Sustainable Application of TDA in Stormwater Infiltration and Treatment

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16. Abstract (Limit: 250 words)

The objective of this research was to determine the efficacy and cost-effectiveness of the application of tire-derived aggregate (TDA) in stormwater treatment and management systems. We reaffirmed that TDA is an excellent means of retaining phosphate (soluble reactive phosphorus) in stormwater runoff. In addition, we found that biofilms grow on TDA flushed by river water in sufficient quantities to retain zinc and copper to below the U.S. Environmental Protection Agency's chronic toxicity criteria within one to four, 72-h flushes, designed to simulate the flushes of an underground runoff storage facility. A four-week antecedent dry period after the 13th flush did not cause the total loss of the biofilm, indicating that the TDA could also be used in biofilters that have high phosphate release due to degradation of compost. We can therefore conclude the following: 1) TDA is a media that can retain phosphate (SRP) for more than 72 flushes (Singh and Gulliver 2024), or roughly 8 to 9 years in the upper Midwest of the United States. 2) Biofilms growing on the TDA will retain much of the zinc, copper and iron that is released from the TDA, even when applied in surface infiltration practices. 3) The per- and polyfluoroalkyl substances (PFAS) leached from TDA were relatively low in our study and appear to be similar to typical urban concentrations, including residential land. 4) TDA that avoids disposal and can be installed as an underground stormwater storage or infiltration facility can reduce the lifetime costs of the material.

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Sustainable Application of TDA in Stormwater Infiltration and Treatment

Final Report

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Executive Summary

This is a report on research to determine the efficacy and cost-effectiveness of the application of tire-derived aggregate (TDA) in stormwater treatment and management systems. Traditional TDA (Trad-TDA) and wire-exposed TDA (WE-TDA) were used in this study. Traditional TDA is categorized as ASTM 6270 Type-B TDA while wire-exposed TDA is a manufacturing by-product and currently does not have a well-defined market (Yang et al. 2002; Singh et al. 2023). The Trad-TDA used in this experiment was roughly 15-30 cm in size, while the WE-TDA was approximately 5-8 cm in size with exposed wires. Both types of TDA are manufactured from tires discarded from tire stores and shredded into TDA, and for Trad-TDA, used in engineering applications.

The primary section of the report is Section 3, where we reaffirm that Trad-TDA and especially WE-TDA are excellent means of retaining phosphate (soluble reactive phosphorus) in stormwater runoff. This observation was tempered by the observation that the TDA would also leach zinc and copper in an abiotic water environment to above the U.S. Environmental Protection Agency's (U.S. EPA's) chronic toxicity criteria for the freshwater biota (Singh et al. 2023). Singh and Gulliver (2024), however, found that a biofilm grown on TDA in water for a month before experimental initiation would capture and retain much of the zinc and copper leached from the TDA, with the resulting water concentrations all below the U.S. EPA's chronic toxicity criteria. This report documents the continuation of Singh and Gulliver's findings toward the determination of zinc and copper and other metal concentrations leached by Trad-TDA and WE-TDA under more realistic conditions, where there is no pre-growth of the biofilm on the TDA.

The results are that biofilms grow on TDA flushed by river water in sufficient quantities to retain zinc and copper to below the U.S. EPA chronic toxicity criteria within one to four, 72-h flushes, designed to simulate the flushes of an underground runoff storage facility. Iron leaching was more variable, requiring between zero and seven flushes to have a flushed effluent below the U.S. EPA chronic toxicity criteria. In an oxic water body (DO > 1 mg/L), however, most of this iron would be Fe^{+3}, which is generally insoluble and would be present as precipitates in the water. It was also noted that no single effluent sample violated acute toxicity standards (U.S. EPA 2007) for zinc, copper or iron. There was minimal change in phosphate retention by the TDA with the biofilm present. A four-week antecedent dry period after the 13th flush did not cause the total loss of the biofilm, indicating that the TDA could also be used in biofilters (bioretention systems or rain gardens with an active underdrain) that have high phosphate release due to degradation of compost.

We can therefore conclude the following:

1. TDA is a media that can retain phosphate (SRP) for more than 72 flushes (Singh and Gulliver 2024), or roughly 8 to 9 years in the upper Midwest of the United States.
2. The WE-TDA retained phosphate somewhat better than the Trad-TDA, but not markedly. The Trad-TDA used in this study also had some exposed wires that could have increased retention of phosphate. A higher adsorption from WE-TDA indicates an opportunity for reutilization of a manufacturing byproduct, produced while generating Trad-TDA.

3. Biofilms growing on the TDA will retain much of the zinc, copper and iron that is released from the TDA. Zinc and iron were found to be below the U.S. EPA's chronic toxicity criteria after one and between one and seven flushes, respectively. Copper was not released from the TDA above the chronic toxicity criteria. No single effluent sample violated acute toxicity standards (U.S. EPA 2007) for zinc, copper or iron.
4. While there was a measurable release of per- and polyfluoroalkyl substances (PFAS) from TDA, the concentrations were relatively low and appeared to be similar to typical urban concentrations, including residential land. The information supports the notion that TDA, with its low PFAS release and low adsorption capacity, could be considered for various applications, including stormwater treatment, without significant PFAS-release concerns.
5. Sorption of zinc and copper to biochar's surfaces has generally resulted in greater than an order of magnitude reduction in leachate, regardless of the biochar used. Therefore, biochar would be an appropriate choice as a mix with TDA to reduce the leaching of zinc and copper. One drawback, however, was the cost of biochar, which may be prohibitive for a large water storage system.
6. Wood chunks were identified as an alternative source to mix in with TDA that would not fluidize. Zinc and Copper can be removed with the help of cedar wood chunks, but one must consider the possibility of phosphorus and metal release from wood chunks. In the end, the biofilm was an appropriate leaching remediation, so that no mixture of supplementary material with TDA was deemed necessary.
7. TDA exposed to the atmosphere (Lid-off) grew biofilm at roughly half the rate of TDA that was kept in high humidity (Lid-on) of 97% ± 3.7%. The Lid-off biofilm, however, was still capable of retaining leached zinc, copper and iron, for the most part, even after a 4-week dry period. This indicates that a metal-retaining biofilm will grow on the TDA even when exposed to the atmosphere, such as in bioretention facilities and other surface infiltration practices.
8. TDA is a porous material with a ~50% porosity after compaction that is presumed to result in the following properties:
    a. Greater water storage per unit volume than achieved with gravel or sand
    b. Less resistance to flow through a TDA system (This assumption needs to be verified with experiments.)
9. TDA that avoids disposal and can be installed as an underground facility can reduce the lifetime costs of the material. A ton of whole end-of-life tires, taken to a confined licensed disposal facility in the Twin Cities Metropolitan Area would cost approximately $240/ton for disposal. The same tires, manufactured and sold as TDA for stormwater treatment in an underground facility, would currently generate approximately $33/ton for TDA and freight from the manufacturer as value added. Thus, the value added for the application of 1 ton of TDA would be $273.
10. Currently, the only means of removing phosphate from stormwater runoff in Minnesota is the Iron Enhanced Sand Filter (Erickson et al. 2012), which is designed for surface filtration and has requirements of the site that cannot always be met. A sand filter needs to be designed and installed, which is not always practical and can be expensive. The underground TDA application is another means of removing phosphate from runoff, developed for a different application,

underground practices that can fit under parking lots and other locations where surface treatment of stormwater is not practical or cost-effective.

Chapter 1: Introduction

In the United States, there is approximately one discarded tire per person per year, and these tires often end up in landfills. Tire-derived aggregates (TDA), a waste product from automobile tires, are used in many engineering applications. In underground stormwater storage systems, tire-derived aggregate (TDA) can be a substitute for stone aggregate. The application of TDA in underground stormwater infiltration and storage/filtration systems is thus a strategy to divert discarded tires and recycle them for beneficial uses in urban settings. However, there are questions about TDA's suitability for use as a stormwater infiltration/filtration media. A previous investigation on the applicability of two-inch TDA for stormwater treatment showed good phosphate retention but with substantial leaching of zinc and some copper (Singh et al. 2023). In a subsequent research study, Singh and Gulliver (2024) determined that biofilms growing naturally on the TDA can prevent metal leaching from a TDA-based stormwater treatment system and estimated the life span of a TDA-based stormwater treatment system. The biofilms, however, were pre-grown for one month before application of leaching tests and were not exposed to long periods of no flushing. This project is a continuation of Singh and Gulliver (2024) to test the phosphate adsorption and leaching of metals when TDA is placed in an underground chamber under more realistic conditions, i.e., without pre-growth of biofilm and with extended dry periods in which biofilm survival may be challenging.

The overall objective of this research was to develop a system of TDA-based media that will utilize the phosphate retaining characteristics of TDA while reducing zinc and copper release. Three major tests were performed in the laboratory to understand the role of biofilms when TDA is subjected to underground stormwater chambers and to determine if TDA is safe to use in stormwater infiltration and underground storage practices, as follows:

1. TDA material without pre-grown biofilm was exposed to river water with intermittent dry periods to investigate the role of biofilms in minimizing metal leaching from the TDA.
2. Batch tests were performed to evaluate the potential leaching or removal of per- and polyfluoroalkyl substances (PFAS) by TDA.
3. An alternative material to mix in with TDA for reducing metal leaching from TDA was tested.

The stated objectives and tasks were designed to deliver a treatment system that is affordable and sustainable while simultaneously addressing the pollution caused by waste tires and stormwater runoff from urban areas.

Chapter 2: Review of literature and available data

2.1 Treatment of stormwater runoff

Stormwater runoff from the environment remains a water pollution control challenge. As stormwater runs over roads, rooftops, and compacted land it picks up chemicals which are a principal contributor to water quality impairment of water bodies in the United States and many locations worldwide (Xu et al. 2020). These chemical compounds include antifreeze, grease, oil, and heavy metals from cars; fertilizers, pesticides, and other chemicals from gardens, homes, and businesses; bacteria from animal wastes and failing septic systems; and sediment from poor construction sites practices (Xiong et al. 2019). The sources of stormwater pollutants trace back to many anthropogenic activities. Nutrients present in urban stormwater runoff (Houtz and Sedlak 2012) contribute to harmful algal blooms and eutrophication (Paerl et al. 2016). For example, the presence of phosphorus in stormwater runoff is the second largest cause of water impairment, affecting over 7,000 water bodies in the United States (EPA 2016). Additionally, the presence of metals and organic and biological contaminants in urban stormwater runoff can pollute receiving waters and pose risks to aquatic and human health (Houtz and Sedlak 2012). Uncontrolled stormwater runoff also impacts humans and the environment in other ways, such as flooding, threatening public health and increasing water and wastewater treatment costs. As a result, stormwater management focuses on addressing the total runoff volume and peak rate and improving the stormwater quality, as untreated stormwater runoff may eventually lead to contamination of the environment, including surface waters, groundwater, and soil (Kayhanian et al. 2019). To mitigate the impacts, a stormwater management strategy is needed.

Management of stormwater runoff has been practiced over many centuries. It dates to the Mesopotamian civilization, to our knowledge, who also focused on flood management. However, elimination of waste from runoff was rarely practiced (National Research Council 2009). With the increase in population and advent of many emerging pollutants, treatment of pollutants in stormwater runoff also became imperative. For the treatment of stormwater pollution, physical removal practices such as infiltration, sedimentation, filtration have conventionally been utilized (Gulliver et al. 2011). Biological methods and application of chemicals have also been utilized to limit the pollution caused by stormwater runoff to nearby water bodies. However, these practices either required substantial investment or were complicated in operation. Thus, further efforts are needed to find sustainable alternatives for stormwater treatment.

2.2 Tire-derived aggregate as a replacement for gravel

Annually, over 270 million automobile and truck tires are removed from service and scrapped in the United States (Takallou and Takallou 1991). Scrap tires have been beneficially utilized as: 1) an alternative fuel source for electricity generation; 2) a fuel source for cement kiln operations; 3) a raw material to produce industrial and consumer goods; and 4) a raw material for civil engineering construction (Rubber Manufacturers Association 2009). Scrap tires that are not beneficially used are often disposed of in various legal or illegal manners. One typical disposal practice is to place scrap tires in large mono-fill stockpiles. These stockpiles create potentially undesirable and hazardous conditions, such as increased mosquito breeding, rodent activity, and combustion. To avoid these conditions, an effective solution is reducing the quantity of stockpiled scrap tires through recycling and alternative-use programs. In 1990, only 11 % of annually generated scrap tires were consumed in beneficial end-use markets, with the remainder stockpiled. As of 2017, the U.S. Tire Manufacturers Association reported that beneficial end-use markets consumed 81.4 % of scrap tires generated in the United States. Tire shreds or tire-derived aggregate (TDA) are increasingly used instead of raw materials (e.g., sand and gravel) for road and landfill construction (Shao and Zarling 1995), septic tank leach fields (Osuji and Uwakwe 2006), alternative daily cover for landfills, and many other construction applications (Wright et al. 2013). The benefits include vibration and sound control (Wolfe et al. 2004; Humphrey and Wolfe 2009) as well as lightweight fill to prevent erosion and landslides (Cheng 2016). Tires also facilitate drainage in septic, leachate, and landfill gas systems. The engineering market consumed over 19 million scrap tires in 2017, about 7.9 percent of the generated total. The American Society for Testing and Materials (ASTM) provides a comprehensive list of terms and definitions for scrap tires used in civil engineering applications (ASTM 2008).

Sand is often used as a stormwater treatment media that has a high infiltration capacity. Gravel is often used as a stormwater storage or infiltration media with high porosity. If it is safe to use, the application of TDA to treat stormwater quality has the potential to help achieve the stormwater management goals while turning discarded tire waste into a valuable product source that can be used in urban settings where there is no land available. In addition, the application of TDA for stormwater has a high potential as it offers the advantages of a lightweight, free draining, aggregate alternative with an improved capillary break, increased shear strength, and reduced lateral loading, vibration mitigation, and thermal infiltration.

2.3 Leaching of chemicals from TDA under different conditions

This section will review measurements of leaching from TDA in three types of studies: field studies above the groundwater table, which are probably most applicable to underground infiltration and underground storage; field studies below the groundwater table, which are more applicable to standing water in the TDA; and laboratory studies of leaching, which can be used to estimate leaching during inundation periods of underground infiltration and underground storage applications of stormwater.

2.3.1 Field studies above the groundwater table

Although field measurements above the groundwater table are very similar to infiltration basin and underground storage applications, residence time could be significantly longer than the 48 to 72 hours of these applications, resulting in a higher leached concentration. The iron and manganese concentrations in the TDA were greater than the control with a significance of 90% (Exponent 2003; Humphrey and Katz 2001). For cadmium, aluminum, copper, and lead, the percentage of samples below the test method limit of detection (LOD) for the TDA sections was greater than or equal to that of the control sections. These results suggest that TDA does not release a substantial amount of these metals into the environment when the TDA is placed above the groundwater level (Exponent 2003; Humphrey and Katz 2001). However, when samples were collected from the adjacent wells, high iron and cadmium were found to be above the U.S. EPA limits (Dickson et al. 2001). The concentration of organic compounds was also lower than the level of detection, except for Cis-1,2-dichloroethlene in one instance (Exponent 2003; Humphrey and Katz 2001). In other studies, total organic carbon (TOC) and total organic halides (TOX) were not seen to be increased in the presence of TDA (Hoppe and Mullen 2004).

Maeda and Finny (2018) also suggested that TDA-soil system provides removal of many constituents from urban stormwater runoff, including cadmium, iron, lead, manganese, phosphate, and zinc. However, quantification of influent pollutant concentration and the adsorption capacity of the soil and its characterization was not performed. Thus, the results were inconclusive on the role of TDA in the TDA based stormwater treatment system.

2.3.2 Field studies below the groundwater table

After analysis of filtered samples collected below the groundwater table, high iron and zinc concentrations were observed (Exponent 2003). On the other hand, metals such as arsenic, cadmium, copper, and lead were seen to be below the level of detection (Humphrey and Katz, 2001). The concentrations of metals, other than iron and zinc, were lower in the unfiltered samples collected below the groundwater table beneath a TDA bed. This is most likely due to the iron oxide precipitate that was visible in water directly contacting the TDA. However, there is a general trend of decreasing iron and zinc concentration with time. For organic compounds, cis-1,2-dichloroethene was found in samples from the TDA trenches on most sampling dates, although concentrations, except for one sample which had a concentration of 85.5 µg/L, were below the U.S. EPA Drinking Water Standard (Humphrey and Katz 2001). Phenol was also found below the level of detection when samples were collected below groundwater in the TDA trenches.

2.3.3 Laboratory studies

The metals of concern in the lab test were barium, cadmium, chromium, copper, iron, mercury, lead, selenium, and zinc (Ealding 1992). None of the metal leachates exceeded the U.S. EPA water quality criteria at a pH between 7.59 and 8. In another study by Edil et al. (1992), the leaching of iron and zinc, which are present in tire material or wire rasp, was higher than the control. A study by the Minnesota Pollution Control Agency (MPCA) concluded that higher leaching of metals from TDA occurred when subjected to lower pH conditions (Twin City Testing Corporation 2009). The Twin City Testing Corporation (2009) further found that the U.S. EPA Drinking Water Standards were generally exceeded for carcinogenic PAHs and noncarcinogenic PAHs under all conditions for both tire composite samples and asphalt samples.

2.3.4 Chloride

The removal of chloride from winter and spring snow melt runoff is a concern in Minnesota. There was no mention of chloride in the studies mentioned above. To the authors knowledge, the only way to remove the tremendous chloride concentration that comes from road runoff is source reduction and reverse osmosis. Reverse osmosis would not be cost effective for the quantity of water that needs to be treated. We believe that TDA will not have any impact on chloride concentration.

2.4 Insights from a funded MnDRIVE project

The project team has utilized TDA in stormwater in prior laboratory experiments, which was funded as a research grant from MnDRIVE. Results of this study were published in Singh and Gulliver (2023). Two-inch TDA obtained from the tire waste management industry (First State Tire Recycling Co.) was applied to batch studies containing synthetic stormwater with a total phosphorus concentration of 0.2 mg/L. In the batch study, multiple flushes were performed, and samples were collected at multiple times for analysis. The concentration of different metals at each time were utilized to determine the sorption potential of TDA and the leaching possibility while treating stormwater. The results revealed that the release of aluminum, nickel, cadmium, chromium, lead, calcium, boron, sodium, magnesium, and potassium was either negligible or remained equal to the respective metal concentration within the initial/influent stormwater. The release of these metals was well within the U.S. EPA's freshwater criteria for chronic exposure. However, the release of copper, zinc and iron from the reactors with TDA was higher than the aquatic criteria for freshwater. The copper, zinc, and iron concentrations from the reactors with TDA were even found to have a maximum average of 0.12, 2.64, and 47.4 mg/L, respectively, while the aquatic criteria for chronic exposure to copper, zinc, and iron are reported to be 0.013, 0.12, and 1.0 mg/L, respectively. One means of rectifying these metal concentrations would be to blend material with a high metal adsorption capacity in or around the TDA.

On the other hand, the analysis of manganese and phosphorus from different reactors revealed that the reactors with TDA had a reduced concentration compared with the control reactors, meaning that the TDA was adsorbing phosphate and manganese. The results of the study suggest that TDA has a great potential for phosphate retention but leaches a considerable amount of zinc and copper. The leachability of zinc is a concern as its concentration was above the water quality criteria for freshwater habitats. Similarly, the leachability of copper can harm aquatic environments and the health of consumers. Consequently, to apply TDA in stormwater management, we are required to check the leachability of copper and zinc while phosphate retention by TDA is not compromised. In addition, the fate of contaminants of emerging concern in the application of TDA in stormwater management is needed.

2.5 Role of biofilms in metal removal

Compared to physical and chemical remediation methodologies, bioremediation/microbial remediation is considered to be a more eco-friendly solution due to its cost-effectiveness, environmental sustainability, and limited impact on the functioning of a system (Ahmad et al. 2014). Biofilms, in any aquatic treatment system, are observed to facilitate the remediation of metal (potentially toxic elements) pollution in most aquatic systems (Rene et al. 2016). The dominant mechanism of metal removal is reported to be the biosorption of metals (Bradney et al. 2019). It is also observed that some bacteria in aquatic environments can interact with certain elements and/or change their physiological properties. Thus, bacteria present in the biofilm matrix can enhance metal sorption by increasing the surface area of the media, which can potentially minimize metal concentration from polluted waters (Antoniadis et al. 2017; Palansooriya et al. 2019). Even the cell walls of bacteria can sorb metals via phosphoryl ligands, carboxyl groups, and other binding methodologies (Beveridge and Murray 1980).

