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Wildfire Impacts on Stormwater Biofilter Functions:
Implications on Their Design and Resilience

A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy
in Civil Engineering

by

Onja Davidson Raelison

2024

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ABSTRACT OF THE DISSERTATION

Wildfire Impacts on Stormwater Biofilter Functions:
Implications on Their Design and Resilience

by

Onja Davidson Raelison

Doctor of Philosophy in Civil Engineering
University of California, Los Angeles, 2024

Professor Sanjay K. Mohanty, Chair

Wildfires are becoming more frequent and intense due to climate change, especially in the southwestern US. Wildfires occur in vulnerable urban areas prone to intense droughts and extreme floods, exacerbating water scarcity issues. Polluted runoff from wildfires can contaminate the limited surface water available for drinking water. To protect downstream water quality, green infrastructure such as stormwater biofilters could be implemented to remove pollutants from post-fire runoff. However, the impacts of wildfire residues on their functions remain unknown. This dissertation aims to understand how green infrastructure can mitigate wildfire impacts on water quality and how to design innovative wildfire-resilient stormwater biofilters.

This dissertation specifically addresses four research questions. (1) How and to what extent are wildfires impacting surface water quality? (2) How do wildfire residues affect the physical and chemical functions of stormwater biofilters? (3) How do wildfire residues affect the biological function of stormwater biofilters? (4) Can waste-derived amendments remove pollutants from wildfire residues? Finally, a study explored whether a cohort-based research experience can increase STEM engagement and persistence.

To address these questions, I used a combination of field experiments, bench-scale laboratory experiments with column setups, physical-chemical processes, and geochemical and spectroscopic techniques, as well as quantitative and qualitative research methods. Natural stormwater was collected from Ballona Creek in Los Angeles, CA, and wildfire residues were collected from the Santa Monica Mountains, CA.

Results showed that wildfires can have a lasting impact on water quality, releasing pollutants into surface water even years after the wildfire. Deposited wildfire residues can negatively affect the infiltration capacity of biofilters by clogging filter media but do not affect their pollutant removal capacity. Wildfire residues did not appear to impact the germination and growth of plants, although sensitivity to wildfire residues varied among species. Drinking water treatment residuals (WTR) enhanced biofilter capacity to remove wildfire-associated pollutants such as phosphate released from fire retardants. Engaging undergraduate students in cohort-based research fostered their science identity, increasing STEM retention, particularly among underrepresented minority students. Overall, the results inform when, where, and how green infrastructure may be used to reduce the negative impacts of wildfires on water quality.

The dissertation of Onja Davidson Raelison is approved.

Jennifer Ayla Jay

Shaily Mahendra

Jane Valentine

Sanjay K. Mohanty, Committee Chair

University of California, Los Angeles

2024

Dedication

I dedicate this Ph.D. Dissertation to my parents, Haja Fifaliana Andriamasy Davidson and Voahirana Davidson. Words are not enough to express my love and my gratitude for having them in my life. They have been my rock and the reason why I am here today. My parents left Madagascar, our native country, in 1998 with only one piece of luggage to give me and my sister a better life in France knowing that their MD degrees would not be recognized there. With great perseverance and resilience, my father became an amazing doctor in France, loved by everyone. That's the reason they have been a source of inspiration and an example not only for me but also for everyone who has crossed paths with them, even just once. They shine with love, kindness, generosity, and most importantly, humility.

For all the sacrifices you made for us, for all the struggles and challenges you faced, and for your faith in God, this dissertation is for you.

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1. CHAPTER 1 – DEVELOPING ENGINEERING SOLUTIONS TO MITIGATE THE NEGATIVE IMPACTS OF WILDFIRES ON WATER QUALITY.

1.1. Introduction

Wildfire frequency and intensity are increasing because of warmer and drier climates in many regions of the world including the southwestern USA (Abatzoglou et al., 2021; Brown et al., 2023; Dong et al., 2022; Parks and Abatzoglou, 2020). Wildfires affect both human health and environmental implications including the loss of human lives, economic loss (Wang et al., 2020), air pollution (Adachi et al., 2022; Jerrett et al., 2022; McClure and Jaffe, 2018; O’Dell et al., 2020), and degradation of soil quality (Lopez et al., 2024). The impacts of wildfire can occur beyond the burned regions due to the deposition of wildfire residues— mostly of ash, black carbon, and other pollutants—by wind and water. Wildfire residues can be carried away by surface runoff from wildfire-affected areas to surface water and subsurface soil downstream, leaving behind their lingering impacts on water quality for years (Cheung and Giardino, 2023; Stein et al., 2012; Thurman et al., 2023). These wildfires residues contain high concentrations of heavy metals such as Hg, Cu, Zn, and As (Burton et al., 2016; Cerrato et al., 2016; Lopez et al., 2023), trace elements (Campos et al., 2016), nutrients (Crandall et al., 2021; Sánchez-García et al., 2023), and toxic organic pollutants (Hickenbottom et al., 2023; Li et al., 2023; Wang et al., 2015). The alkalinity of ash can increase soil pH (Plumlee et al., 2007; Raoelison et al., 2023), impacting plants and soil microbial community (Dove et al., 2022; Nelson et al., 2022), responsible for the natural cycling of elements such as C and N (Gustine et al., 2022; Lu et al., 2021). Impacts on microbial communities and plants could alter the emission of greenhouse gases such as CO₂, NO₂, and CH₄ from sediments and soils mixed with wildfire residues (Bowring et al., 2022; VanderRoest et al.,

2024). However, the extent to which the deposition of wildfire residues can affect water bodies and their ecosystems remains unclear.

The negative impact of wildfire residues on water quality can be minimized by implementing management methods or green infrastructure typically used to treat surface runoff. For instance, stormwater treatment systems such as biofilters are designed to infiltrate and treat stormwater runoff. These systems are engineered to mimic natural processes by retaining and infiltrating runoff in urban areas to minimize flooding and provide water quality benefits. However, studies examining the potential of stormwater treatment systems to mitigate the impacts of post-fire runoff further downstream are limited. Stormwater biofilters could intercept the contaminated runoff, remove wildfire residues pollutants, and increase groundwater infiltration. However, the deposition of wildfire residues and pollutants associated could also adversely affect the physical, chemical, and biological functions of biofilters, potentially compromising their ability to recover after disturbance and fulfill their ecosystem functions. The physical function includes the infiltration capacity of stormwater or clogging. The chemical function includes the pollutant removal capacity of biofilters such as heavy metals, nutrients, and pathogens. The biological function includes germination and growth of plants. Thus, it is important not only to examine the potential of biofilters to remove wildfire residues and wildfire-derived pollutants from runoff but also to evaluate the negative effects of deposited wildfire residues and associated pollutants on biofilter functions.

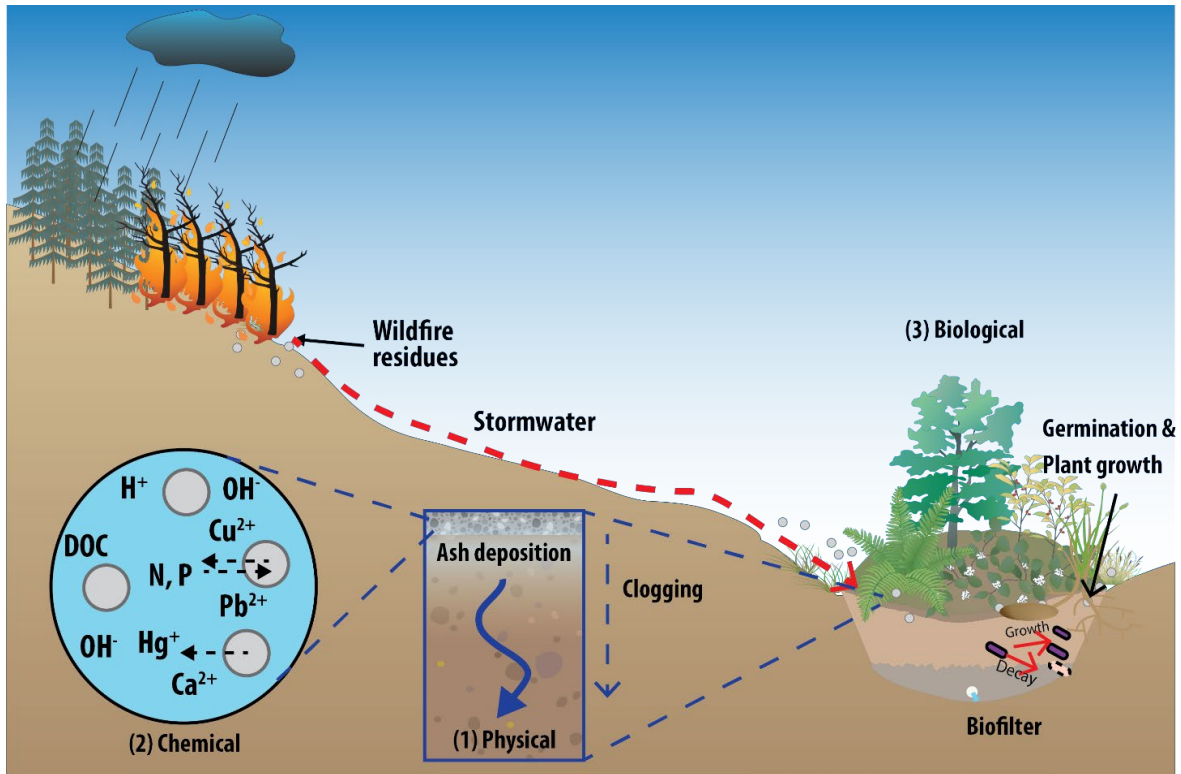


Figure 1-1. Schematics of the potential effect of wildfire residues deposition on the physical, chemical, and biological functions of stormwater biofilters.

1.2. Research gaps

1.2.1. Lack of consistency in data collection for post-fire studies

Wildfires can negatively alter downstream water quality although predicting the extent to which water quality may deteriorate after a wildfire is challenging due to various factors. First, a lack of data on water quality both before and after a wildfire hinders accurate assessments of changes following a wildfire (Paul et al., 2022). Second, inconsistencies in reporting information related to sampling methods and fire characteristics make it challenging to compare results across different studies (Robinne et al., 2020; Rust et al., 2019; Santos et al., 2019). For example, the water quality after a wildfire is influenced by factors such as the type of debris generated during the wildfire, as well as the resulting physical and geochemical alterations in the affected landscape. The water pollution after a wildfire depends on the burned area contributing to runoff and debris

flow (Caldwell et al., 2020; Rhoades et al., 2019), the rate of discharge in rivers or streams that can dilute the concentration (Caldwell et al., 2020), and the sampling time, considering that pollutant concentration may decrease over time (Santos et al., 2019). However, it remains unclear how long and to what extent burned areas, sampling time, and flow rate impact pollutant concentrations in surface water following a wildfire.

1.2.2. Impact of wildfire residues deposition on biofilters functions

Physical Functions. Green infrastructure can reduce excess surface runoff by physically retaining runoff water or infiltrating water into the ground or underground drainage. In biofilters, surface runoff flows through a filter layer typically composed of sandy soil or a mixture of sand and compost to increase the infiltration capacity and prevent clogging (Tirpak et al., 2021). The deposition of wildfire residues may impact the ability of biofilters to infiltrate stormwater, as these wildfire residues are larger ($> 2 \mu\text{m}$) than the pore size of the filter media (Valenca et al., 2020), potentially leading to their entrapment in the interstitial spaces and subsequently clogging. Yet, no study to date has evaluated when and how the biofilters get clogged in the presence of wildfire residues in the runoff, thus affecting the infiltration capacity of biofilters.

Chemical Functions. Moreover, deposited wildfire residues such as ash and black carbon can affect the pore water chemistry and the pollutant removal capacity from stormwater biofilters. For instance, the dissolution of ash can lead to an increase in pore water pH (Brito et al., 2021), which could prevent the dissolution of heavy metals (Lee and Saunders, 2003). Additionally, wildfires can increase dissolved organic carbon (DOC) concentration which may affect the capacity of biofilters to remove organic pollutants, heavy metals (HongE et al., 2022), and microbial pollutants (Zhang et al., 2015). Wildfire residues can leach heavy metals (Fernandez-Marcos, 2022), nutrients (Gustine et al., 2022; Valenca et al., 2020), and polyaromatic

hydrocarbons (PAHs) (Campos and Abrantes, 2021; Cooke et al., 2022), and other pollutants into the pore water in the root zone (Pereira and Úbeda, 2010). These pollutants could potentially compromise the biofilter's ability to provide water quality benefits. Therefore, it is important to understand how deposited wildfire residues influence the pollutant removal capacity of stormwater biofilters to ensure effective stormwater management.

Biological Functions. Plants play an important role in helping capture and remove pollutants such as nutrients and other organic pollutants from stormwater especially since plant roots help microorganisms to thrive in soils. Plant root structure can also help maintain the hydraulic conductivity of the biofilter media (Archer et al., 2002; Bartens et al., 2008). The presence of heavy metals and other contaminants in the wildfire residues, along with an increase in pH resulting from ash, as well as the presence of hydrophobic organic carbon, could have detrimental effects on the root zones, which may affect plant growth and soil microbiome within stormwater biofilters (Fernandez-Marcos, 2022; Nelson et al., 2022). It is not clear to what extent wildfire residues can affect the plant's roots and health in biofilters.

1.2.3. Design of wildfire-resilient stormwater biofilters

Conventional biofilters are not effective in removing phosphate and pathogens from stormwater runoff (Chahal et al., 2016; Tirpak et al., 2021). However, wildfires can contribute to increased phosphate levels and pathogen loads in post-fire runoff through two primary mechanisms: burned debris and fire-suppressing agents. First, the combustion of organic biomass during wildfires can release N and P compounds present in vegetation and soil (Bladon et al., 2014). These phosphate-rich residues, such as ash and charred materials, can be carried by stormwater runoff, leading to elevated phosphate concentrations. Second, many fire-suppressing agents, including foams and retardants, contain significant amounts of phosphate-based

compounds (Yu et al., 2021). While these chemicals are intentionally applied to control and extinguish fires and support vegetation post-fire, the residual phosphates can subsequently be washed off by stormwater runoff, contributing to increased phosphate levels in the post-fire runoff. Finally, wildfires can increase pathogen levels in water bodies after wildfires due to the turbidity of the post-fire runoff that causes solar inactivation of pathogens (Cira et al., 2022). Post-fire runoff can be considered a potential source of phosphate and pathogen pollution, highlighting the importance of addressing its impact on stormwater management strategies, especially in areas affected by recent wildfire events.

Biofilters remove pollutants from runoff mostly by adsorption of pollutants on amendments used in filter media (LeFevre et al., 2015; Tirpak et al., 2021). The amendments include for example compost and water treatment residual (WTR). However, the potential of these amendments to remove wildfire-derived pollutants has not been investigated. Numerous studies have examined the potential of WTR for the removal of phosphate (Ali and Pickering, 2023; Ament et al., 2022, 2021; Guo et al., 2015; Hsieh et al., 2007; Liu et al., 2014; Lucas and Greenway, 2010; O'Neill and Davis, 2012; Palmer et al., 2013; Poor et al., 2019; Qiu et al., 2019; Sidhu et al., 2021; Wang et al., 2021; Yan et al., 2017), but far fewer studies have investigated WTR's ability to remove *E. coli* from stormwater (Xu et al., 2019; Zoski et al., 2013). Most studies were conducted under controlled laboratory conditions (Ament et al., 2021; Zoski et al., 2013), which may not fully account for field complexities such as the presence of other amendments used in conventional biofilters for plant growth. For instance, no study to date has examined whether or how the presence of compost or mulch, the most commonly used amendments in conventional biofilters (Tirpak et al., 2021), would affect the pollutant removal capacity of WTR. It is unknown if the mixture of compost-WTR may leach pollutants. Therefore, evaluating how compost affects

WTR's ability to remove stormwater pollutants is an important research gap with practical implications for stormwater biofilter design.

1.2.4. Innovative cohort-based research opportunity

I used my dissertation research to provide mentoring opportunities to undergraduate students through an innovative research method. The unique research opportunity could significantly contribute to the key factors driving science identity and enhance STEM engagement. Some studies have previously shown the beneficial role of laboratory experience in thriving science identity because laboratory work helps develop connections between theoretical concepts and experiences while developing a sense of belonging with student collaboration and critical thinking (Hefferan et al., 2002; Kamen and Leri, 2019; Sidebottom, 2020; VanMeter-Adams et al., 2014). Laboratory experience could become a key component of developing science identity by influencing positively student attitudes (Simmons et al., 2008) and integrating knowledge by strengthening their interest in science (VanMeter-Adams et al., 2014). On the other hand, some studies have shown the beneficial role of a learning community that helps create a positive learning environment and improve STEM retention (Alcéna-Stiner and Markowitz, 2020; Brownell et al., 2012; Patrick et al., 2023; Polmear et al., 2024). Yet, no study has evaluated the impact of a cohort-based research experience on fostering all the factors that drive science identity, increasing student interest, and simultaneously maximizing a strong sense of community.

1.3. Objectives

The overall objective of this dissertation is to understand how green infrastructure can be integrated to mitigate the negative impacts of wildfires on water quality and how to design innovative wildfire-resilient stormwater biofilters able to effectively remove contaminants associated with wildfires. The dissertation consists of five research chapters. While Chapter 2

analyzes the impacts of wildfires on water quality using historical data to inform future monitoring efforts, Chapters 3 and 4 focus on the impacts of wildfire residues on stormwater biofilter physiochemical and biological functions, respectively. Chapter 5 provides a solution to improve the design and performance of stormwater biofilters to increase the pollutant removal capacity of biofilters. Chapter 6 presents the education study conducted in a classroom setting to provide an innovative research opportunity to undergraduate students. Specific goals are described below.

Chapter 2 contains an analysis of data reported in 44 wildfire studies to understand how wildfires can negatively alter downstream water quality throughout the world and quantifies the post-fire pollutant concentration as a function of sampling time, surface water and wildfire characteristics, and fire-affected watershed size. This study also highlights current issues with monitoring water quality following wildfires due to a lack of consistency in data collection and reporting, thus providing a framework to improve monitoring. The outcome of Chapter 2 is a peer-reviewed journal article:

Raoulison, O.D., Valenca, R., Lee, A., Karim, S., Webster, J.P., Pouline, B.A., and Mohanty, S. (2022). Wildfire impacts on surface water quality parameters: Cause of data variability and reporting needs. *Environmental Pollution*. 120713.
<https://doi.org/10.1016/j.envpol.2022.120713>

Chapter 3 examines the effects of wildfire residues on the physical and chemical functions of stormwater biofilters. This study shows that wildfire residues could decrease their infiltration capacity but may not affect the pollutant removal capacity of biofilters. The outcome of the chapter 3:

Raoelison, O.D., Das, T., Guyett, K., Merrifield, R., Indiresan, S., Yang, K., Visweswaran, A., Pierce, G., and Mohanty, S.K. (2024) Resilience of stormwater biofilters following the deposition of wildfire residues: Implication on downstream water quality management in wildfire-prone regions. *Journal of Hazardous Materials*.
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Chapter 4 examines the effects of wildfire residues on the biological functions of stormwater biofilters by analyzing germination, early root growth, and aboveground biomass. This study shows that wildfire residues do not appear to impact the germination and growth of plants in stormwater biofilters but plants exhibit varying sensitivity to wildfire residues. The outcome of Chapter 4:

Raoelison, O.D., Achziger, C., Gallardo, L., Santana, D., Hermsmeyer, L., Belinsky, C., Dayan, C., Choo, J., Nguyen, K., Vilchis, M., Belikov N., Min, S., and Mohanty, S.K. Deposited Wildfire Residues Impacts on Plant Health in Stormwater Green Infrastructure. [In preparation]

Chapter 5 investigates the ability of drinking water treatment residuals (WTR) to serve as a wildfire-resilient biofilter media and shows their effectiveness in removing wildfire-associated contaminants like phosphate released from fire retardants and pathogens. The outcome of Chapter 5:

Raoelison, O.D., Das, T., Guyett, K., Visweswaran, A., Spallone, S., Ramos, R., Merrifield, R., Pierce, G., and Mohanty, S.K. (2023) Compost decreases bacterial and phosphate removal capacity of drinking water treatment residuals in stormwater biofilters.

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Chapter 6 focuses on integrating methods from earlier chapters into a classroom environment. This education study shows that a cohort-based hands-on laboratory experiment can serve as an innovative teaching approach to increase self-efficacy, sense of belonging, and interest in science, all of which are crucial factors fostering science identity. The results have implications for STEM retention, particularly among underrepresented minorities. The outcome of Chapter 6:

Raoulison, O.D., Dixie, K., Mohanty, S.K. Innovative Cohort-Based Research Experience: Fostering Science Identity and STEM Engagement to Promote STEM Retention. [In preparation]

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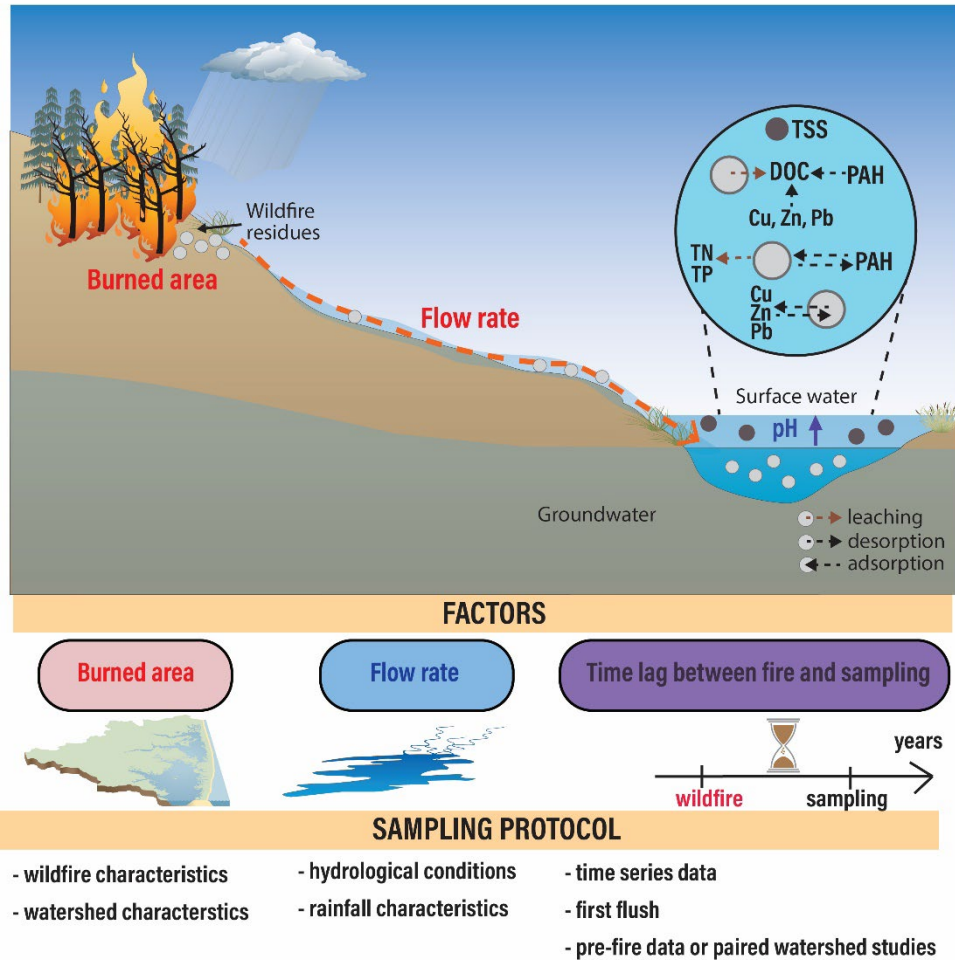
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2. CHAPTER 2 – WILDFIRE IMPACTS ON SURFACE WATER QUALITY PARAMETERS: CAUSE OF DATA VARIABILITY AND REPORTING NEEDS



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Abstract

Surface runoff mobilizes the burned residues and ashes produced during wildfires and deposits them in surface waters, thereby deteriorating water quality. A lack of a consistent reporting protocol precludes a quantitative understanding of how and to what extent wildfire may affect the water quality of surface waters. This study aims to review pre- and post-fire water quality data to inform the data reporting and highlight research opportunities. A comparison of the pre- and post-fire water quality data from 44 studies reveals that wildfire could increase the concentration of many pollutants by two orders of magnitude, but the concentration increase is sensitive to when the sample was taken after the wildfire, the wildfire burned area, discharge rate in the surface water bodies where samples were collected, and pollutant type. Increases in wildfire-burned areas disproportionately increased total suspended solids (TSS) concentration, indicating TSS concentration is dependent on the source area. Increases in surface water flow up to $10 \text{ m}^3 \text{ s}^{-1}$ increased TSS concentration but any further increase in flow rate decreased TSS concentration, potentially due to dilution. Nutrients and suspended solids concentrations increase within a year after the wildfire, whereas peaks for heavy metals occur after 1-2 years of wildfire, indicating a delay in the leaching of heavy metals compared to nutrients from wildfire-affected areas. The concentration of polycyclic aromatic hydrocarbons (PAHs) was greatest within a year post-fire but did not exceed the surface water quality limits. The analysis revealed inconsistency in the existing sampling protocols and provides a guideline for a modified protocol along with highlighting new research opportunities. Overall, this review underlines the need for consistent reporting of post-fire water quality data along with environmental factors that could affect the data so that the post-fire water quality can be assessed or compared between studies.

