from oxidation (e.g., through ozonation). It is highly toxic to aquatic organisms, especially coho salmon.

Aeration: The process of exposing materials or water to air, often to promote oxidation reactions or simulate environmental conditions.

Analytical Method: A laboratory procedure used to detect and quantify chemical compounds in a sample. In this report, it refers to LC-MS and related techniques.

Bioretention: A stormwater management practice using soil and plants to treat runoff by filtering pollutants and promoting infiltration.

Compost: Decomposed organic matter used in filtration media to increase organic content and promote chemical sorption.

Crumb Rubber: Small particles of recycled rubber from end-of-life tires, often used in landscaping, asphalt paving, sports fields, or experimental leachate generation.

Dechlorinated Potable Water: Tap water that has been treated to remove chlorine, typically used in lab experiments to avoid interference with chemical reactions or microbial activity.

Effluent: Outflowing water from a treatment system or filter (e.g., soil column) that is often analyzed for residual contaminant levels, such as 6PPD-Q.

Filtration Column: A vertical container filled with soil or sand media used to test the removal of contaminants from water through gravity percolation.

First Flush: The initial portion of runoff or effluent which often contains higher concentrations of pollutants due to limited contact time with filtration media.

Glass Fiber Filter (GF Filter): A type of filter used to separate solid particles from liquid samples, often before chemical analysis.

HDPE (High-Density Polyethylene): A durable plastic material used in tanks and pipes; in this study, used to construct filtration columns.

Influent: Incoming water to a treatment system or filter (e.g., soil column) that is used as the basis for evaluating removal efficiency.

Isotope Dilution: A technique used in chemical analysis to improve accuracy and compensate for matrix interference, often applied in LC-MS.

LC_{50} (Lethal Concentration 50%): The concentration of a chemical that is lethal to 50% of a test population (e.g., fish) within a specific time frame.

LC-MS (Liquid Chromatography-Mass Spectrometry): An analytical method combining liquid chromatography and mass spectrometry to detect and quantify chemical compounds, such as 6PPD-Q.

Leachate: Water that has percolated through a material (e.g., tire rubber), potentially dissolving and carrying chemical constituents like 6PPD-Q.

Matrix Interference: Contamination or background components in a sample that interfere with accurate analytical measurement of the target analyte.

ng/l (Nanograms per Liter): A unit of concentration commonly used to measure trace levels of contaminants in water.

Non-Detect (ND): An analytical result indicating that the concentration of a compound is below the method detection limit.

Organic Mass Fraction: The proportion of organic material in a filtration media, typically measured to evaluate its capacity for contaminant removal.

Potable Water: Water that is safe for human consumption; used in experiments as a base solution for leachate preparation.

Replicate Samples: Multiple samples collected under identical conditions to assess variability and improve confidence in results.

Rubber Mulch: Recycled tire material, typically shredded, used in landscaping and experimental studies due to its manageable size and lack of embedded wire.

Soil Media: A mixture of soil, compost, or sand used in filtration experiments to remove contaminants from water.

Solid Phase Extraction (SPE): A sample preparation technique used to isolate and concentrate analytes from water prior to chemical analysis.

Stormwater Runoff: Water from precipitation that flows over surfaces and can carry pollutants into waterways.

TDA (Tire Derived Aggregate): Shredded tire material used as a lightweight fill in civil engineering applications such as retaining walls or drainage layers.

TDA-A (Tire Derived Aggregate Type A): A course, shredded tire material (3 to 4 inches in size) often containing steel wire, used in civil engineering for drainage, lightweight fill, and landfill applications.

Transformation Product: A chemical compound formed from the degradation or alteration of a parent compound (e.g., 6PPD to 6PPD-Q).

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