Metals are reported to be first diffused to the surface of the organism, then react with sites on their surface (adsorption/desorption), where some micronutrient metals can be transported to the biofilm matrix biologically. The other reason for metal accumulation in biofilms are biosorption, bioprecipitation, intracellular accumulation, and redox immobilization (Edwards and Kjellerup 2013). However, more research is needed to investigate the role of biofilm in removing metals being leached out from TDA after application to stormwater.

Chapter 3: Contribution of biofilms present on TDA and blend material in stormwater treatment

3.1 Material and methods

3.1.1 Tire-derived aggregates

Traditional TDA (Trad-TDA) and wire-exposed TDA (WE-TDA) were used in this experiment. Traditional TDA is categorized as ASTM 6270 Type-B TDA while wire-exposed TDA is a manufacturing by-product and currently does not have a well-defined market (Yang et al. 2002; Singh et al. 2023). The Trad-TDA utilized in this experiment was roughly 15-30 cm in size, while WE-TDA was approximately 5-8 cm in size with exposed wires (Figure 1). Both types of TDA were obtained from First State Tire Recycling Company (Isanti, MN, USA), who collect tires discarded from stores and shred them into TDA for engineering applications.

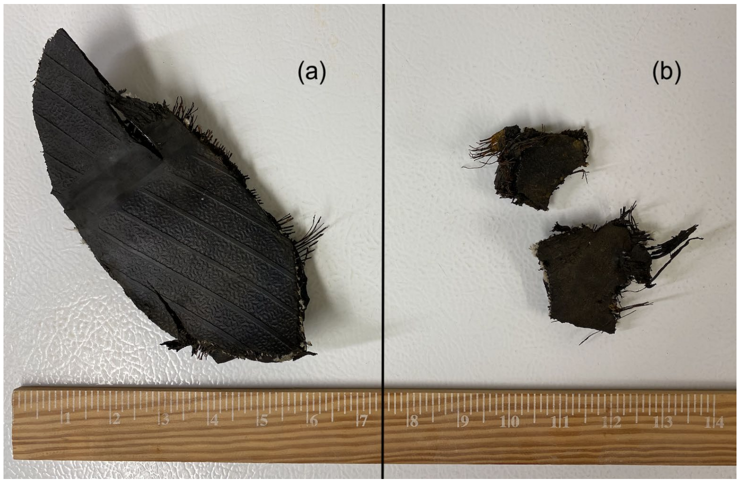

Figure 1. Tire-derived aggregates used in this study a) Traditional TDA (Trad-TDA) and b) Wire-exposed TDA (WE-TDA).

3.1.2 Material preparation

The batch reactor containers used in this study were 1-gallon high-density polyethylene buckets that were purchased from Uline (WI, USA). First, the buckets and lids were acid-washed by soaking in a 5% nitric acid bath and triple-rinsed with Milli-Q water and then allowed to air-dry completely. Approximately 11 kg of each type of TDA material was rinsed with Milli-Q water to remove dirt and debris on the tire surfaces, wiped with a paper towel to remove excess water, and air-dried for use in the batch experiments.

3.1.3 Influent preparation

The river water used in this experiment was collected from the Mississippi River upstream of Saint Anthony Falls in Minneapolis, Minnesota, USA (44°58'58.2"N 93°15'18.7"W). There are limited industrial facilities upstream of the collection points, thus the presence of heavy metals in the river water was minimal. The primary source of phosphorus to the river upstream is agricultural and urban runoff. The collection of river water was done from August to December 2023, approximately three hours before each flush was performed. The river water collected during this period had mean concentrations of 2.3 ± 1.4 mg/L for total suspended solids (TSS; 15 samples), 59 ± 48 µg/L for total phosphorus (TP), 39 ± 22 µg/L for total dissolved phosphorus (TDP), 28 ± 16 µg/L for soluble reactive phosphorus (SRP), 8.5 ± 0.17 for pH, and 15 ± 6.9 °C for water temperature; all analytes were tested (APHA 1998) on duplicate or triplicate samples collected throughout the experimental period.

After collection, the river water was filtered through 1.5 µm glass fiber filters to minimize the suspended solids and associated particulate fractions of the metals to be analyzed. The filtered river water was used as the influent water for the batch studies. However, it must be noted that unfiltered river water was used for the first flush of the study. Data from the 1st flush are included in the results because the dissolved metals and dissolved phosphorus concentrations were still similar in the unfiltered and filtered water (see Results section).

3.1.4 Experiment protocol

3.1.4.1 Batch studies

A total of 26 batch reactors were set up at room temperature (22 ± 2.1 °C) at the Saint Anthony Falls Laboratory (SAFL; Figure 2). Each TDA type was set up in buckets with lids kept either closed (Lid-on) or open (Lid-off) to simulate different humidity conditions in an underground chamber. Five replicates were used for each group – Trad-TDA Lid-on, Trad-TDA Lid-off, WE-TDA Lid-on, and WE-TDA Lid-off (20 buckets total). Two sets of three control buckets (no TDA) were also set up with Lid-on or Lid-off (six buckets total). In each bucket with TDA, 600 g of the prescribed type of TDA was placed and filled with 2.25 L filtered river water using a calibrated bucket. The TDA to water mass ratio of 1:3.75 was adopted following the previous experiments done with TDA at SAFL (Singh et al. 2023; Singh et al. 2024). The same ratio was maintained throughout the experiments.

Figure 2. Experimental setup of batch buckets with TDA kept at room temperature at SAFL. Top shelf: batch buckets with Lid-on treatment, bottom shelf: batch buckets with Lid-off treatment.

3.1.4.2 Flush protocol

A flush cycle started with collecting, filtering, and adding 2.25 L of prepared river water to each reactor (Figure 3). This was done between 9 a.m. and 12 p.m. on Monday of each cycle. After 72 h of contact time between the water and TDA (Thursday afternoon), the water in the buckets was drained (as much as possible) and the buckets were kept without water for 96 h. After the 96-h dry period, water was filled into the buckets, kept for 72 h, and flushed again. This 3-day wet period and 4-day dry period is considered a flush cycle and was repeated for a total of 13 flushes. After that, the buckets were kept dry for 24 days to simulate drought conditions and investigate the effects of drought on biofilm viability. Four more flushes were then performed. Thus, a total of 17 flushes were performed in the batch reactors from August 19, 2023, to January 3, 2024.

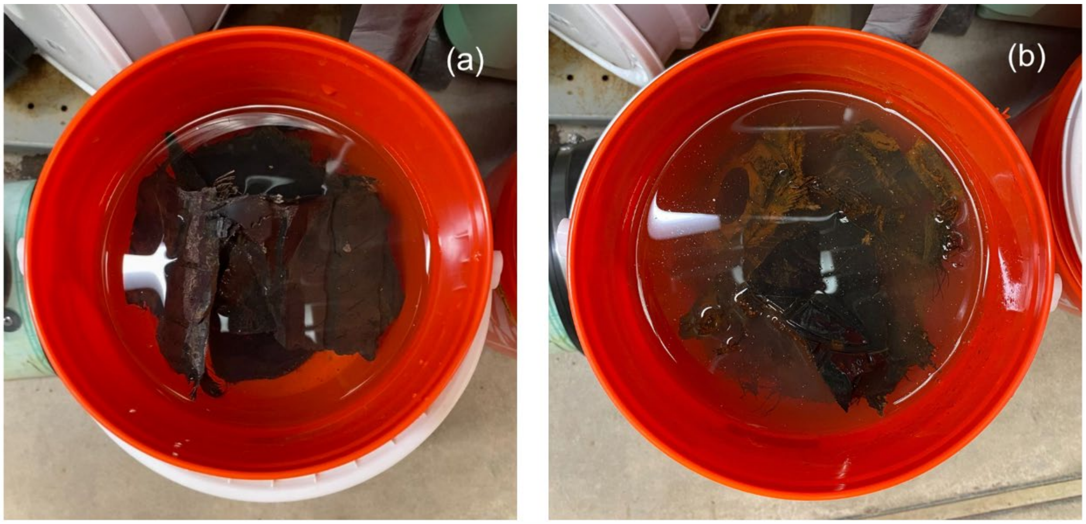

Figure 3. Reactors used in this study with influent (filtered river water) and TDA; (a) Trad-TDA = Traditional TDA and (b) WE-TDA = wire-exposed TDA. Photos were taken at the end of the 6th flush.

3.1.5 Sampling protocol and analysis

3.1.5.1 Water samples

Samples of the influent river water were taken at the beginning of each flush to characterize the water for pH, phosphorus and metal concentrations. Three unfiltered river water samples, five 1.5 µm-filtered river water samples, and five 0.45 µm-filtered samples (12 mL each) were collected for phosphorus analysis (TP, TDP, SRP; APHA 1998) at SAFL. An additional set of three 0.45 µm-filtered influent river water samples were saved for metals analysis only on the weeks with effluent sampling. Sampling of the effluent (12 mL) was performed at the end of 72 h for flushes numbered 1, 2, 3, 5, 9, 13, 14, 15, and 17.

The influent and effluent samples collected for metal analysis were preserved with 2% nitric acid (trace metal grade) and sent to the Research Analytical Laboratory at the University of Minnesota. The total dissolved metal concentrations of fifteen different metals were determined by the Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) method: phosphorus (P), iron (Fe), zinc (Zn), copper (Cu), magnesium (Mg), lead (pb), sodium (Na), potassium (K), nickel (Ni), chromium (Cr), calcium (Ca), boron (B), aluminum (Al), manganese (Mn) and cadmium (Cd). The limit of detection (LOD) for each metal is presented in Table 1. Samples were typically analyzed within three weeks after collection. Randomly selected samples were analyzed in duplicate for quality assurance, and blanks were sent with each set of samples.

Table 1. Laboratory limits of detection for the 15 metals analyzed by the ICP-OES method.

Metal	Detection limit (mg/L)
Aluminium (Al)	<0.011
Boron (B)	<0.003
Calcium (Ca)	<0.038
Cadmium (Cd)	<0.002
Chromium (Cr)	<0.001
Copper (Cu)	<0.001
Iron (Fe)	<0.001
Potassium (K)	<0.024
Manganese (Mg)	<0.003
Magnesium (Mn)	<0.001
Sodium (Na)	<0.024
Nickel (Ni)	<0.001
Phosphorus (P)	<0.004
Lead (Pb)	<0.003
Zinc (Zn)	<0.001

The concentrations of different metals were then analyzed to determine the leaching or adsorption of metals in a given TDA-based treatment system. The concentrations observed were later converted to flux in terms of mg metal per kg of TDA, considering the TDA:water mass ratio of 1:3.75. The flux of metals was compared with the U.S. Environmental Protection Agency's (U.S. EPA's) chronic toxicity levels for the freshwater biota (U.S. EPA, 2007) if a typical 50% porosity of compressed TDA is assumed. The equation for this conversion is as follows:

$$\frac{M_C}{M_{TDA}} = \frac{C}{\rho_{TDA}\,(1-\eta_{TDA})} \qquad (1)$$

where,

M_C = Mass of chemical leached from the TDA

M_{TDA} = Mass of TDA

C = Concentration of chemical (U.S. EPA chronic toxicity criteria for freshwater biota)

ρ_{TDA} = Density of TDA ≅ 1.22 kg/L (Park, et al. 2023), and

η_{TDA} = Porosity of TDA ≅ 0.5 (Singh and Gulliver 2024)

3.1.5.2 Other parameters

The relative humidity and temperature in the batch reactors were monitored daily using sensors installed on the lids of the buckets along with monitoring of ambient conditions using a reference sensor placed adjacent to the experimental setup. The pH and temperature of the water in the batch reactors were taken to characterize changes in the water after the 72-h contact period with TDA. At the end of flush 10, the water in the batch buckets was found to have low dissolved oxygen DO (< 2 mg/L). Therefore, from flush 11 to 13, the DO concentration in the water in each of the batch buckets was measured daily until the flushing was performed (i.e., at 0, 24, 48 and 72 h) to monitor the oxygen deficit due to biofilm growth.

3.1.5.3 Biofilm samples

Biofilm analysis was done according to Shin et al. (1999) after flushes 7, 13, 14, and 17. Flushes 7 and 13 were during the first series of weekly flushes. Flush 14 was preceded by the 24-day dry period to simulate the effects of drought on biofilm growth. Biofilm sampling was again performed at the end of flush 17. To collect the biofilm samples from the rubber surface, TDA with biofilm was scraped from an area with typical biofilm growth using toothbrushes and the scraped area was recorded. For the first sampling (after flush 7), biofilm was scraped from a 7.92 or 23.6 cm^2 area on the TDA's rubber surface and the dry mass of biofilm collected was very small as biofilm was still developing. Therefore, in the subsequent sampling events (flushes 13, 14 and 17), biomass was sampled at multiple locations on the TDA (up to four times using the 23.6 cm^2 sampler) to collect a larger mass of biofilm to analyze. The scrapings were washed using Milli-Q water and collected in aluminum tins. The tins with scraped biofilm and water were subjected to oven drying at 105 °C and the weight of the dried residue was recorded. The dried residue was then transferred to crucibles and dried for 4 h in a muffle furnace at 550 °C. The weight difference between 105 °C and 550 °C was recorded as the weight of volatile solids. The volatile solids present (mg) over a unit surface area scraped (cm^2) for biofilm analysis were used to quantify the biofilm growth over a unit surface area of TDA (mg/cm^2). After the 17th flush, the batch reactors were kept dry for two months and biofilm samples were collected to determine the effect of extended dry period on the biofilm.

Biofilm samples were also collected from the exposed wires in the TDA at the end of the batch experiments, i.e., after the two-month dry period post flush 17. The exposed wires in the TDA material consisted of thicker bead wires and thinner belt wire clusters that either protruded from the rubber or connected the rubber segments. The bead wire is typically thicker gauge steel wire that sits near the rim of the wheel, while the belt wire is thinner gauge steel wire that is layered into the rubber of the tire. An account of the lengths of the exposed wire types was performed in two or three out of the five replicate reactors in each treatment containing Trad-TDA and WE-TDA. It must be noted the process of wire accounting was challenging because of the variety of wires in the TDA, some of which were difficult to access for length measurement. Biofilm mass (i.e., volatile solids mass, mg) on known lengths of the exposed wires were determined using the same protocol followed for the rubber as described above. Surface area of the bead and belt wires were calculated using respective average diameters of non-oxidized wires in unused TDA material and the wire lengths sampled for biofilm; the sampled wire surface areas were 1.8 to 9.8 cm^2 for the thinner belt wires and 3.6 to 14 cm^2 for the thicker bead wires. The mass of exposed wires (g) was calculated by dividing the volume of the measured lengths of wires by the wire density (7.81 g/cm^3 for bead wire and 7.85 g/cm^3 for belt wire).

3.2 Results

3.2.1 Environmental conditions

3.2.1.1 Water pH

The influent pH (8.6 ± 0.13; n = 60) did not change significantly after contact with the TDA material in the batch reactors. The mean effluent pH after the 72-h contact period was 7.9 (± 0.19) in Trad-TDA Lid-on, 8.2 (± 0.15) in WE-TDA Lid-on, 8.1 (± 0.18) in Trad-TDA Lid-off, 8.3 (± 0.18) in WE-TDA Lid-off, 8.6 (± 0.15) in Control Lid-on, and 8.8 (± 0.12) in Control Lid-off reactors. This suggests that the TDA material will not alter pH of the runoff flowing and detained in an underground storage chamber.

3.2.1.2 Humidity

The relative humidity was tracked in all batch reactors that were kept closed (i.e., Trad-TDA Lid-on , WE-TDA Lid-on, control Lid-on) to see if moisture levels varied between the wet and dry periods. The relative humidity inside the reactors was 99% when the TDA was kept with influent water. After the reactors were drained, relative humidity continued to be high (97 ± 3.7 %) at the end of the 4-day intermittent dry period from flush #1 to #13. After the 13th flush, all reactors were kept dry for 24 days to simulate drought conditions during which the relative humidity levels maintained at 98% in the Lid-on reactors with TDA. Such high relative humidity levels are conducive for biofilm survival (Else et al. 2003) suggesting biofilm may continue to thrive if similar conditions exist in an underground chamber. The impact on biofilm growth during the dry period is discussed in Section 3.2. From the 13th to 17th flush, the relative humidity after the 4-day dry period was on average 80% (± 3.8%) in the reactors with TDA and 73% (± 4.8%) in the control reactors. It is not clear why the humidity readings were lower in the control reactors. The ambient relative humidity level was 38% (± 13%) and the air temperature was 22 (± 2.1) °C on average during the entire experimental duration.

3.2.1.3 Dissolved oxygen

The dissolved oxygen (DO) concentration in the batch reactors was tracked from flush 10 to flush 17 primarily to monitor for changes due to the presence of biofilm on the TDA material. Unlike the control reactors, the initial DO level in the water decreased over the 72-h contact period in all batch reactors with TDA; however, there were small differences in the extent to which the DO dropped across different treatments (Figure 4). After a sharp decline in 24 h, the DO in the reactors with Trad-TDA dropped to 2 mg/L while that in WE-TDA reached almost 1 mg/L when the reactors were kept with the lid closed (Lid-on). The DO drop was less in the reactors with lids open (Lid-off) likely due to exchange with surrounding air; final DO levels were 4 to 3 mg/L in Trad-TDA reactors and 3 to 2 mg/L in the WE-TDA reactors. The decrease in DO not only suggests consumption of oxygen by the biofilm growth but also by the oxidation of iron in the tire wires, especially in the WE-TDA that may form oxidized iron (rust) in the exposed wires (Stumm and Morgan 1995).

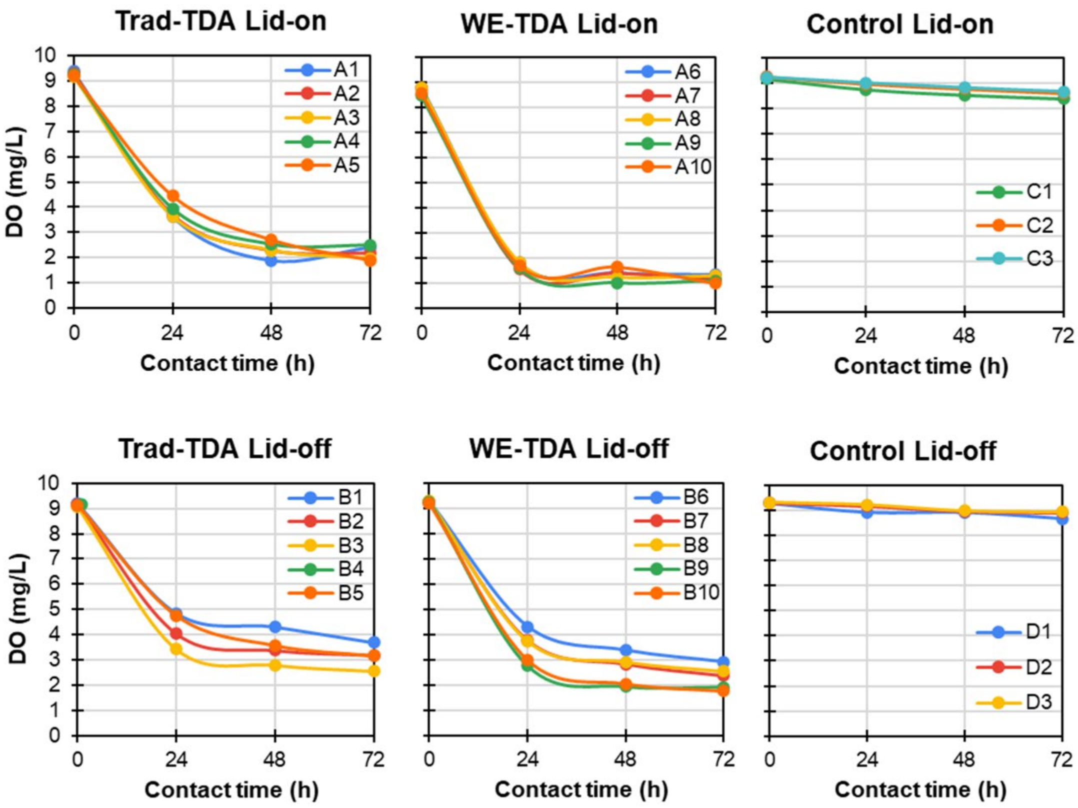

Figure 4. Dissolved oxygen concentrations in the batch reactors with TDA (Trad-TDA and WE-TDA) and the control reactors (no TDA). Data shown for the 12th flush.