2.1. Introduction

Surface waters such as lakes and rivers are critical resources to meet drinking water demand in many regions (Delpla et al., 2009). Climate change and associated extreme events are not only depleting these resources but affecting water quality (Leveque et al., 2021; Ma et al., 2022). Wildfire is one of the extreme events that is projected to increase in intensity, frequency, and duration with longer wildfire seasons during climate change (Westerling et al., 2006). Wildfires release many pollutants into the air and distribute them on the surface in surrounding areas (**Figure 2- 1**). Those pollutants include, for example, mercury (Hg), nitrogen oxides (NO_x), sulfur oxides (SO_x), carbon oxides (CO_x), and polycyclic aromatic hydrocarbons (PAH) (O'Dell et al., 2020; Schneider et al., 2021). In addition to the dry deposition of air-borne pollutants after the fire, fire management practices such as prescribed fire and the addition of fire retardants containing high concentrations of nutrients during wildfire could affect water quality after the fire (Crouch et al., 2006; Paul et al., 2022; Richter et al., 1982). Wildfires also leave behind ash, black carbon, and many pollutants, and surface runoff mobilizes and conveys them to surface waters, thereby deteriorating water quality during post-fire seasons (Hohner et al., 2019; Smith et al., 2011). Collectively, left-over burned debris on land, atmospheric fallout burned residues, and fire management practices could influence the pollutant loading to surface waters.

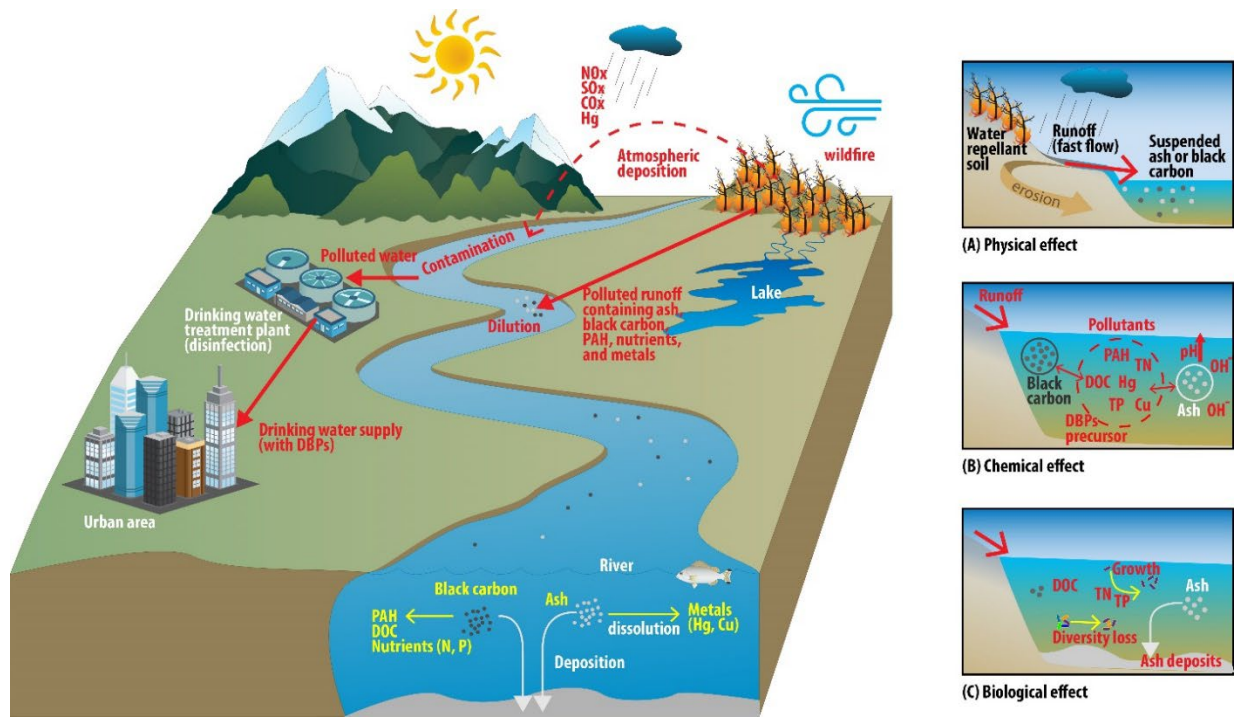


Figure 2-1. Conceptual depiction of physical, chemical, and biological processes that affect the release of different pollutants after wildfires including mercury (Hg), Nitrogen Oxides (NO_x), Sulfur oxides (SO_x), Carbon oxides (CO_x) into the atmosphere, polycyclic aromatic hydrocarbons (PAH), dissolved organic carbon (DOC), total nitrogen (TN) and total phosphorus (TP), Copper (Cu) and mercury (Hg) in water bodies and disinfection by-product (DBPs) in drinking water.

Wildfires can alter the physical, chemical, and biological properties of soil and water bodies around them, which in turn can affect water quality (**Figure 2-1**). Wildfires could increase runoff volume and speed (Ebel et al., 2012; Moody and Martin, 2001) because of changes in land surface properties such as tree cover and water repellency. Wildfires can also eliminate tree canopies that abstract rainwater and shield the soil from rainfall splash, thereby increasing the erosion of soil during post-fire seasons (Ebel et al., 2012; Ice et al., 2004). Fire can increase the hydrophobicity of soil due to the deposition of plant-derived waxy substances burned during a hot fire (DeBano, 2000; Ice et al., 2004) and limits subsurface infiltration. The surface runoff mobilizes the burned residues produced during the fire and flows into surface water bodies (Bodí et al., 2014). These particulates could release a wide range of pollutants including heavy metals (Ager et al., 2019; Bento-Gonçalves and Vieira, 2020), and polycyclic aromatic hydrocarbons

(PAHs) (Campos et al., 2019; Gorshkov et al., 2021; Mansilha et al., 2019). These pollutants are a public health concern due to their high level of toxicity and their detrimental impacts on human health (Fernandez-Marcos, 2022). PAHs are highly toxic and carcinogenic to human health and persist in the environment (Li et al., 2021; Wang et al., 2022). Similarly, heavy metals can bioaccumulate in plants and animal tissues (Campos and Abrantes, 2021) and continued consumption of water containing high concentrations of toxic metals may cause developmental abnormalities, cancer, and other deleterious health effects (Gavhane et al., 2021).

Decreased surface water quality increases the burden on drinking water treatment facilities to treat polluted surface water before distribution (Hohner et al., 2019; Robinne et al., 2021). Some studies showed that wildfire can change dissolved organic carbon (DOC) quality and produce more nitrogen-rich aromatic compounds (Davidson et al., 2019; Hohner et al., 2019; Uzun et al., 2020; Wang et al., 2015). An increase in nitrogen-rich organics can increase the formation of disinfection byproducts or DBPs (Chow et al., 2019; Hohner et al., 2019; Wang et al., 2015). Organic-rich ash produced during wildfires is more reactive to form N-DBPs than C-DBPs (Wang et al., 2015). Wildfires can also alter the levels of inorganic precursors such as bromide, iodide, and nitrite in surface waters, leading to the formation of inorganic DBPs (Chang et al., 2011; Uzun et al., 2020). Degradation of surface water quality can have significant impacts on recreational water use (Cira et al., 2022) and aquatic habitats (Rust et al., 2019a). Deposition of wildfire-derived residues such as ash and black carbon could have many impacts on other ecosystems (Brito et al., 2017; Earl and Blinn, 2003; McCullough et al., 2019; Oliveira-Filho et al., 2018; Rust et al., 2019a). For instance, the deposition of ash could affect the soil pH (Plumlee et al., 2007), plants, and soil microbial communities (Noyce et al., 2016), and alter the natural cycling of elements (Granath et al., 2020). Changes to water quality can, in turn, affect downstream water uses, and these impacts could

intensify (Stein et al., 2012; Wan et al., 2021) because of the projected increase in the frequency and intensity of wildfires in a warming climate (Westerling et al., 2006).

Despite the link between wildfire and post-fire water quality deterioration, the extent to which water quality may deteriorate after wildfire in a region is difficult to predict because of several reasons. First, there is a paucity of pre- and post-fire water quality data to ascertain net changes in water quality because of fire (Paul et al., 2022). Second, underreporting of supporting data such as sampling protocol and fire characteristics, makes it difficult to compare results across studies (Robinne et al., 2020; Rust et al., 2019b; Santos et al., 2019). For example, water quality after wildfires often depends on the characteristics of debris produced during a wildfire, and the resulting physical and geochemical changes in the landscape where wildfires have occurred. Water pollution levels following wildfires have been shown to depend on many factors including burned area contributing to the flow that controls the amount of debris available (Caldwell et al., 2020; Rhoades et al., 2019a), discharge rate in rivers or streams that could dilute the concentration (Caldwell et al., 2020), and the time of sampling assuming the source of pollutants deplete with time (Santos et al., 2019). Yet, it is unclear to what extent and how long after wildfires the burned areas affect the concentration of pollutants in the surface water. Therefore, it is critical to identify the limitations of current data reporting so that future monitoring protocols can produce the data set required to quantitatively link wildfire with post-fire surface water quality. To identify the limitations of data reporting methods, it is essential to aggregate pre- and post-fire water quality data and the confounding factors that could affect water quality.

The objectives of the review article are to create and analyze the dataset including the concentration of most common pollutants reported in the field after wildfires and identify potential gaps in the data collection and reporting methods. Although there are many reviews on the effects

of wildfires on water quality (Abraham et al., 2017; Bitner et al., 2001; Hohner et al., 2019; Ranalli, 2004; Rhoades et al., 2019b; Rust et al., 2018; Smith et al., 2011), these reviews either reported overall trends without a quantitative dataset or presented the trend based on data of a few selected parameters. In contrast, we have provided a comprehensive dataset including all water quality parameters changed after wildfire and local conditions. We analyzed the data reported in 44 studies to estimate pollutant concentration maxima or peaks as a function of the burned area, surface water flow rate, and time lag between fire and sampling. The pollutants considered were total suspended sediments, nutrients, dissolved organic carbon (DOC), heavy metals, and polycyclic aromatic hydrocarbons (PAHs) as these pollutants were commonly reported in the studies to enable comparison between pre- and post-fire data. The analysis of available limited data revealed potential missing information or issues with available data. The results identified the reporting or monitoring needs, which could help develop better protocols to report water quality parameters so that all studies can be comparable.

2.2. Data collection and management

We searched peer-reviewed articles on the Web of Science using a combination of keywords including “wildfire” and “water quality”, “fire” and “water”, “postfire”, and “forest fire” to collect peer-reviewed articles published by January 10, 2022. We excluded the articles that are not written in English and analyzed only air or soil samples without reporting water quality. The exclusion criteria reduced the total of 429 research articles collected to 142 studies focused on aquatic environments, which were further analyzed by reading the full text. These selected articles were analyzed to extract data that includes: (1) contaminant concentrations before and after wildfire, (2) area of watershed burned by wildfire, (3) total watershed area, (4) time lag between fire and sampling, (5) type of surface water bodies, and (6) flow rate of surface water. Out of 142

studies, only 44 studies reported data that could be used for our review because of missing pre and post-fire data or incomplete information related to water quality parameters and watershed characteristics. These studies were further analyzed for wildfire characteristics including type of fire, location, date, size, severity, name of the surface water, and biomass type. Detailed information on all the studies including these data was provided in **Table 2-1** and **Table 2-2**. Out of the 44 studies used in our review from different parts of the world (**Figure 2-2**), nearly 80% of studies were from the U.S., Canada, and Australia, with no studies from Asia or South American continents despite severe wildfires in the Amazon (Lizundia-Loiola et al., 2020; Xu et al., 2020). Not all studies reported changes in the concentration of all parameters due to wildfire.

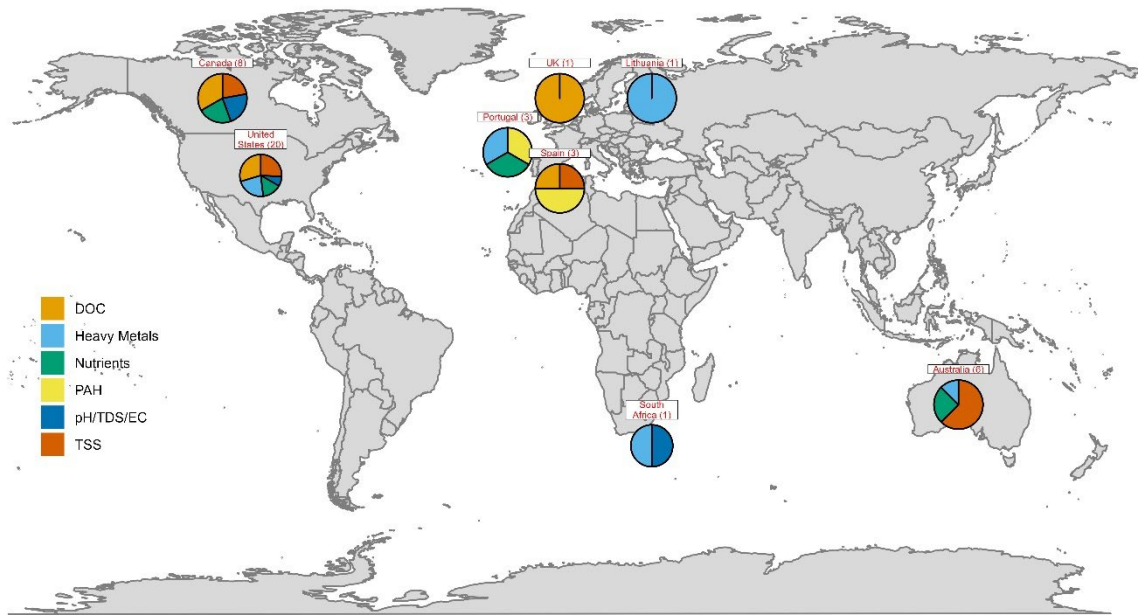


Figure 2-2. Locations of the 44 studies that measured and reported pre-and post-fire water quality parameters including dissolved organic carbon (DOC), polycyclic aromatic hydrocarbon (PAH), total dissolved solids (TDS), electrical conductivity (EC), and total suspended solids (TSS). Pie-graphs represent the distribution of the studies in each country regarding their reported water quality parameters.

Table 2-1. Characteristics of the selected studies.

Reference	Type of fire	City	Country	Köppen Geiger ^a	Latitude	Longitude	Wildfire name	Date started	Stream name	Surface water type	Burn severity	Type of biomass
Alexander 2004	natural	Dartmouth	Australia	Cfb	-36.55633	147.52156	The Victorian Alpine Fires	1/8/2003	Dartmouth Reservoir	reservoir	severe	Alpine Bogs and Fens
Arlke and Piffiod 2010	natural	Swifts Creek	Australia	Cfb	-37.25177	147.71368	The Victorian Alpine Fires	1/8/2003	Tambo River	river	severe	
	prescribed	Warren, ID	United States	Dsb	44.95861	-115.53679	Parks-eiguren	5/8/2004	Parks, Reegan, Buckhorn, Blackmare, Fourmile	creek going to river	low	Ponderosa pine forest
							Williams	05/2006	Parks, Reegan, Buckhorn, Blackmare, Fourmile	creek going to river	low	
Basso et al. 2020	natural	Pedrogao Grande	Portugal	Csb	39.921856	-8.131199	Pedrogao Grande and Gros Fire	6/17/2017	Rio Zezere	river going to a reservoir	severe	Shrublands and Forests (Pine, Eucalyptus, Oak)
	natural	Kenora, ON	Canada	Dfb	49.661215	-93.729006	1973 fire	6/26/1974	Lake 239	stream to lake	severe	Boreal forests and Fen (Black spruce, Jackpine and Aspen)
Bayley et al. 1992a	natural	Kenora, ON	Canada	Dfb	49.661215	-93.729006	1980 fire	1980 fire	Lake 239	stream to lake	severe	
Bayley et al. 1992b	natural	Kenora, ON	Canada	Dfb	49.661215	-93.729006	1980 fire	1980 fire	Lake 239	lake to stream	severe	
Betts and Jones Jr 2009	prescribed	Fairbanks, AK	United States	Dfb	65.140617	-147.45733	1999 prescribed fire	1999	Caribou-Poker Creeks (CA)	stream	moderate	Boreal forests (Paper birch, Aspen, Black spruce, feathermosses)
Bladon et al. 2008	natural	Fairbanks, AK	United States	Dfb	65.140617	-147.45733	Boundary Fire	6/2004	Caribou-Poker Creeks (P6)	stream	moderate to severe	
	natural	Crowsnest Pass, Alberta	Canada	Dfb	49.558833	-114.55975	2003 Lost Creek wildfire	7/2003	South York Lynx	creek	severe	Alpine forests
Britton 1991	prescribed	Stellenbosch	South Africa	Csb	-33.9907	18.95651	N/A	3/17/1987	Swarboskloof stream	stream	low to moderate	Mediterranean Shrubland
	prescribed	Stellenbosch	South Africa	Csb	-33.98779	18.96273	N/A	3/17/1987	Jubilee Creek	creek	low to moderate	
Brown 1972	natural	Cabramurra	Australia	Cfb	-35.7935	148.41427	Chatsbury/Bungonia bushfires	3/3/1965	Wallaces Creek	creek	moderate to high	Alpine forests (Eucalypt)
	natural	Cabramurra	Australia	Cfb	-35.78936	148.41423	Chatsbury/Bungonia bushfires	3/3/1965	Yarrangobilly River	river	low to moderate	
Burke et al. 2013	natural	La Cañada Flintridge, CA	United States	Csb	34.222222	-118.1775	Station Fire	8/26/2009	Arroyo Seco	river	moderate	Chaparral, coniferous forest
Campos et al. 2012	natural	Colmeal	Portugal	Csb	40.146111	-7.993056	N/A	8/24/2008	hill slope runoff	hill slope runoff	moderate to low	Mediterranean (Eucalypt, Pine)

Chessman et al. 1986	natural	Victoria	Australia	Cfb	-37.38583	148.00194	1983 wildfires	1/31/1983	Errimundra	river	severe	Temperate rainforest, ancient wet eucalypt forest
Chow et al. 2019	natural	Bailey, CO	United States	Dfb	39.234672	-105.3027	2002 Hayman Fire	6/8/2002	Cabin Creek/Wigwam Creek	creek to river	severe	Dry conifer forest
Costa et al. 2014	natural	Westcreek, CO	United States	Dfb	39.207301	-105.23396	2002 Hayman Fire	6/8/2002	Fourmile Creek	creek to river	severe	
Davidson et al. 2019	natural	Serra do Marão	Portugal	Csb	41.24847	-7.886821	N/A	6/2006	Marão River	river	moderate	Pine forest
Davis 1989	prescribed	Fort McMurray, Alberta	Canada	Dfb	56.933333	-111.5489	Horse River Wildfire	5/3/2016	Poplar Fen	runoff to wetland (fen)	severe	Boreal fen
Emelko et al. 2011	natural	Central Arizona	United States	Bsk	33.43	-111.19	N/A		"Experimental watersheds"	stream	low	Chaparral forest
Evans et al. 2017	natural	Crowsnest Pass, Alberta	Canada	Dfb	49.558833	-114.55975	2003 Lost Creek wildfire	7/2003	South York	creek	severe	Alpine forest
Ewing 1996	natural	Montana	UK	Cfb	54.159134	-5.968549	N/A	5/1/2011	Blue Lough	mountain lake	severe	Mountain forest
Gallaher and Koch 2004	natural	New Mexico	United States	Dfb	44.423691	-110.58852	Red Bench Fire	9/6/1988	Yellowstone river	river	severe	Alpine pine forest
García-Comendador et al. 2017	natural	Wyoming	United States	Dfa	44.86922	-110.16624	Red Bench Fire	9/6/1988	Lamar River station	river	severe	Alpine pine forest
Hauer and Spencer 1998	natural	Mallorca	United States	BWk	35.869468	-106.41253	Cerro Grande fire	5/11/2000	Pueblo	Canyon	severe	Mixed conifer forest
Hohnert et al. 2016	natural	Montana	Spain	Bsk	39.5730	3.3667	N/A	7/2013	Sa Coma Freda	river	moderate	Mediterranean forest
Ignatavicius et al. 2006	natural	Multiple	United States	Dfb	44.423691	-110.58852	Red Bench Fire	9/6/1988	Can Cabrit	river	moderate	Alpine pine forest
Lane et al. 2006	natural	Victoria	United States	Dfa	40.589	-105.404	High Park wildfire	6/9/2012	Cache la Poudre	river	Mixed (mainly moderate)	Mixed conifer forest
Mast and Clow 2008	natural	Montana	Lithuania	Cfb	55.261111	21.306667	N/A	2002	N/A	N/A	N/A	Forest and peat bogs
Olefaldt et al. 2013	natural	Alberta	Australia	Cfb	41.064	-80.0565	The Canberra bushfires	1/2003	Slippery Rock Creek	creek	severe	Alpine forest
	natural	Montana	United States	Dfb	58.665806	-136.90021	The Robe, Trapper, Rampaage fires the Utkama	7/23/2003	Springs Creek McDonald creek	creek lake	severe moderate to severe	Subalpine coniferous forest
	natural	Alberta	Canada	Dfb	55.92	-115.18	Complex fire	5/15/2011	Utkama Lake	lake to stream	moderate	Boreal peatland (Black spruce)

Oliver et al. 2012	natural	Catalonia	Spain	Cfb	42.292863	1.6189803	N/A	8/1994	The Llobrega	river	mixed	Mediterranean coniferous forest
Owens et al. 2013	natural	El dorado, CA	United States	Cfa	38.863	-120.05	The Angora Fire	6/24/2007	Angora Creek	creek	severe	Mixed conifer forest
Pinedo-Gonzalez et al. 2017	natural	Kamloops, BC	Canada	Dfb	51.123333	-120.2094	The McLure wildfire	7/30/2003	The Fishtrap Creek	creek	severe	Mountain forest (Pine, Spruce, Fir)
Ré et al. 2020	natural	Azusa, CA	United States	Csa	34.239	-117.822	Williams Fire	9/2/2012	San Gabriel	river	moderate	Chaparral forest, old coniferous forest
Rust et al. 2019	natural	Miranda do Corvo	Portugal	Csb	40.0941	-8.33355	N/A	8/8/2015	Ceira river	river	moderate-severe	Mediterranean forest
	natural	Colorado	United States	Dfa	37.373431	-107.00293	The West Fork Complex (WFC) fire	6/5/2013	Rio Grande	river	moderate to severe	Mixed conifer forest (spruce)
	natural	Idaho	United States	Bsk	44.068203	-114.742043	Foothills	8/19/1992	Boise	river	severe	Mountain forest
	natural	California	United States	Cwb	33.745571	-117.86784	Old	10/25/2003	Santa Ana	river	severe	Dry conifer forest
	natural	Colorado	United States	Dfa	37.373431	-107.00293	2002 Hayman Fire	6/8/2002	South Platte	river	Mixed (mainly moderate)	Mixed conifer forest
	natural	Colorado	United States	Dfa	37.373431	-107.00293	High Park wildfire	6/9/2012	Cache la Poudre	river	severe	Mountain forest (lodgepole and ponderosa pines)
	natural	El dorado, CA	United States	Cfa	38.863	-120.05	The Angora Fire	6/24/2007	Angora Creek	creek	severe	Coniferous forest
	natural	Montana	United States	Dfb	58.665806	-136.90021	Taylor Creek	7/3/2012	Otter creek	creek	N/A	Wetland
	natural	Texas	United States	Cfa	31.968	-99.9018	Riley Road & Dyer Mill	6/19/2011	Spring creek	creek	N/A	Riparian forest
Ryan et al. 2011	natural	Wyoming	United States	Dfa	43.07597	-107.29028	The Boulder Creek fire	7/30/2000	Little Granite Creek	creek	N/A	Riparian forest (pine, spruce)
Shibata et al. 2003	prescribed	Alaska	United States	Cfb	65.166667	-147.5	N/A	7/8/1999	Caribou Poker Creeks	creek	low	Boreal forest (black spruce)
Silins et al. 2009	natural	Crowsnest Pass, Alberta	Canada	Dfb	49.55278	-114.43118	The 2003 Lost Creek wildfire	July of 2003	Drum	creek	N/A	Subalpine forest (pine, spruce, fir)

Son et al. 2015	natural	Colorado	United States	Dfa	40.70431	-105.2472	High Park wildfire	6/9/2012	Cache la Poudre	river	severe	Mountain forest (lodgepole and ponderosa pines)
Stein et al. 2012	natural	La Cañada Flintridge, CA	United States	Csb	34.222222	-118.1775	Station Fire	8/28/2009	Arroyo Seco and Big Tujunga wash	creek	moderate	Mediterranean chaparral, coniferous forest
	natural	Orange, CA	United States	Csc	33.769739	-117.89089	Santiago	10/21/2007	Santiago Creek	creek	severe	
	natural	Ventura, CA	United States	Csc	34.523047	-118.25704	Day	9/4/2006	Piru Creek	creek	severe	
	natural	Ventura, CA	United States	Csc	34.286391	-118.74926	Simi Valley	10/25/2003	Dry Canyon	creek	severe	Mountain forest (lodgepole and ponderosa pines)
	natural	San Bernardino, CA	United States	Csc	34.185564	-117.18004	Old	10/25/2003	City Creek	creek	severe	
Townsend and Douglas 2004	natural	Darwin	Australia	Cfa	-13.09236	132.393837	N/A	5/22/1998	Kapalga	stream	mixed (moderate)	Tropical savanna forest
Uzun et al. 2020	natural	Lake, CA	United States	Csc	38.923564	-122.32648	Rocky fire	7/29/2015	Cache creek	creek	N/A	Mixed forest (savanna, oak, chaparral)
	natural	Napa, CA	United States	Csc	38.512031	-122.09723	Wrags fire	7/22/2015	Cold Creek	creek	N/A	
Vila-Escalé et al. 2007	natural	Catalonia	Spain	Cfb	41.390205	2.154007	N/A	8/11/2003	The Gallifa creek	creek	severe	Mediterranean forest
Writer et al. 2014	natural	Colorado	United States	Dfa	40.589	-105.404	High Park wildfire	6/9/2012	Mura Cache la Poudre	creek river	severe	Mountain forest (lodgepole and ponderosa pines)
Yu et al. 2019	natural	Sydney	Australia	Cfa	-33.86514	151.2099	N/A	12/3/2001	Lake Burrigawang	lake to stream	severe	Shrubland forest
										lake to stream	severe	
										lake to stream	severe	
										lake to stream	severe	

^a The local weather classification based on Koppen-Geiger: BSk = Cold semi-arid climate; BWk = Cold desert climate; Cfa = Humid subtropical climate; Cfb = Temperate oceanic climate; Csa = Hot-summer Mediterranean climate; Csb = Warm-summer Mediterranean climate; Cwb = Subtropical highland climate; Csc = Cold-summer Mediterranean climate; Dfa = Hot-summer humid continental climate; Dsb = Mediterranean-influenced warm-summer humid continental climate; Dfb = Warm-summer humid continental climate.