3.2.2 Biofilm growth

Biofilm gradually established on the TDA material over the first 13 flushes (Figure 5), indicating the presence of nutrients in river water that support biofilm growth. One to four locations in each batch reactor on the TDA were identified to take a 3.2 or 5.5-cm diameter sample of the biofilm mass accumulation, which was different based on the treatment (Figure 6). First, the length of the standard deviation values in Figure 6 indicates that biofilm formation on Trad-TDA was lower and more variable than that on WE-TDA, which could be related to the lower surface area and surface roughness of Trad-TDA for a given weight (Singh and Gulliver 2024). Second, the Lid-off TDA had, with one exception, lower biofilm mass than the equivalent Lid-on TDA. This is likely because the biofilm growth continued in the 96-h dry period between flushes in the lid-on reactors, due to the high relative humidity. After the 13th flush, the Lid-on and Lid-off reactors were kept dry without any river water for 24 days. There was some loss in biofilm mass at the end of 24 days only in the WE-TDA Lid-off reactors. The biofilm mass, however, appeared to drop further after the subsequent wet and dry cycle up to the 17th flush. It is possible that biofilm growth was impacted by the extended dry period, but the biofilm can be expected to grow over time with continued contact with river water. This is supported by the biofilm mass sampled after a two-month dry period, wherein the Lid-on and Lid-off reactors were kept dry without any river water for two months after the 17th flush. The biofilm mass increased in both lid-on and lid-off reactors of Trad-TDA and WE-TDA materials over the dry period.

Biofilm growth on the exposed wires was found to be similar for Trad-TDA and WE-TDA, although a higher mass density (mg biomass/cm^2 wire) was measured in the Lid-on reactors than that in the Lid-off reactors. At the end of the two-month dry period, the mean (± std dev) biofilm density on the wires was 1.6 (± 1.1) mg/cm^2 in Trad-TDA Lid-on, 1.8 (± 1.1) mg/cm^2 in WE-TDA Lid-on, 0.49 (± 0.57) mg/cm^2 in Trad-TDA Lid-off, 0.60 (± 0.38) mg/cm^2 in WE-TDA Lid-off reactors. The mass of wires in the TDA (g wire/kg TDA, where mass of TDA in the reactor includes rubber and wires) was 8.2 (± 3.9) g/kg in Trad-TDA Lid-on, 15 (± 6.7) g/kg in WE-TDA Lid-on, 8.2 (± 6.3) g/kg in Trad-TDA Lid-off, 29 (± 2.4) g/kg in WE-TDA Lid-off reactors. It must be noted that our sampling method did not include biofilm growing on all of the exposed wires in all reactors, which could account for the high variability and uncertainty in the measurements.

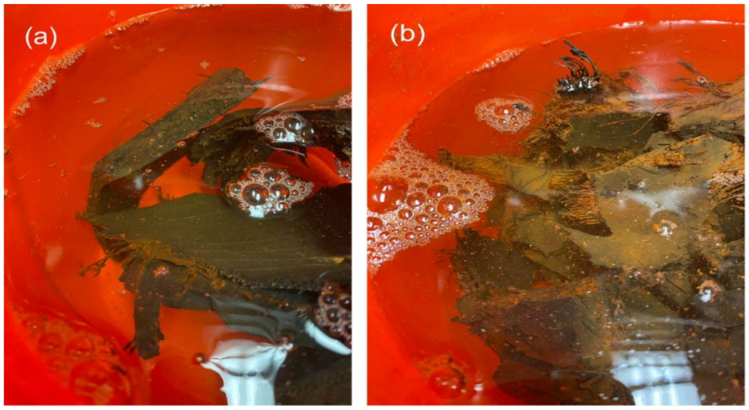

Figure 5. Biofilm growth on TDA in the 0th hour of the fifth flush (a) Trad-TDA and (b) WE-TDA; (Trad-TDA = traditional TDA and WE-TDA = wire-exposed TDA).

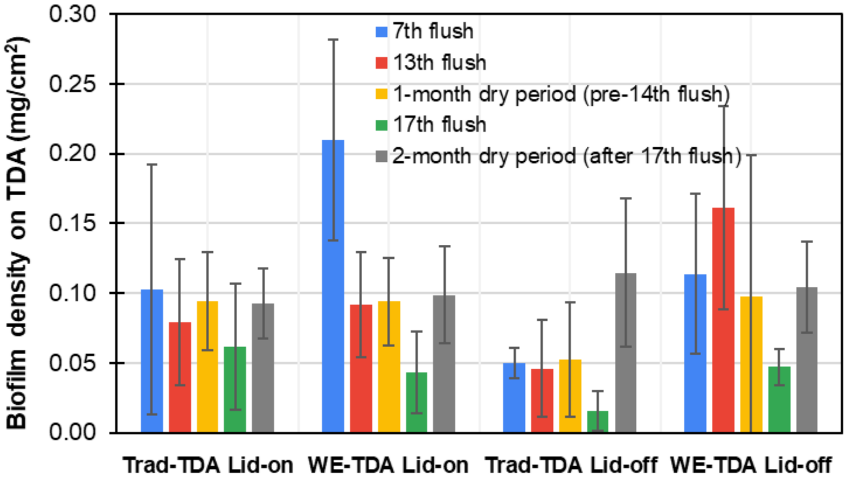

Figure 6. Biofilm growth on TDA was sampled in each reactor and averaged according to replicate groups (Trad-TDA = traditional TDA and WE-TDA = wire-exposed TDA). Biofilm was sampled after flushing the reactors on the 7th, 13th, 14th, and 17th flush. There was a 24-day dry period between flush 13 and 14, and biofilm samples were taken at the end of the 14th flush. The reactors were kept dry for 2 months after the 17th flush and biofilm was sampled at the end of the 2-month dry period. The error bars represent the standard deviation of the mean for each set of five replicate reactors. Biofilm developed on the exposed wires is not included in the plot shown.

3.2.3 Fate of chemicals

3.2.3.1 Concentrations of chemicals

As there was no phosphate added to the river water, influent phosphate concentration varied over time, reaching 0.1 mg/L on the 3rd flush and falling to 0.024 mg/L on the 9th flush (Figure 7, Table A1). The effluent phosphate concentrations were lower than the influent concentrations across all treatments, while the control had virtually no reduction in phosphate. At the end of 72-h contact period, effluent concentrations in the four groups of reactors were consistently below the 0.05 mg/L U.S EPA limit from the 1st to 17th flush, except for Trad-TDA Lid-on in the 1st flush. The WE-TDA removed more phosphate than Trad-TDA until Flush 9, after which removal performances were similar. The mean reduction in concentrations for the 17 flushes were 71% (± 7.6%) for Trad-TDA Lid-on, 60% (± 15%) for Trad-TDA Lid-off, 76% (± 9.9%) for WE-TDA Lid-on, and 80% (± 6.8%) for WE-TDA Lid-off.

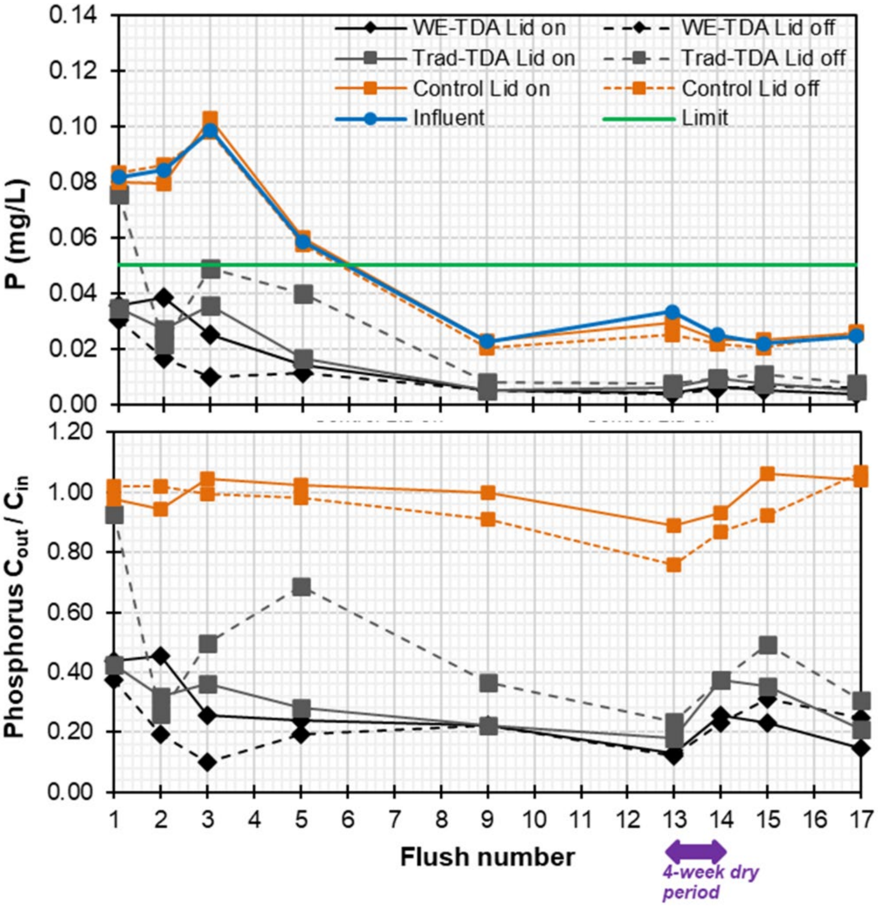

Figure 7. (a) Phosphate concentrations (mean of five replicate values) after application of TDA in river water. Trad = Traditional TDA, WE = wire-exposed TDA, Influent = filtered river water, Limit = U.S. EPA criteria of phosphate concentration for prevention of eutrophication in lakes (Litke 1999); (b) Phosphate concentrations in the reactors relative to the influent, where C_{out} represents the effluent concentration after 72-h contact and C_{in} represents the influent river water concentration. A C_{out}/C_{in} value greater than one indicates leaching of metal from TDA into the river water.

The effluent zinc concentrations in the Trad-TDA reactors were substantially and consistently higher than that of the influent for all flushes (Figure 8, Table A2). The concentrations, however, fell below the chronic toxicity limit for zinc after the first flush. After the first flush, the WE-TDA reactors had approximately the same concentration as the influent with the exception of WE-TDA Lid-off during the 9th flush. Table A2 indicates that no single effluent sample violated acute toxicity standards (U.S. EPA 2007) for zinc. Influent river water concentrations of zinc were low.

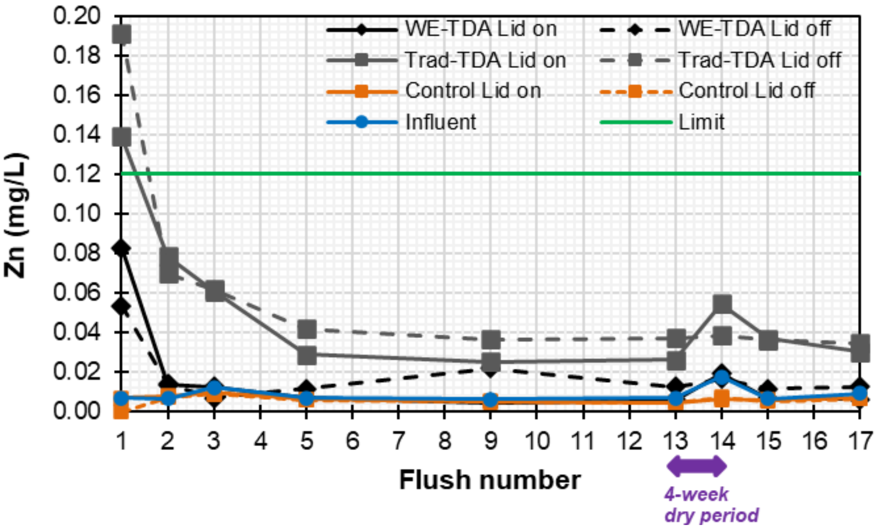

Figure 8. Zinc concentrations (mean of five replicate values) after application of TDA in river water. Trad = Traditional TDA, WE = wire-exposed TDA, Influent = filtered river water, Limit = chronic toxicity criteria for freshwater biota (U.S. EPA 2007).

Effluent copper concentrations in the reactors were slightly greater than influent concentrations during some of the flushes (Figure 9, Table A3). The effluent concentrations were, however, still well below the U.S. EPA chronic toxicity criteria throughout the experiment. Table A3 indicates that no single effluent sample violated acute toxicity standards (U.S. EPA 2007) for copper. Influent river water concentrations of copper were low.

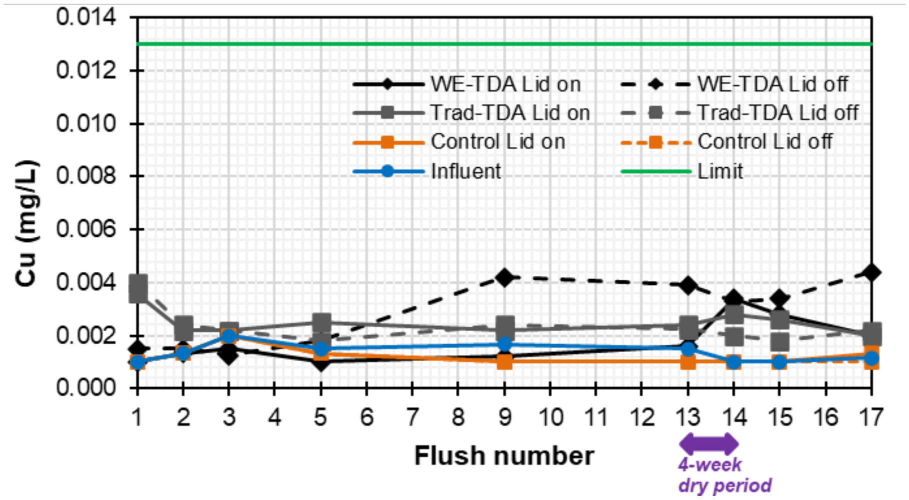

Figure 9. Copper concentrations (mean of five replicate values) after application of TDA in river water. Trad = Traditional TDA, WE = wire-exposed TDA, Influent = filtered river water, Limit = chronic toxicity criteria for freshwater biota (U.S. EPA 2007).

Iron concentrations increased in the water after the 72-h contact with TDA in all reactor groups during the experiment (Figure 10, Table A4). For the same TDA type, the Lid-on treatments showed more iron leaching from the TDA than the Lid-off treatments until the 5th or 9th flush. With the exception of the first flush, influent concentrations of iron were low. Table A4 indicates that no single effluent sample violated acute toxicity standards (U.S. EPA 2007) for iron. Influent river water concentrations of iron were low.

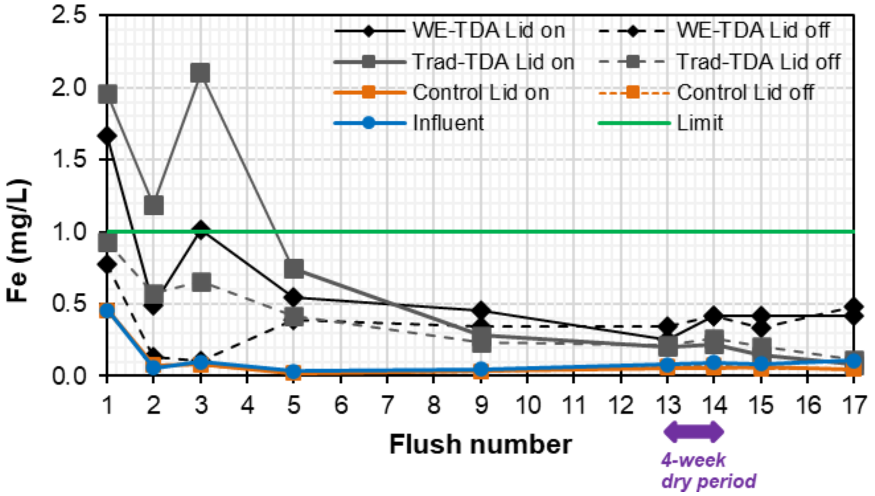

Figure 10. Iron concentrations (mean of five replicate values) after application of TDA in river water. Trad = Traditional TDA, WE = wire-exposed TDA, Influent = filtered river water, Limit = chronic toxicity criteria for freshwater biota (U.S. EPA 2007).

Manganese leaching from TDA was observed for both traditional and wire-exposed TDA, with substantial release observed in reactors with WE-TDA until the last flush of the batch studies (Figure 11). There is no U.S. EPA chronic toxicity criterion for manganese, but the secondary drinking water recommendations, related to taste, are identified as “Limit” in Figure 11. Release of manganese can be linked to its presence in tires (Park et al. 2023). On the other hand, metals such as aluminum, cadmium, chromium, lead, and nickel were not found at concentrations above their respective laboratory limits of detection (LOD), which are substantially below the freshwater chronic toxicity limits (U.S. EPA 2007). Boron, which is allowed up to a 0.5 mg/L in drinking water (U.S. EPA 2007), was below 0.07 mg/L in all reactors. Metals such as calcium, potassium, magnesium, and sodium were present in influent and as such no increase or decrease in the concentration of these metals was observed, which indicates that adsorption or leachability of these metals was minimal. Plots showing concentrations of all these metals are provided in Appendix A.

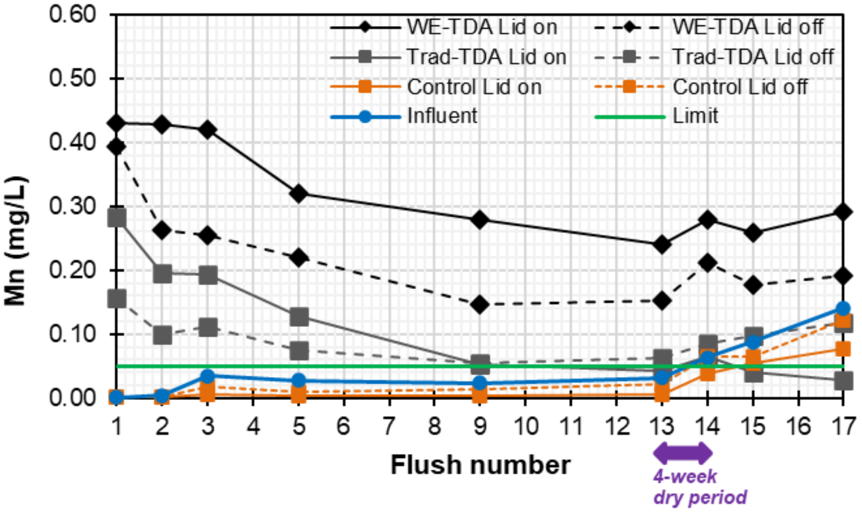

Figure 11. Manganese concentrations (mean of five replicate values) after application of TDA in river water. Trad = Traditional TDA, WE = wire-exposed TDA, Influent = filtered river water, Limit = U.S. EPA's national secondary drinking water regulation.

3.2.3.2 Flux of chemicals in a typical TDA underground chamber

Concentrations of leached metals per liter of water were converted to concentrations per kg of TDA mass by multiplying by the liters of water (2.25 L) in each reactor and dividing by the mass of TDA (600 g) in each reactor. Figures 12 through 15 show the effluent concentration after 72 h in a typical TDA underground chamber with the influent concentrations given converted to concentration per unit mass of TDA in the chamber. The U.S. EPA chronic criteria for freshwater biota were converted to an equivalent concentration per mass of TDA in a typical TDA underground chamber by applying Eq. 1. The purpose of applying Eq. 1 is to show how the leached or adsorbed chemicals would relate to the chronic criteria (or limit) in a typical TDA underground chamber.

The zinc effluent from the typical TDA chamber (Figure 12) would fall below the U.S. EPA chronic criteria for freshwater by the 2nd (WE-TDA) and 5th flush (Trad-TDA). This indicates that the biofilm growth is sufficient in the early flushes to retain zinc leaching, especially for the WE-TDA.

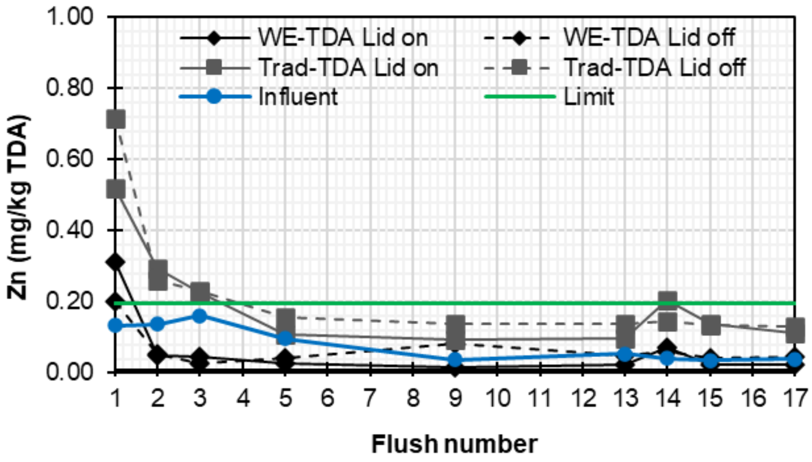

Figure 12. Cumulative zinc flux (mean of five replicate values) after application of TDA in river water. Trad = Traditional TDA and WE = wire-exposed TDA. Limit = chronic toxicity criteria for freshwater biota (U.S. EPA 2007) assuming 50% porosity.

Copper in the effluent does not exceed the U.S. EPA chronic criteria in any of the flushes (Figure 13). This again indicates the ability of the biofilm to capture dissolved metals.

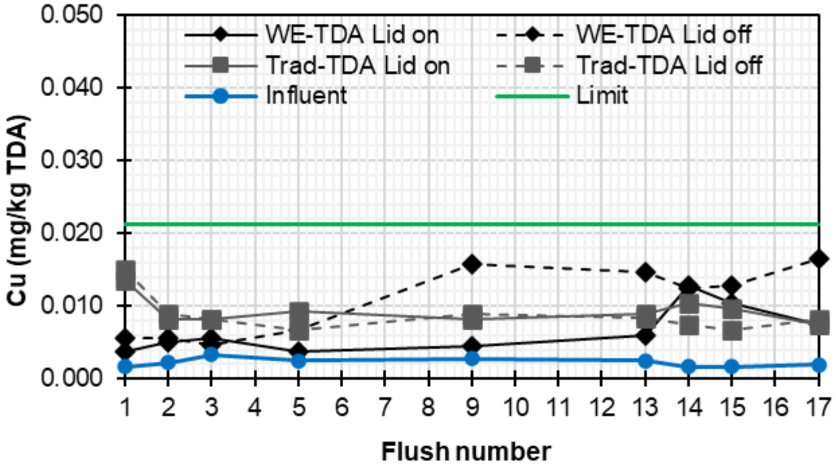

Figure 13. Cumulative copper flux (mean of five replicate values) after application of TDA in river water. Trad = Traditional TDA and WE = wire-exposed TDA. Limit = chronic toxicity criteria for freshwater biota (U.S. EPA 2007) assuming 50% porosity. Values not shown were below the scale of the vertical axis.

The iron concentration in the effluent (Figure 14) is above the U.S. EPA suggested criteria for chronic toxicity until the 5th or 9th flush. In an oxic water body (DO > 1 mg/L), however, most of this iron would be Fe^{+3}, which is generally insoluble and would be present as precipitates in the water. It is believed that most of these precipitates would settle in the compressed TDA, before leaving the chamber, or settle in the storm sewer, where there is typically good access to oxygen (Huisman et al. 2004).

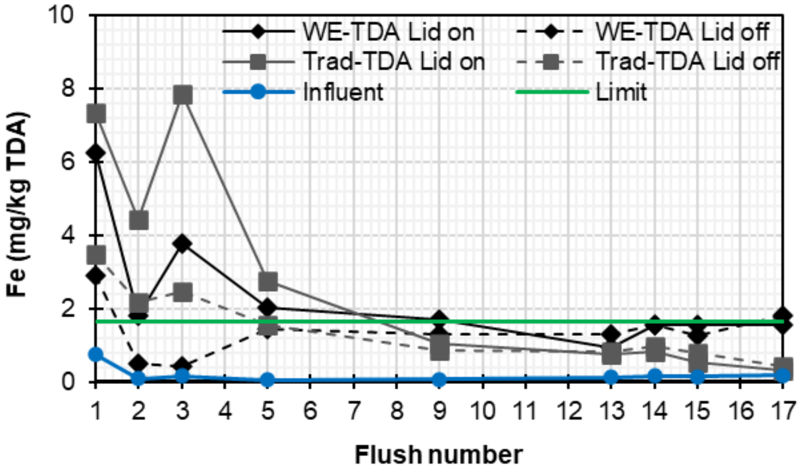

Figure 14. Cumulative iron flux (mean of five replicate values) after application of TDA in river water. Trad = Traditional TDA and WE = wire-exposed TDA. Limit = chronic toxicity criteria for freshwater biota (U.S. EPA 1986) assuming 50% porosity.

The manganese concentration in the effluent is above the U.S. EPA suggested criteria for drinking water from flush 1 to 17 (Figure 15).

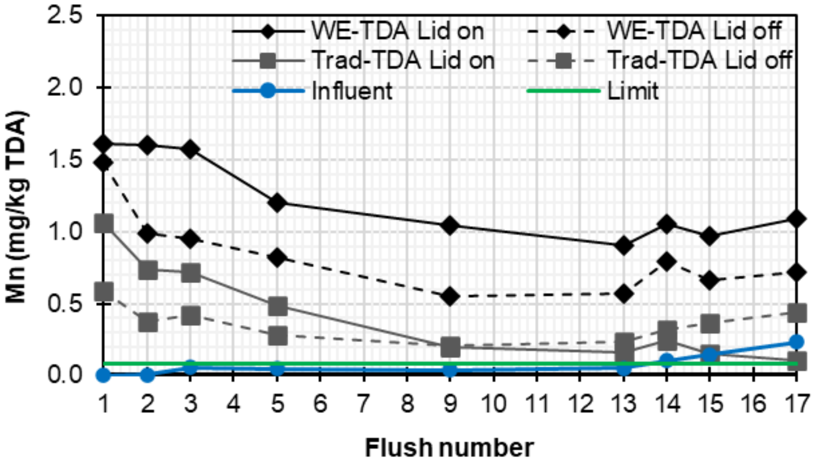

Figure 15. Cumulative manganese flux (mean of five replicate values) after application of TDA in river water. Trad = Traditional TDA and WE = wire-exposed TDA. Limit = secondary drinking water standard (U.S. EPA) assuming 50% porosity.

3.3 Discussion

The biofilm growth on the TDA did not uniformly result in more mass on the wire-exposed versus traditional TDA. This is different than found by Singh et al. (2024), where the WE-TDA had more biofilm growth. The difference is that the biofilm in this study did not have one month under water to develop. In addition, we could not measure the biofilm on the wires protruding from the TDA, so the WE-TDA may have had a higher mass of biofilm than the Trad-TDA. WE-TDA, being a byproduct extracted from the TDA process by a large magnet, has a lot of wires and ripped surfaces, which serve as optimal sites for biofilm growth (Braem et al. 2014).

A comparison of the iron and zinc leaching between TDA with and without biofilms reveals that biofilms contribute to the prevention of the leaching of metals in TDA. The prevention of metal leaching by biofilms could be attributed to biosorption, in which heavy metals are tied to live microbe cells or inert matter present within the biofilm (Azizi et al. 2016; van Hullebusch et al. 2003). Extra polymeric substances (EPS) present within the biofilms serve as an organic ligand source for metal uptake (Costa et al. 2018). The presence of biofilms is also seen to convert metals from a toxic state to a non-toxic state using bioprecipitation and efflux pumping (Edwards and Kejellrup 2013).

Field studies of TDA effluent have observed zinc and copper concentrations that are below the chronic toxicity criteria for the freshwater biota, and biofilms may be a reason for that observation. In a field study by Humphry and Katz (2001), the metal leaching from TDA coming in contact with groundwater was seen to gradually reduce over time. It should be noted that the concentrations of these metals were below the chronic limit suggested by the U.S. EPA. In another study done by Hennebert et al. (2014), TDA kept in embankment fills had minimal leaching of metals over time. The occurrence of no leaching or gradual reduction of leaching over time in different studies could be attributed to the prevention of metal leaching due to biofilm growth on TDA.

Chapter 4: Adsorption of chemicals of emerging concern (CECs) to tire-derived aggregate (TDA)

4.1 Background

Per- and polyfluoroalkyl substances (PFAS)are a group of contaminants of emerging concern (CECs), often referred to as "forever chemicals" due to their extremely slow degradation rates in the environment. As these chemicals accumulate, their increasing concentration poses significant risks to human health and ecosystems. Stormwater runoff, which carries pollutants from various sources, transports them to receiving water bodies. Therefore, treating PFAS before discharge presents a valuable strategy for reducing their spread and mitigating their environmental impact. In this study, TDA was evaluated as a stormwater treatment media through lab batch tests to assess its potential to remove PFAS. Additionally, the study also examined if interactions between TDA and stormwater could potentially release PFAS from this material.

PFAS consists of nearly 15,000 chemicals, but our study primarily focused on the species containing four to eight carbons, perfluorobutanoic acid (PFBA), perfluorobutanesulfonic acid (PFBS), perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), and related compounds. These are the main PFAS species proposed limits in drinking water set by both the U.S. Environmental Protection Agency (U.S. EPA) and the Minnesota Department of Health (MDH; Table 2).

Table 2. Advisory limit of PFAS contents for drinking water by U.S. EPA and Minnesota Department of Health (MDH).

Name	EPA proposed MCL (µg/L)*	2022 EPA Health Advisory (µg/L)*	Type of HA value	Lowest MDH Value (µg/L)	Type and date of MDH value	Duration of exposure
PFBS	0.003	2	life-time	0.1	HRL23	Short Term
PFBA				7	HRL18	Short Term
PFHxS	0.01			0.047	HRL23	Short Term
PFHxA	0.01			0.2	HRL23	Short Term
PFOA and salts	0.004	0.004 (interim)	life-time	0.035	HRL18 & HBV22	Short Term
PFOA and salts	0.004	0.004 (interim)	life-time	0.0000079	HRV24	Short Term
PFOS and salts	0.004	0.02 (interim)	life-time	0.3	HRL09	Chronic
PFOS and salts	0.004	0.02 (interim)	life-time	0.015	HBV20	Short Term

Note: MCL - maximum contaminant level; HBV- MDH Health-Based Value; HRL - MDH Health Risk Limit
* Comparison of State Water Guidance and Federal Drinking Water Standards, cited on February 3, 2025

Notably, current regulatory/advisory frameworks lack defined limits or standardized methods for determining the presence of PFAS in solid materials. Recognizing this gap, our experimental design was initially drafted from methodologies used by the NRRI Environmental Chemistry Lab. Through a series of trials, we refined the testing procedures.

4.2 Experimental methods

Lab batch tests were performed separately for the PFAS release and adsorption tests by different procedures and different sizes of TDA materials. PFAs measurement is performed by Liquid chromatography-quadrupole time-of-flight mass spectrometry (LC-QTOF-MS).

4.2.1 Leaching test procedures

Two small-size TDA rubber materials (TDA rubber nuggets and shredded TDA rubber, Figure 16) were selected for the leaching test to fit the 50-mL conical poly-propylene centrifuge. Wires have been removed from both materials before the testing. These materials were rinsed by tap water for five or less minutes to remove the dust. Both the materials before and after tap water rinse were used for the leaching test.

Figure 16. Pictures of two TDA materials used for PFAS leaching test. On the left are the wire-off TDA rubber nuggets, and on the right are the wire-off shredded TDA rubber.

To perform the leaching test, 5 g of TDA material were transferred into a 50-mL conical tube, which was rinsed by methanol before the test. Subsequently, 50 mL of HPLC water was added to the tube to create a mixture with a liquid-to-solid ratio of 10:1. This process was performed in three replicates for each mixture. The mixed solution was then placed on a shaking table, agitating at 150 RPM for a duration of 72 h (Figure 17). After that, the solution was separated through centrifugation at 4000 RPM for 10 minutes. The resultant solution is then carefully transferred to another conical tube and concentrated through solid phase extraction (SPE) and evaporation by nitrogen gas to reach a volume of 1 mL, in preparation for LC-QTOF-MS analysis.

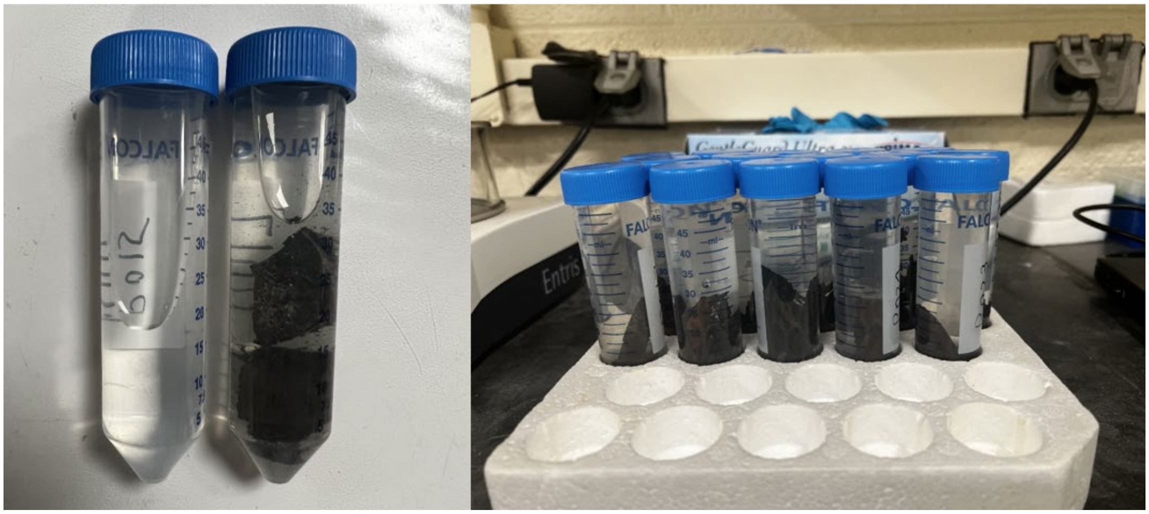

Figure 17. The example mixture of TDA and HPLC water after they were shaken for 72 hours.

Besides the TDA materials tested, two blank controls and two spike recovery tests were performed with the exact same experimental procedures. The blank was 50 mL HPLC water only without any TDA to test any potential contamination in the workflow. The spike solution incorporated a 100-µL diluted EPA standard solution (5 µg/L, prepared by serial dilution from Wellington standard EPA533-PAR) to the 50-mL HPLC water to validate the preservation of PFAS throughout the testing process.

During the test, the tube, material and solution weights were measured at every step to count for the materials added, the solution added, and the final solution used to concentrate.

4.2.2 Adsorption test procedures

The adsorption test was conducted by checking the PFAS concentration changes in the solution after mixing TDA and PFAS solutions with known concentrations (namely spike solution) for five days.

The concentrated stock solution was prepared from concentrated solutions of PFBS, PFBA, PFOS and PFOA in methanol (1 mg/mL), which were prepared from individual neat standards. The concentrated stock was serial diluted with 70:30 methanol:water to create a spike solution at the concentration of 2 µg/L for each PFAS chemical.

To achieve the maximum adsorption capacity, TDA powder was used for this test. TDA powder was first rinsed with methanol three times and air-dried for 48 h before use. TDA was weighed at 100 mg, 500 mg, and 1 g three times and then placed into separate 50 mL falcon tubes. Each tube was then added with 40 mL of DI water, which was measured to contain minimal concentrations of studied PFAS chemicals. After that, 200 µL of the spike solution was added to each TDA-containing solution in the falcon tubes to achieve a concentration around 15 µg/L. These tubes were then placed on a shaker table (150 RPM) for 5 days. After 24-h and 5-day shaking period, the tubes were centrifuged at 4500 RPM for 15 minutes. Post-centrifugation, 420 µL sample was taken from the falcon tubes and diluted to 30% by adding 980 µL of surrogate. After that, 150 µL of the 1.4 mL solution was transferred to an auto sampling vial for LC-QTOF-MS measurement.

4.3 Results and discussion

4.3.1 Leaching test results

In the leaching testing, 22 PFAS species exhibited recovery rates falling within the 50% and 150% range (Table 3), which is considered as reliable results were achieved for these species. Additional four PFAS species were detected with spike recovery rates around 20% and one compound had a recovery rate at 160%. Because of this, the measurement results for these five species were biased low or high.

Table 3. List of PFAS components measured for the leachate solution.

No.	PFAS species	Formula	Blank control avg (stdev), ng/L	Spike recovery, %	Detected in TDA leachate?
1	PFBA	C4HF7O2	0	103%	Yes
2	PFPeA	C5HF9O2	0	101%	Yes
3	PFBS	C4HF9O3S	0	95%	Yes
4	PFEESA	C4HF9O4S	0	89%	No
5	4:2 FTS	C6H5F9O3S	0	23%	No
6	PFHxA	C6HF11O2	6.10 (3.5)	100%	Yes
7	PFPeS	C5HF11O3S	0	92%	Yes
8	HFPO-DA	C6HF11O3	0	94%	No
9	PFHpA	C7HF13O2	3.52 (3.85)	106%	Yes
10	PFHxS	C6HF13O3S	0	105%	No
11	DONA	C7H2F12O4	0	96%	No
12	6:2 FTS	C8H5F13O3S	81.12 (114.72)	29%	Yes
13	PFOA	C8HF15O2	16.00 (2.47)	108%	Yes
14	PFHpS	C7HF15O3S	0	160%	Yes
15	PFOS	C8HF17O3S	0	81%	Yes
16	PFNA	C9HF17O2	0	95%	No
17	9Cl-PF3ONS	C8HF16ClSO4	0	51%	No
18	8:2 FTS	C10H5F17O3S	0	23%	No
19	PFDA	C10HF19O2	0	106%	Yes
20	N-MeFOSAA	C11H6F17NO4S	0	82%	No
21	PFUdA	C11HF21O2	0	88%	No
22	PFMBA	C5HF9O3	0	89%	No
23	NFDHA	C5HF9O4	0	84%	No
24	PFMPA	C4HF7O3	0	84%	No
25	3:3 FTCA	C6H5F7O2	0	118%	No
26	5:3 FTCA	C8H5F11O2	0	49%	No
27	7:3 FTCA	C10H5F15O2	0	15%	No

Among the 27 species examined, eleven, including PFBA, PFBS, PFPeA, PFPeS, PFHxA, PFHpA, PFOA, PFOS, PFHpS, 6:2 FTS and PFDA, were detected in the solution. Meanwhile, another sixteen species (PFEESA, 4:2 FTS, HFPO-DA, PFHxS, DONA, PFNA, 9Cl-PF3ONS , N-MeFOSAA,8:2 FTS, PFUdA, PFMBA,

NFDHA, PFMPA, 3:3 FTCA, 5:3 FTCA, 7:3 FTCA) were not detectable in the TDA leachate. Notably, four species (PFHxA, PFHpA, PFOA and 6:2 FTS) were also present in the blank samples, implying potential contamination from the containers or the experimental process. Despite this, most concentrations measured in the blank samples were lower than those in the mixture samples except for 6:2 FTS (Figure 18). Consequently, we concluded that these three species were released from the TDA as well.

The released PFAS concentrations were calculated based on the mass (approximately 5 g) of TDA added, providing a measure of mass PFAS released per gram of TDA (Figure 18). In general, PFBA and PFBS were detected to have the highest concentration, approximately 0.1-0.6 ng/g for both types of TDAs, likely attributed to their high-water solubility for the short-chain PFAS. Most other PFAS species exhibited concentrations ranging from 0.001 to 0.02 ng/g. Generally, the shredded TDA demonstrated higher released PFAS contents compared to TDA nuggets, potentially attributed to the smaller size of the latter, resulting in larger surface area/weight of TDA.

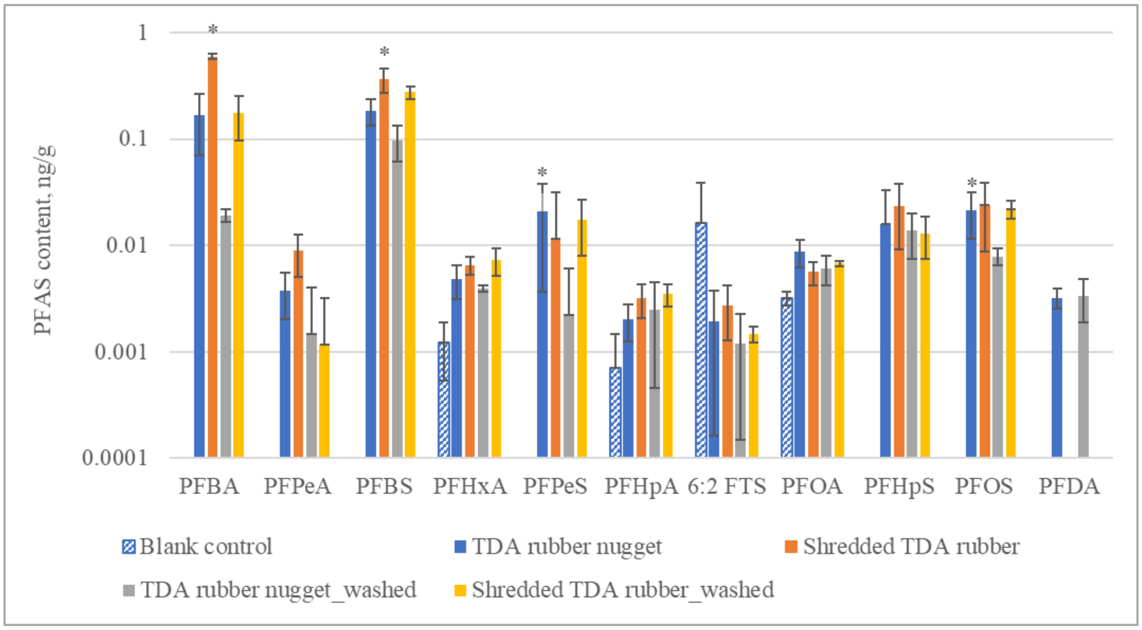

Figure 18. The contents of PFAS species in two TDA materials before and after rinsed by tap water. The significant difference (t-test with $p<0.05$) between the same material before and after tap rinse is marked by an asterisk. The blank control was 50-ml HPLC water only without any TDA but was tested with the exact same leaching procedure.