Table 2-2. Summary of the references used for the data analysis and the constituents that the references contributed for the study. EC: electrical conductivity; TDS: total dissolved solids; TSS: total suspended solids; DOC: dissolved organic carbon; PAH: polycyclic aromatic hydrocarbons; TN: total nitrogen; TP: total phosphorous.

References	Constituents																
	Heavy metals											Nutrients					
	pH	EC	TDS	TSS	DOC	PAH	As	Cd	Cu	Fe	Mn	Ni	Pb	V	Zn	TN	TP
(Alexander, 2004)				×												×	×
(Arkle and Pilliod, 2010)	×				×											×	×
(Basso et al., 2020)																×	×
(Bayley et al., 1992a)																×	×
(Bayley et al., 1992b)	×																
(Betts and Jr, 2009)					×												
(Bladon et al., 2008)																	×
(Britton, 1991)	×	×	×														
(Brown, 1972)				×													
(Burke et al., 2013)				×				×					×				×
(Campos et al., 2012)																	×
(Chessman, 1986)				×													
(Chow et al., 2019)					×												
(Costa et al., 2014)	×																
(Davidson et al., 2019)																	×

(Davis, 1989)	×	×																	
(Emelko et al., 2011)			×																
(Evans et al., 2017)	×																		
(Ewing, 1996)				×															
(Gallaher and Koch, 2004)				×															×
(García-Comendador et al., 2017)				×															
(Hauer and Spencer, 1998)				×															
(Hohner et al., 2016)				×															×
(Ignatavičius et al., 2006)								×											×
(Lane et al., 2006)						×													
(Mast and Clow, 2008)						×													
(Olefelt et al., 2013)							×												
(Olivella et al., 2006)									×										
(Oliver et al., 2012b)																			×
(Owens et al., 2013)																			
(Pinedo-Gonzalez et al., 2017)																			×
(Ré et al., 2020)										×									×
(Rust et al., 2018)																			×
(Rust et al., 2019)																			×

(Ryan et al., 2011)	×									
(Shibata et al., 2003)		×								
(Silins et al., 2009)	×									
(Son et al., 2015)			×							
(Stein et al., 2012)	×		×						×	×
(Townsend and Douglas, 2004)					×		×			×
(Uzun et al., 2020)				×						
(Vila-Escalé et al., 2007)		×						×		
(Writer et al., 2014)									×	
(Yu et al., 2019)	×									

To analyze the variability of contaminant concentration before and after a given wildfire, we calculated the log-ratio of contaminant concentrations before and after the wildfire using the equation: $LR = \log(C_{post}/C_{pre})$, where C_{pre} and C_{post} are the concentrations before and after wildfires respectively. A positive LR indicates an increase in contaminant concentration after the wildfire while a negative LR indicates a reduction of the contaminant concentration after the wildfire. LR values near zero represent a scenario when the wildfire had no significant impact on the contaminant concentration. To analyze the effect of wildfire on pH, we compared the values of these variables reported before and after the wildfire in the same surface water body. To verify the effect of burned area on total suspended solids and nutrient concentration, we normalized the data by dividing the extent of the burned area by the total area of the watershed and categorized them based on the extent of burned area relative to the total watershed: low (< 20%), medium (between 20 to 80%), and high (>80%). The time lag between fire and sampling was sometimes referred to as “sampling time” or “time after the fire” in some studies. For total suspended solids, the flow rate was divided into three categories—less than $1 \text{ m}^3 \text{ s}^{-1}$, between 1 and $10 \text{ m}^3 \text{ s}^{-1}$, and more than $10 \text{ m}^3 \text{ s}^{-1}$. For DOC data, three types of surface water bodies were surveyed: creek, river, and stream. We identified the water body type based on how it was reported in the original study. Due to a lack of reported data from wildfire studies that analyzed heavy metals, we estimated changes in metal concentrations when burned area increases by an order of magnitude from 4 to 40 km^2 as the spatial distribution of heavy metals can be influenced by the burn severity, which is correlated to the burned area (Cocke et al., 2005; Pereira and Úbeda, 2010). In contrast to metals, PAH can be strongly associated with suspended particles or particulate organic matter released during fire (Nielsen et al., 2015). As most suspended particles are released in the first few rainfalls after the fire, it is important to correlate PAH concentration with sampling the time lag after the

fire. To examine if PAH concentration peaked initially potentially due to their association with suspended particles, we analyzed reported PAH concentration as a function of their aromatic rings at two sampling times: less than 4 months after the wildfire and more than 4 months after the wildfire. The statistical analysis for this study was conducted using R (version 4.2.1). Wilcoxon test was used to calculate the statistical difference between boxplots, where p-values lower than 0.05 represent a significant difference between results.

2.3. Wildfire impacts on specific water quality

2.3.1. pH

Only 9 of 44 surveyed studies had reported pre- and post-fire pH values (**Table 2-4**). Based on the limited studies, pH appears to increase within a year after a fire but returns to pre-fire level a year following the wildfire (**Figure 2-3**). Of the 9 studies, 6 of the studies that reported no change in pH had collected water samples one year after the fire (Arkle and Pilliod, 2010; Bayley et al., 1992; Britton, 1991; Davis, 1989; Evans et al., 2017; Olefeldt et al., 2013) and only 2 studies recorded an increase in pH within a year after the fire (Costa et al., 2014; Son et al., 2015). It is expected that the presence of wildfire residues would mostly increase the pH due to the dissolution of ashes (Harper et al., 2019; Rust et al., 2018). In some cases, it could also decrease pH due to carboxyl groups present in burned residues (Cheng et al., 2006) and wet deposition of dissolved acids (Evans et al., 2017, 2021). Analysis of changes in pH as a function of sampling time after fire confirmed that any changes in pH of surface water may dissipate within a year after the fire (**Figure 2-3**), potentially because the natural buffering capacity of sediment might neutralize any impacts of wildfire residues on pH (Muñoz-Rojas et al., 2016). Furthermore, wildfires in most of the reported studies were of low to moderate severity including 3 prescribed burns, which could affect the nature of the ash produced (Arkle and Pilliod, 2010; Britton, 1991; Davis, 1989).

Prescribed burns are intentional and controlled to reduce hazardous fuels on lands (Miller et al., 2020). Under low-temperature combustion (< 450 °C), organic carbon is the main component of ash, which could decrease the pH (Lodeiro et al., 2020). At high temperatures (450 °C), ash contains calcium, magnesium, sodium, potassium, silicon, and phosphorous in the form of inorganic carbonates, which increase the pH of the water (Bodí et al., 2014). Thus, both burn intensity and the time lag between fire and sampling can influence pH in surface water receiving runoff from wildfire-affected areas. Therefore, they should be reported consistently in water quality monitoring studies. Overall, monitoring pH within one year of wildfire and reporting the burn severity or nature of ash produced during wildfires in future studies could help link wildfire properties to changes in pH in affected surface waters.

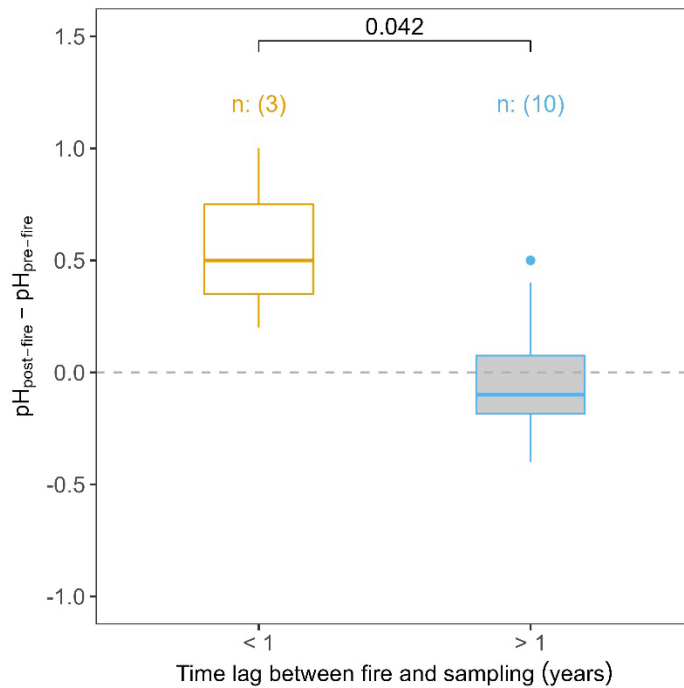


Figure 2-3. Difference of pH in surface water before and after wildfires based on the time lag between fire and sampling: “<1” represents the sampling time occurring within a year after fire (white-filled box plot), “>1” represents the sampling time occurring a year after fire (gray-filled boxplot). The horizontal dashed line represents no difference in pH before and after wildfire. Statistical differences were determined by the Wilcoxon rank sum test: no significant difference (p-value > 0.05). The number between parentheses represents the number (n-value) of data points available for analysis.

Table 2-3. Effect of wildfires on mean pH value measured in surface waters based on the time lag between fire and sampling. The literature review was based on 9 peer-reviewed articles.

Wildfire type (year)	Burned area (Catchment area) in km ²	Water bodies (Location)	Time lag between fire and sampling (days)	pH before fire	pH after fire	References
Prescribed (2004)	32 (219)	Blackmare and Fourmile creeks (Warren, USA)	1095	7.56	7.42	Arkle and Pilliod 2010
Natural (1980)	0.56 (0.56)	Lake 239 (Kenora, Canada)	365	5.15	4.92	Bayley et al. 1992
			730	5.15	4.76	-
Prescribed (1987)	3.73 (3.73)	Swartboskloof stream (Stellenbosch, South Africa)	365	5.31	5.61	Britton 1991
			365	5.06	5.17	-
Natural (2006)	2.55	Jubilee Creek (Stellenbosch, South Africa)	365	4.86	4.25	
		Marão River (Portugal)	150	5.9	6.4	Costa et al. 2014
				5.9	6.1	
Prescribed (1969)	NA (0.28)	Unnamed stream (Roosevelt, South Africa)	365	7.90	8.00	Davis 1989
Natural (2011)	100 (-)	Blue Lough Lake (Newry, U.K.)	365	4.98	4.78	Evans et al. 2017
Natural (2011)	218 (900)	Utikuma Lake (Alberta, Canada)	420	4.27	4.76	Olefeldt et al. 2013
			420	7.46	7.32	
Natural (multiple)	2,044 (11,358)	Western USA	NA	8.0	8.0	Rust et al., 2018
Natural (2015)	900 (-)	Cache la Poudre River (Colorado, USA)	25	7.9	8.5	Son et al. 2015

2.3.2. *Total suspended solids*

Analyzing data available in 16 studies (**Table 2-5**), we show that the relative increase in TSS concentration post-fire could vary up to 3 orders of magnitude (**Figure 2-4**). A wide variation in TSS has been attributed to the complex role of wildfire, surface hydrology, and land properties (Lane et al., 2006; Mast and Clow, 2008; Owens et al., 2013; Rust et al., 2019b; Townsend and Douglas, 2004; Yu et al., 2019). Our analysis shows that the TSS concentration is sensitive to the percentage of watershed burned during a wildfire. Post-fire TSS concentration increased slightly when the burned area is below 20 % and then decreased until the burned area reached 80% of the watershed area; any further increase in the burned area increased TSS concentration by nearly 2 orders of magnitude. An increase in the burned area would ensure sufficient burned residues are available for conveyance into the surface water bodies long after a wildfire (Owens et al., 2013; Wilson et al., 2020). The unburned area particularly in downstream locations can also trap TSS from runoff, thereby decreasing the loading to surface waters. Our analysis also revealed that TSS concentration decreased one year after the fire (**Figure 2-4**). TSS concentration within the first two years post-fire was high, possibly due to the availability of a pool of wildfire-derived debris in the first rainfall events (García-Comendador et al., 2017). After 2 years, depletion of the source and dilution may have decreased TSS. Concentration maxima can also vary with flow rate as flow rate can affect the deposition or removal of TSS from surface water and erosion power. Typically, high TSS concentration has been attributed to high flow rates (Wilson et al., 2020) on barren land caused by wildfires (Chen et al., 2020; Stoof et al., 2012). Our analysis revealed that the flow rate did not affect TSS concentration. However, when the flow rate in surface water exceeded $10 \text{ m}^3 \text{ s}^{-1}$, TSS concentration slightly decreased, although not significant ($p > 0.05$), possibly due to the dilution of TSS by mixing with uncontaminated water. Thus, the sampling protocol should include

the number of rainfalls before the sampling events, the flow rate in surface water, the burned area, and the watershed area.

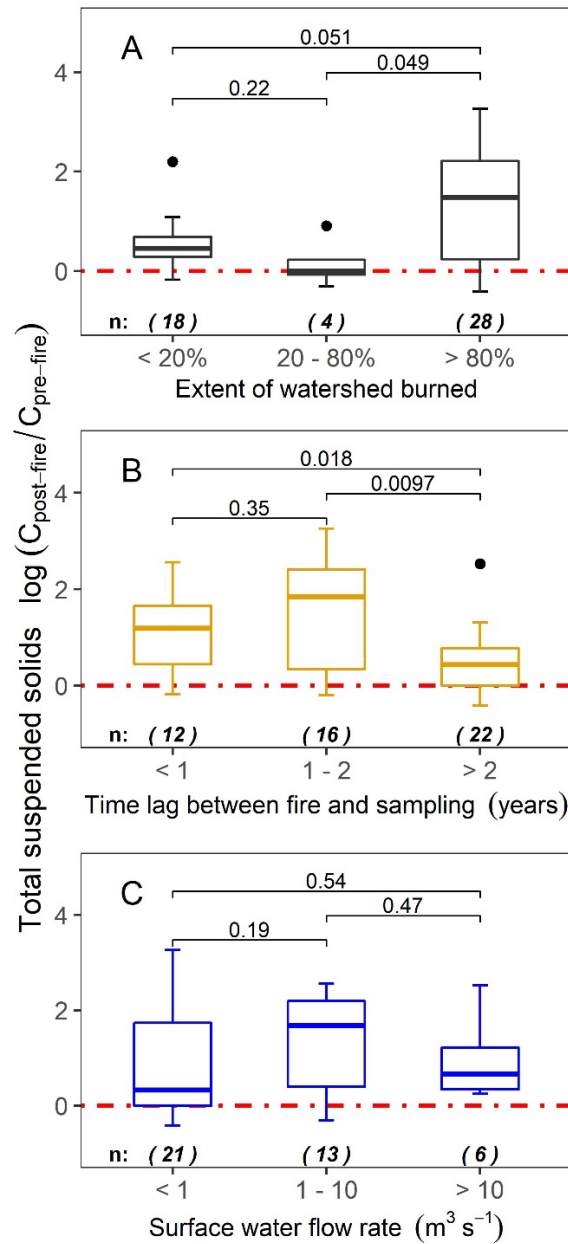


Figure 2-4. The relative concentration of total suspended sediments (TSS) in surface water varies based on (A) the percent of the burned area of the watershed, (B) the time lag between fire and sampling, and (C) the surface water flow rate. $C_{\text{post-fire}}$ and $C_{\text{pre-fire}}$ represent the concentration TSS after and before the wildfire, respectively. The horizontal dashed line represents no variability of TSS before and after the wildfire. Statistical significance is presented above each pair of boxplots and it was determined by the Wilcoxon rank-sum test. The numbers between parentheses and below each boxplot represent the “n-values” used to create each boxplot analysis. Data analysis was based on 16 peer-reviewed articles.

Table 2-4. Effect of wildfires on total suspended solids (TSS) (Alexander, 2004; Brown, 1972; Burke et al., 2013; Chessman, 1986; Ewing, 1996; Gallaher and Koch, 2004; García-Comendador et al., 2017; Hauer and Spencer, 1998; Lane et al., 2006; Mast and Clow, 2008; Owens et al., 2013; Rust et al., 2019; Ryan et al., 2011; Silins et al., 2009; Townsend and Douglas, 2004; Yu et al., 2019).

References	Surface water	Flow rate (m ³ /s)	Time lag between fire and sampling (days)	Type of data	Cpre-fire (mg/L or ppm)	Cpost-fire (mg/L or ppm)	Log removal
Alexander et al. 2004	Runoff	13.75	60		4	91	1.36
		1.60	30		1	360	2.56
	Creek	5.30	270	max	1	157	2.20
		1.31	120		2	122	1.79
Brown 1972	River	19.54	2160		334	112000	2.53
	Stream	9.46	1800	max	7052	143000	1.31
Burke et al. 2013	Stream	0.28	322		157.0	6380	1.61
			379		51.6	71800	3.14
			394	max	882.0	47900	1.73
	Stream	0.28	365		363.4	51700	2.15
			322		25.8	517	1.30
			379	mean	25.4	46200	3.26
Chessman 1986	River	5.25	394		16.3	11600	2.85
			365		22.5	26400	3.07
			485	max	880	80500	1.96
Ewing 1996	River	45.29	1460	max	163.0	2300	1.15
			52	mean	84.0	159	0.28
Gallaher and Koch 2004	Stream	7.76	365		56.0	99	0.25
			N/A	max	43140.0	71400	0.22
García-Comendador 2017	River	0.20	61	max	5244.7	33618	0.81
			1825	mean	3.0	32	1.03
Hauer and Spencer 1998	Stream	N/A	365		3.0	15	0.70
			730		250.3	45540	2.26
Lane 2006	Stream	1.77	1095		250.3	741	0.47
			365	max	250.3	275	0.04
			730		946.3	45564	1.68
	Stream	0.29	1095		946.3	575	-0.22
			365		946.3	365	-0.41

Mast and Clow 2008	Creek	N/A	1365	max	1497.0	147	-1.01
Owens et al. 2013	Creek	7.58	970	max	1320.0	652	-0.31
Rust et al. 2019	Creek	6.20	730		3.5	8.8	0.40
			180		13.0	157.0	1.08
			365		1.5	3.5	0.37
			180		3.0	2.0	-0.18
			180		3.0	9.0	0.48
		N/A	365		6.1	5.6	-0.04
			365		6.1	17.0	0.45
	Stream			median	4.0	5.6	0.15
					4.0	14.3	0.55
			31.87	730		4.0	13.6
Ryan et al. 2011 Silins 2009 Townsend and Douglas 2004		37.75			4.0	25.2	0.80
		N/A			4.0	18.4	0.66
	Creek	0.16	180		19.8	14.3	-0.14
			365		3.0	6.4	0.33
	Stream	5.95	365	peak	10.5	19.6	0.27
	Creek		1460	mean	107.0	17000.0	2.20
					2.7	21.9	0.91
	Stream	0.15	425	mean	11.0	7.0	-0.20
		0.01			0.5	0.5	1.00
		0.06	3650	min	0.5	0.5	1.00
Yu, M et al. 2019		0.65			1.0	0.5	0.50
		0.37			0.5	0.5	1.00
		0.01			1.0	7.0	7.00
	Stream	0.06	3650	median	1.0	1.0	1.00
		0.65			1.0	1.3	1.25
		0.37			4.0	7.0	1.75
		0.01			15110.0	1998.0	0.13
		0.06	3650	max	97.0	3850.0	39.69
		0.65			149.0	35.0	0.23
		0.37			803.0	496.0	0.62

2.3.3. *Dissolved organic carbon*

Our analysis based on 13 peer-reviewed articles that reported DOC concentration shows that, in a majority of studies, wildfire slightly increased DOC immediately after the wildfire (**Table 2-5**). DOC concentration did not vary with the time lag between fire and sampling ($p>0.05$), but the variation of DOC concentration was more apparent in creeks than in a river. The results indicate that lower flows in creeks could make them more susceptible to concentration variability (**Figure 2-4**). The increase in DOC after a wildfire is mainly explained by the combustion of organic matter, leaching from charred litter and dead vegetation, and the fragmentation of particulate organic matter which dissolves in stream water (Betts and Jr, 2009; Uzun et al., 2020). Although some studies observed an increase in DOC concentration after a wildfire (Cawley et al., 2018; Emelko et al., 2011; McEachern et al., 2000), other studies did not find a consistent trend (Jensen et al., 2017; Mast and Clow, 2008). The effect of fires on a net decrease in DOC content in topsoil and plant detritus is short-termed, while its effect in the decomposition of organic matter via disrupting the soil microbial communities and transformation of the organic biomass to black carbon can be long-lasting (Knicker et al., 2006; Wang et al., 2012). Black carbon is resistant to microbial degradation, thus creating recalcitrant particulate carbons or black carbon that may not release a significant amount of DOC compared to the unburned particulate organic carbon (Schmidt et al., 2011). The DOC leached could also be quickly diluted to suppress any impact of wildfires on the DOC concentration (Hohner et al., 2016; Wagner et al., 2015).

Moreover, burn severity can affect DOC export as the highest DOC concentration occurs for low and moderate burn temperatures (250 ° C) (Chow et al., 2019). Furthermore, burn severity can influence the percentage and the type of ash produced during a wildfire which impacts DOC concentration as the ash could adsorb DOC (Wu et al., 2020). The percentage of ash and aging of

ash in runoff could affect its DOC content as freshly burned ash could release a higher concentration of DOC than weathered ash (Revchuk and Suffet, 2014). We did not observe a correlation between DOC concentration and the time lag between fire and sampling (**Figure 2-4**). However, DOC was rarely measured during the first flush when most of the labile organic carbon could be leached out (Vila-Escalé et al., 2007). The increase in DOC concentration could diminish with time due to the washing off of wildfire debris by runoff (Shibata et al., 2003). Moreover, the sorption of DOC to soil particles could decrease DOC export, which often occurs in boreal forests. 4 out of our 13 studies were conducted in boreal forests with some post-fire values lower than pre-fire values (Betts and Jr, 2009; Davidson et al., 2019; Olefeldt et al., 2013; Shibata et al., 2003) because permafrost acts as a barrier preventing infiltration of rainfall in subsoil (Betts and Jr, 2009). The wildfire burns the upper organic soil layer available above permafrost and converts the soil organic carbon in the surface soil to more recalcitrant and soluble organic compounds (Davidson et al., 2019). Thus, the characteristic of the burned area should be reported. Local precipitation can affect the DOC concentration as low precipitation can delay the delivery of DOC or other chemicals generated during a wildfire (Betts and Jr, 2009). Sampling seasons could influence the concentration of DOC in downstream water as the season can affect the hydrology and biogeochemistry processes related to the organic carbon (Burd et al., 2018; Carignan et al., 2000).

Table 2-5. Effect of wildfires on the concentration of dissolved organic carbon (DOC) in surface water based on the time lag between fire and sampling, and the different types of moving surface water. $C_{\text{post-fire}}$ and $C_{\text{pre-fire}}$ represent the concentration of DOC after and before the wildfire, respectively. ΔDOC represents the difference between post-fire and pre-fire measurements. The literature review was based on 13 peer-reviewed articles.