This high solubility of PFBA and PFBS led to their easy removal with a 5-minute tap water rinse. This was evident in the significant difference observed for PFBA and FPBS in shredded TDA before and after the tap water rinse. Additionally, the water rinse also reduced PFPeS and PFOS contents in the TDA nuggets.

4.3.2 Adsorption test results

The concentration changes of PFAS species were recorded from the start to 24 h and to the fifth day (Figure 19). The short-chain PFAS, like PFBA and PFBS, showed minimal concentration changes between day one and day five. This suggested that their release or adsorption reached equilibrium relatively quickly. Conversely, significant differences were noted in concentrations of PFOA and PFOS, compounds with eight carbons, between the first and fifth days. This indicated that these long-chain PFAS compounds required a longer equilibration period to observe changes in their adsorption behavior accurately.

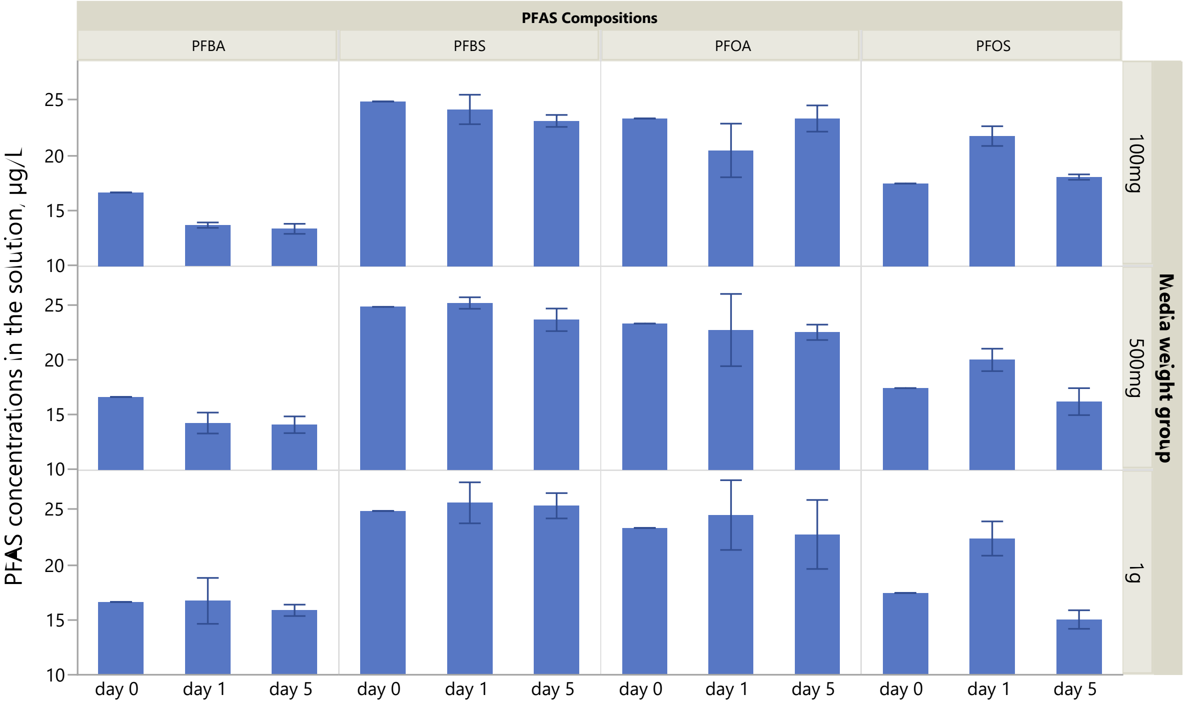

Figure 19. The concentrations of four PFAS species at the beginning (day 0), the first day (day 1) and the fifth days (day 5) during the adsorption test.: 100 mg (top), 500 mg (middle) and 1 g (bottom) of TDA were added to 40 ml of water containing the PFAS species with triple replicates for each.

In contrast to the behavior expected for sorption of PFAS to TDA, PFBA and PFBS concentrations in the solutions increased as TDA mass increased (Figure 20). This may be attributed to the release from the TDA material itself, as PFBA and PFBS showed the highest level of leaching from TDA.

In the case of PFOA, there were no statistically significant differences between the concentrations in the tests with and without PFOA, suggesting little to no sorption or leaching of PFOA. However, for PFOS, the concentration in solution decreased as TDA mass increased, suggesting that PFOS is sorbed somewhat by TDA. Calculations based on the mass used revealed an approximate removal rate of 95 ng PFOS per gram of TDA when utilizing both 500 mg and 1 g mass in the testing. Sorption or partitioning, often characterized by K_d value representing the ratio of chemical content in the solid (adsorbed) to that in the liquid phase, was computed for PFOS, resulting in a K_d value of 6.3 L/kg, translating to a log K_d of 0.8, which is within the range of a typical soil. Comparatively, commercial sorbents like GAC typically exhibit log K_d values for PFOS above 4 (Xiao et al. 2017). This suggests the adsorption of PFOS on TDA was similar to that of a typical soil and was minimal relative to commercial filter media products.

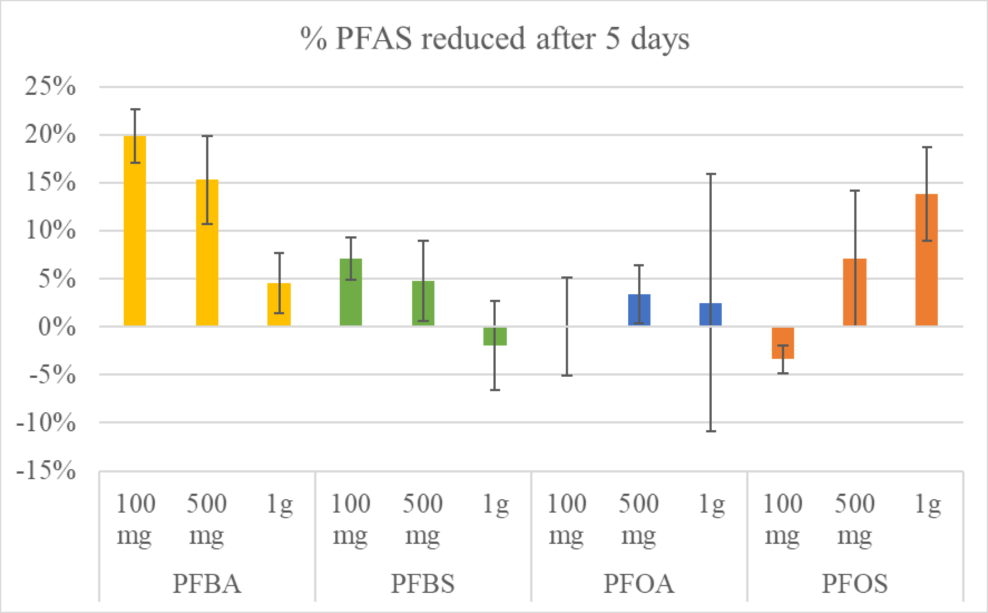

Figure 20. The amount of PFAS reduced from the liquid after a 5-day shaking period.

For the four PFAS species studied, PFBA and PFBS represented the short-chain species while PFOA and PFOS represented the long-chain species. Typically, adsorption is often less effective for the short-chains due to their more hydrophilic properties compared to long-chain species (Li et al. 2020). As a general trend, PFAS sorption tends to increase when the carbon chain number increases. Since the adsorption of PFOS was minimal, it was estimated that the TDA's adsorption capacity for PFAS with carbon chain number less than eight would also be minimal or negligible. Furthermore, among compounds with an equal number of carbon atoms, perfluorinated sulfonic acids like PFOS were usually more efficiently removed via adsorption compared to perfluorinated carboxylic acids, such as PFOA (Yao et al. 2014). This aligns with our experiment findings where more PFOS than PFOA were removed by TDA.

4.4 Summary

This study indicated that, although there was an observable release of PFAS from the roughly 2.54 cm X 1.27 cm (1 in. X ½ in.) TDA nuggets and the roughly 2.54 cm X 1.27 cm (1 in. X ¼ in.) shredded tire rubber, the quantities were relatively low. Most PFAS species exhibited releases below 0.1 ng/g, with PFBA and PFBS releasing 0.6 ng/g or less. It is believed that the release from 15 cm X 5.1 cm (6 in. X 2 in.) ASTM 6270-B TDA would be lower than that from the TDA nuggets and shredded tire rubber.

The adsorption tests with TDA powder indicated that the short chained PFAS compounds, such as PFBA, PFBS and PFOA had minimal adsorption on TDA powder. Only the longer-chained compounds, such as PFOS, had adsorption to the TDA powder, which was still relatively small at a maximum of 14% after 5 days. It is believed that sorption to 15 cm X 5.1 cm (6 in. X 2 in.) ASTM 6270-B TDA would be lower than that from the TDA powder.

Comparative analyses with other sites revealed that the PFAS contents in TDA were lower than firefighting or former PFAS manufacturer sites, where the contents in soil often exceeded 1 ng/g and may reach several hundred ng/g (Xiao et al. 2015; Wang et al. 2023). Instead, the released PFAS contents from TDA aligned with or fell below levels observed in residential land (Brusseau et al. 2020; Wang et al. 2023). For instance, the average content of 34 sites in residential land was reported as 2.9 ng/g for PFOS and 1.7 ng/g for PFOA (Wang et al. 2023), both exceeding the released contents measured in TDA.

In summary, while there was a measurable release of PFAS from TDA, the concentrations were relatively low and appeared to be similar to typical urban concentrations, including residential land. The information supports the notion that TDA, with its low PFAS release and low adsorption capacity, could be considered for various applications, including stormwater treatment, without significant PFAS-release concerns. Continued research can further enhance our understanding of the environmental impact of TDA in different contexts.

Chapter 5: Selection of blend materials and mixing ratio to minimize leaching of zinc and copper from TDA

5.1 Background

Leaching of zinc and copper from tire-derived aggregate (TDA) was previously found in Singh and Gulliver (2023) and described in the Task 2 Interim Report for this project, along with retention of phosphate through adsorption on iron wires in the TDA and/or precipitation due to the prevalence of dissolved iron in the water. While the retention of phosphate is a major accomplishment due to its prevalence as an impairment of water bodies in Minnesota, the leaching of zinc and copper is a concern. Singh and Gulliver (2024) found that a biofilm that was grown over 1 month in water with nutrients and river water was capable of retaining the copper and zinc that leached from TDA. The 1-month growth period in water is unlikely to be replicated in the field, so a blend of materials was investigated in case there were still concerns about zinc and copper leaching from TDA. This report thus investigated materials, if required, to mix into the TDA to capture the leached zinc and copper from the TDA. Biochar is known to capture metals but is more costly than some other potential materials. This section will start with a review of biochar's ability to adsorb copper and zinc and then investigate some less costly materials.

5.2 Review of metal retention by biochar

Biochar selection for metal retention is currently challenging because most commercially available biochars are not well characterized. In general, biochar properties can vary widely depending on various aspects of the production process (typically pyrolysis, or the burning biomass under conditions of low temperatures and minimal oxygen), including the feedstock type and production temperature. Biochars produced at lower pyrolysis temperatures typically have more polar surface chemistries and lower intraparticle surface area, while biochars produced at higher temperatures have more hydrophobic surface chemistry and higher surface area. Biochar properties, for example, vary substantially depending on several aspects of the biochar production processes (Ulrich et al. 2024). However, wood-based biochars produced in the 500–600 °C range (a threshold for "high-temperature" biochars) are the most widely available.

Sorption of zinc and copper to biochar's surfaces have generally resulted in greater than an order of magnitude reduction in leachate concentrations (Beesley and Mirmiroli 2011, Xiong et al. 2022, Alsahli et al. 2021, Premarathna et al. 2023), regardless of the biochar used. Therefore, biochar would be an appropriate choice as a mix with TDA to reduce the leaching of zinc and copper. One drawback, however, is the cost of biochar, which may be prohibitive for a large water storage system. Wood chunks were identified as an alternative source to mix in with TDA that would not fluidize and may retain zinc and copper.

5.3 Selection of other material for laboratory experiments

The selection of material had the following considerations:

1. Natural organic materials have an excellent adsorption of metals, and will be selected for zinc and copper retention,
2. Many organic materials also leach phosphate, negating the phosphate capture of the TDA. However, wood chunks are not known to leach phosphate and will be selected for zinc and copper retention without releasing phosphate.
3. Movement of particles within a granular material is a concern when the material is exposed to flushing with water and may become fluidized. The wood chunks should be of a size that will limit movement within the TDA material.
4. If possible, the wood chunks should be commonly manufactured for use and therefore cost-effective.

To meet the above considerations, it was decided to purchase cedar wood chunks that were approximately 1 – 2 inches in plan view and ¼ inch in thickness (Figures 21 and 22), to be close to the size of the TDA material while having a relatively low cost.

Figure 21. A sample of 1 – 2-inch X ¼ inch wood chunks used in the experiment.

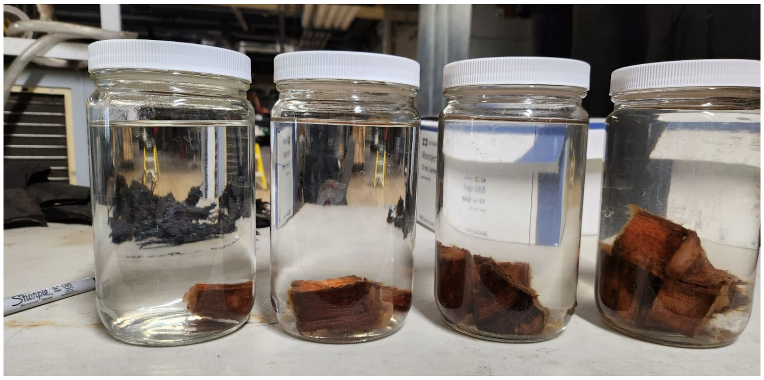

Figure 22. Wood chunks placed in batch containers.

5.4 Experimental methods

5.4.1 Stormwater preparation

Synthetic stormwater (SS) was prepared with a carbonate buffer (1.5 mM) added for pH control to assess the leaching of the metals. The synthetic stormwater (SS) recipe was prepared considering the composition of runoff presented in the NPDES database (Maestre and Pitt 2005); 113 mg/L sodium bicarbonate and 77.4 mg/L magnesium chloride were added to Milli-Q water, followed by pH adjustment of the solution to 7.4 using 0.1 M HCl. The zinc and copper were added according to the leaching observed in the study conducted by Singh and Gulliver (2023). The chemicals zinc chloride and chlorophyllin sodium copper were added to the synthetic stormwater to achieve concentrations of approximately 7.5 mg/L zinc and 0.6 mg/L copper in the water. There was no phosphate added to investigate leaching of phosphate from the wood chunks.

Two types of influents were prepared and utilized: 1) synthetic stormwater (without nutrients; SS) and 2) synthetic stormwater with nutrients (SSWN). The nutrients were added to support biofilm growth while SS without nutrients were used to assess effectiveness of wood chunks without biofilms.

5.4.2 Batch studies

Two sets of four experiments were conducted, one with biofilm development and one without. Eight clear glass 1 L jars (Uline) were used to carry out the batch studies for comparison of leaching and phosphorus adsorption. A 5% nitric acid solution was used to wash these jars, followed by rinsing with Milli-Q water. Four bottles were filled with 750 mL SSWN each to promote biofilm growth while other four bottles were similarly filled with 750 mL SS without nutrients to result in wood chunks without biofilm. After adding the desired stormwater to each group of jars, the cedar wood chunks were added to each reactor in the quantities shown in Table 4 (Figure 22). The wood chunks added in the bottles were decided based on a TDA/water ratio previously identified by Singh and Gulliver (2023). It must be noted that TDA was not added in the bottles as the motive behind this study is to assess the role of biofilms when TDA is leaching copper and zinc.

Table 4. Wood chunk placed in river water and synthetic stormwater reactors.

Reactor and Mass of Wood Chunks	Equivalent wood chunks mix with TDA
R1 = 12.5 g Wood chunks	TDA/16
R2 = 25 g Wood chunks	TDA/8
R3 = 50 g Wood chunks	TDA/4
R4 = 100 g Wood chunks	TDA/2

The hypothetical TDA/water mass ratio was maintained at 1:3.75, which means that the wood chunk/water mass ratio varied from 1:7.5 (100 g wood chunks) to 1:60 (12.5 g wood chunks). After influent sample collection, effluent samples from the eight reactors were collected at 72 h, the reactors were drained while wood chunks were retained. Fresh influent was refilled to all eight reactors for the four flushes.

5.4.3 Water sample collection and analysis

At each sampling event, 12 mL samples were collected with a syringe and disc filters (pore size 0.45 µm) into 15 mL centrifuge tubes. A 2% nitric acid solution was applied for the preservation of samples for Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) analysis for fifteen different metals: phosphorus (P), iron (Fe), zinc (Zn), copper (Cu), magnesium (Mg), lead (pb), sodium (Na), potassium (K), nickel (Ni), chromium (Cr), calcium (Ca), boron (B), aluminum (Al), manganese (Mn) and cadmium (Cd).

5.5 Results

The concentration of various metals obtained after ICP-OES was analyzed to determine the leaching or adsorption in the given TDA-based treatment system (Table A-5 in Appendix A). These concentrations were later converted to flux in terms of mg metal or phosphate per kg of wood chunks, considering the wood chunk/water mass ratio between 1:7.5 and 1:60. The phosphate results are given in Figure 23 and Figure 24.

The wood chunks were shown to release phosphate at substantial rates, contrary to the reason that they were chosen for this study. The release of phosphate decreased with flushes, but concentrations were still high compared to acceptable concentrations of phosphate that will be released to receiving waters. With a 50% porosity of TDA and wood chunks, a 5 mg/kg release over 72 h will result in roughly 14 mg/L phosphate concentration released from the storage facility.

Reactor 4 (R4) with 100 g wood chunks (1/2 of TDA weight) was observed to show the highest release of phosphate without biofilm growth and among the lowest with biofilm growth. The reason for this is unclear. The impact of biofilm growth on phosphate release is also unclear in the first two flushes, but there was not much difference in phosphate release in the third and fourth flushes.

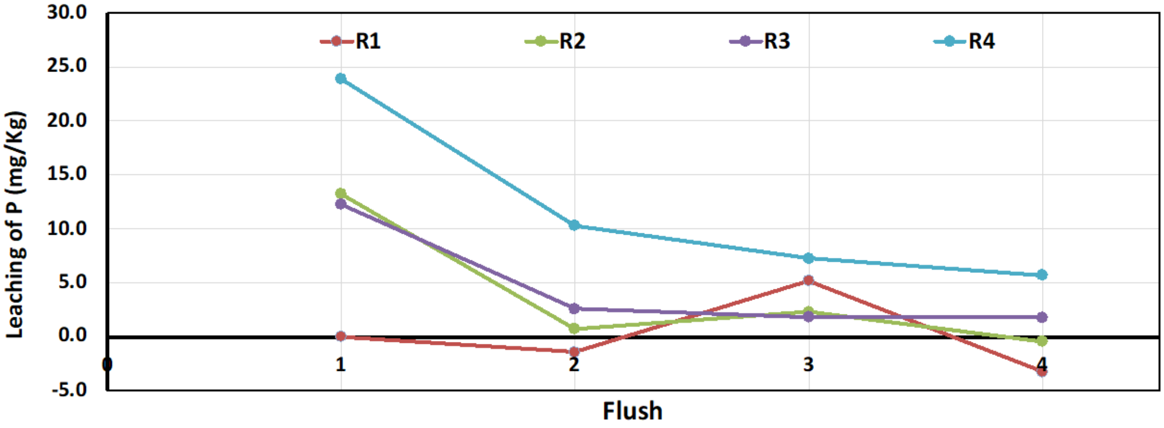

Figure 23. Phosphate leached (mg P per kg wood chunks) after 72 h for each flush of four reactors without biofilm.