Wildfire type (year)	Burned area (Catchment area) in km ²	Water bodies (Location)	Time lag between fire and sampling (days)	$C_{\text{pre-fire}}$ (mg/L or ppm)	$C_{\text{post-fire}}$ (mg/L or ppm)	ΔDOC	References
Prescribed (2004)	26 (219)	Parks, Reegan, Buckhorn, Blackmare, Fourmile streams (Warren, USA)	1,095	0.95	1.13	0.18	Arkle and Pilliod 2010
Natural (2004)	2,170 (3,338)	Caribou-Poker Creeks (Fairbanks, USA)	30	3.54	3.84	0.30	Betts and Jones 2009
			365	4.68	5.66	0.98	
			730	3.54	3.61	0.07	
			1,095	7.2	6.32	-0.88	
Natural (2002)	215 (215)	Goose (Colorado, USA)	4,380	1.8	3.6	1.80	Chow et al. 2019
	530 (2,408)	Horse (Colorado, USA)	4,380	1.8	2.9	1.10	
	43 (123)	Wigman (Colorado, USA)	4,380	1.8	2.2	0.40	
	20 (53)	Cabin (Colorado, USA)	4,380	1.8	4	2.20	
	179 (388)	West (Colorado, USA)	4,380	1.8	2.6	0.80	
	20 (28)	Fourmile Creek (Colorado, USA)	4,380	1.8	1.5	-0.30	
	5.9 (6.5)	Brush (Colorado, USA)	4,380	1.8	1	-0.80	
Natural (2016)	5,890 (NA)	Poplar Fen (Alberta, Canada)	365	46.8	23.6	-23.20	Davidson et al. 2019
			365	46.4	26.8	-19.60	

Natural (2003)	210 (NA)	South York (Alberta, Canada)	730	3.8	4.6	0.80	Emelko et al. 2011
			730	7.9	8.1	0.20	
			730	1.5	3	1.50	
			1,461	1.5	2.5	1.00	
Natural (2012)	353	Cache la Poudre (Colorado, USA)	335	3.7	4.1	0.40	Hohner et al. 2016
			450	3.7	11.8	8.10	
Natural (2003)	700	McDonald Creek (Montana, USA)	1,365	0.7	1.1	0.40	Mast and Clow 2008
			1,365	3.5	2.3	-1.20	
Natural (2011)	900	Utikuma Lake (Alberta, Canada)	420	28.3	16.6	-11.70	Olefeldt et al. 2013
			420	71.3	88.6	17.30	
Natural (multiple)	2,044 (11,358)	Western USA	NA	5.2	5.3	0.10	Rust et al. 2018
Prescribed (1999)	NA (11)	Caribou Poker Creeks (Alaska, USA)	30	30	11	-19.00	Shibata et al. 2003
Natural (2015)	281 (3,017)	Cache creek (Clearlake, USA)	365	5.4	4.9	-0.50	Uzun et al. 2020
	33 (3,017)	Cold Creek (Napa, USA)	365	5.4	9	3.60	
Natural (2003)	45 (56.25)	The Gallifa creek (Catalonia, Spain)	45	1.57	410	408.43	Vila-Escale, M. et al. (2007)
	45 (56.25)	Mura (Catalonia, Spain)	78	1.57	10	8.43	
Natural (2012)	350 (4,900)	Cache la Poudre (Colorado, USA)	60	6.8	2.6	-4.20	Writer et al. 2014
			60	2.6	5.9	3.30	
			60	2.6	6	3.40	

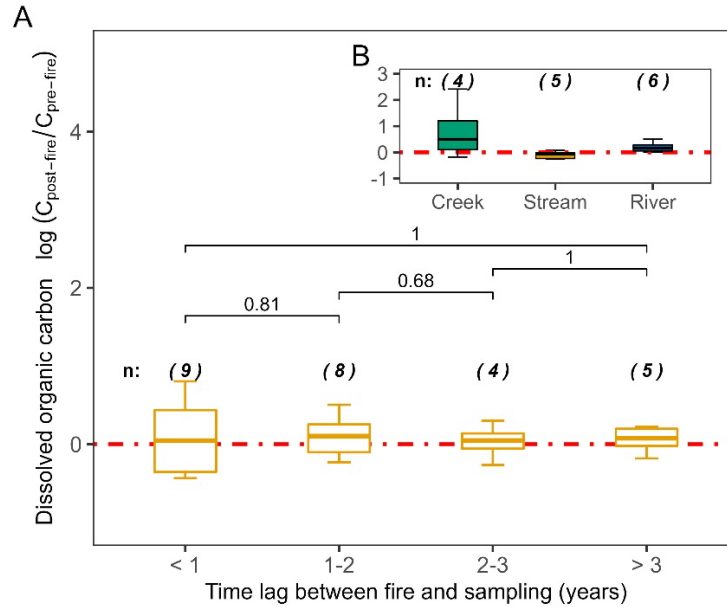


Figure 2-5. The variance of the relative concentration of Dissolved Organic Carbon (DOC) in surface water varies based on (A) the time lag between fire and sampling (B) the different types of moving surface water (e.g. creek, river, and stream). The numbers above each boxplot and between parentheses represent the “n-values” used to create each boxplot analysis. $C_{\text{post-fire}}$ and $C_{\text{pre-fire}}$ represent the concentration DOC after and before the wildfire, respectively. The horizontal red dashed line represents no variation of DOC before and after wildfire. The literature review was based on 13 peer-reviewed articles.

2.3.4. Nutrients

Analyzing results from 10 studies, we show that wildfire increased nutrients TN and TP in stream water (**Table 2-6**). The nutrient concentration typically increases significantly during post-fire storm events, especially during the first flush as solute concentrations reach their maximum (Alexander, 2004; Gallaher and Koch, 2004). Small decreases in TN and TP concentrations have been reported 3 years after the fire even though these concentrations return to pre-fire background levels a couple of years after the fire (Arkle and Pilliod, 2010). Our analysis revealed that nutrient concentrations were highest within the first year after the wildfire and then decreased with time (**Figure 2-6**), indicating most dissolved nutrients were washed off from burned areas within 1 year after the fire (Pierson et al., 2019). Nutrients concentration in surface waters after a wildfire could increase (Earl and Blinn, 2003; Emelko et al., 2011; Hohner et al., 2019; Rhoades et al., 2019a)

because runoff after a fire can erode burned litter, a source of organic nitrogen (Gray and Dighton, 2006) and phosphorus (García-Oliva et al., 2018), and export particulate nutrients to surface water (de Koff et al., 2006; Pierson et al., 2019). However, a couple of studies reported the nutrient concentration could become similar to the background level after several weeks (Spencer et al., 2003) to a few months after wildfire (Corbin, 2012). A faster recovery time in these studies could be attributed to a smaller area burned where the available nutrients pool can be depleted after the first few rainfall events. Similarly, increased precipitation within the first post-fire season or high-intensity rainfall could increase the peak due to the high loading rate (Sherson et al., 2015). An increase in the burned area increases the contributing area for the runoff (Burke et al., 2005) and thus should affect the nutrient loading or availability for leaching during a rainfall event. Our analysis shows that wildfire increased the export of nutrients post-fire relative to the pre-fire level based on the time lag between sampling time and the fire (**Figure 2-6**), and the increase in nutrient concentration after the fire is significant when the time lag is within a year. However, the percentage of area burned did not affect the extent to which nutrient concentration would increase after the fire. More data is needed to understand how an increase in burned area percent affects nutrient export.

Our analysis revealed that wildfire effect on nutrient concentration in water varies with species type. After the wildfire, the relative increase in TN concentration was higher than TP. While TP concentrations returned to pre-fire levels within 2 years, TN concentrations remained slightly elevated beyond 2 years of post-fire sampling (**Figure 2-7**). Most studies did not report the speciation of N and P in surface water, which could vary with an increase in the pH of water polluted with wildfire ash within one year after the fire (Earl and Blinn, 2003; Fidel et al., 2018). Higher pH could also slow down the biological decomposition of organic materials in soil and the

release of nutrients (Hanan et al., 2020), which explains a delay in TN concentration post-fire (Mast et al., 2016). Although sulfate released post-fire can also be a source of nutrients (Hinckley et al., 2020), few studies have evaluated the impact of wildfires on sulfate (Hubbert et al., 2015; Murphy et al., 2006). Our analysis also reveals that total N (TN) and total P (TP) increased following the wildfire, but the increase depended on the time lag between fire and sampling (**Figure 2-7**). The most noticeable increase after the wildfire is the nitrate concentration, which elevates TN concentration (Oliver et al., 2012) remaining high over 5 years (Bayley et al., 1992; Bladon et al., 2008). The slope of the burned area, post-fire rainfall frequency, wildfire extent, and burn severity could affect nutrient concentration either by increasing or delaying the delivery of the nutrients to streams (Blake et al., 2020; Gustine et al., 2022; Rhoades et al., 2011). As a high temperature could break down organic nutrients to inorganic form, which can be easily dissolved in rainwater, burn severity should be reported in the studies. Similarly, heavy post-fire rainfall could increase stream sediment loading and the associated increase in nutrients (Ice et al., 2004).

Table 2-6. Effect of wildfires on the concentration of nutrients (Total Nitrogen and Total Phosphorous) in surface water varies based on time lag between fire and sampling. $C_{\text{post-fire}}$ and $C_{\text{pre-fire}}$ represent the concentration of nutrients after and before the wildfire, respectively. ΔTN represents the difference between post-fire and pre-fire total nitrogen measurements and ΔTP represents the difference between post-fire and pre-fire total phosphorus measurements. The literature review was based on 10 peer-reviewed articles.

Wildfire type (year)	Burned area (Catchment area) in km ²	Water bodies (Location)	Time lag between fire and sampling (days)	Type of nutrients	$C_{\text{pre-fire}}$ (mg/L or ppm)	$C_{\text{post-fire}}$ (mg/L or ppm)	ΔTN	ΔTP	References
Natural (2003)	3,611 (3,801)	Dartmouth Reservoir (Dartmouth, Australia)	120	N	0.07	9.02	8.95		Alexander et al. 2004
		Tambo River (Swifts Creek, Australia)	120	N	0.20	1.60	1.40		-
		Parks, Reegan, Buckhorn, Blackmare, Fourmile (Warren, USA)	120	P	0.02	0.14	0.12		
Prescribed (2004)	26 (219)		1095	N	0.02	0.01	-0.01		Arkle and Pilliod 2010
			1095	P	0.19	0.14		-0.05	
Natural (2017)	1,000 (3,333)	Rio Zezere (Pedrogao Grande, Portugal)	NA	N	0.04	1.72	1.68		Basso al. 2020
			NA	N	351.60	744.73	393.13		
			NA	P	52.08	96.39		44.31	-
			NA	P	0.03	0.26		0.23	
			NA	P	0.21	1.08		0.87	-
			NA	P	56.13	317.72		261.59	
Natural (1974)	1.74 (2.39)	Rawson Lake (Kenora, Canada)	548	N	0.31	0.54	0.24		Bayley 1991

Natural (1974)		548	N	0.39	0.78	0.40	Bayley 1991
Natural (1980)	2.33 (2.39)	548	N	0.41	0.74	0.33	-
		548	P	0.01	0.01	0	
		548	P	0.02	0.03	0.01	
		548	P	0.02	0.04	0.02	
Natural (2003)	1.91 (3.60)	365	N	0.20	1.07	0.87	Bladon et al. 2008
		730	N	0.35	0.92	0.57	
		1095	N	0.23	0.35	0.12	
Natural (2000)	30 (NA)	1095	P	2.00	15.00	13.00	Gallaher and Koch 2004
Natural (2012)	384 (NA)	450	N	0.29	0.66	0.37	Hohner et al. 2016
		450	P	0.02	0.06	0.04	
Natural (2007)	8 (15)	365	N	0.25	0.25	0	Oliver et al. 2012
		365	N	0.25	0.25	0	
		365	N	0.25	0.30	0.05	
		365	N	0.25	0.35	0.10	
		365	P	0.03	0.01	-0.02	
		365	P	0.03	0.02	-0.01	
		365	P	0.03	0.03	0	
		365	P	0.03	0.04	0.01	
Natural (multiple)	2,044 (11,358)	NA	N	1.7	1.20	-0.5	Rust et al., 2018
Natural (1998)	6.27 (6.60)	425	N	0.25	0.32	0.07	Townsend and Douglas 2004
		425	P	0.01	0.01	0	

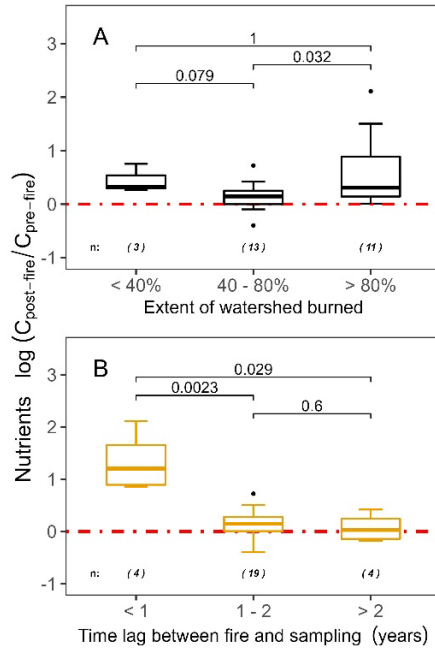


Figure 2-6. The variance of the relative concentration of nutrients (Total Nitrogen and Total Phosphorous) in surface water varies based on (A) percentage of the watershed burned area and (B) the time lag between fire and sampling. $C_{\text{post-fire}}$ and $C_{\text{pre-fire}}$ represent the concentration of nutrients after and before the wildfire, respectively. The horizontal red dashed line represents no variation of nutrients before and after wildfire. Statistical significance is presented above each pair of boxplots, and it was determined by the Wilcoxon rank sum test. The number between parentheses represents the number (n-value) of data points available for analysis. The literature review was based on 10 peer-reviewed articles.

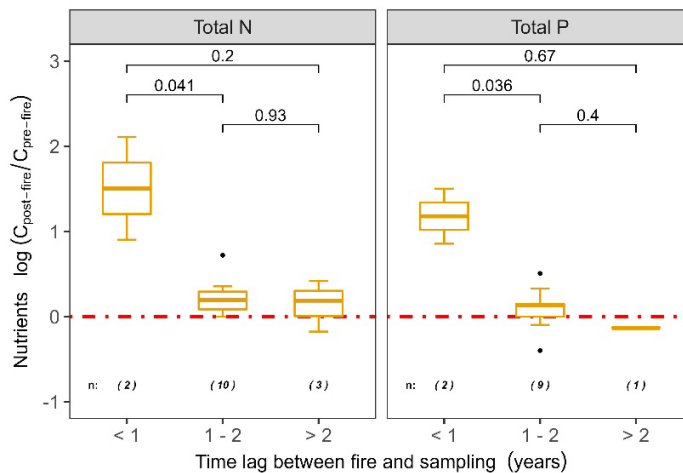


Figure 2-7. Concentration of total nitrogen (N) and total phosphorus (P) in surface waters varies with time lag between fire and sampling. The numbers below each boxplot and between parentheses represent the “n-values” used to create each boxplot analysis. $C_{\text{post-fire}}$ and $C_{\text{pre-fire}}$ represent the concentration of nutrients after and before the wildfire, respectively. The number between parentheses represents the number (n-value) of data points available for analysis. Statistical significance is presented above each pair of boxplots, and it

was determined by the Wilcoxon rank sum test. The horizontal red dashed line represents no variation of nutrient concentration before and after wildfire.

2.3.5. Heavy metals

Only 6 of the 44 surveyed studies reported heavy metal concentrations (**Table 2-7**). Based on the limited data, heavy metal concentration in surface water increased after a wildfire, but the extent of the increase depended on the extension of the burned area, the time lag between fire and sampling, and on heavy metal species (**Figure 2-8**). Due to the lack of data about the watershed from the reported studies that measured heavy metals after wildfires, the normalized area of the burned watershed for heavy metals concentration was not calculated. Nevertheless, an increase in the burned area by one order of magnitude resulted in an increase in the heavy metal concentration by 1.6 logs. The result is attributed to an increased amount of burned residues in a large area. Wildfires can affect heavy metal concentration in surface water by introducing residues containing metals (Ignatavičius et al., 2006) or by altering the pH of water via the deposition of ash which can change the speciation of metals (Nayak et al., 2015). Moreover, large wildfire areas are partially related to more intense fires (Laurent et al., 2019), which typically produce ash enriched with metals (Harper et al., 2019; Murphy et al., 2020). Heavy metals are naturally present in soil and can accumulate in plant biomass via root uptake (Peralta-Videa et al., 2009). The burning of biomass unlocks the metals and concentrates them in the ash (Burton et al., 2016; Øygard et al., 2005; Stein et al., 2012). The high temperatures during wildfires can break the metal-humic acid bonds in soil organic matter and release heavy metals adsorbed in the soil (Abraham et al., 2018). Post-fire conditions can also lower soil organic content – a natural adsorbent for heavy metals, thereby increasing the release of heavy metals (Stein et al., 2012).

The increase in heavy metals after wildfire also appears to depend on the species of heavy metal (**Figure 2-8**). Comparing the heavy metals concentration in studies with the burned area

above 40 km², we found that heavy metals concentration decreased in the following order: Pb > Cu ≈ Zn. While Cu, Pb, and Zn exhibit elevated concentrations even after one year of the wildfire, the levels of Fe, Mg, and Mn returned to pre-fire levels after 1 year (**Figure 2-9**). A larger variation in Pb concentrations compared to Cu and Zn concentrations could be attributed to the variable spatial distribution of Pb on topsoil (Yang et al., 2009). Because some metals such as Pb and Cu have higher affinity to soil organic matter (Abraham et al., 2017), their leaching could be slower depending on the species and organic matter quality affected by the fire. Thus, the variability in the release of these heavy metal species can depend upon soil and fire characteristics. Interestingly, our results suggest that the concentration of heavy metals was delayed by at least a year after the wildfire (**Figure 2-8**), indicating a phase lag in peak concentration relative to other contaminants such as nutrients or TSS. As pH increased within a year post-fire (**Figure 2-3**), elevated pH created by ash dissolution in the first 12 months post-fire, could decrease the solubility of the metals and their concentration in the water (Kashem and Singh, 2001). Therefore, it is critical to measure pH within 12 months after a fire in the sampling protocol to link the change in concentration of pollutants with water chemistry post-fire. Unlike dissolved metals, particulate metal concentration could continue to increase even 5 years after a wildfire (Rust et al., 2018), but such a correlation was not observed in this study due to the unavailability of long-term data. Although many studies have reported a post-fire increase in Hg concentration (Abraham et al., 2018; Jensen et al., 2017; Kelly et al., 2006; Ku et al., 2018; Webster et al., 2016), they rarely reported pre-fire concentration—one criterion for our analysis. Thus, Hg is not included in our analysis.

Table 2-7. Effect of wildfires on heavy metals (As, Cd, Cu, Fe, Mg, Mn, Ni, Pb, V, Zn). (Burke et al., 2013; Ignatavičius et al., 2006; Pinedo-Gonzalez et al., 2017; Ré et al., 2020; Stein et al., 2012; Townsend and Douglas, 2004).

References	Surface water	Flow rate (m ³ /s)	Species	Time lag between fire and sampling (days)	Type of data	Cpre-fire (mg/L or ppm)	Cpost-fire (mg/L or ppm)	Log removal
Burke et al. 2013	Stream	0.28	Cu	322		0.0066	0.0908	1.14
				398		0.004	0.207	1.71
				379	max	0.0023	0.256	2.05
				394		0.034	0.0365	0.03
				365		0.0117	0.148	1.10
				322		0.0044	0.0208	0.67
				398		0.0026	0.169	1.81
				379	mean	0.0014	0.114	1.91
			394		0.0052	0.0226	0.64	
			365		0.0034	0.0815	1.38	
			322		0.0011	0.954	2.94	
			398		0.0017	2.08	3.09	
			379	max	0.0001	1.29	4.11	
			394		0.035	0.277	0.90	
			365		0.0095	1.15	2.08	
			322		0.0007	0.0788	2.05	
			Pb	398		0.0007	1.23	3.24
				379	mean	0.0001	0.831	3.92
				394		0.0009	0.0813	1.96
				365		0.0006	0.555	2.97
				322		0.034	0.606	1.25
				398		0.026	2.54	1.99
				379	max	0.015	1.67	2.05
				394		0.12	0.601	0.70
			Zn	365		0.0488	1.36	1.45
				322		0.0138	0.0828	0.78
				398		0.0173	1.48	1.93
				379	mean	0.006	0.956	2.20
394		0.0051	0.178	1.54				
365		0.0105	0.674	1.81				

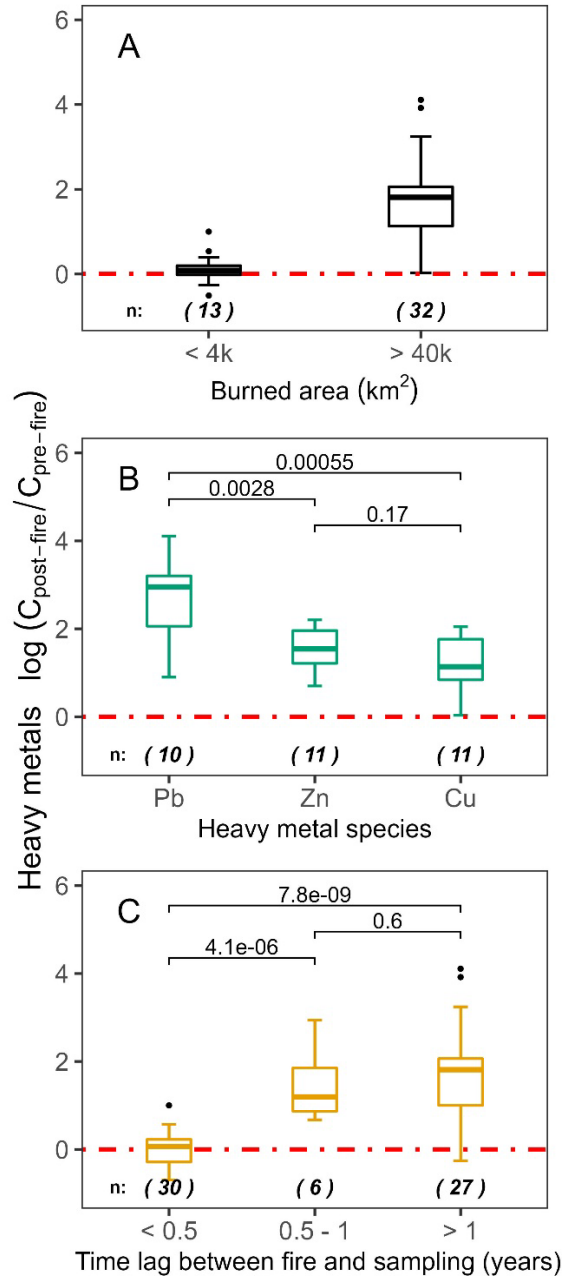


Figure 2-8. The relative concentration of heavy metals (As, Cd, Cu, Fe, Mg, Mn, Ni, Pb, V, Zn) in surface water varies based on (A) burned area of the watershed, (B) heavy metals species (Cu, Pb, and Zn) and (C) time lag between fire and sampling. $C_{\text{post-fire}}$ and $C_{\text{pre-fire}}$ represent the concentration of heavy metals after and before the wildfire, respectively. The horizontal dashed line represents no variation of heavy metals before and after the wildfire. Statistical significance is presented above each pair of boxplot and it was determined by the Wilcoxon rank-sum test. The numbers between parentheses and below each boxplot represent the “n-values” used to create each boxplot analysis. The literature review was based on 6 peer-reviewed articles.

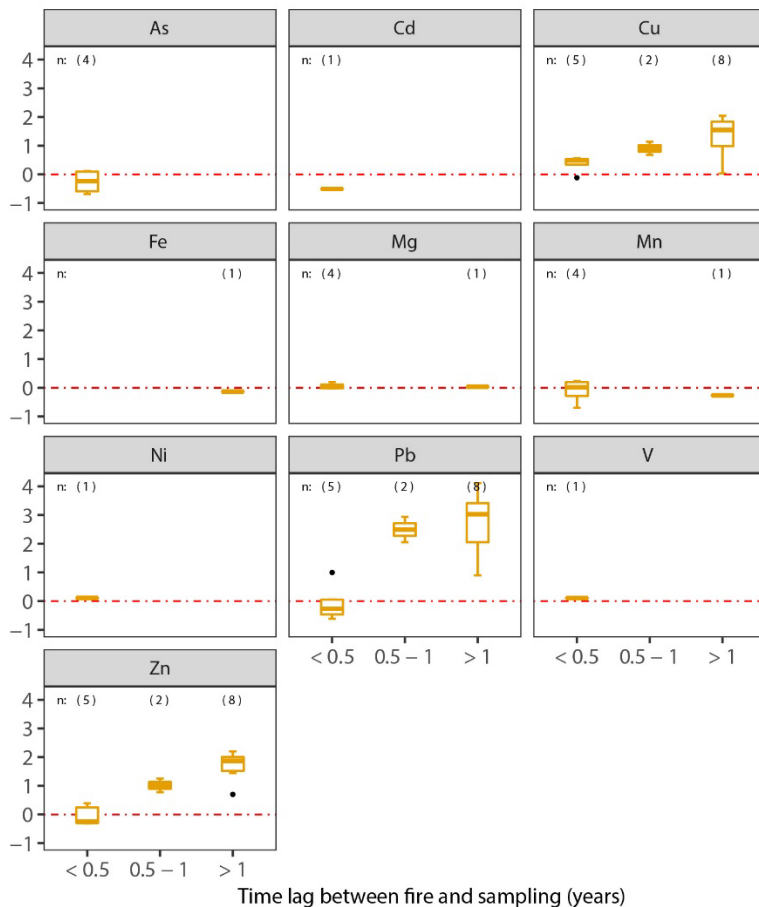


Figure 2-9. Relative concentration of different heavy metal species after wildfire in surface waters. The numbers below or above each boxplot represent the “n-values” used to create each boxplot analysis. $C_{\text{post-fire}}$ and $C_{\text{pre-fire}}$ represent the concentration of heavy metals after and before the wildfire, respectively. The horizontal red dashed line represents no variation of heavy metals before and after wildfire. The number between parentheses represents the number (n-value) of data points available for analysis.