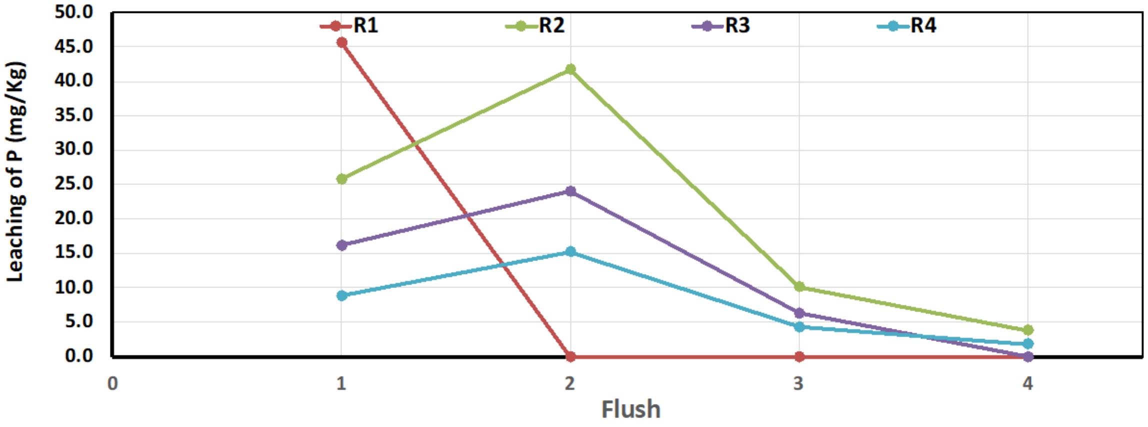

Figure 24. Phosphate leached (mg P per kg wood chunks) after 72 h for each flush of four reactors with biofilm growth. Flushes 2, 3 and 4 for R1 had concentrations below the limit of detection for phosphate.

Copper adsorption was fairly constant with flushes for the batch without biofilm growth (Figure 25). The adsorption decreased with mass of wood chunks in the reactor, probably due to exposure of the wood surface to the water (Figure 25 and Figure 26). In the reactor where biofilms were allowed to grow (Figure 26), however, copper adsorption seemed to increase in flushes 2 and 3, reaching a steady state for flush 4. The big difference is, in the system with biofilm, the removal rate was substantially higher than the systems without biofilms, which confirms our previous observation (Singh and Gulliver 2024) about the role of biofilms in removal of metals.

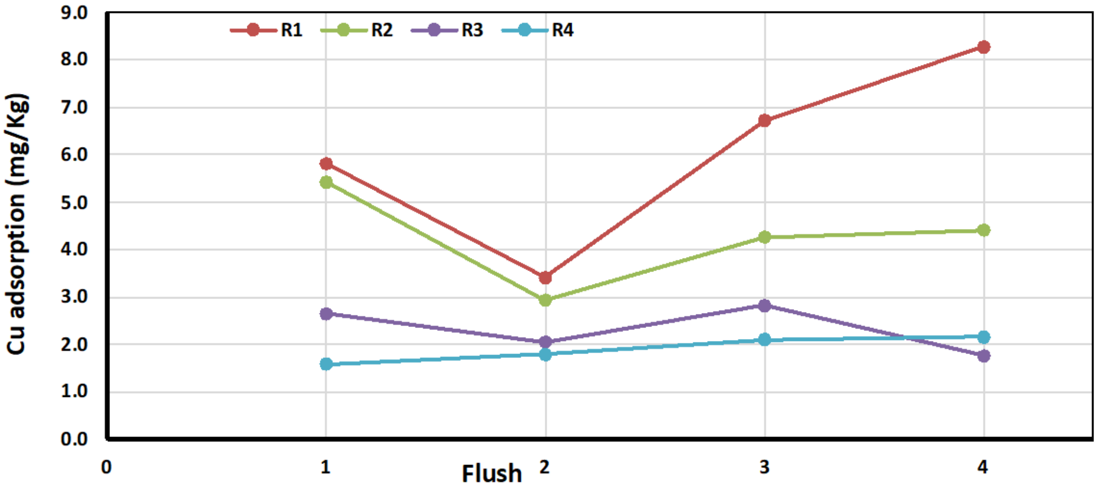

Figure 25. Copper adsorption (mg Cu per kg wood chunks) after 72 h for each flush of four reactors without biofilm growth.

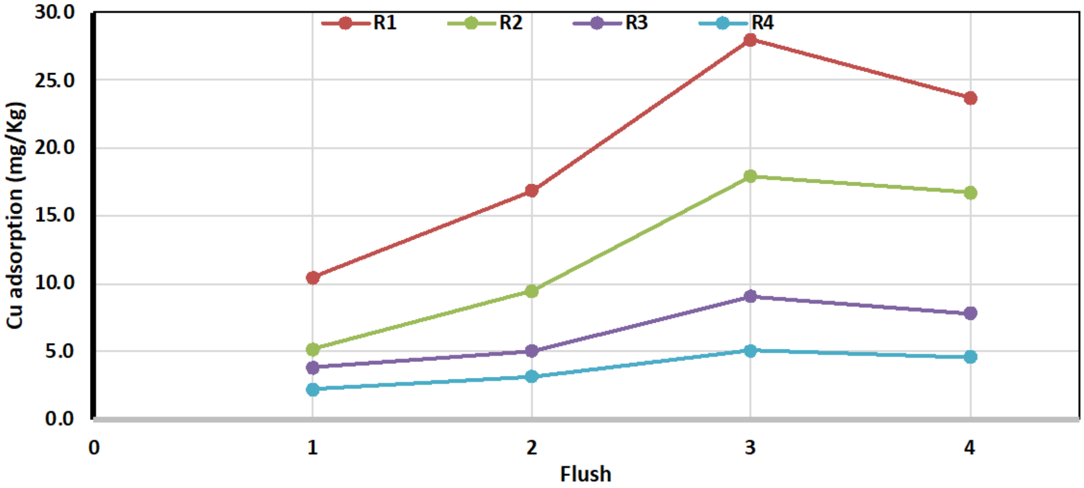

Figure 26. Copper adsorption (mg Cu per kg wood chunks) after 72 h for each flush of four reactors with biofilm growth.

Zinc adsorption per kg of wood chunk mass was again generally higher in the reactors with the least mass, probably due to a better exposure to the water (Figure 27 and Figure 28). The Zn adsorbed with biofilms allowed to grow was roughly 1.5 to 2 times that in the reactors without biofilms. We cannot explain the drop in adsorption from flush 1 to 2 with biofilm, but the adsorption increase in flushes 3 and 4 is likely due to biofilm growth.

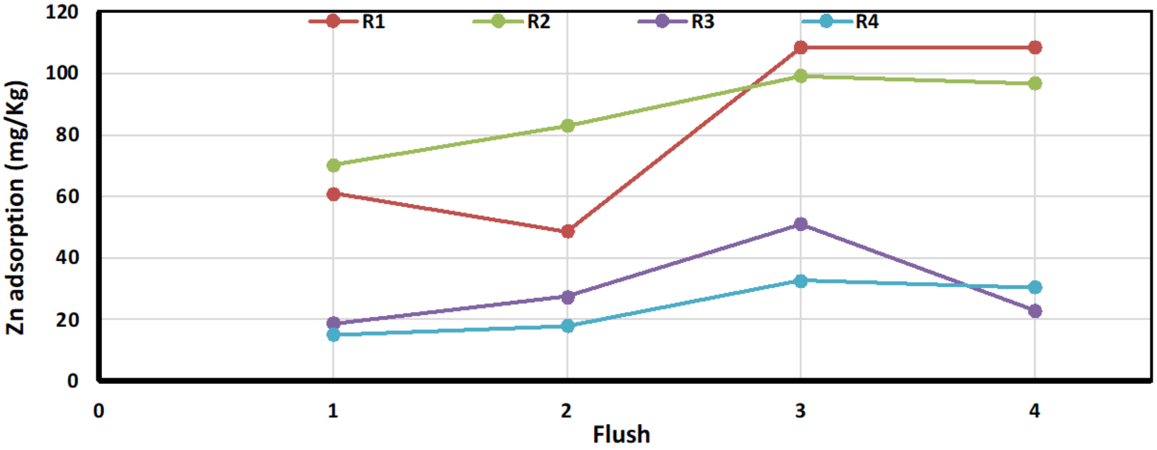

Figure 27. Zinc adsorption (mg Zn per kg wood chunks) after 72 h for each flush of four reactors without biofilm.

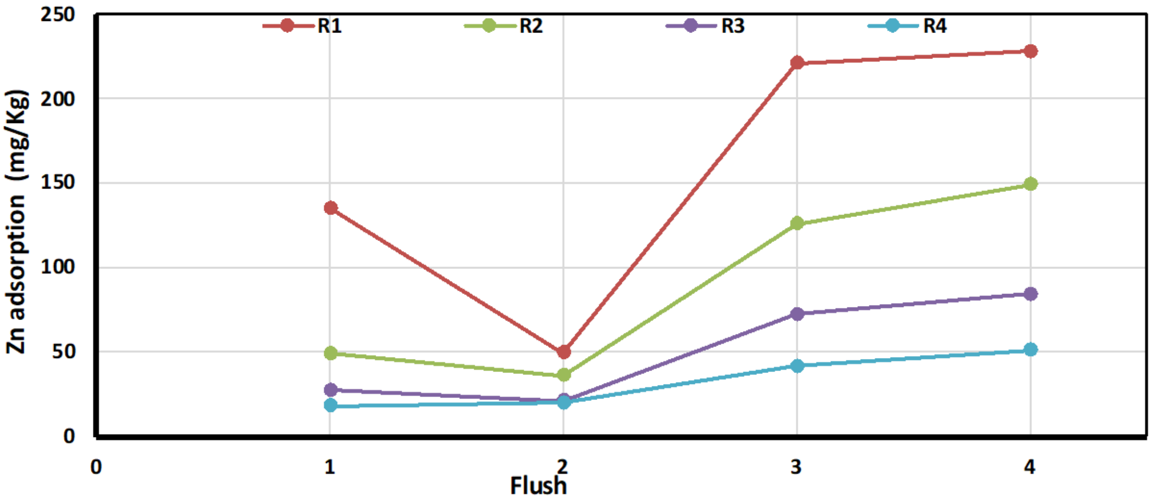

Figure 28. Zinc adsorption (mg Zn per kg wood chunks) after 72 h for each flush of four reactors with biofilm.

Leaching and adsorption of all 15 chemicals from the wood chunks indicated differences between the samples with biofilm and those without (see Table A-5 in Appendix). As stated previously, Cu and Zn were adsorbed by the wood chunks with substantially greater adsorption with a biofilm. Most of the chemicals not spiked into the samples leached from the wood chunks, but Al ,Ca, K, Mg, Mn, and Ni leached substantially less with the biofilm. Fe and P did not show much difference between leaching with and without biofilm, and Na leached substantially more with the biofilm. Virtually all samples of B, Cd, Cr, and Pb were below the limits of detection.

5.6 Summary

Zinc and Cu can be removed with the help of cedar wood chunks but one must consider the possibility of P and metal release from the wood chunks. However, long-term studies need to be conducted to see if P and metals leaching is persistent in or after 6 -10 flushes. It is possible that the wood chunks were contaminated with the leached metals, which would not be good as these wood chunks were designed for use in gardens.

Chapter 6: Expected research benefits

A primary benefit of this research is to establish the conditions under which TDA could be used in underground stormwater infiltration and storage/filtration facilities. A second benefit of this research would be to minimize eutrophication of the lakes receiving stormwater from underground stormwater storage/filtration facilities, which will ultimately benefit the aquatic ecosystem. The reduction of eutrophication in lakes receiving stormwaters will make lakes relatively more aesthetic, thereby increasing tourism, recreation, and additional revenue for the upkeep of lakes. In fact, the benefits will not only be limited to the aquatic ecosystem but to humans and other animals as well since we are dependent on the water bodies for our food/protein and freshwater needs. It will also find a useful application for the discarded tires, thereby limiting the environmental pollution caused by the dumping/landfilling of tires. In addition, it will minimize the space and funds invested in landfilling the discarded tire wastes.

In short, this research determines the potential of TDA for the remediation of pollutants (specifically, phosphorus and organic compounds) and prevent the leaching of zinc and copper from TDA during its application for the treatment of stormwater runoff.

TDA that avoids disposal and can be installed as an underground facility can reduce the lifetime costs of the material. A ton of whole end-of-life tires, taken to a confined licensed disposal facility in the Twin Cities Metropolitan Area would cost approximately $240 per ton for disposal. The same tires, manufactured and sold as TDA for stormwater treatment in an underground facility, would generate approximately $33/ton for TDA and freight from the manufacturer as value added. Thus, the base value gained from redistribution of used tires as TDA can be calculated as follows:

$$\frac{Value\ Added}{ton} = \frac{\$240}{ton} + \frac{\$33}{ton} = \frac{\$273}{ton} \tag{2}$$

An example of bids on underground storage costs is given in Table 5. An equivalent cost of a TDA system was approximated by TDA Manufacturing with review and approval by the authors of the report. Table 5 indicates that a TDA system would cost substantially less but would require more surface space due to the 50% porosity of the compressed TDA.

Table 5. Cost and other considerations of 810,000 cubic feet underground storage volume by the City of Wilmette, OR, compared to a similar cost of a TDA detention system (Wilmette Engineering and Public Works Department). Common items normalized by typical unit prices include Earth Excavation (Haul Excess Offsite, $50/Cubic Yard), Backfill (Aggregates and Excavated Stockpiled Materials, $50/Cubic Yard), Concrete Base Pad ($9/Square Foot) and Site Restoration ($6/Square Yard). A 20% allowance was applied to the construction cost subtotals for contingency. The equivalent TDA system was approximated by TDA Manufacturing for this report.

System	Normalized System Cost	Foot-print (ac)
Contech aluminized corrugated metal pipe and structures	$8,742,200	4.2
StormTrap modular precast concrete units	$9,808,700	3.5
Concrete box culvert	$11,242,100	3.7
GeoStorage reinforced walls overtopped by precast concrete plank roof	$11,892,000	3.9
Storm Tech elliptical arch segments of polypropylene and polyethylene resins	$13,772,400	5.4
TDA Manufacturing Tire-Derived Aggregate System	$4,800,000	~6.5-7

Currently, the only means of removing phosphate from stormwater runoff in Minnesota is the Iron Enhanced Sand Filter (Erickson et al. 2012), which is designed for surface filtration and has requirements of the site which cannot always be met. A sand filter needs to be designed and installed, which is not always practical and can be expensive. The underground TDA application is another means of removing phosphate from runoff, developed for a different application, underground practices that can fit under parking lots and other locations where surface treatment of stormwater is not practical or not cost-effective.

Thus, the research will result in:

- Cost savings – As shown in Eq. 2 and Table 5, reduction in the investment needed for the individual management of stormwater and discarded tires would result in cost savings.
- Land savings – No need to acquire a landfill space to dispose of discarded tires would save land and reduce the cost of developing new landfill space.
- Increased environmental benefits – The retention of phosphate by the TDA would reduce lake eutrophication and harmful algal blooms. In addition, the reduction of discarded tires would create environmental benefits.

Chapter 7: Conclusions

In addition to being a media that will adsorb phosphate, TDA in field applications is unlikely to release zinc and copper to result in effluent concentrations that are above the U.S. EPA's chronic toxicity criteria for freshwater biota. Singh et al. (2023) found that TDA would leach zinc, copper and iron to levels that exceed the chronic toxicity criteria for freshwater (U.S. EPA 2007). Subsequently, Singh et al. (2024) found that the presence of the one-month pre-developed biofilm reduced all zinc and copper leached from both Trad-TDA and WE-TDA to a value below the chronic toxicity criteria. One purpose of this study was to determine how soon a biofilm without a one-month predevelopment would result in zinc and copper being leached from the TDA that would not exceed chronic toxicity criteria. The result, assuming a chamber with a 50% porosity, is that pre-rinsed zinc was below the criteria by the second flush of river water and copper did not exceed the criteria. Iron exceeded the toxic criteria for between zero and 7 flushes; however, iron in oxic water (DO > 1 mg/L) would be mostly present in the particulate form, which would settle in the TDA and downstream of the chamber. If the chamber becomes anoxic, it is still likely that the iron would precipitate when it reaches the storm sewer due to a typically high degree of aeration (Huisman, et al. 2004). Finally, Tables A2 - A4 indicate that no single effluent sample violated acute toxicity standards (U.S. EPA 2007) for zinc, copper or iron. Indications are that biofilms capable of adsorbing zinc and copper will develop quickly when exposed to stormwater, which has nutrient concentrations similar to river water at the Saint Anthony Falls Laboratory.

We can therefore conclude the following:

1. TDA is a media that can retain phosphate (SRP) for more than 72 flushes (Singh and Gulliver 2024), or roughly 8 to 9 years in the upper Midwest of the United States.
2. The WE-TDA retained phosphate somewhat better than the Trad-TDA, but not markedly. The Trad-TDA used in this study also had some exposed wires that could have increased retention of phosphate. A higher adsorption from WE-TDA indicates an opportunity for reutilization of a manufacturing byproduct, produced while generating Traditional TDA.
3. Biofilms growing on the TDA will retain much of the zinc, copper and iron that is released from the TDA. Zinc and iron were found to be below the U.S. EPA's chronic toxicity criteria after one and between one and seven flushes, respectively. Copper was not released from the TDA above the chronic toxicity criteria. No single effluent sample violated the U.S. EPA's acute toxicity standards for zinc, copper or iron.
4. While there was a measurable release of PFAS from TDA, the concentrations were relatively low and appeared to be similar to typical urban concentrations, including residential land. The information supports the notion that TDA, with its low PFAS release and low adsorption capacity, could be considered for various applications, including stormwater treatment, without significant PFAS-release concerns.
5. Sorption of zinc and copper to biochar's surfaces has generally resulted in greater than an order of magnitude reduction in leachate, regardless of the biochar used. Therefore, biochar would be an appropriate choice as a mix with TDA to reduce the leaching of zinc and copper. One drawback, however, was the cost of biochar, which may be prohibitive for a large water storage system.

6. Wood chunks were identified as an alternative source to mix in with TDA that would not fluidize. Zinc and copper can be removed with the help of cedar wood chunks but one must consider the possibility of phosphorus and metal release from wood chunks. In the end, the biofilm was an appropriate leaching remediation, so that no mixture of supplementary material with TDA was deemed necessary.
7. TDA exposed to the atmosphere (Lid-off) grew biofilm at roughly half the rate of TDA that was kept in high humidity (Lid-on) of 97% ± 3.7%. The Lid-off biofilm, however, was still capable of retaining leached zinc, copper and iron, for the most part, even after a 4-week dry period. This indicates that a metal-retaining biofilm will grow on the TDA even when exposed to the atmosphere, such as in bioretention facilities and other surface infiltration practices.
8. TDA is a porous material with a ~50% porosity after compaction that are presumed to result in the following properties:
    a. Greater water storage per unit volume than achieved with gravel or sand
    b. Less resistance to flow through a TDA system (This assumption needs to be verified with experiments.)
9. TDA that avoids disposal and can be installed as an underground facility can reduce the lifetime costs of the material. A ton of whole end-of-life tires, taken to a confined licensed disposal facility in the Twin Cities Metropolitan Area would cost approximately $240/ton for disposal. The same tires, manufactured and sold as TDA for stormwater treatment in an underground facility, would currently generate approximately $33/ton for TDA and freight from the manufacturer as value added. Thus, the value added for the application of 1 ton of TDA would be $273.
10. Currently, the only means of removing phosphate from stormwater runoff in Minnesota is the Iron Enhanced Sand Filter (Erickson et al. 2012), which is designed for surface filtration and has requirements of the site that cannot always be met. A sand filter needs to be designed and installed, which is not always practical and can be expensive. The underground TDA application is another means of removing phosphate from runoff, developed for a different application, underground practices that can fit under parking lots and other locations where surface treatment of stormwater is not practical or cost-effective.