2.3.6. Polycyclic aromatic hydrocarbons (PAHs)

Only 3 studies reported the concentration of specific PAH after a wildfire (**Table 2-8**). Overall, 44 studies were selected for this review, of which 40 reported pre-fire data. However, none of them reported PAH concentration before the wildfire or after 1 year of the wildfire, which limits our understanding of the fate of PAH in long term. Analyzing the limited dataset, we found that PAH concentration before and after 4 months post-fire depended on the number of PAH rings and a time lag between fire and sampling (**Figure 2-10, and Figure 2-11**). Although our results show that the concentration of PAH exceeded the limits set by US EPA (100 ng L^{-1}) or European

Union (100 ng L⁻¹) or World Health Organization (200 ng L⁻¹) on some occasions, the concentrations of individual PAH species in the majority of samples (>95% of data) were below EPA's limits (US EPA, 2018). As the PAH concentration slightly increased with the delay in the sampling period, the concentration may continue to increase if the samples were taken beyond one year. Thus, future studies should monitor PAH concentration beyond 1 year to examine the exceedance of PAH levels above limits in the U.S. and Europe. Furthermore, the total PAH concentration could exceed the limit when individual concentration may not (Felemban et al., 2019; Karyab et al., 2013).

PAH concentration was higher if sampled after 4 months of fire than within 4 months of fire, but the difference was significant if the aromatic ring number was 4 or 6 (**Figure 2-11**). Our analysis also reveals after 4 months, the concentration of PAH with 3-4 aromatic rings was consistently higher than that of heavier PAH (with 5 or 6 rings) that dissolved concentration of heavier PAH did not increase after 4 months, potentially because they are more likely associated with particulate matters. An overall increase in PAH concentration after 4 months of fire indicates the slow release of PAH from the burned materials after the initial washing of particulate-bound PAH. PAHs can be adsorbed onto soil particles or ash (Kim et al., 2003) and mobilized with fine particles (Vila-Escalé et al., 2007). Post-fire surface runoff could carry dissolved and particle-bound PAH from burned areas to surface water bodies through increased erosion in post-fire rainfall (Campos et al., 2019; Vila-Escalé et al., 2007). Heavier PAH is more likely to adsorb on particles and sediments (Tucca et al., 2020), which explains why a lower dissolved concentration of PAH with >4 rings was found within or after 4 months after fire (**Figure 2-10**). The concentration of PAH after a fire can also depend on the burn intensity of the wildfire and the type of forests (Vergnoux et al., 2011). For instance, black ash – usually produced at lower temperatures

– typically contains more PAHs and has a higher size of aromatic structures (Chen et al., 2018) than the white ash, which is produced at higher burn temperatures. Thus, an increase in the concentration of black ash – and possibly organic-rich sediment – can increase high molecular weight PAH concentrations in runoff (Campos et al., 2019; Kim et al., 2003). Although post-fire heavy rainfall is likely to decrease low molecular weight PAHs due to dilution and subsequent photo-oxidation (Campos et al., 2012; Olivella et al., 2006; Vila-Escalé et al., 2007), the hydrophobicity and environmental recalcitrance of PAH seems to increase with their molecular weight (Quantin et al., 2005). Thus, both particulate and dissolved PAH should be measured in surface waters for at least 2 years after the fire to estimate the total export of PAH after a wildfire, and the nature of the fire should be reported to explain the variability of the results.

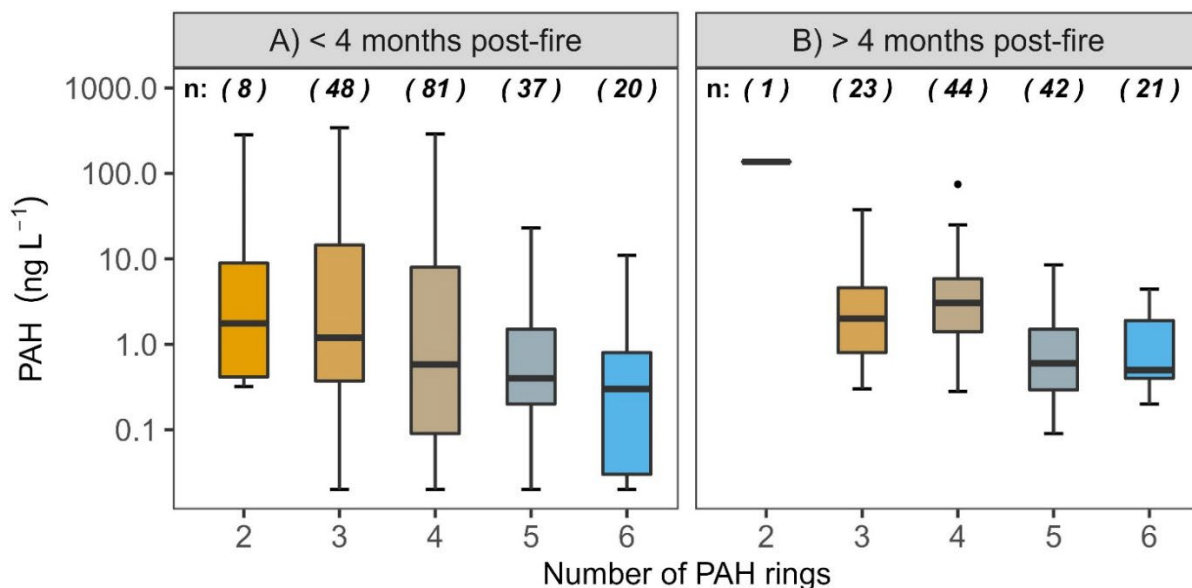


Figure 2-10. Concentrations of polycyclic aromatic hydrocarbons (PAH) in surface waters after wildfire. PAH compounds were divided into 5 categories depending on the number of rings of their chemical structure. Graphical data was separated into two sets based on the time lag between fire and sampling: “< 4 months” samples were collected between 12 and 107 days after a wildfire, while “> 4 months” samples were collected between 122 and 445 days after the wildfire. The numbers between parenthesis and above each boxplot represent the “n-values” used to create the boxplot analysis. Data were collected from 3 peer-reviewed articles (Campos et al., 2012; Olivella et al., 2006; Vila-Escalé et al., 2007).

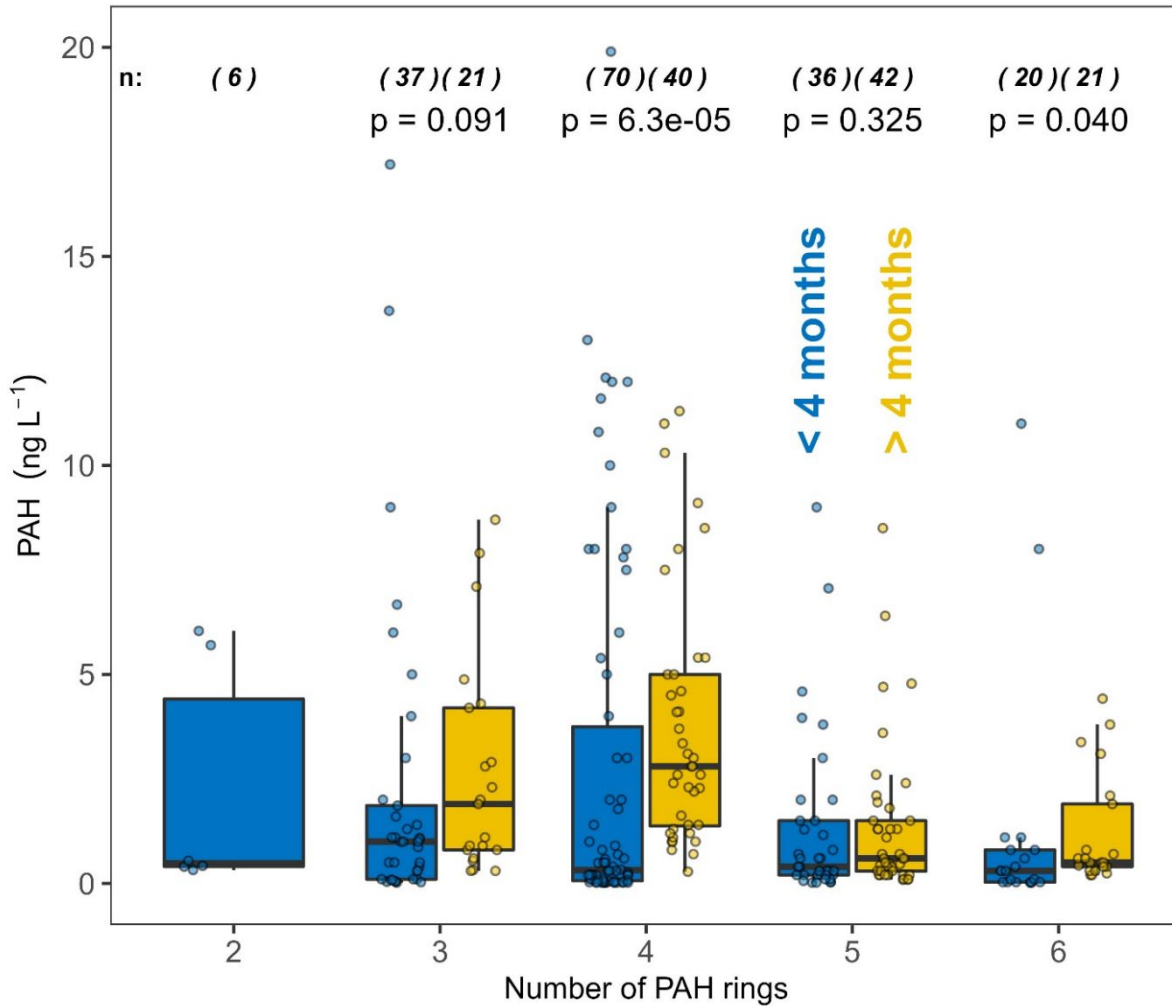


Figure 2-11. Comparison of polycyclic aromatic hydrocarbons (PAH) concentration in surface waters after wildfires for each type of PAHs (rings) between post-fire concentration within 4 months post-fire (blue boxplot) and after 4 months after the fire (yellow boxplot). PAH compounds were divided into 5 categories depending on the number of rings of their chemical structure. The number between parenthesis represents the number (n-value) of data points available for the analysis. Statistical significance is presented above each pair of boxplots, and it was determined by the Wilcoxon rank sum test.

Table 2-8. Effect of wildfires on polycyclic aromatic hydrocarbons (PAHs) (Campos et al., 2012; Olivella et al., 2006; Vila-Escalé et al., 2007).

Reference s	Surface water	Flow rate (m ³ /s)	Numbe r of rings	Type of data	Total Contaminant	Time lag between fire and samplin g (days)	Cpre- fire (ng/L)	Cpost -fire (ng/L)					
Campos et al. 2012	Overlan d flow	N/A	2	dissolved	Naphthalene	47	N/A	14.8					
					Acenaphthylene			0.105					
			3		Acenaphthene			0.105					
					Fluorene			5.32					
					Phenanthrene			0.105					
					Anthracene			0.105					
					Fluoranthene			0.105					
					Pyrene			1.86					
			4		Chrysene			14.6					
					Benzo[a]anthracene			53.4					
			5		Benzo[b]fluoranthene			0.105					
					Benzo[k]fluoranthene			0.105					
					Benzo[a]pyrene			0.105					
			6		Dibenz[a,h]anthracene			0.105					
					Benzo[g,h,i]perylene			0.105					
					Indeno[1.2.3-cd]pyrene			0.105					
			2		dissolved			N/A	2	Naphthalene	365	N/A	24.5
										Acenaphthylene			0.105
			3						Acenaphthene	0.105			
									Fluorene	0.105			
									Phenanthrene	1.68			
			4						Anthracene	0.105			
									Fluoranthene	1.22			
			4						Pyrene	1.21			
									Chrysene	14.3			
			5						Benzo[a]anthracene	0.105			
									Benzo[b]fluoranthene	0.98			
									Benzo[k]fluoranthene	1.99			
6	Benzo[a]pyrene	0.105											
	Dibenz[a,h]anthracene	0.105											
	Benzo[g,h,i]perylene	0.105											
2	particulat e	N/A	2	Naphthalene		47	N/A		284				
				Acenaphthylene					343				
3	particulat e		Acenaphthene	0.105									
			Fluorene	41.5									
	dissolved		Phenanthrene	42.4									
4	particulat e		Anthracene	0.105									
			Fluoranthene	10.8									
5	dissolved		Pyrene	11.6									
			Chrysene	81.6									
			Benzo[a]anthracene	290									
5	Benzo[b]fluoranthene		0.105										

				Benzo[k]fluoranthene		0.105
				Benzo[a]pyrene		0.105
				Dibenz[a,h]anthracene		0.105
			6	Benzo[g,h,i]perylene		0.105
				Indeno[1.2.3-cd]pyrene		0.105
			2	particulate	Naphthalene	137
				dissolved	Acenaphthylene	0.105
					Acenaphthene	0.105
			3	particulate	Fluorene	30.9
					Phenanthrene	37.7
				dissolved	Anthracene	0.105
				particulate	Fluoranthene	8
			4		Pyrene	3.35
					Chrysene	74.6
				dissolved	Benzo[a]anthracene	0.105
				particulate	Benzo[b]fluoranthene	1.94
			5		Benzo[k]fluoranthene	4.78
				dissolved	Benzo[a]pyrene	0.105
					Dibenz[a,h]anthracene	0.105
			6	particulate	Benzo[g,h,i]perylene	3.38
					Indeno[1.2.3-cd]pyrene	4.42
			3		Phenanthrene	88
					Anthracene	56
					Fluoranthene	5
					Pyrene	8
			4		Benzo[a]anthracene	0.4
					Chrysene+Triphenylene	1.4
						30
					Benzo[b]fluoranthene	0.2
					Benzo[k]fluoranthene	0.3
			5		Benzo[a]pyrene	0.2
					Dibenz[a,h]anthracene	0.01
					Indeno[1.2.3-cd]pyrene	0.01
			6		Benzo[g,h,i]perylene	0.01
					Phenanthrene	0.1
			3	particulate	Anthracene	0.02
					Fluoranthene	0.02
					Pyrene	0.02
			4		Benzo[a]anthracene	0.01
					Chrysene+Triphenylene	0.06
						60
					Benzo[b]fluoranthene	0.01
					Benzo[k]fluoranthene	0.01
			5		Benzo[a]pyrene	0.01
					Dibenz[a,h]anthracene	0.01
					Indeno[1.2.3-cd]pyrene	0.01
			6		Benzo[g,h,i]perylene	0.01
					Phenanthrene	2
			3		Anthracene	0.6
					Fluoranthene	1.2
			4		Pyrene	1.3
						150

[Olivella et al. 2006](#)

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0.006

N/A

		Benzo[a]anthracene	1
		Chrysene+Triphenylene	4.1
5		Benzo[b]fluoranthene	0.6
		Benzo[k]fluoranthene	0.09
		Benzo[a]pyrene	0.4
		Dibenz[a,h]anthracene	0.09
6		Indeno[1.2.3-cd]pyrene	0.2
		Benzo[g,h,i]perylene	0.24
3		Phenanthrene	1.4
		Anthracene	0.04
		Fluoranthene	0.09
		Pyrene	0.05
4		Benzo[a]anthracene	0.01
		Chrysene+Triphenylene	0.3
	30		
		Benzo[b]fluoranthene	0.03
5		Benzo[k]fluoranthene	0.01
		Benzo[a]pyrene	0.01
		Dibenz[a,h]anthracene	0.01
6		Indeno[1.2.3-cd]pyrene	0.02
		Benzo[g,h,i]perylene	0.03
3		Phenanthrene	1
		Anthracene	0.04
		Fluoranthene	0.02
		Pyrene	0.02
4		Benzo[a]anthracene	0.01
		Chrysene+Triphenylene	0.03
	60		
		Benzo[b]fluoranthene	0.01
5		Benzo[k]fluoranthene	0.01
		Benzo[a]pyrene	0.01
		Dibenz[a,h]anthracene	0.01
6		Indeno[1.2.3-cd]pyrene	0.01
		Benzo[g,h,i]perylene	0.01
3		Phenanthrene	2.3
		Anthracene	0.3
		Fluoranthene	1
		Pyrene	0.8
4		Benzo[a]anthracene	0.7
		Chrysene+Triphenylene	2.2
	150		
		Benzo[b]fluoranthene	0.7
5		Benzo[k]fluoranthene	0.2
		Benzo[a]pyrene	0.4
		Dibenz[a,h]anthracene	0.2
6		Indeno[1.2.3-cd]pyrene	0.2
		Benzo[g,h,i]perylene	0.4
3		Phenanthrene	5
		Anthracene	0.4
		Fluoranthene	3
4		Pyrene	25
	30		

		Benzo[a]anthracene	0.01
		Chrysene+Triphenylene	12
5		Benzo[b]fluoranthene	0.01
		Benzo[k]fluoranthene	0.01
		Benzo[a]pyrene	0.01
		Dibenz[a,h]anthracene	0.01
6		Indeno[1.2.3-cd]pyrene	0.01
		Benzo[g,h,i]perylene	0.01
3		Phenanthrene	0.5
		Anthracene	0.1
		Fluoranthene	0.05
		Pyrene	0.03
4		Benzo[a]anthracene	0.01
		Chrysene+Triphenylene	0.05
	60		
		Benzo[b]fluoranthene	0.01
5		Benzo[k]fluoranthene	0.01
		Benzo[a]pyrene	0.01
		Dibenz[a,h]anthracene	0.01
6		Indeno[1.2.3-cd]pyrene	0.03
		Benzo[g,h,i]perylene	0.01
3		Phenanthrene	1.1
		Anthracene	0.9
		Fluoranthene	1
		Pyrene	2.6
4		Benzo[a]anthracene	1.1
		Chrysene+Triphenylene	5.4
	150		
		Benzo[b]fluoranthene	1.3
5		Benzo[k]fluoranthene	0.3
		Benzo[a]pyrene	0.7
		Dibenz[a,h]anthracene	0.1
6		Indeno[1.2.3-cd]pyrene	0.5
		Benzo[g,h,i]perylene	0.7
3		Phenanthrene	1.3
		Anthracene	1
		Fluoranthene	0.2
		Pyrene	0.3
4		Benzo[a]anthracene	0.01
		Chrysene+Triphenylene	2
	30		
		Benzo[b]fluoranthene	0.01
5		Benzo[k]fluoranthene	0.6
		Benzo[a]pyrene	0.3
		Dibenz[a,h]anthracene	0.01
6		Indeno[1.2.3-cd]pyrene	0.01
		Benzo[g,h,i]perylene	0.01
3		Phenanthrene	0.3
		Anthracene	0.03
4		Fluoranthene	0.02
	60		
		Pyrene	0.02

		Benzo[a]anthracene	0.01
		Chrysene+Triphenylene	0.02
5		Benzo[b]fluoranthene	0.01
		Benzo[k]fluoranthene	0.01
		Benzo[a]pyrene	0.01
		Dibenz[a,h]anthracene	0.01
6		Indeno[1.2.3-cd]pyrene	0.01
		Benzo[g,h,i]perylene	0.01
3		Phenanthrene	4.2
		Anthracene	0.8
		Fluoranthene	2.8
		Pyrene	3.1
4		Benzo[a]anthracene	21
		Chrysene+Triphenylene	7.5
	150		
		Benzo[b]fluoranthene	2.6
5		Benzo[k]fluoranthene	0.6
		Benzo[a]pyrene	1.3
		Dibenz[a,h]anthracene	0.2
6		Indeno[1.2.3-cd]pyrene	0.5
		Benzo[g,h,i]perylene	0.6
3		Phenanthrene	3
		Anthracene	2
		Fluoranthene	0.8
		Pyrene	0.9
4		Benzo[a]anthracene	13
		Chrysene+Triphenylene	21
	30		
		Benzo[b]fluoranthene	23
5		Benzo[k]fluoranthene	9
		Benzo[a]pyrene	3
		Dibenz[a,h]anthracene	1.5
6		Indeno[1.2.3-cd]pyrene	8
		Benzo[g,h,i]perylene	11
3		Phenanthrene	1.6
		Anthracene	0.3
		Fluoranthene	0.3
		Pyrene	0.6
4		Benzo[a]anthracene	0.5
		Chrysene+Triphenylene	1
	60		
		Benzo[b]fluoranthene	0.8
5		Benzo[k]fluoranthene	0.2
		Benzo[a]pyrene	0.2
		Dibenz[a,h]anthracene	0.3
6		Indeno[1.2.3-cd]pyrene	0.8
		Benzo[g,h,i]perylene	0.6
3		Phenanthrene	2.8
		Anthracene	0.8
		Fluoranthene	1.4
4		Pyrene	2.3
	150		

		Benzo[a]anthracene	1.2
		Chrysene+Triphenylene	5
5		Benzo[b]fluoranthene	1.8
		Benzo[k]fluoranthene	0.3
		Benzo[a]pyrene	1.1
		Dibenz[a,h]anthracene	0.2
6		Indeno[1.2.3-cd]pyrene	0.5
		Benzo[g,h,i]perylene	0.8
3		Phenanthrene	29
		Anthracene	26
		Fluoranthene	34
		Pyrene	234
4		Benzo[a]anthracene	0.01
		Chrysene+Triphenylene	12
	30		
		Benzo[b]fluoranthene	0.01
5		Benzo[k]fluoranthene	0.01
		Benzo[a]pyrene	0.01
		Dibenz[a,h]anthracene	0.01
6		Indeno[1.2.3-cd]pyrene	0.01
		Benzo[g,h,i]perylene	0.01
3		Phenanthrene	0.5
		Anthracene	0.05
		Fluoranthene	0.04
		Pyrene	0.03
4		Benzo[a]anthracene	0.01
		Chrysene+Triphenylene	0.1
	60		
		Benzo[b]fluoranthene	0.03
5		Benzo[k]fluoranthene	0.01
		Benzo[a]pyrene	0.01
		Dibenz[a,h]anthracene	0.01
6		Indeno[1.2.3-cd]pyrene	0.02
		Benzo[g,h,i]perylene	0.03
3		Phenanthrene	7.9
		Anthracene	1.9
		Fluoranthene	5.4
		Pyrene	5
4		Benzo[a]anthracene	11
		Chrysene+Triphenylene	21
	150		
		Benzo[b]fluoranthene	8.5
5		Benzo[k]fluoranthene	1.5
		Benzo[a]pyrene	4.7
		Dibenz[a,h]anthracene	1.5
6		Indeno[1.2.3-cd]pyrene	1.9
		Benzo[g,h,i]perylene	3.1
3		Phenanthrene	60
		Anthracene	28
-		Fluoranthene	10
4		Pyrene	44
	30		

		Benzo[a]anthracene	0.2
		Chrysene+Triphenylene	9
5		Benzo[b]fluoranthene	1.5
		Benzo[k]fluoranthene	0.2
		Benzo[a]pyrene	0.7
		Dibenz[a,h]anthracene	0.01
6		Indeno[1.2.3-cd]pyrene	1.1
		Benzo[g,h,i]perylene	0.01
3		Phenanthrene	0.5
		Anthracene	0.08
		Fluoranthene	0.08
		Pyrene	0.2
4		Benzo[a]anthracene	0.08
		Chrysene+Triphenylene	0.2
	60		
		Benzo[b]fluoranthene	0.1
5		Benzo[k]fluoranthene	0.02
		Benzo[a]pyrene	0.2
		Dibenz[a,h]anthracene	0.06
6		Indeno[1.2.3-cd]pyrene	0.1
		Benzo[g,h,i]perylene	0.09
3		Phenanthrene	8.7
		Anthracene	0.9
		Fluoranthene	3
		Pyrene	2.4
4		Benzo[a]anthracene	2.8
		Chrysene+Triphenylene	8.5
	150		
		Benzo[b]fluoranthene	2.4
5		Benzo[k]fluoranthene	0.5
		Benzo[a]pyrene	1.3
		Dibenz[a,h]anthracene	0.2
6		Indeno[1.2.3-cd]pyrene	0.3
		Benzo[g,h,i]perylene	0.3
3		Phenanthrene	1.1
		Anthracene	0.08
		Fluoranthene	0.2
		Pyrene	0.1
4		Benzo[a]anthracene	0.2
		Chrysene+Triphenylene	8
	30		
		Benzo[b]fluoranthene	0.3
5		Benzo[k]fluoranthene	N/A
		Benzo[a]pyrene	0.1
		Dibenz[a,h]anthracene	0.01
6		Indeno[1.2.3-cd]pyrene	0.3
		Benzo[g,h,i]perylene	0.3
3		Phenanthrene	0.1
		Anthracene	N/A
4		Fluoranthene	0.03
	60		
		Pyrene	0.02