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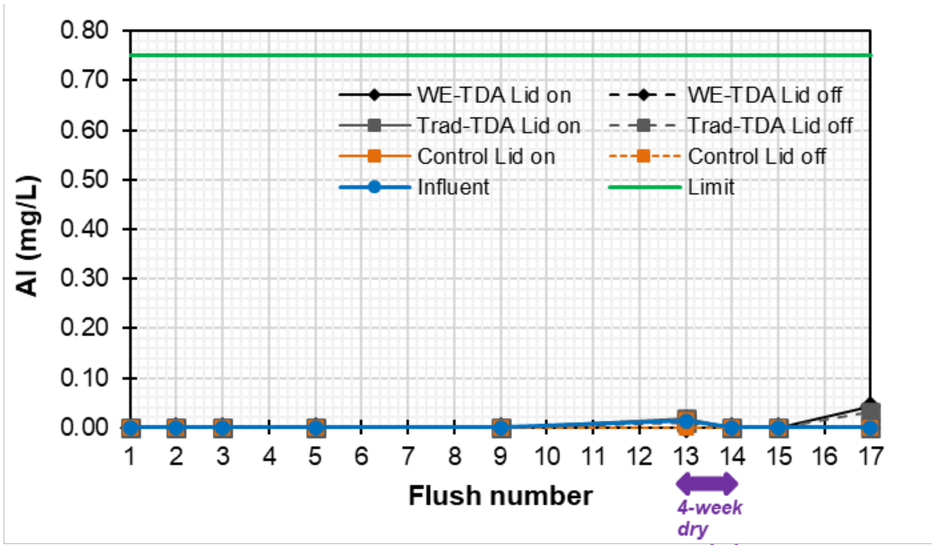
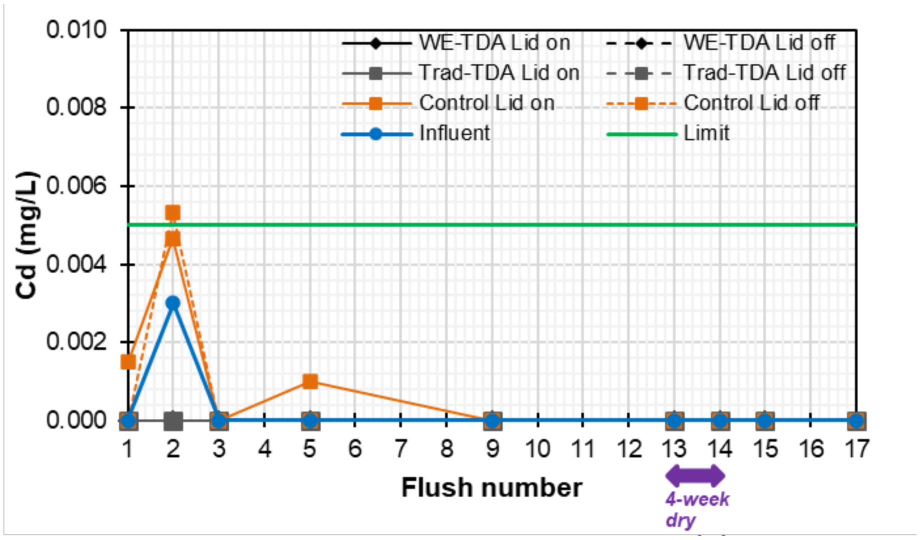
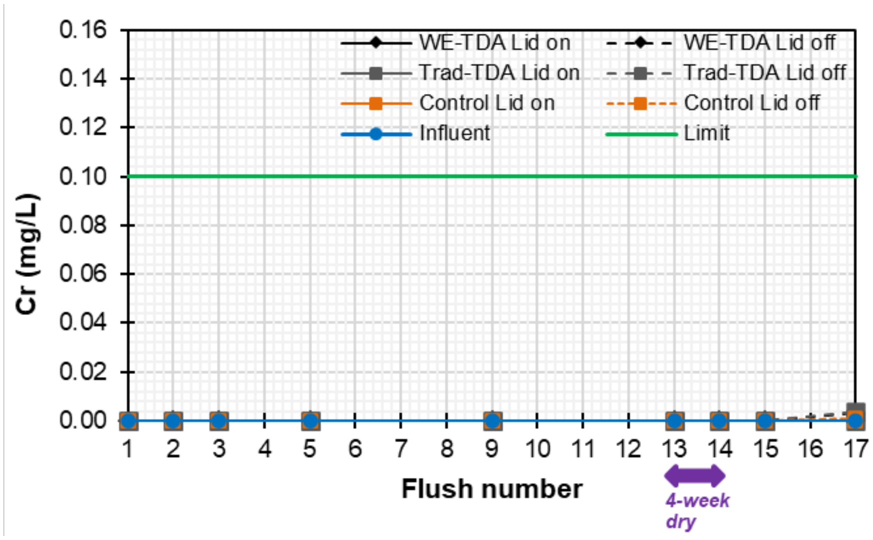
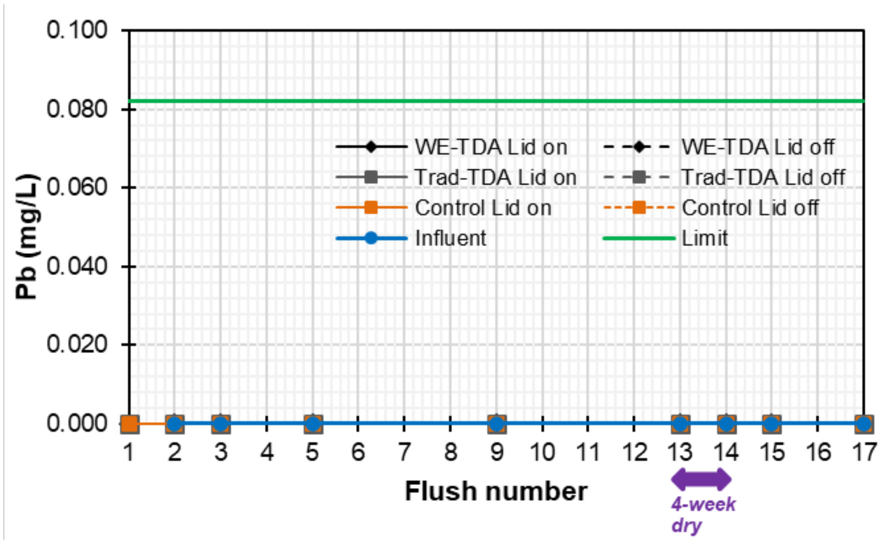
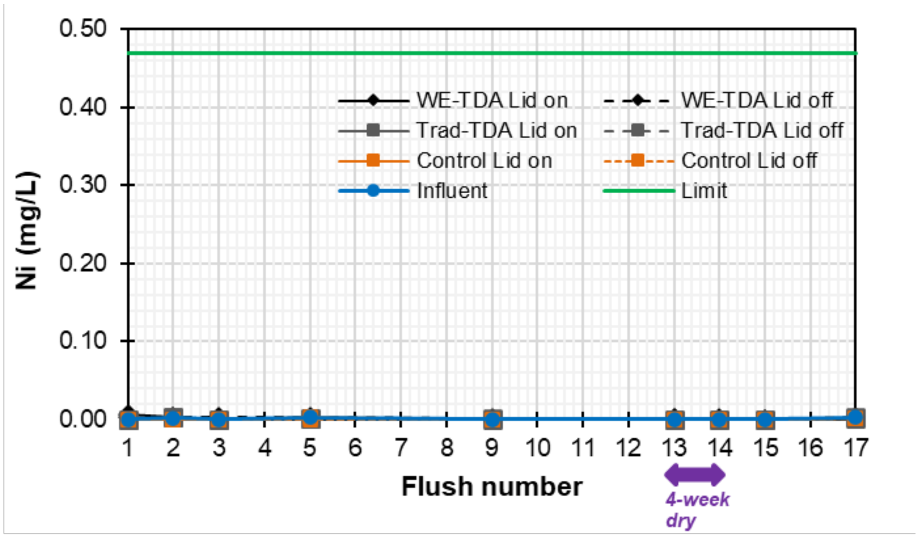
Appendix A: Phosphate and Metal Concentrations from Adsorption and Leaching Tests on TDA

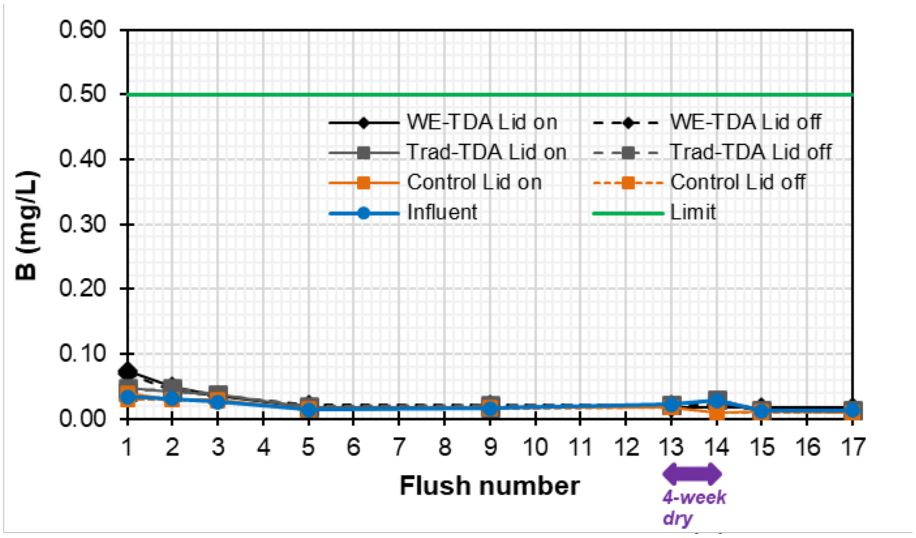

Al (mg/L)
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
Flush number
4-week dry
WE-TDA Lid on
WE-TDA Lid off
Trad-TDA Lid on
Trad-TDA Lid off
Control Lid on
Control Lid off
Influent
Limit

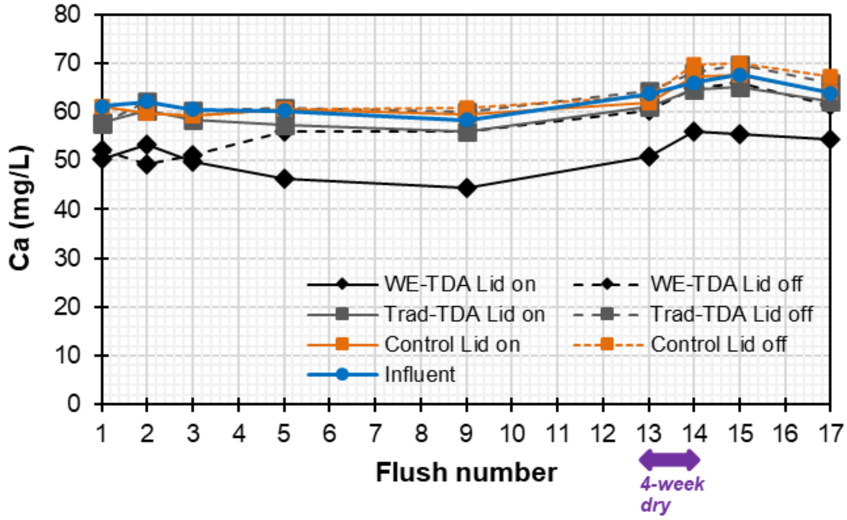

Cd (mg/L)
0.010
0.008
0.006
0.004
0.002
0.000
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
Flush number
4-week dry
WE-TDA Lid on
WE-TDA Lid off
Trad-TDA Lid on
Trad-TDA Lid off
Control Lid on
Control Lid off
Influent
Limit

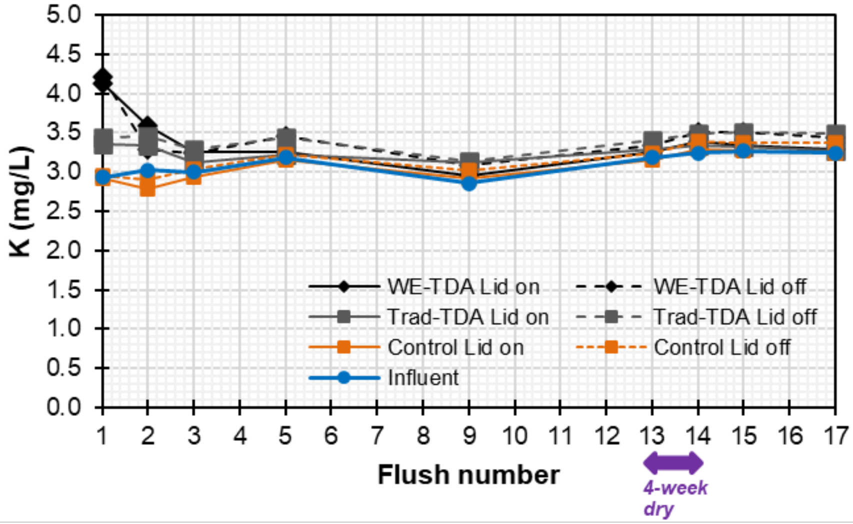

Cr (mg/L)
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
Flush number
4-week dry
WE-TDA Lid on
WE-TDA Lid off
Trad-TDA Lid on
Trad-TDA Lid off
Control Lid on
Control Lid off
Influent
Limit


Pb (mg/L)
0.100
0.080
0.060
0.040
0.020
0.000
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
Flush number
4-week dry
WE-TDA Lid on
Trad-TDA Lid on
Control Lid on
Influent
WE-TDA Lid off
Trad-TDA Lid off
Control Lid off
Limit


Ni (mg/L)
0.50
0.40
0.30
0.20
0.10
0.00
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
Flush number
4-week dry
WE-TDA Lid on
Trad-TDA Lid on
Control Lid on
Influent
WE-TDA Lid off
Trad-TDA Lid off
Control Lid off
Limit


B (mg/L)
0.60
0.50
0.40
0.30
0.20
0.10
0.00
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
Flush number
4-week dry
WE-TDA Lid on
Trad-TDA Lid on
Control Lid on
Influent
WE-TDA Lid off
Trad-TDA Lid off
Control Lid off
Limit


Ca (mg/L)
0
10
20
30
40
50
60
70
80
WE-TDA Lid on
WE-TDA Lid off
Trad-TDA Lid on
Trad-TDA Lid off
Control Lid on
Control Lid off
Influent
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
Flush number
4-week dry


K (mg/L)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
WE-TDA Lid on
WE-TDA Lid off
Trad-TDA Lid on
Trad-TDA Lid off
Control Lid on
Control Lid off
Influent
1
2
3
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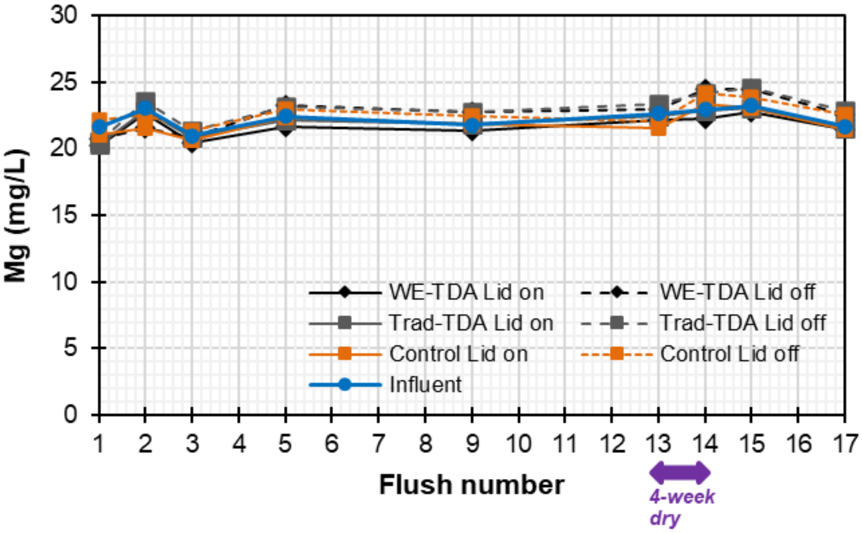
6
7
8
9
10
11
12
13
14
15
16
17
Flush number
4-week dry


Mg (mg/L)
0
5
10
15
20
25
30
WE-TDA Lid on
WE-TDA Lid off
Trad-TDA Lid on
Trad-TDA Lid off
Control Lid on
Control Lid off
Influent
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
Flush number
4-week dry

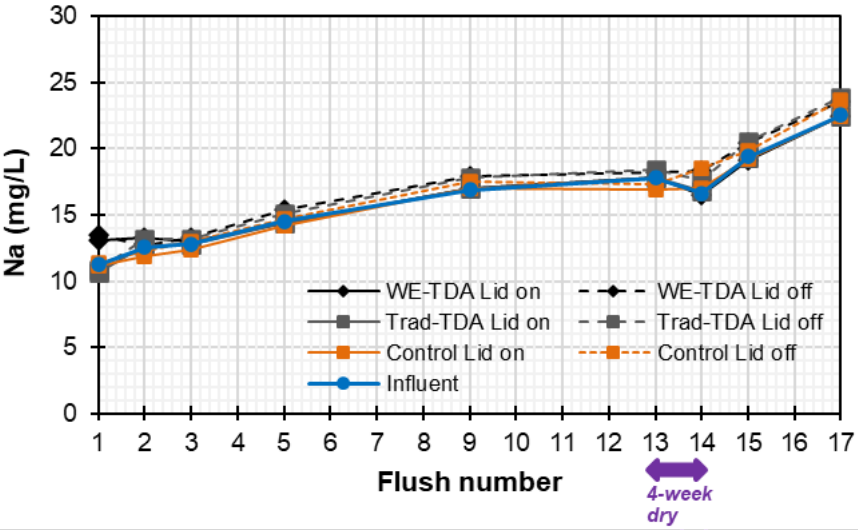


Figure A-1. Concentrations (mean of five replicate values) of metals after application of TDA in river water. Trad = Traditional TDA, WE = wire-exposed TDA, Influent = filtered river water, Limit = chronic toxicity criteria for freshwater biota (U.S. EPA 2007) if shown. Plots shown are for aluminum (Al), cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni), boron (B), calcium (Ca), potassium (K), magnesium (Mg), and sodium (Na).

Table A-1. Data for concentrations of phosphate after application of TDA in river water. Trad = Traditional TDA, WE = wire-exposed TDA, Influent = filtered river water. Concentrations in the five replicate batch buckets are provided for each treatment. The phosphorus water quality limit is 0.050 mg/L, which is the U.S. EPA criteria of phosphate concentration for prevention of eutrophication in lakes (Litke 1999).

Influent: Phosphate (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	n/a	0.085	0.102	0.053	0.023	0.034	0.025	0.021	0.023
2	n/a	0.084	0.098	0.061	0.023	0.034	0.025	0.024	0.027
3	n/a	0.084	0.096	0.062	0.022	0.032	0.025	0.021	0.024

Trad-TDA Lid ON: Phosphate (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	0.0445	<0.027	0.0400	0.0170	<0.005	0.0060	0.0090	0.0070	0.0040
2	0.0300	<0.027	0.0360	0.0140	<0.005	0.0070	0.0100	0.0080	0.0050
3	0.0450	<0.027	0.0395	0.0140	<0.005	0.0040	0.0100	0.0090	0.0060
4	0.0340	<0.027	0.0390	0.0210	<0.005	0.0070	0.0090	0.0080	0.0060
5	0.0200	<0.027	0.0240	0.0170	<0.005	0.0060	0.0090	0.0070	0.0050

WE-TDA Lid ON: Phosphate (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	0.042	0.038	0.023	0.013	<0.005	0.004	0.007	0.004	0.004
2	0.026	<0.027	0.02	0.0095	<0.005	0.004	0.008	0.005	0.004
3	0.043	0.038	0.033	0.018	<0.005	0.005	0.006	0.007	0.004
4	0.022	<0.027	0.017	0.013	<0.005	<0.003	0.005	0.005	0.003
5	0.045	0.039	0.034	0.017	<0.005	0.004	0.006	0.005	0.003

Trad-TDA Lid OFF: Phosphate (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	0.038	<0.027	0.018	0.017	0.006	0.006	0.008	0.010	0.008
2	0.071	<0.027	0.025	0.019	0.007	0.008	0.009	0.009	0.006
3	0.194	0.027	0.160	0.126	0.012	0.012	0.012	0.017	0.013
4	0.061	0.029	0.025	0.024	0.008	0.007	0.011	0.010	0.005
5	0.015	0.010	0.017	0.015	<0.005	0.006	0.007	0.008	0.006

WE-TDA Lid OFF: Phosphate (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	0.037	0.018	0.009	0.01	<0.005	0.005	0.006	0.006	0.006
2	0.022	0.009	<0.008	0.01	<0.005	0.004	0.007	0.008	0.006
3	0.024	0.02	0.011	0.012	<0.005	0.004	0.006	0.009	0.0045
4	0.035	0.017	0.008	0.013	<0.005	0.003	0.004	0.005	0.008
5	0.035	0.018	0.011	0.011	<0.005	0.004	0.006	0.006	0.006

Control Lid ON: Phosphate (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	0.073	0.078	0.104	0.060	0.023	0.030	0.021	0.023	0.024
2	0.086	0.078	0.104	0.062	0.022	0.030	0.026	0.025	0.027
3	0.081	0.083	0.101	0.058	0.023	0.029	0.023	0.022	0.026

Control Lid OFF: Phosphate (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	0.080	0.084	0.097	0.058	0.020	0.025	0.022	0.020	0.026
2	0.087	0.086	0.098	0.057	0.023	0.024	0.021	0.021	0.026
3	0.083	0.088	0.099	0.058	0.019	0.027	0.022	0.020	0.027

Table A-2. Data for concentrations of zinc after application of TDA in river water. Trad = Traditional TDA, WE = wire-exposed TDA, Influent = filtered river water. Concentrations in the five replicate batch buckets are provided for each treatment. For zinc, 0.12 mg/L is the chronic toxicity criteria for freshwater biota (U.S. EPA 2007).

Influent: Zinc (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	n/a	0.007	0.011	0.007	0.008	0.009	0.035	0.007	0.009
2	n/a	0.007	0.010	0.007	0.006	0.006	0.008	0.007	0.009
3	n/a	0.006	0.016	0.007	0.005	0.006	0.010	0.006	0.010

Trad-TDA Lid ON: Zinc (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	0.151	0.079	0.064	0.027	0.028	0.033	0.084	0.047	0.030
2	0.070	0.057	0.036	0.017	0.021	0.014	0.029	0.020	0.016
3	0.211	0.131	0.102	0.048	0.032	0.037	0.070	0.046	0.043
4	0.129	0.061	0.051	0.034	0.027	0.027	0.051	0.038	0.037
5	0.134	0.064	0.051	0.019	0.018	0.020	0.038	0.034	0.026

WE-TDA Lid ON: Zinc (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	0.07	0.015	0.012	0.006	0.005	0.01	0.046	0.007	0.006
2	0.084	0.012	0.012	0.009	0.005	0.004	0.015	0.007	0.005
3	0.091	0.011	0.009	0.006	0.003	0.004	0.01	0.005	0.006
4	0.061	0.008	0.008	0.005	0.004	0.004	0.011	0.006	0.005
5	0.109	0.022	0.022	0.009	0.006	0.008	0.015	0.009	0.009

Trad-TDA Lid OFF: Zinc (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	0.228	0.093	0.075	0.058	0.061	0.060	0.061	0.055	0.051
2	0.162	0.091	0.084	0.060	0.053	0.053	0.054	0.046	0.045
3	0.279	0.089	0.074	0.048	0.032	0.029	0.034	0.032	0.032
4	0.223	0.064	0.060	0.030	0.025	0.032	0.031	0.037	0.033
5	0.064	0.012	0.016	0.014	0.012	0.012	0.013	0.012	0.012

WE-TDA Lid OFF: Zinc (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	0.042	0.007	0.005	0.005	0.051	0.009	0.012	0.010	0.011
2	0.026	0.007	0.005	0.008	0.008	0.009	0.012	0.009	0.011
3	0.059	0.011	0.007	0.012	0.016	0.017	0.022	0.013	0.012
4	0.088	0.022	0.012	0.023	0.019	0.017	0.020	0.016	0.017
5	0.052	0.023	0.006	0.010	0.016	0.012	0.017	0.011	0.013

Control Lid ON: Zinc (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	<0.003	0.007	0.008	0.006	0.005	0.005	0.006	0.006	0.007
2	<0.003	0.004	0.008	0.007	0.005	0.004	0.006	0.005	0.007
3	0.007	0.013	0.013	0.006	0.005	0.005	0.007	0.007	0.007

Control Lid OFF: Zinc (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	<0.003	0.006	0.008	0.006	0.005	0.004	0.008	0.006	0.007
2	<0.003	0.007	0.01	0.006	0.006	0.005	0.007	0.005	0.007
3	<0.006	0.009	0.009	0.006	0.005	0.005	0.007	0.005	0.006

Table A-3. Data for concentrations of copper after application of TDA in river water. Trad = Traditional TDA, WE = wire-exposed TDA, Influent = filtered river water. Concentrations in the five replicate batch buckets are provided for each treatment. For copper, 0.013 mg/L is the chronic toxicity criteria for freshwater biota (U.S. EPA 2007).

Influent: Copper (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	n/a	0.001	0.002	<0.001	0.002	0.002	<0.001	<0.001	0.0015
2	n/a	0.002	0.002	0.001	0.002	0.001	<0.001	<0.001	0.001
3	n/a	0.001	0.002	0.002	0.001	<0.001	0.001	<0.001	0.001

Trad-TDA Lid ON: Copper (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	0.002	0.002	0.002	0.004	0.002	0.002	0.002	0.002	0.002
2	0.003	0.002	0.002	0.002	0.002	0.002	0.003	0.003	0.002
3	0.004	0.002	0.002	<0.001	0.002	0.002	0.003	0.002	0.002
4	0.004	0.003	0.003	0.002	0.003	0.003	0.003	0.003	0.002
5	0.005	0.002	0.002	0.002	0.002	0.003	0.003	0.003	0.002

WE-TDA Lid ON: Copper (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	0.001	0.001	0.001	0.001	0.002	0.001	0.003	0.002	0.002
2	<0.001	<0.001	0.001	0.001	0.001	0.001	0.003	0.003	0.002
3	<0.001	0.001	0.002	<0.001	0.001	0.002	0.003	0.003	0.002
4	<0.001	0.002	0.002	0.001	0.001	0.002	0.005	0.003	0.002
5	<0.001	<0.001	<0.001	0.001	0.001	0.002	0.003	0.003	0.002

Trad-TDA Lid OFF: Copper (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	0.003	0.003	0.003	0.002	0.002	0.002	0.002	0.002	0.002
2	0.002	0.002	0.002	0.001	0.002	0.002	0.002	0.001	0.002
3	0.003	0.003	0.002	0.001	0.002	<0.001	0.001	0.001	0.002
4	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
5	0.010	0.002	0.002	0.003	0.004	0.003	0.003	0.003	0.003

WE-TDA Lid OFF: Copper (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	0.001	0.002	0.001	0.002	0.006	0.005	0.004	0.004	0.004
2	<0.001	<0.001	0.001	0.002	0.004	0.004	0.003	0.003	0.003
3	0.002	0.001	0.001	0.002	0.004	0.0035	0.0035	0.003	0.004
4	0.002	0.002	0.002	0.002	0.003	0.003	0.003	0.003	0.004
5	0.001	0.001	<0.001	0.001	0.004	0.004	0.003	0.004	0.007

Control Lid ON: Copper (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	<0.001	0.001	0.002	0.002	0.001	0.001	<0.001	<0.001	0.001
2	<0.001	0.002	0.002	0.001	0.001	<0.001	0.001	0.001	0.001
3	<0.001	0.001	0.002	0.001	0.001	0.001	0.001	<0.001	0.002

Control Lid OFF: Copper (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	<0.001	0.001	0.002	0.002	0.001	<0.001	0.001	<0.001	0.001
2	<0.001	0.002	0.002	0.001	0.001	<0.001	0.001	<0.001	0.001
3	<0.001	0.001	0.002	0.001	0.001	0.001	0.001	<0.001	0.001

Table A-4. Data for concentrations of iron after application of TDA in river water. Trad = Traditional TDA, WE = wire-exposed TDA, Influent = filtered river water. Concentrations in the five replicate batch buckets are provided for each treatment. For iron, 1 mg/L is the chronic toxicity criteria for freshwater biota (U.S. EPA 2007).

Influent: Iron (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	n/a	0.057	0.097	0.036	0.0415	0.0785	0.0885	0.077	0.095
2	n/a	0.058	0.097	0.036	0.051	0.078	0.095	0.095	0.108
3	n/a	0.058	0.098	0.036	0.051	0.079	0.102	0.081	0.115

Trad-TDA Lid ON: Iron (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	1.945	0.913	1.825	0.742	0.25	0.194	0.268	0.114	0.064
2	2.244	1.264	2.789	0.504	0.256	0.168	0.203	0.115	0.055
3	1.927	1.259	2.848	0.916	0.257	0.188	0.175	0.14	0.085
4	1.677	1.154	1.419	0.791	0.275	0.24	0.26	0.17	0.098
5	2.006	1.338	1.629	0.752	0.376	0.23	0.211	0.173	0.098

WE-TDA Lid ON: Iron (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	1.136	0.626	1.063	0.361	0.212	0.176	0.219	0.245	0.18
2	1.478	0.386	0.666	0.3915	0.407	0.22	0.392	0.321	0.188
3	2.237	0.373	0.78	0.483	0.211	0.201	0.396	0.227	0.205
4	2.073	0.238	0.685	0.748	0.588	0.18	0.476	0.3265	0.235
5	1.416	0.81	1.873	0.743	0.845	0.482	0.607	0.454	0.419

Trad-TDA Lid OFF: Iron (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	1.131	0.714	0.787	0.435	0.217	0.176	0.217	0.155	0.078
2	0.894	0.8	0.823	0.365	0.13	0.132	0.325	0.231	0.121
3	0.363	0.458	0.562	0.432	0.306	0.211	0.288	0.231	0.145
4	1.606	0.709	0.688	0.446	0.226	0.266	0.184	0.192	0.107
5	0.651	0.21	0.427	0.415	0.287	0.304	0.276	0.227	0.129

WE-TDA Lid OFF: Iron (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	0.873	0.138	0.112	0.248	0.375	0.408	0.532	0.529	0.593
2	0.268	0.104	0.088	0.310	0.260	0.393	0.414	0.400	0.557
3	1.046	0.077	0.100	0.434	0.345	0.363	0.450	0.364	0.545
4	1.046	0.224	0.163	0.630	0.315	0.335	0.351	0.145	0.365
5	0.648	0.139	0.086	0.316	0.442	0.234	0.336	0.224	0.370

Control Lid ON: Iron (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	0.055	0.041	0.058	0.019	0.031	0.053	0.044	0.047	0.031
2	0.268	0.104	0.088	0.018	0.032	0.060	0.058	0.059	0.054
3	1.046	0.077	0.100	0.018	0.037	0.063	0.069	0.073	0.064

Control Lid OFF: Iron (mg/L)

Replicate	Flush #1	Flush #1	Flush #2	Flush #4	Flush #8	Flush #12	Flush #13	Flush #14	Flush #16
1	0.055	0.041	0.058	0.019	0.029	0.057	0.078	0.043	0.034
2	0.268	0.104	0.088	0.018	0.038	0.065	0.084	0.060	0.055
3	1.046	0.077	0.100	0.018	0.031	0.072	0.084	0.058	0.070

Table A-5. Adsorption and Leaching results for 15 chemicals. Samples 1 through 20 are of wood chunks leaching into synthetic stormwater. Samples 21 through 26 indicate the water that the biofilm was exposed to for the month of biofilm growth. Samples 27 through 46 are of wood chunks with biofilm leaching into synthetic stormwater.

Flush	Sample ID	Reactor	Al <0.020	B <0.010	Ca <0.017	Cd <0.003	Cr <0.001	Cu <0.001	Fe <0.001	K <0.039	Mg <0.002	Mn <0.001	Na <0.005	Ni <0.004	P <0.077	Pb <0.016	Zn <0.013
Flush 1	**1**	**Influent**	0.110	<0.010	0.260	<0.003	<0.001	0.519	0.051	0.060	0.016	0.012	0.102	<0.004	<0.077	<0.016	7.116
	1 DUP	**Influent**	0.102	<0.010	0.233	<0.003	<0.001	0.520	0.051	0.040	0.016	0.013	0.099	<0.004	<0.077	<0.016	7.165
	2	**1**	0.247	<0.010	1.839	<0.003	<0.001	0.422	0.069	20.654	2.675	0.369	0.195	0.022	<0.077	<0.016	6.099
	3	**2**	0.624	<0.010	2.642	<0.003	<0.001	0.338	0.185	37.850	9.741	1.031	0.255	0.028	0.479	<0.016	4.776
	4	**3**	1.533	<0.010	5.912	<0.003	<0.001	0.342	0.173	78.246	16.153	1.701	0.325	0.091	0.856	0.026	5.866
	5	**4**	1.494	0.016	8.097	<0.003	<0.001	0.307	0.375	98.506	16.976	2.555	0.530	0.139	3.221	0.019	5.103
Flush 2	**6**	**Influent**	<0.020	<0.010	0.324	<0.003	<0.001	0.407	0.040	1.992	0.312	0.045	0.040	<0.004	0.121	<0.016	6.683
	7	**1**	0.103	<0.010	1.053	<0.003	<0.001	0.350	0.037	8.637	1.447	0.163	0.349	0.009	0.097	<0.016	5.873
	8	**2**	0.217	<0.010	1.389	<0.003	<0.001	0.309	0.067	14.586	5.046	0.383	0.078	0.012	0.145	0.017	3.917
	9	**3**	0.666	<0.010	3.069	<0.003	<0.001	0.270	0.083	33.599	8.054	0.753	0.171	0.041	0.294	<0.016	4.855
	10	**4**	0.874	<0.010	5.334	<0.003	<0.001	0.168	0.108	60.159	11.291	1.374	0.267	0.073	1.492	<0.016	4.279
Flush 3	**11**	**Influent**	<0.020	<0.010	0.117	<0.003	<0.001	0.468	0.034	0.062	0.006	0.002	0.024	<0.004	<0.077	<0.016	7.537
	12	**1**	0.067	<0.010	0.723	<0.003	<0.001	0.356	0.033	5.529	1.036	0.114	0.097	0.006	0.125	<0.016	5.730
	13	**2**	0.171	<0.010	1.299	<0.003	<0.001	0.326	0.057	8.064	3.835	0.289	0.105	0.009	0.115	<0.016	4.233
	14	**3**	0.434	<0.010	2.437	<0.003	<0.001	0.280	0.053	19.743	6.164	0.561	0.179	0.025	0.160	<0.016	4.129
	15	**4**	0.508	<0.010	3.403	<0.003	<0.001	0.187	0.051	35.119	6.948	0.811	0.180	0.040	1.005	<0.016	3.176
Flush 4	**16**	**Influent**	<0.020	<0.010	0.137	<0.003	<0.001	0.472	0.033	0.043	0.009	0.002	0.029	<0.004	0.093	<0.016	7.196
	17	**1**	0.091	<0.010	0.863	<0.003	<0.001	0.334	0.033	4.454	1.082	0.117	0.084	0.006	<0.077	<0.016	5.391
	18	**2**	0.130	<0.010	1.198	<0.003	<0.001	0.325	0.039	5.597	3.634	0.281	0.078	0.008	0.078	<0.016	3.976
	19	**3**	0.384	<0.010	2.399	<0.003	<0.001	0.354	0.043	13.056	6.198	0.546	0.050	0.024	0.211	<0.016	5.666
	20	**4**	0.427	<0.010	3.211	<0.003	<0.001	0.183	0.035	25.457	6.710	0.748	0.151	0.033	0.854	<0.016	3.127
Biofilm Influent (day 1) before	**21**		0.050	0.018	26.390	<0.003	<0.001	0.002	0.174	39.173	86.049	0.129	122.29	0.005	39.705	<0.016	0.031
	21 DUP		0.069	<0.010	26.965	<0.003	<0.001	0.003	0.181	39.550	84.392	0.135	123.60	<0.004	41.572	<0.016	0.060
	22		0.041	0.017	26.143	<0.003	0.001	0.002	0.178	38.778	84.775	0.130	120.76	0.006	39.186	<0.016	0.033
	23		0.055	0.017	26.502	<0.003	<0.001	0.001	0.175	39.338	84.838	0.134	122.37	0.005	40.267	<0.016	0.029
Influent (Day 28) after	**24**		0.212	0.025	36.770	<0.003	<0.001	0.011	0.040	117.06	97.725	0.710	126.16	0.049	30.046	<0.016	0.039
	25		0.226	0.024	37.066	<0.003	<0.001	0.010	0.038	118.12	97.211	0.716	126.56	0.049	30.334	<0.016	0.040
	26		0.237	0.023	37.190	<0.003	<0.001	0.010	0.041	118.42	98.557	0.721	127.37	0.047	30.642	<0.016	0.043

			Al	B	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	Zn
Flush	**Sample ID**	**Reactor**	<0.020	<0.010	<0.017	<0.003	<0.001	<0.001	<0.001	<0.039	<0.002	<0.001	<0.005	<0.004	<0.077	<0.016	<0.013
Flush 1	**27**	**Influent**	<0.020	<0.010	0.209	<0.003	<0.001	0.588	0.029	0.322	0.026	0.003	0.183	<0.004	<0.077	<0.016	9.072
	28	**1**	<0.020	<0.010	0.749	<0.003	<0.001	0.414	0.033	2.272	0.980	0.067	1.755	<0.004	0.796	<0.016	6.817
	29	**2**	<0.020	<0.010	0.751	<0.003	<0.001	0.416	0.031	3.563	1.076	0.068	2.368	<0.004	0.894	<0.016	7.437
	30	**3**	<0.020	<0.010	0.926	<0.003	<0.001	0.333	0.026	4.304	1.294	0.083	2.887	<0.004	1.111	<0.016	7.246
	31	**4**	<0.053	<0.008	1.312	<0.003	<0.001	0.296	0.032	4.606	1.851	0.135	3.317	<0.008	1.216	<0.013	6.661
Flush 2	**32**	**Influent**	<0.053	<0.008	0.117	<0.003	<0.001	0.575	0.033	<0.045	0.003	<0.001	0.020	<0.008	<0.239	<0.013	5.887
	33	**1**	<0.053	<0.008	1.630	<0.003	<0.001	0.294	0.037	0.635	0.664	0.081	0.769	<0.008	<0.239	<0.013	5.067
	34	**2**	0.055	<0.008	1.482	<0.003	<0.001	0.260	0.041	2.119	1.648	0.320	1.604	<0.008	1.510	<0.013	4.697
	35	**3**	0.132	<0.008	3.931	<0.003	0.006	0.239	0.342	3.550	2.363	0.402	59.784	0.024	1.723	<0.013	4.505
	36	**4**	0.146	<0.008	2.927	<0.003	<0.001	0.154	0.040	5.713	3.992	0.517	4.304	0.010	2.145	<0.013	3.237
Flush 3	**37**	**Influent**	<0.053	<0.008	0.163	<0.003	<0.001	0.787	0.039	<0.045	0.003	0.001	0.018	<0.008	<0.239	<0.013	8.514
	38	**1**	<0.053	<0.008	0.626	<0.003	<0.001	0.320	0.033	0.210	0.477	0.047	0.221	<0.008	<0.239	<0.013	4.835
	39	**2**	<0.053	<0.008	0.936	<0.003	<0.001	0.189	0.036	1.034	1.019	0.162	0.823	<0.008	0.457	<0.013	4.316
	40	**3**	<0.053	<0.008	1.256	<0.003	<0.001	0.184	0.040	2.406	1.558	0.187	1.815	<0.008	0.540	<0.013	3.705
	41	**4**	0.150	<0.008	2.209	<0.003	<0.001	0.110	0.044	3.122	2.629	0.300	2.181	<0.008	0.690	<0.013	3.003
Flush 4	**42**	**Influent**	<0.053	<0.008	0.162	<0.003	<0.001	0.727	0.031	<0.045	0.004	<0.001	0.007	<0.008	<0.239	<0.013	9.217
	43	**Influent**	<0.053	<0.008	0.552	<0.003	<0.001	0.332	0.042	0.128	0.438	0.040	0.118	<0.008	<0.239	<0.013	5.416
	43 DUP	**1**	<0.053	<0.008	0.654	<0.003	<0.001	0.336	0.042	0.177	0.444	0.040	0.123	<0.008	<0.239	<0.013	5.721
	44	**2**	<0.053	<0.008	0.874	<0.003	<0.001	0.170	0.036	0.562	1.005	0.137	0.407	<0.008	0.246	<0.013	4.253
	45	**3**	<0.053	<0.008	1.073	<0.003	<0.001	0.206	0.032	1.831	1.414	0.135	1.299	<0.008	<0.239	<0.013	3.603
	46	**4**	0.119	<0.008	1.903	<0.003	<0.001	0.116	0.039	2.107	2.310	0.225	1.419	<0.008	0.363	<0.013	2.421