		Benzo[a]anthracene	0.01
		Chrysene+Triphenylene	0.02
5		Benzo[b]fluoranthene	0.02
		Benzo[k]fluoranthene	0.01
		Benzo[a]pyrene	0.01
		Dibenz[a,h]anthracene	0.01
6		Indeno[1.2.3-cd]pyrene	0.03
		Benzo[g,h,i]perylene	0.03
3		Phenanthrene	7.1
		Anthracene	0.3
		Fluoranthene	9.1
		Pyrene	4.5
4		Benzo[a]anthracene	1.4
		Chrysene+Triphenylene	3.7
	150		
		Benzo[b]fluoranthene	1.3
5		Benzo[k]fluoranthene	0.3
		Benzo[a]pyrene	0.6
		Dibenz[a,h]anthracene	0.1
6		Indeno[1.2.3-cd]pyrene	0.4
		Benzo[g,h,i]perylene	0.6
3		Phenanthrene	4
		Anthracene	1.1
		Fluoranthene	0.5
		Pyrene	0.2
4		Benzo[a]anthracene	6
		Chrysene+Triphenylene	N/A
	30		
		Benzo[b]fluoranthene	N/A
5		Benzo[k]fluoranthene	0.6
		Benzo[a]pyrene	0.4
		Dibenz[a,h]anthracene	0.01
6		Indeno[1.2.3-cd]pyrene	0.3
		Benzo[g,h,i]perylene	0.4
3		Phenanthrene	6
		Anthracene	1
		Fluoranthene	2
		Pyrene	8
4		Benzo[a]anthracene	4
		Chrysene+Triphenylene	3
	60		
		Benzo[b]fluoranthene	2
5		Benzo[k]fluoranthene	0.4
		Benzo[a]pyrene	2
		Dibenz[a,h]anthracene	0.6
6		Indeno[1.2.3-cd]pyrene	1.1
		Benzo[g,h,i]perylene	0.8
3		Phenanthrene	4.3
		Anthracene	2.9
4		Fluoranthene	4.6
	150		
		Pyrene	10.3

					Benzo[a]anthracene		2.6
					Chrysene+Triphenylene		25
			5		Benzo[b]fluoranthene		6.4
					Benzo[k]fluoranthene		2.1
					Benzo[a]pyrene		3.6
					Dibenz[a,h]anthracene		0.2
			6		Indeno[1.2.3-cd]pyrene		2.1
					Benzo[g,h,i]perylene		3.8
			2		Naphthalene		0.94
					Methyl-naphthalene[1]		0.34
					Methyl-naphthalene[2]		1.03
					Acenaphthylene		0.05
			3		Acenaphthene		0.05
					Fluorene		0.05
					Phenanthrene		0.64
					Anthracene	12	0.23
			4		Fluoranthene		0.85
					Pyrene		0.11
					Benzo[b]fluoranthene		0.24
					Benzo[k]fluoranthene		0.3
			5		Benzo[a]pyrene		0.05
					Indeno[1.2.3-cd]pyrene		0.05
					Dibenz[a,h]anthracene		0.05
			6		Benzo[g,h,i]perylene		0.58
					Naphthalene		0.05
			2		Methyl-naphthalene[1]		0.22
					Methyl-naphthalene[2]		0.19
					Acenaphthylene		0.05
			3	dissolved	Acenaphthene	N/A	0.05
					Fluorene		0.05
					Phenanthrene		0.69
					Anthracene		0.37
					Fluoranthene	45	0.24
			4		Pyrene		0.26
					Benzo[a]anthracene		0.16
					Chrysene		0.17
					Benzo[b]fluoranthene		0.05
					Benzo[k]fluoranthene		0.05
			5		Benzo[a]pyrene		0.05
					Indeno[1.2.3-cd]pyrene		0.05
					Dibenz[a,h]anthracene		0.05
			6		Benzo[g,h,i]perylene		0.05
					Naphthalene		0.05
			2		Methyl-naphthalene[1]		0.05
					Methyl-naphthalene[2]		0.05
					Acenaphthylene	64	0.05
					Acenaphthene		0.05
			3		Fluorene		0.05
					Phenanthrene		0.19
					Anthracene		0.15

[Vila-Escale et al. 2007](#)

Creek

0.009

dissolved

N/A

		Fluoranthene	0.05
		Pyrene	0.05
4		Benzo[a]anthracene	0.05
		Chrysene	0.05
		Benzo[b]fluoranthene	0.05
		Benzo[k]fluoranthene	0.05
5		Benzo[a]pyrene	0.05
		Indeno[1.2.3-cd]pyrene	0.05
		Dibenz[a,h]anthracene	0.05
6		Benzo[g,h,i]perylene	0.05
		Naphthalene	0.05
2		Methyl-naphthalene[1]	0.05
		Methyl-naphthalene[2]	0.05
		Acenaphthylene	0.05
		Acenaphthene	0.05
3		Fluorene	0.05
		Phenanthrene	0.75
		Anthracene	0.44
		Fluoranthene	0.19
	78	Pyrene	0.4
4		Benzo[a]anthracene	0.13
		Chrysene	0.14
		Benzo[b]fluoranthene	0.15
		Benzo[k]fluoranthene	0.05
5		Benzo[a]pyrene	0.05
		Indeno[1.2.3-cd]pyrene	0.05
		Dibenz[a,h]anthracene	0.05
6		Benzo[g,h,i]perylene	0.05
		Naphthalene	0.05
2		Methyl-naphthalene[1]	0.05
		Methyl-naphthalene[2]	0.05
		Acenaphthylene	0.05
		Acenaphthene	0.05
3		Fluorene	0.05
		Phenanthrene	0.71
		Anthracene	0.36
		Fluoranthene	0.22
	107	Pyrene	0.33
4		Benzo[a]anthracene	0.12
		Chrysene	0.11
		Benzo[b]fluoranthene	0.14
		Benzo[k]fluoranthene	0.05
5		Benzo[a]pyrene	0.12
		Indeno[1.2.3-cd]pyrene	0.05
		Dibenz[a,h]anthracene	0.05
6		Benzo[g,h,i]perylene	0.05
		Naphthalene	0.05
2		Methyl-naphthalene[1]	0.05
		Methyl-naphthalene[2]	0.1
	122	Acenaphthylene	0.05
3		Acenaphthene	0.05

		Fluorene		0.05
		Phenanthrene		0.88
		Anthracene		0.39
		Fluoranthene		0.22
4		Pyrene		0.37
		Benzo[a]anthracene		0.11
		Chrysene		0.14
		Benzo[b]fluoranthene		0.15
5		Benzo[k]fluoranthene		0.05
		Benzo[a]pyrene		0.11
		Indeno[1.2.3-cd]pyrene		0.05
		Dibenz[a,h]anthracene		0.05
6		Benzo[g,h,i]perylene		0.05
		Naphthalene		0.05
2		Methyl-naphthalene[1]		0.05
		Methyl-naphthalene[2]		0.05
		Acenaphthylene		0.05
		Acenaphthene		0.05
3		Fluorene		0.05
		Phenanthrene		0.32
		Anthracene		0.05
		Fluoranthene		0.48
4		Pyrene	445	0.89
		Benzo[a]anthracene		0.31
		Chrysene		0.13
		Benzo[b]fluoranthene		0.43
		Benzo[k]fluoranthene		0.16
5		Benzo[a]pyrene		0.34
		Indeno[1.2.3-cd]pyrene		0.42
		Dibenz[a,h]anthracene		0.47
6		Benzo[g,h,i]perylene		0.34
		Naphthalene		28.9
2		Methyl-naphthalene[1]		6.04
		Methyl-naphthalene[2]		5.7
		Acenaphthylene		0.1
		Acenaphthene		0.1
3		Fluorene		9
		Phenanthrene		90.8
		Anthracene		0.1
		Fluoranthene		53.5
4	particulat e	Pyrene	12	1.78
		Benzo[a]anthracene		0.33
		Chrysene		0.31
		Benzo[b]fluoranthene		7.06
		Benzo[k]fluoranthene		0.1
5		Benzo[a]pyrene		0.1
		Indeno[1.2.3-cd]pyrene		1.29
		Dibenz[a,h]anthracene		0.2
6		Benzo[g,h,i]perylene		0.15
		Naphthalene		0.32
2		Methyl-naphthalene[1]	45	0.1

		Methyl-naphthalene[2]	0.1
		Acenaphthylene	0.1
		Acenaphthene	0.1
3		Fluorene	1.09
		Phenanthrene	28.9
		Anthracene	0.1
		Fluoranthene	12.1
4		Pyrene	38.7
		Benzo[a]anthracene	0.26
		Chrysene	0.58
		Benzo[b]fluoranthene	3.96
		Benzo[k]fluoranthene	0.1
5		Benzo[a]pyrene	0.1
		Indeno[1.2.3-cd]pyrene	0.15
		Dibenz[a,h]anthracene	1.16
6		Benzo[g,h,i]perylene	0.15
		Naphthalene	0.4
2		Methyl-naphthalene[1]	0.54
		Methyl-naphthalene[2]	0.42
		Acenaphthylene	0.1
		Acenaphthene	0.1
3		Fluorene	0.87
		Phenanthrene	6.67
		Anthracene	0.1
		Fluoranthene	5.39
4	64	Pyrene	19.9
		Benzo[a]anthracene	0.1
		Chrysene	0.15
		Benzo[b]fluoranthene	3.8
		Benzo[k]fluoranthene	0.1
5		Benzo[a]pyrene	0.1
		Indeno[1.2.3-cd]pyrene	0.15
		Dibenz[a,h]anthracene	0.2
6		Benzo[g,h,i]perylene	0.15
		Naphthalene	0.1
2		Methyl-naphthalene[1]	0.1
		Methyl-naphthalene[2]	0.1
		Acenaphthylene	0.1
		Acenaphthene	0.1
3		Fluorene	1.86
		Phenanthrene	17.2
		Anthracene	0.1
		Fluoranthene	7.5
4	78	Pyrene	29.5
		Benzo[a]anthracene	0.49
		Chrysene	0.69
		Benzo[b]fluoranthene	4.59
		Benzo[k]fluoranthene	0.1
5		Benzo[a]pyrene	0.1
		Indeno[1.2.3-cd]pyrene	0.15
		Dibenz[a,h]anthracene	0.2

6	Benzo[g,h,i]perylene		0.15
	Naphthalene		0.1
2	Methyl-naphthalene[1]		0.1
	Methyl-naphthalene[2]		0.1
	Acenaphthylene		0.1
	Acenaphthene		0.1
3	Fluorene		1.06
	Phenanthrene		13.7
	Anthracene		0.1
	Fluoranthene	107	7.8
4	Pyrene		27.8
	Benzo[a]anthracene		0.1
	Chrysene		0.15
	Benzo[b]fluoranthene		0.15
	Benzo[k]fluoranthene		0.1
5	Benzo[a]pyrene		0.1
	Indeno[1.2.3-cd]pyrene		0.15
	Dibenz[a,h]anthracene		0.2
6	Benzo[g,h,i]perylene		0.15
	Naphthalene		0.1
2	Methyl-naphthalene[1]		0.1
	Methyl-naphthalene[2]		0.1
	Acenaphthylene		0.1
	Acenaphthene		0.1
3	Fluorene		0.1
	Phenanthrene		4.88
	Anthracene		0.1
	Fluoranthene	122	4.11
4	Pyrene		11.3
	Benzo[a]anthracene		0.1
	Chrysene		0.15
	Benzo[b]fluoranthene		0.15
	Benzo[k]fluoranthene		0.1
5	Benzo[a]pyrene		0.1
	Indeno[1.2.3-cd]pyrene		0.15
	Dibenz[a,h]anthracene		0.2
6	Benzo[g,h,i]perylene		0.15
	Naphthalene		0.1
2	Methyl-naphthalene[1]		0.1
	Methyl-naphthalene[2]		0.1
	Acenaphthylene		0.54
	Acenaphthene		0.1
3	Fluorene		0.1
	Phenanthrene	445	0.32
	Anthracene		0.1
	Fluoranthene		1.62
4	Pyrene		2.28
	Benzo[a]anthracene		0.28
	Chrysene		0.15
5	Benzo[b]fluoranthene		0.46
	Benzo[k]fluoranthene		0.1

	Benzo[a]pyrene	0.29
	Indeno[1.2.3-cd]pyrene	0.43
	Dibenz[a,h]anthracene	0.48
6	Benzo[g,h,i]perylene	0.43

2.4. Opportunities for modified sampling protocol

Sampling protocols: Our review provides the first quantitative dataset on how wildfire may affect water quality and highlights the need to have more monitoring efforts for pollutants and basic water quality parameters after wildfires. Our analysis also revealed that pre-fire data is rarely reported in most studies, thereby making it difficult to compare with post-fire data and assess the extent to which wildfire may affect water quality. Thus, future studies should report, if possible, pre-fire water quality data. The opportunistic nature of most post-fire studies means that the watershed of interest likely was not monitored and that water quality variables are therefore not available. In that case, data from a nearby unburned catchment with similar characteristics should be collected to offer a relevant proxy to pre-fire conditions (Mahat et al., 2015). Alternatively, recourse to water quality modeling simulating pre-fire conditions may also work. Hydrologists could plan their post-fire studies by using wildfire probability layers which could inform locations of unburned catchments with a high probability of burning (Villarreal et al., 2022) to install monitoring stations. The sampling protocol also rarely includes wildfire characteristics including burn severity, unburned area, and ecosystem or vegetation types in the affected areas. In addition to reporting these parameters, the sampling protocol also should include the distance of the sampling point in the water bodies from the wildfire-affected area and the time of sampling. The sampling protocol should include time series data that captures the effect of the first flush (runoff from the first rainfall after the wildfire) and the residual effect lasting for several months or years. The time series data could inform the duration until which wildfire continues to affect the water quality. The post-fire water quality data rarely include information about rainfall characteristics such as the frequency of rainfalls, their intensity, their seasonality, and their time after the fire. The

sampling protocol should include information about rainfall characteristics. The sampling protocol should be modified based on specific water quality parameters as shown below:

pH: Although pH can be easily measured using in situ or portable meters, many of the studies surveyed did not report pH. The aggregated data shows that the pH of water one year after the wildfire may be similar to the pre-fire pH level and most changes can occur within a year (**Figure 2-3**). Thus, reported studies failed to capture changes in pH during the first flush—runoff generated during the first rainfall after a wildfire. Future studies should record the pH of water during the first flush when the effect is more severe. Extensive monitoring and reporting of these parameters could help mechanistically link changes in pH with fire severity, climate, topography, soil type, vegetation, and the time lag between fire and sampling (Britton, 1991; A. A. Oliver et al., 2012).

Total suspended solids: Our analysis showed that wildfire increases TSS (Emmert et al., 2020; Ice et al., 2004; Moody and Martin, 2001), but the extent to which TSS could increase depends on the burned area, and the time lag between fire and sampling, and flow rate in the surface waters. These parameters affect the strength or depletion of TSS sources after the fire and their release or dilution in the surface water. The aggregated data shows that when the burn area is more than 80%, the source of TSS is strong enough to provide TSS to surface water and increase the concentration (**Figure 2-4**). When the burn area is less than 80%, the source is depleted quickly after a few rainfalls, which explains why the increase in TSS concentration is not prominent in this condition. Moreover, rivers can store sediments for a long time, which can be remobilized downstream slowly after each high-flow event releasing pollutants contained in these stocks (Crawford et al., 2022). Thus, the sampling protocol must include these parameters along with TSS values. Most of the debris created during a wildfire is carried by surface runoff during the

first rainfall after the wildfire. This first flush could contain most of the pollutants released due to wildfire. Yet rarely the water quality is monitored during the first rainfall event after a wildfire due to potential hazards near the fire-affected area. Future sampling protocols should collect first flush water samples after wildfire and get high-frequency temporal data at locations near as well as beyond the hazard area. High-frequency temporal and spatial data could help understand the total loading of suspended solids based on the characteristics of burned areas (e.g slope) and rainfall events (Blake et al., 2020).

Dissolved organic carbon: Limited data is available on temporal variation in DOC concentration at a location after a wildfire. Long-term monitoring could help improve our understanding of whether and how DOC quantity changes with time. The sampling protocol should include the time lag between fire and sampling, antecedent rainfall events, burn severity, and ash content when DOC data was reported as these factors would affect DOC. Furthermore, DOC quality was rarely reported or monitored. Wildfires can also alter the levels of inorganic precursors such as bromide, iodide, and nitrite in surface waters, leading to the formation of inorganic DBPs (Chang et al., 2011; Uzun et al., 2020). Future studies should link wildfire characteristics with DOC quality and DBP formation.

Nutrients: Land properties such as soil types and vegetation cover and hydrological conditions such as rainfall intensity, runoff volume, and flow rate can affect nutrient concentration in the water bodies. Without information about these confounding factors, it is difficult to compare the effect of wildfire on nutrient concentration between sites. The sampling protocol should report these factors in the field to improve the link of how wildfires affect nutrient concentration in surface bodies. Most studies only reported total N and P, assuming most of them were associated

with suspended particles. Future studies should report dissolved N and P species such as nitrate, ammonium, and orthophosphate.

Heavy metals: A lack of temporal data immediately after fire precludes our understanding of the link between metal release kinetics from wildfire residues and their concentration in water. Furthermore, most studies did not report supporting data such as pH, DOC, and particulate matter, all of which can affect the speciation of metals in water. Thus, the sampling protocol for metals should include these parameters. DOC quality is particularly important to bind metals such as mercury, which concentration typically increases after a fire. Wildfire results in the re-emission of some mercury to the atmosphere (Webster et al., 2016) and hydrologic mobilization of Hg(II) in both dissolved and particulate forms to neighboring riparian zones, wetlands, and downgradient lakes where Hg(II) can be converted to neurotoxic methylmercury. Notably, however, the transport of dissolved Hg(II) was observed to be largely unaffected by a low-severity wildfire but strongly correlated to DOC concentration (Jensen et al., 2017; Patel et al., 2019); this observation may be influenced by sampling efforts that do not capture the first flush or the low fire intensity for the sole study on this topic (Jensen et al., 2017). Thus, the sampling protocol must include reporting mercury concentration in the first flush. TSS generated during wildfires may carry toxic pollutants including heavy metals (Chalmers et al., 2007). Therefore, future studies should measure the amount of contaminant loading via suspended solids. Particulate-bound Hg(II), however, was observed to significantly increase as a result of wildfires due to an increase in TSS levels, and the wildfire effects diminished to pre-burn levels approximately 8 months following the wildfire (Jensen et al., 2017). Future research efforts are needed to identify the combined effects of increased mobilization of mercury and release of nutrients and chemicals that could accept

electrons to facilitate the formation of methylmercury in water bodies and uptake in aquatic food webs.

Organic micropollutants: This review analyzed the effect of wildfire on PAH based on only 3 studies. More data on PAH will help address the knowledge gaps on how PAH concentration is affected by wildfire and watershed characteristics. Future sampling protocols should also include monitoring of other organic pollutants in addition to PAH. Although PAHs are the most reported organic pollutants, other organic pollutants such as polychlorinated di-benzo-q-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) could be produced during the combustion (Gabos et al., 2001; Ghosh, 2007; Gorshkov et al., 2021; Kim et al., 2003; Salamanca et al., 2016). Furthermore, fire retardants are extensively used to extinguish forest fires, which contain nutrients, corrosion inhibitors, stabilizers, and bactericides (Crouch et al., 2006; Yu et al., 2021). The concentration of organic chemicals used in fire retardants should be monitored particularly during the first few rainfalls after the fire.

2.5. Conclusions

This study provided a quantitative understanding of the extent to which different pollutants may increase after a wildfire by analyzing the effects of wildfire characteristics such as burned area, surface water flow rate, and the time lag between fire and sampling on the concentration of pollutants and water quality parameters in surface waters. The pH of surface water mostly increased within one year after the fire, not after that, potentially due to washing off all ash in the first year. The concentration of contaminants in surface water after a wildfire could increase by over 100-fold, but the extent of concentration would increase varied with contaminant type, flow rate, time lag between fire and sampling, and area of the burned watershed. TSS concentration increased up to 3 order magnitude post-fire. An increase in the burned area increased the TSS

concentration disproportionately, indicating that post-fire TSS concentration is sensitive to the burned area. TSS concentration increased significantly when the burn area is >80% of the watershed area indicating large burn area increased the source strength to supply TSS during postfire seasons. TSS concentrations increased within the first two years post-fire and then decreased to almost pre-burn levels with time, indicating source-limiting conditions. TSS concentration increased in surface waters up to a flow of $10 \text{ m}^3 \text{ s}^{-1}$, beyond which higher flow decreased TSS concentration possibly due to dilution. Wildfires slightly increased DOC immediately after the wildfire but the DOC concentration did not vary with the time lag between fire and sampling ($p>0.05$). Nutrient concentration was greatest within a year after the fire before returning to the background level after 2 years. In contrast with TSS and nutrients, heavy metal concentrations of Pb, Cu, and Zn were greatest a year after the fire indicating a phase lag, possibly due to delay in their dissolution. Compared to background levels, heavy metal concentration (Pb, Cu, and Zn) was higher with increases in the burned area. The increase in concentration was sensitive to metal types: $\text{Pb} > \text{Cu}$ and Zn . The mean concentration of PAH increased 4 months after the wildfire and the increase dissolve PAH is more prominent for heavier PAH. Nevertheless, the increase in PAH did not exceed the regulatory limit within a year following a wildfire in the majority of studies. Global environmental change is making these water quality issues more acute. Thus, there is a greater need to support international water monitoring networks to collect critical data needed to inform how to best manage watersheds prone to wildfire to protect water resources.

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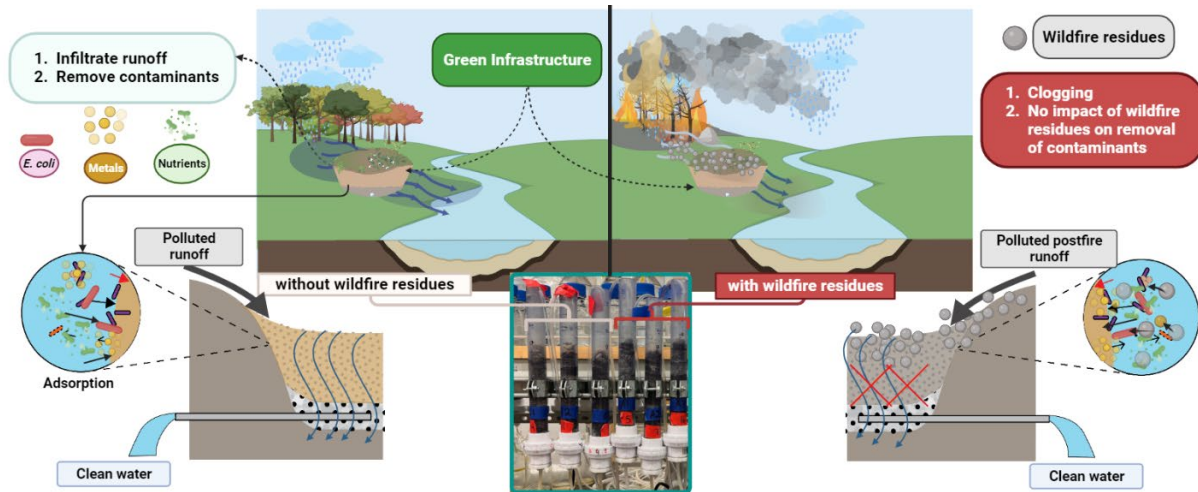
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3. CHAPTER 3 – RESILIENCE OF STORMWATER BIOFILTERS FOLLOWING THE DEPOSITION OF WILDFIRE RESIDUES: IMPLICATION ON DOWNSTREAM WATER QUALITY MANAGEMENT IN WILDFIRE-PRONE REGIONS



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Raelison, O.D., Das, T., Guyett, K., Merrifield, R., Indiresan, S., Yang, K., Visweswaran, A., Pierce, G., and Mohanty, S.K. (2024) Resilience of stormwater biofilters following the deposition of wildfire residues: Implication on downstream water quality management in wildfire-prone regions. *Journal of Hazardous Materials*. <https://doi.org/10.1016/j.jhazmat.2023.132989>

Abstract

Stormwater treatment systems such as biofilters could intercept and remove pollutants from contaminated runoff in wildfire-affected areas, ensuring the protection of water quality downstream. However, the deposition of wildfire residues such as ash and black carbon onto biofilters could potentially impair their stormwater treatment functions. Yet, whether and how wildfire residue deposition could affect biofilter functions is unknown. This study examines the impact of wildfire residue deposition on biofilter infiltration and pollutant removal capacities. Exposure to wildfire residues decreased the infiltration capacity based on the amount of wildfire deposited. Wildfire residues accumulated at the top layer of the biofilter, forming a cake layer, but scraping this layer restored the infiltration capacity. While the deposition of wildfire residues slightly changed the pore water geochemistry, it did not significantly alter the removal of metals, and *E. coli*. Although wildfire residues leached some metals into pore water within the simulated root zone, the leached metals were effectively removed by the compost present in the filter media. Collectively, these results indicate that biofilters downstream of wildfire-prone areas could remain resilient or functional and protect downstream water quality if deposited ash is periodically scraped to restore any loss of infiltration capacity following wildfire residues deposition.

3.1. Introduction

Wildfires are becoming more intense and frequent due to climate change, especially in the southwestern US, where the wildfires are increasingly encroaching into suburban areas (Abatzoglou et al., 2021; Brown et al., 2023; Dong et al., 2022; Holden et al., 2018). Most wildfires occur in vulnerable regions that have been experiencing warming, drought, and water scarcity (Libonati et al., 2022; Parks and Abatzoglou, 2020). In these regions, wildfire is likely to make the water scarcity issue worse because wildfire affects both the quality and quantity of surface water (Hallema et al., 2018b; Hohner et al., 2019; Paul et al., 2022; Raoelison et al., 2023; Robinne et al., 2020; Rust et al., 2018). For instance, while vegetation loss during wildfires decreases the natural abstraction of water during rainfall, an increase in soil hydrophobicity after wildfires limits runoff infiltration and increases overland flow, thereby significantly decreasing groundwater recharge (Atwood et al., 2023; Ebel and Martin, 2017; Hallema et al., 2018b; Ren and Leslie, 2020; Williams et al., 2022). Collectively, these effects reduce groundwater availability in an area where the capacity to replenish groundwater is reduced by wildfires in large forest watersheds. This would affect local water balance and reduce the availability of surface water. This energetic surface runoff could also carry wildfire residues such as ash, black carbon, and associated contaminants, and contaminate surface water bodies (Paul et al., 2022; Raoelison et al., 2023). While wildfires can damage public drinking water systems (Jankowski et al., 2023; Whelton et al., 2023), postfire runoff can impact the treatability of drinking water, resulting in increased variability in water quality (Hickenbottom et al., 2023). This variability caused by bio stabilization may lead to shock loads, which could in turn affect the performance of biofilter systems (Blackburn et al., 2023; Emelko et al., 2011; Stone et al., 2011). As wildfires pose a risk to human health, it is imperative

to develop management methods particularly resilience of water supplies to protect surface water resources in wildfire-prone areas (Hallema et al., 2018a; Whelton et al., 2023).

Green infrastructure refers to a network of nature-based solutions designed to provide a range of ecosystem services, which encompass ecological, economic, and societal benefits. Their primary goal is to enhance the natural ecosystem's functions within urban areas in order to improve climate resilience and sustainability, and ultimately human health (Fang et al., 2023; Jungman et al., 2023; Navarrete-Hernandez and Laffan, 2023). Among all green infrastructure types, biofiltration systems also referred to as bioretention, biofilters, and rain gardens, are typically designed to remove a wide range of pollutants from stormwater in a changing climate (Fowdar et al., 2021). The runoff from wildfire-affected areas could contain a high amount of wildfire residues containing ash black carbon and other pollutants (Bisiaux et al., 2011; Bodí et al., 2014; Silva et al., 2016). Their concentration could exceed three orders of magnitude higher concentrations than the background level during the first few rainfall events after the fire (Raoelison et al., 2023). Stormwater biofilters, previously designed to remove many of these pollutants (Grebel et al., 2013; Tirpak et al., 2021), could be strategically implemented downstream of fire-prone areas to protect surface water quality. Considering the complex interplay of factors in fire-prone areas, including the intensity and severity of wildfires, as well as the characteristics of the vegetation and resultant wildfire residues (Raoelison et al., 2023), selection of these areas would require careful consideration of the wildfire characteristics and the local ecosystems, ensuring that the chosen locations are more susceptible to a potential downstream contamination. In biofilters, surface runoff passes through a filter layer that typically consists of sandy soil or a mixture of sand and compost to increase the infiltration capacity and reduce clogging (Tirpak et al., 2021). It is unclear how their capacity to remove pollutants changes after the deposition of wildfire residues.

While one study has explored the resilience of biofiltration to wildfire ash in drinking water treatment (Blackburn et al., 2023), no study to date has examined the effects of the deposited wildfire residues on stormwater biofilter functions. The deposition of wildfire residues could affect the capacity of biofilters to infiltrate and treat stormwater. Wildfire residues due to their large size ($> 2 \mu\text{m}$) are expected to be filtered in the top 10 cm of the subsurface (Valenca et al., 2020). Wildfire residues could be entrapped into interstitial spaces in the filter layer and clog them. Knowledge of when and how the biofilters get clogged in the presence of wildfire residues in runoff could help develop management strategies to restore the infiltration functions. Furthermore, deposited wildfire residues such as ash and black carbon could alter pore water chemistry and affect pollutant removal. For instance, pore water pH could increase due to the dissolution of ash (Brito et al., 2021), and a change in pH could affect the removal of pollutants including heavy metals (HongE et al., 2022) and microbial pollutants (Zhang et al., 2015). Wildfire residues could leach heavy metals and other pollutants into pore water in the root zone based on the composition of the pore water (Pereira and Úbeda, 2010). They could also leach nutrients (Gustine et al., 2022; Valenca et al., 2020) and polycyclic aromatic hydrocarbons or PAH (Campos and Abrantes, 2021; Cooke et al., 2022). Thus, it is important to understand whether and how the deposited wildfire residues affect the infiltration and removal functions of stormwater biofilters.

This study examines the effect of wildfire deposition on the infiltration capacity of stormwater biofilters and their capacity to remove pollutants including heavy metals, and *E. coli*. We hypothesized that the deposited wildfire residues would negatively affect the infiltration and decrease the removal of pollutants by altering the pore water geochemistry of the filter media layer. To test the hypotheses, model biofilters were designed in laboratory with and without wildfire residues and exposed to contaminated stormwater to measure the effects of wildfire residues on

effluent water quality. The result would help inform policy on designing green infrastructure downstream to manage water quality in wildfire-prone areas.

3.2. Materials and methods

3.2.1. Stormwater and wildfire residues collection

Natural stormwater and natural wildfire residues were used in this study. The top 10 cm of the burned soils containing wildfire residues were collected from the Santa Monica Mountains National Recreation Area, USA (34°06'14"N, 118°36'09"W) four weeks after the Palisades Fire, which burned over 4.86 km² between May 14th, 2021, and May 26th, 2021. No recorded rainfall event preceding the wildfire residue collection. The sample was sieved to remove particles larger than 0.83 mm—the maximum size of sand grain used in filter media—as larger residues are less likely to be carried away long-distance by runoff before their deposition on biofilters downstream and deposition of particles larger than 83 mm would create an additional layer of filter media without clogging. Based on the particle size distribution measurement of sieved residues, D10, D50, and D90 of the wildfire residues were 12.0 μm, 42.3 μm, and 172.8 μm, respectively (**Figure 3-1**). In sieve analysis, D10, D50, and D90 represent the particle sizes at which 10%, 50%, and 90% of the particles, by mass, are finer than the specified size, respectively.

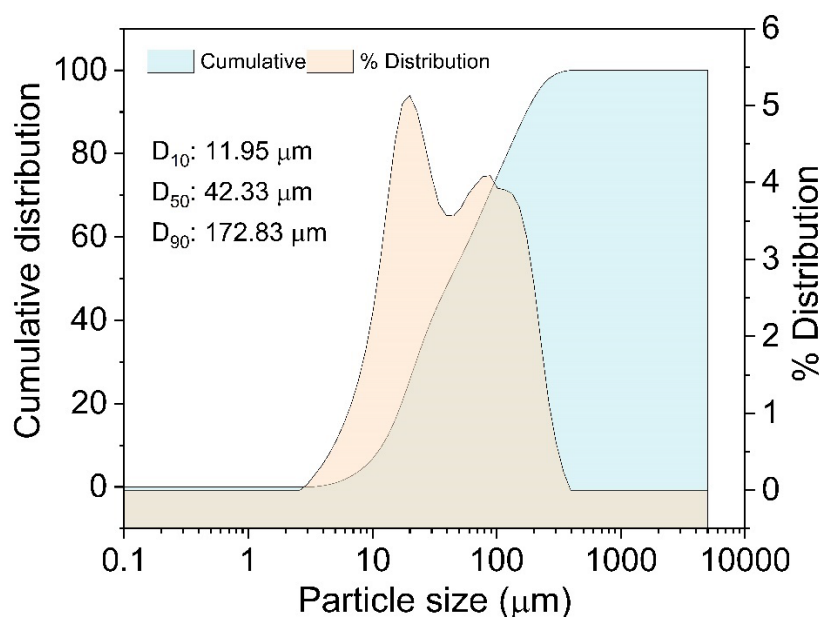


Figure 3-1. Particle size distribution of wildfire residues.

Following the method outlined elsewhere (Valenca et al., 2020), natural stormwater was collected from Ballona Creek in Los Angeles, CA (34° 00'32" N, 118° 23'3" W), which receives both dry- and wet-weather runoff from a 318 km² urban area with 82% developed and 61% impervious surface. This catchment has not been affected by fire in several decades, thereby providing natural control for stormwater during pre-fire seasons. Water quality parameters such as pH, electrical conductivity, and dissolved organic carbon (DOC) of stormwater were monitored to ensure the quality did not fluctuate significantly between experiments.

3.2.2. *Packing and characterization of biofilters*

Conventional biofilters typically use sand to increase infiltration and compost to enhance pollutant removal and support vegetation (Tirpak et al., 2021). In our study, garden compost (Whitter Fertilizer, CA, USA) was first sieved to remove particles larger than 2 mm to prevent preferential flow through the packed column. Coarse sand (0.59 mm – 0.84 mm, Humboldt Mfg.

Co., IL, USA) was mixed with the sieved compost at a ratio of 7:3 based on the specification commonly used in biofilter (Tirpak et al., 2021). Although plants are typically present in biofilters, we did not use plants in this study to isolate the mechanisms of pollutant removal in biofilters and to avoid changes in pore water composition after the deposition of wildfire residues without confounding effects exerted by the vegetation layer and root zone. In this study, model biofilters were designed by packing transparent polyvinyl chloride (PVC) columns (2.54 cm ID x 30 cm length) with a sand-compost or sand-only mixture following the method outlined elsewhere (Borthakur et al., 2022b; Ghavanloughajar et al., 2020). Briefly, a drainage layer was created up to 6 cm using pea gravel at the bottom of each column, and a 100 μm nylon membrane was placed on the top of the drainage layer to prevent biofilter media from falling into the gravel layer. The sand-compost mixture was added incrementally in the column to ensure uniform packing as described in a previous study (Borthakur et al., 2021). An additional 2.5-cm layer of gravel layer was added to the top of the filter media to prevent compost particles from floating in the ponded stormwater. Although the use of small columns may not accurately predict larger-scale heterogeneity typically observed in biofilters in field, small columns are suitable for comparing pollutant removal capacity of filter media with and without wildfire deposits. The small columns did not exhibit wall effects—that is flow through gap between wall and peripheral media near wall— as the ratio between the column diameter and the grain size of the media averages 254, exceeding the threshold of 50 (Mehta and Hawley, 1969). All biofilters were conditioned until the media filter reached equilibrium, ensuring that the pH and ionic strength in the effluent remained stable (Borthakur et al., 2022a) . To ensure consistency and uniformity of the experiment, each type of column was characterized for saturated pore volume (PV), bulk density, and porosity. The hydraulic conductivity was measured with the falling head method (Ghavanloughajar et al., 2020).

The bulk density of filter media was measured by dividing the weight of the media by the inner volume of the column, and the pore volume of filter media was estimated based on the weight difference between the dry columns and completely saturated columns (Borthakur et al., 2022a).

The hydraulic characteristics of filter media are summarized in **Table 3-1**.

Table 3-1. Properties of the media columns.

A) Infiltration capacity experiment:

Properties	Hydraulic conductivity cm s^{-1}	Bulk density (g cm^{-3})	Pore volume (mL)
4 compost-sand columns	0.012 ± 0.001	1.30 ± 0.02	25.67 ± 0.76

B) Removal capacity experiment:

Properties	Hydraulic conductivity cm s^{-1}	Bulk density (g cm^{-3})	Pore volume (mL)
3 compost-sand columns (control)	0.007 ± 0.000	1.29 ± 0.02	23.57 ± 0.76
3 compost-sand columns (wildfire residues)	0.010 ± 0.001	1.37 ± 0.14	24.53 ± 2.71
3 sand columns (control)	0.03 ± 0.0006	1.60 ± 0.07	24.55 ± 0.07
3 sand columns (wildfire residues)	0.03 ± 0.0005	1.63 ± 0.04	23.20 ± 0.04

3.2.3. *Effect of wildfire residues on infiltration capacity of biofilters*

To examine the effects of wildfire residue deposition on the infiltration capacity of filter media in biofilters, a total of four sand-compost biofilter columns were packed. Out of these four columns, three columns, set up in triplicate, were exposed to the same incremental amount of wildfire residues, and one column was used as a control, receiving stormwater without wildfire residues (**Figure 3-2**).

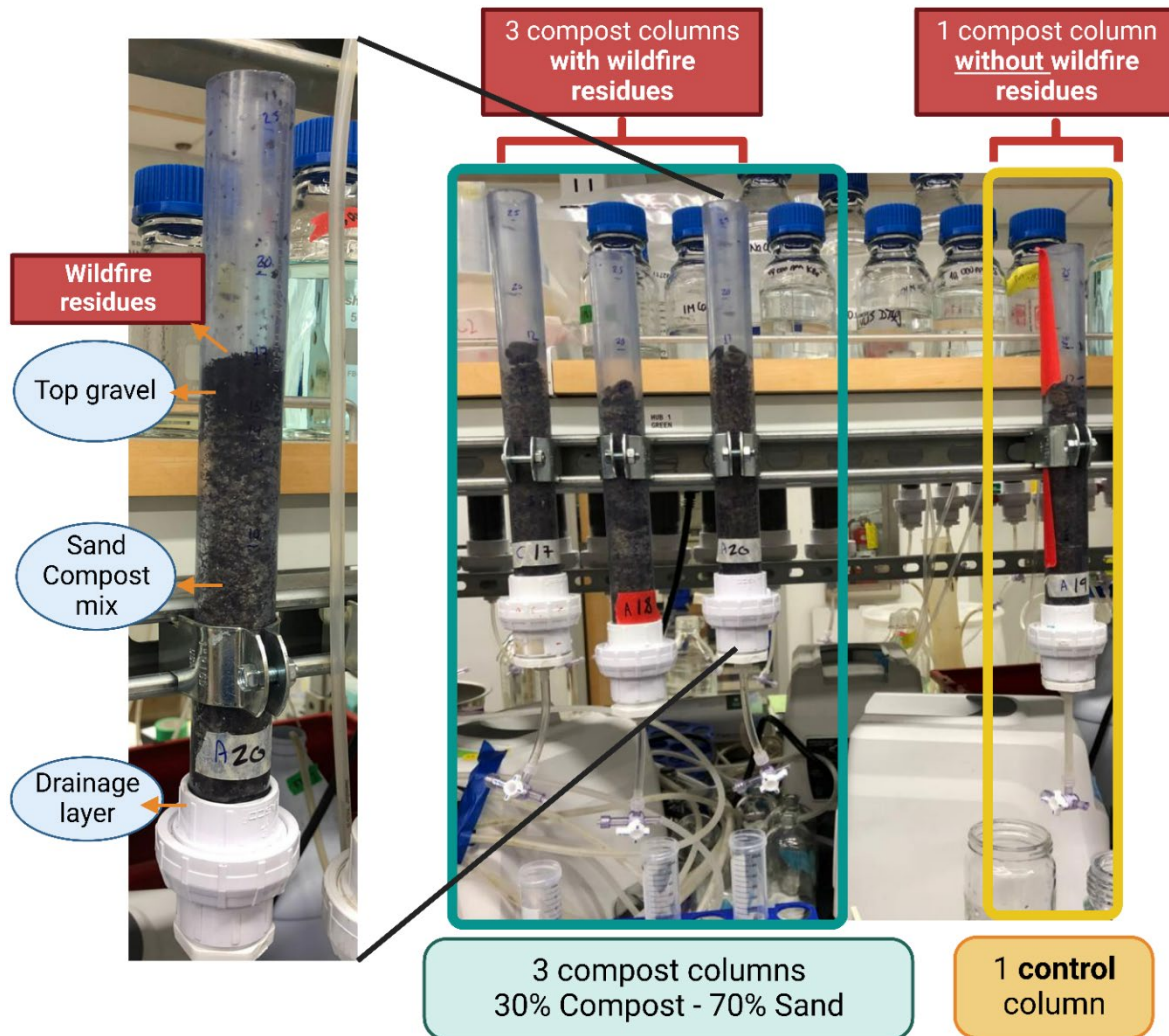


Figure 3-2. Experimental set-up of the 4 compost biofilters used for the infiltration experiment with a zoomed-in compost column configuration.

To simulate runoff containing wildfire residues, an amount equivalent to 1 kg m^{-2} was added incrementally. This amount was achieved by mixing 0.5 g of sieved wildfire residues with 40 mL of deionized water in a centrifuge tube, resulting in a wildfire residues concentration that fell within the range of total suspended solid concentration in runoff generated during the first rainfall after the fire (Raelison et al., 2023). The suspension was hand-shaken and poured out onto the top of triplicate biofilters. For each increment, the hydraulic conductivity was measured using the falling head method described elsewhere (Le et al., 2020). This involved passing an

equivalent amount of ~ 4 PV through each column every 1 kg m^{-2} . This step was repeated by adding another 1 kg m^{-2} of wildfire residues in suspension to the same column incrementally until the filter media became clogged. The clogging was indicated by the formation of a cake layer (Figure 3-3).

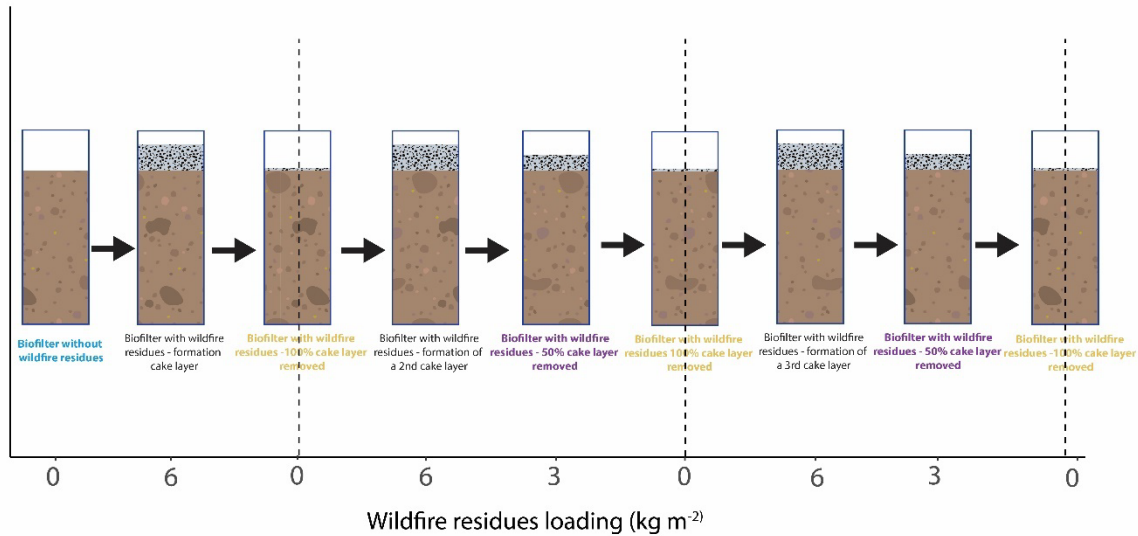


Figure 3-3. Steps of the hydraulic conductivity experiment.

To examine if scraping off the deposited wildfire residues could restore the infiltration capacity of biofilters, half of the cake layer was removed followed by the measurement of the hydraulic conductivity. Then, the remaining cake layer was removed without disturbing the underlying filter media mixture, and the hydraulic conductivity was measured. The entire clogging procedure was repeated twice by depositing the wildfire residues incrementally followed by a measurement of hydraulic conductivity to examine if the restorative maintenance by removing the cake layer could keep the biofilters functional despite multiple exposures to wildfire residues over the designed lifetime of biofilters (Figure 3-3) To estimate the amount of wildfire residue removed by biofilters, effluent turbidity was measured based on the absorbance of effluent at 890 nm. The turbidity measured at 890 nm was converted to concentration as mg L^{-1} using a calibration curve

made by suspensions containing a known quantity (mg) of fine ($< 250 \mu\text{m}$) wildfire residues. The effluent predominantly carries fine particles of this size due to their ability to permeate through the biofilter's pore structure, thus aligning the calibration curve with particles of this size range that could plausibly appear in the effluent.

3.2.4. Effect of deposited wildfire residues on pollutant removal capacity of biofilters

To examine the effects of the deposited wildfire residues on the pollutant removal function of biofilters, a total of twelve biofilter columns were newly packed with six columns containing a sand-compost mixture and six columns containing only sand to monitor the change in chemical properties of pore water due to addition of wildfire residues without influenced by compost leachate. For each media mixture, three columns out of the six were subjected to wildfire residues deposition (**Figure 3-4**) to mimic the field conditions following a wildfire, where wildfire residues can deposit onto biofilters. A 40 mL stormwater suspension containing 1 g of sieved wildfire residues (equivalent to 2 kg m^{-2}) was poured on both triplicate compost-sand and triplicate sand-only columns. Based on the results of the infiltration experiment conducted in this study (**Figure 3-5**), this quantity was found to be a sufficiently large amount to affect pore water chemistry without completely clogging the biofilters, while still falling within the range of post-fire TSS concentration (Raoelison et al., 2023). The three other columns of each media mixture were used as control without deposition of wildfire residues. All experiments were conducted in triplicates.

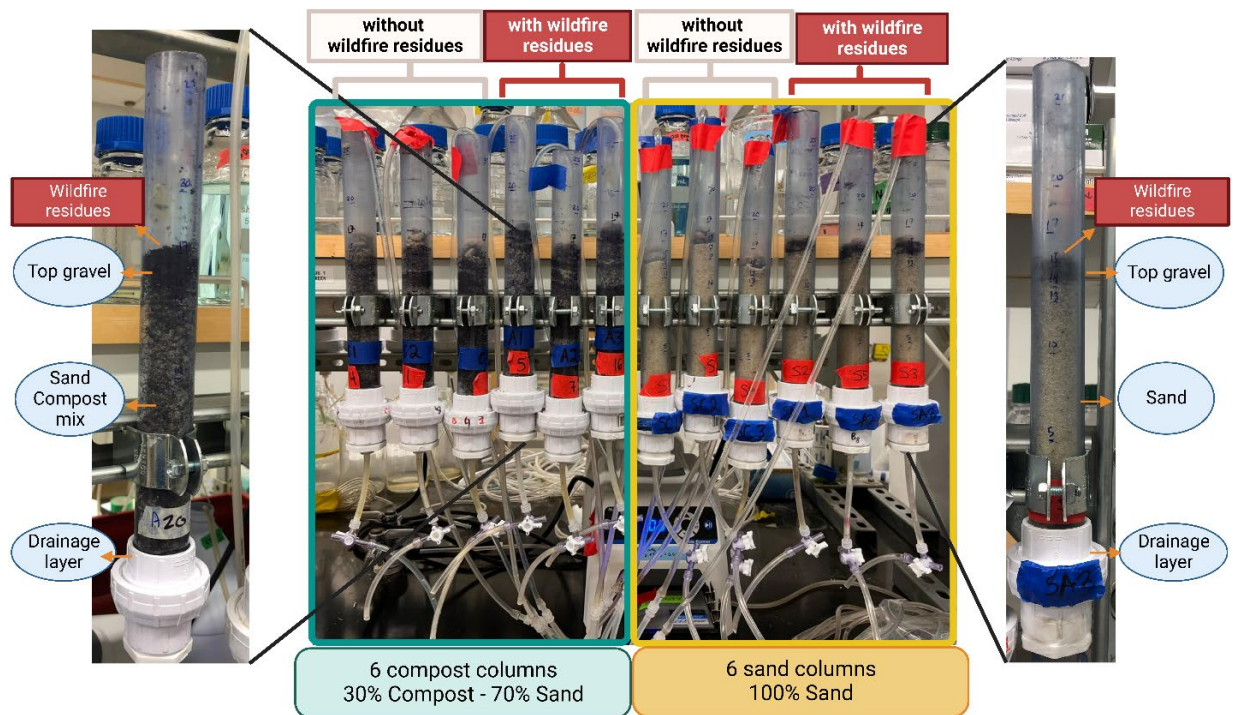


Figure 3-4. Experimental set-up of the 12 biofilter columns with a zoomed-in sand and sand-compost column configuration.

Following a wildfire, potential subsequent rainfall events could result in runoff and erosion of burned soil. Therefore, it is crucial to understand whether these deposited wildfire residues could exert an influence on the removal capacity of biofilters. In order to measure the ability of biofilters to remove pollutants from contaminated stormwater during subsequent post-fire rainfall events, natural stormwater spiked with pollutants such as nitrate (5 mg L^{-1}), phosphate (1 mg L^{-1}), and heavy metals (Pb, Ni, Cu, Zn, As, and Cr, $100 \text{ } \mu\text{g L}^{-1}$) was intermittently applied on the top of biofilters with and without pre-exposure to wildfire residues to simulate rainfall and intermittent infiltration of stormwater runoff in biofilters in a natural environment. These specified target concentrations fall within the typical concentration ranges of metals, nutrients, and *E. coli* found in urban stormwater, as documented in the International BMP Database (Tirpak et al., 2021) and used in prior experimental investigations (Grebel et al., 2013), thereby making the results

applicable across a wide array of locations. For each injection i.e., “dry-wet cycle”, a total of 22.5 PV of contaminated stormwater was injected into the columns at 11.8 cm h⁻¹ for 9 h followed by gravity drainage and 15 h of drying at room temperature (22 °C). The infiltration rate through media filter is influenced by the stormwater loading rate, which depends on the catchment area and rainfall intensity. However, the chosen infiltration rate is typically determined by the hydraulic conductivity of filter media. In our study, the rate of 11.8 cm h⁻¹ was lower than the lowest hydraulic conductivity of biofilters with wildfire residue deposits, which ensured that stormwater would not pond on the top of biofilters. This rate simulates the usual range for urban biofilters (4 – 20 cm h⁻¹) (Tirpak et al., 2021). The dry-wet cycle was repeated four times. Therefore, the experimental design assessed the short-term removal rate, excluding consideration of potential long-term alterations that may occur in natural conditions due to depletion of the media’s filter adsorption capacity. To estimate metal removal, the effluent was analyzed after application of 22.5 PV of contaminated stormwater per day. The inflow volume was chosen to observe the metals removal of the filter media reaching the breakthrough point of the different metals of interest. The removal capacity of biofilters was calculated by using the equation: $1 - (C_e/C_i)$; where C_e and C_i represent the concentration in the effluent and influent, respectively.

The experiments involving metals and nutrients removal were carried out concurrently, while the *E. coli* experiment was conducted subsequently to prevent any deleterious effects of metals on *E. coli* viability or the potential for *E. coli* proliferation due to nutrient availability. The purpose of this approach is to distinctly observe the impact of wildfire residues on *E. coli* removal while minimizing other confounding variables. To examine the effects of deposited wildfire residues on the *E. coli* removal capacity of conventional biofilters, autoclaved natural stormwater spiked with *E. coli* ($2.87 \pm 0.18 \times 10^5$ CFU mL⁻¹) was intermittently applied on the model biofilters,

and effluent was analyzed for *E. coli* using agar plates (Valenca et al., 2020). Briefly, a kanamycin-resistant strain of *E. coli* K-12 was cultivated in Luria-Bertani growth media (LB Broth, Miller, Fisher BioReagents). After centrifugation to remove growth media and subsequent washing with a phosphate-buffered saline (PBS) solution, the bacteria were suspended in stormwater to achieve a concentration ranging from 10^3 to 10^7 colony-forming units (CFU) per milliliter. During each injection, 8 PV of contaminated stormwater was applied on the top of biofilters at 11.8 cm h^{-1} followed by 18 h of no-flow period, when the water in the columns was drained naturally by gravity. This simulates a typical rainfall, which involves a wetting cycle followed by a period of drying cycle. The variation in the inflow volume between the study of metals and nutrients and the study of *E. coli* was influenced by the different breakthrough dynamics of these pollutants. Specifically, the bacterial breakthrough occurred at a faster rate compared to the breakthrough of metals, thus necessitating a smaller volume of water to be injected to observe the breakthrough. The dry-wet cycle was repeated 4 times. During each injection, the effluent samples were collected in two fractions: the first PV eluted after starting the infiltration event and the last PV before stopping the infiltration event. The first PV represents old water from the previous simulated rainfall trapped in biofilters where trapped *E. coli* could either grow or die off depending on the conditions in biofilters (Ghavanloughajar et al., 2021; Valenca et al., 2021). This also represents first-flush effluent, which is found to contain a high concentration of *E. coli* compared to the rest of the effluent due to mobilization of attached *E. coli* (Mohanty et al., 2013). The concentration of *E. coli* in the last PV was used to estimate the steady-state removal capacity of the biofilters as a typical breakthrough occurs within 2 PV of injection (Mohanty et al., 2013). The *E. coli* removal capacity of biofilters was calculated as $-\log(C/C_0)$, where C and C_0 represent the *E. coli* concentration in the effluent and influent water, respectively. To examine if the presence of

wildfire residues could proliferate or inhibit *E. coli* growth during the drying period, the growth-die-off index (GDI) was estimated using the following equation:

$$GDI = -\log \frac{C_2^{i-1}/C_0^{i-1}}{C_1^i/C_0^i}$$

where C_0 , C_1 , C_2 represent *E. coli* concentration in the influent, first flush, and last sample of the injection, respectively, and i and $i-1$ represent current injection and the previous injection. Positive GDI indicates that *E. coli* grow during the drying period and negative GDI indicates *E. coli* die off during the drying period.

3.2.5. Effluent analysis

Effluents were measured for pH using an ion-selective electrode (model #9107BN, Fisher Scientific), dissolved organic carbon using a Total Organic Carbon Analyzer (TOC-L, Shimadzu), and specific ultraviolet absorbance (SUVA) at UV₂₅₄ absorbance using a spectrophotometer (Lambda 365, PerkinElmer). Nitrate and phosphate concentrations were measured using Ion Chromatography (Dionex™ Integrion™ HPIC™ System). A sub-sample was filtered through a 0.45 μm PES syringe filter (Cytiva Whatman™ Uniflo) to remove any suspended solids and then acidified using 5% nitric acid and analyzed for metals using Inductively coupled plasma mass spectrometry (ICP-MS). Preliminary analysis of the total concentration of metal—which is measured in the sample that undergoes acidification to desorb metals from any suspended particles followed by centrifugation—reveals that the contribution of particle-associated concentration to total metal concentration is insignificant. Therefore, we only measured the dissolved metal concentration of metal, which can be assumed to represent the total metal concentration due to the limited contribution of particles. *E. coli* concentration was determined by inoculating the effluent sample onto LB agar plates with kanamycin, following spread plate and counting techniques with

two plates per sample. Dilution was performed to achieve bacteria count within the range of 30 to 300 colony forming units (CFU) mL⁻¹. The final concentration was calculated as the average colony count from the two plates and expressed as CFU per mL.

3.2.6. *Statistical analysis*

All statistical analysis was conducted using R (version 4.2.1). Wilcoxon test was performed to assess the statistical differences between the boxplots of samples exposed to wildfire residues and those without. Differences were considered significant if the p-value was < 0.05.

3.3. Results

3.3.1. *Effect of wildfire residues on infiltration capacity of the biofilters*

The addition of wildfire residues decreased the hydraulic conductivity of all biofilters (**Figure 3-5**). Deposition of wildfire residues up to 7 kg m⁻² on top of biofilters decreased the hydraulic conductivity of biofilters from 441 ± 35 mm h⁻¹ to 158 ± 23 mm h⁻¹. The decrease in hydraulic conductivity depended on the amount of wildfire residues deposited on the top. The hydraulic conductivity decreased with each successive addition of wildfire residues until the loading reached 2 kg m⁻². Beyond this threshold, any further addition of wildfire residues did not significantly decrease the hydraulic conductivity of biofilters, indicating that a cake layer was formed with the accumulated wildfire residues. Removal of 50% of the cake layer did not result in the complete restoration of hydraulic conductivity, but the removal of the entire cake layer restored the hydraulic conductivity of biofilters to its original value.

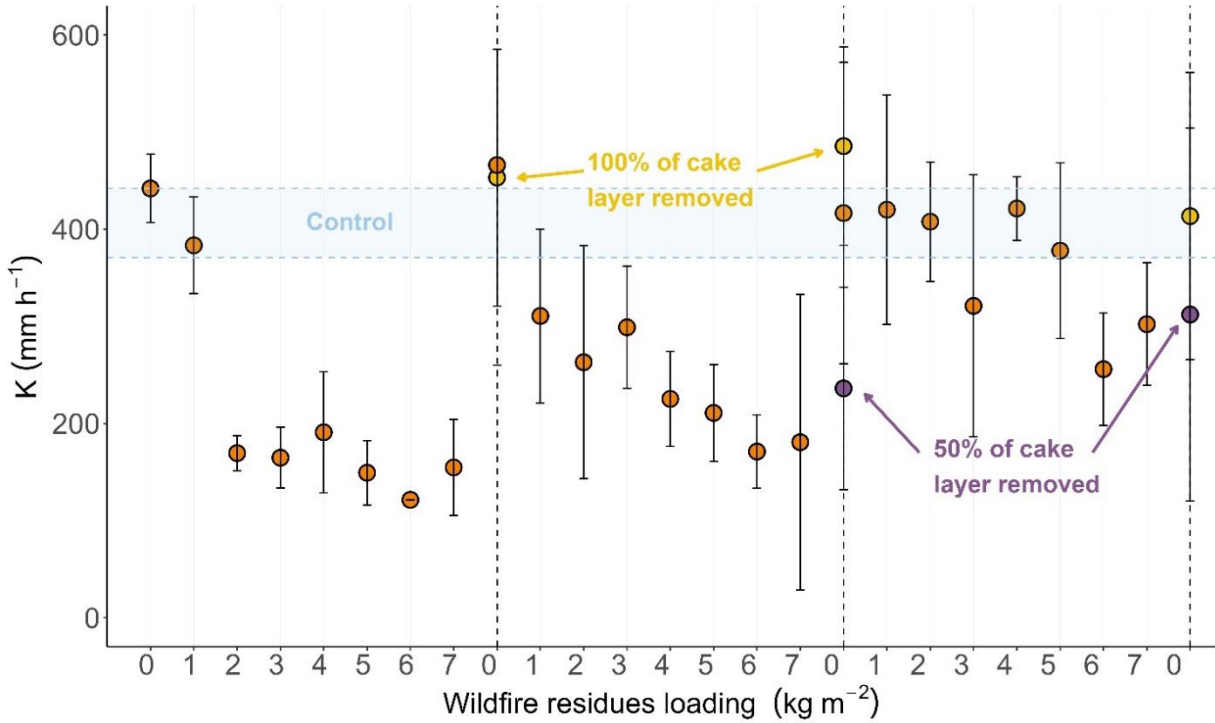


Figure 3-5. Changes in saturated hydraulic conductivity (K) (mm h^{-1}) of sand-compost biofilters with and without exposure to wildfire residue (kg m^{-2}). The blue shaded area represents the hydraulic conductivity of the control column without wildfire residues throughout the experiment. Vertical dashed lines indicate the beginning of the clogging procedure after scraping half of the cake layer (purple dots: “50% of cake layer removed”) and/or the whole cake layer (yellow dots: “100% of cake layer removed”) cf. Fig. 3-3.

3.3.2. Effects of deposited wildfire residues on pore water composition

Deposition of wildfire residues did not alter the water chemistry parameters including pH, SUVA, and TOC in pore water (Figure 3-6). The average pH for pore water in sand and compost columns, respectively, were 7.94 and 7.87. Addition of wildfire residues to both columns did not result in a significant increase in pH. The presented TOC should be referred to as DOC (Dissolved Organic Carbon) because the effluent samples underwent filtration through a $0.45 \mu\text{m}$ filter. For DOC, the sand and compost columns exhibited levels of 5.76 mg L^{-1} and 6.94 mg L^{-1} respectively, indicating organic carbon leaching from DOC did not significantly increase the stormwater DOC. Despite the addition of wildfire residues, DOC levels remained largely unchanged across all columns. The SUVA of sand columns was $1.88 \text{ L mg}^{-1} \text{ M}^{-1}$, reflecting the stormwater SUVA

concentration. Similar to DOC, the addition of compost increased SUVA to 3.59 mg L⁻¹. The deposition of wildfire residues did not affect SUVA values in sand columns but did lead to a slight increase in SUVA in the compost columns.

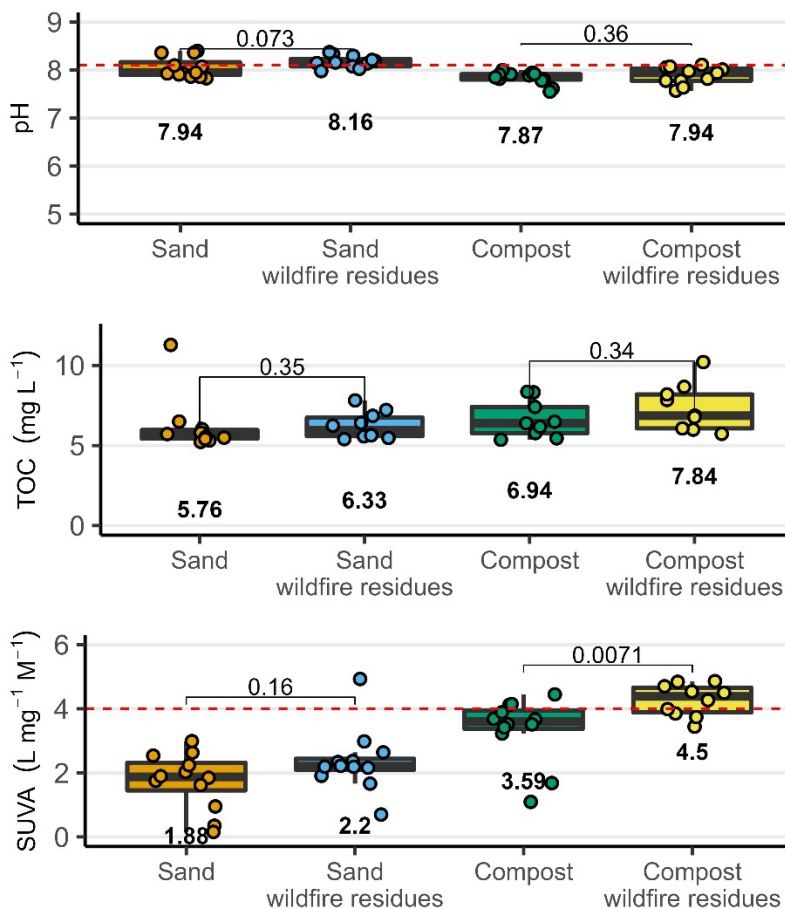


Figure 3-6. Effect of wildfire residues on pH, SUVA, and DOC in sand and compost biofilters. For pH, the horizontal red dashed line for pH represents the stormwater and the number represents the median value of each boxplot. For SUVA, the horizontal dashed line represents the maximum limit recommended by EPA in surface water.

3.3.3. Effects of deposited wildfire residues on the removal of metals and nutrients

Deposited wildfire residues either increased metals removal (Pb, Ni, Cu, and, Zn) or had no significant effect on metals removal (As, Cr) in sand columns while metals removal remained unaltered in compost columns, apart from Pb (**Figure 3-7**). Compared to the removal of metal cations, the removal of anions was not affected by wildfire residues in both sand and compost

columns. Conversely, results were inconclusive for nutrients since our model biofilters without wildfire residues displayed almost zero removal of nitrate and phosphate (**Figure 3-8**). However, the exposure of biofilters to wildfire residues did not appear to affect the removal of phosphate and nitrate during the infiltration of stormwater.

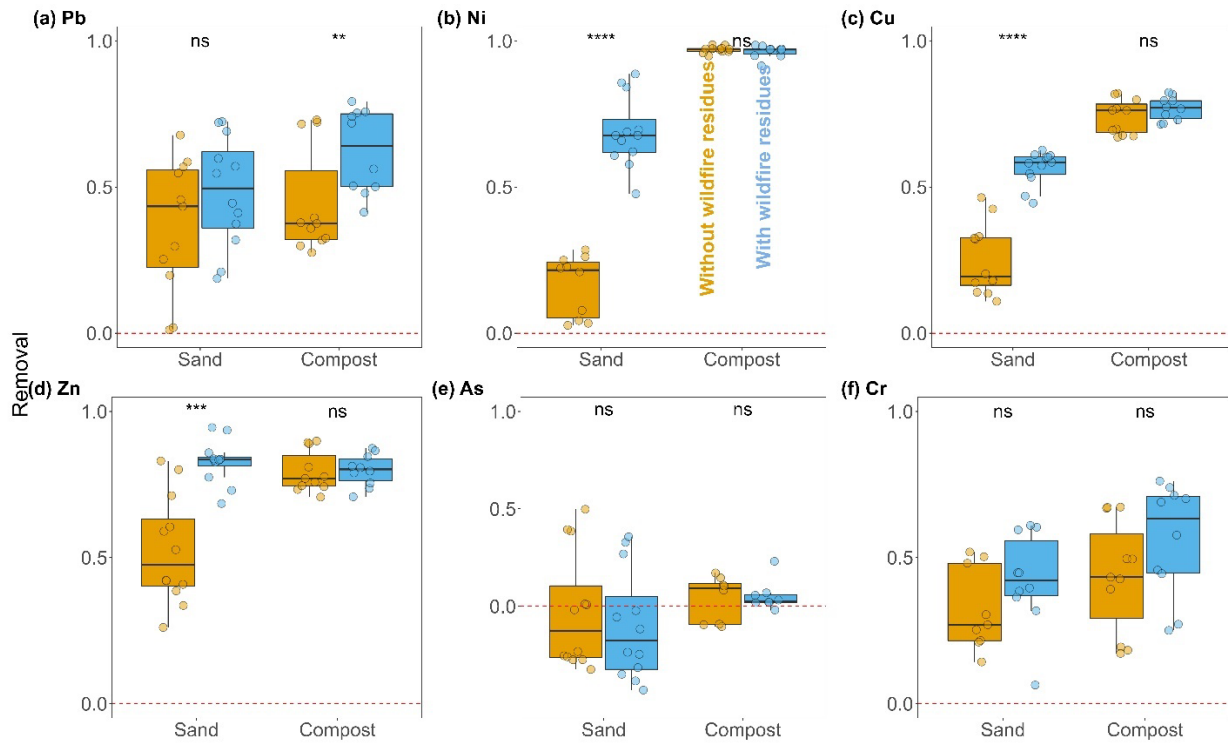


Figure 3-7. Removal of metals without and with wildfire residue deposition (2 kg m⁻²) based on the metal species (a) Pb, (b) Ni, (c) Cu, (d) Zn, (e) As, (f) Cr, and filter media: sand or compost. The red dashed line represents no removal, whereas positive and negative values represent net removal and net export of metals, respectively. The sand columns contain 100% sand, and the compost columns contain 70% sand and 30% compost by volume. ** means p-value < 0.01, **** means p-value < 0.0001, and ns means a non-significant difference between the groups.

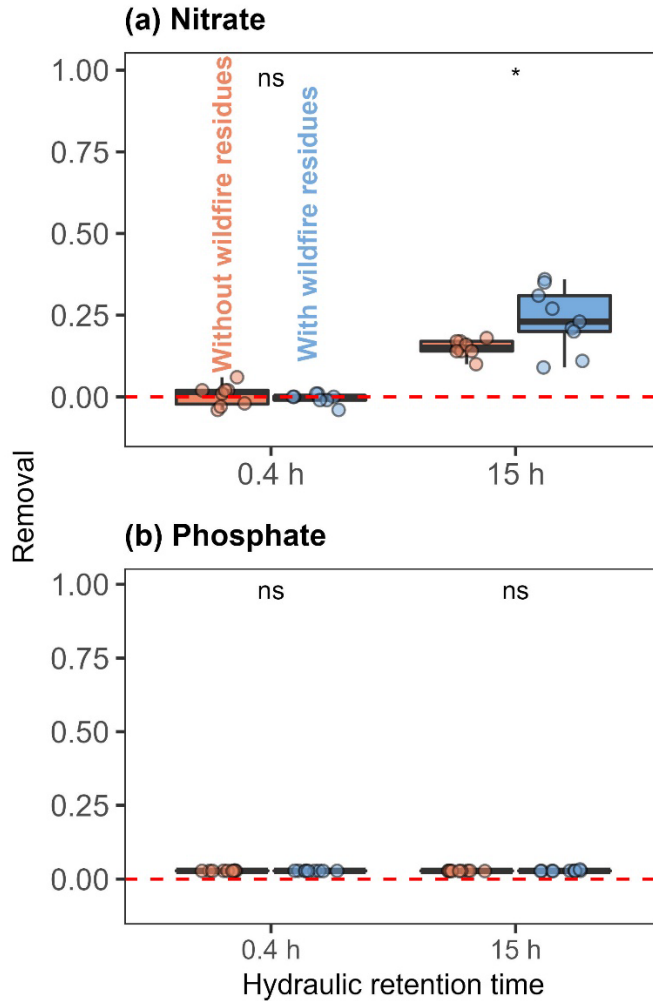


Figure 3-8. Removal of (a) nitrate and (b) phosphate before and after wildfire residue deposition in biofilter containing sand and compost. Hydraulic retention time is calculated as the ratio of pore volume PV (mL) and the flow rate of stormwater (mL min^{-1}). The removal capacity of biofilters was calculated by using the equation: $1 - (C_e/C_i)$; where C_e and C_i represent the concentration in the effluent and influent, respectively. The dashed line represents no removal, whereas positive and negative values represent net removal and net export of nutrients, respectively. ns means a non-significant difference between the groups.

3.3.4. Effect of deposited wildfire residues on *E. coli* removal in biofilters

Wildfire residue deposition did not significantly alter *E. coli* removal in both sand and compost biofilters, although the mean log removal decreased slightly following the exposure to wildfire residues in sand columns (Figure 3-9). The mean log removal in sand columns without and with wildfire residues were 0.09 and 0.06, respectively, whereas the mean log *E. coli* removal in compost columns without and with wildfire residues was higher (~0.51).

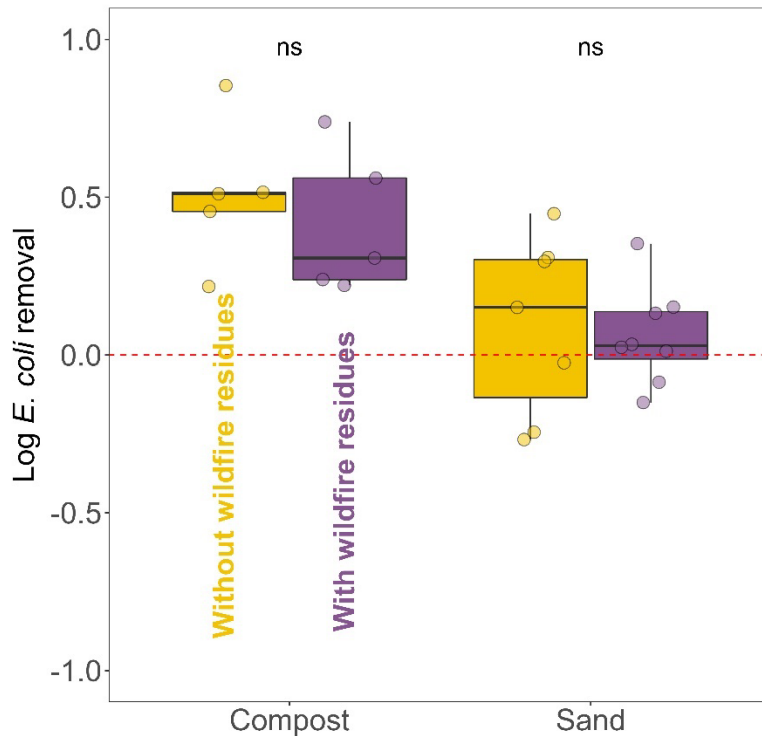


Figure 3-9. Removal of *E. coli* without and with wildfire residue deposition (2 kg m^{-2}) based on filter media: sand or compost. The sand columns contain 100% sand, and the compost columns contain 70% sand and 30% by volume. The dashed line represents no removal, whereas positive and negative values represent net removal and net export of *E. coli*, respectively. ns means a non-significant difference between groups.

3.4. Discussion

3.4.1. Effects of wildfire residues on clogging potential of stormwater biofilters

Most stormwater biofilters are installed near roadways or downstream, where they are designed to capture sediments from runoff. However, it is not clear whether they could remain functional hydraulically after the deposition of high amounts of wildfire residues released from catchments affected by wildfires. Our results (**Figure 3-5**) show that the deposition of wildfire residues, based on the amount deposited, could rapidly decrease the hydraulic conductivity of biofilters to a threshold value, beyond which any additional deposition of wildfire residues did not change hydraulic conductivity due to the formation of a cake layer. The result is consistent with other studies that examined a decrease in infiltration rate in the subsurface of stormwater biofilters

with suspended sediments (Le et al., 2020; Siriwardene et al., 2007). While residues $>10\ \mu\text{m}$ can also be removed by filtration, interception, and adsorption, size residues $< 2\ \mu\text{m}$ are expected to pass through sand filters (Bradford et al., 2002; Liu et al., 2016). A previous study with an identical experimental design on wildfire residue transport confirmed that sand filters can remove all wildfire residues greater than $3\ \mu\text{m}$ (Valenca et al., 2020). As compost has an average size smaller than sand, the mean pore size of the compost and sand mixture is expected to be smaller than that of sand only. Thus, some of the residues below $3\ \mu\text{m}$ are expected to be filtered in our study. Measuring particle size distribution of wildfire residue (**Figure 3-1**), we found that 50 % of wildfire residues had an average size of $42\ \mu\text{m}$, suggesting that nearly all deposited wildfires should be removed through straining. Consequently, the formation of the cake layer indicates that most deposited residues remained on the top surface without penetrating into deeper layers. Moreover, this finding was corroborated by comparing particle concentrations of influent and effluent (**Figure 3-10**), which demonstrated that all wildfire residues were indeed filtered out of the stormwater. Thus, the removal of the entire cake layer completely restored the capacity of biofilters. The hydraulic conductivity after the formation of the cake layer remained at nearly 35% of the initial hydraulic conductivity, which should be the hydraulic conductivity of the cake layer, the layer with the least hydraulic conductivity (Subramaniam et al., 2018). The addition of more wildfire residues only increased the thickness of the cake layer to $2.8 \pm 0.4\ \text{cm}$ without affecting the filter layer underneath (**Figure 3-11**). This explained why the hydraulic conductivity did not change after the deposition of $2\ \text{kg}$ of residue per m^2 of biofilter area in our study. Our results show that the removal of the cake layer could restore the infiltration capacity.

The results have both practical and scientific implications for biofilter functions. Knowledge of cake layer formation would help restoration efforts, whereas knowledge of how far

wildfire residues may migrate into biofilters helps understand their impact on the biochemical functions of biofilters. However, in the field conditions, the depth of the cake layer would depend on the area of biofilters, and the quantity of wildfire residues deposited on the biofilters. Thus, the depth of the cake layer should be measured based on site conditions (Haile et al., 2015) before any measure to restore the infiltration capacity of biofilters.

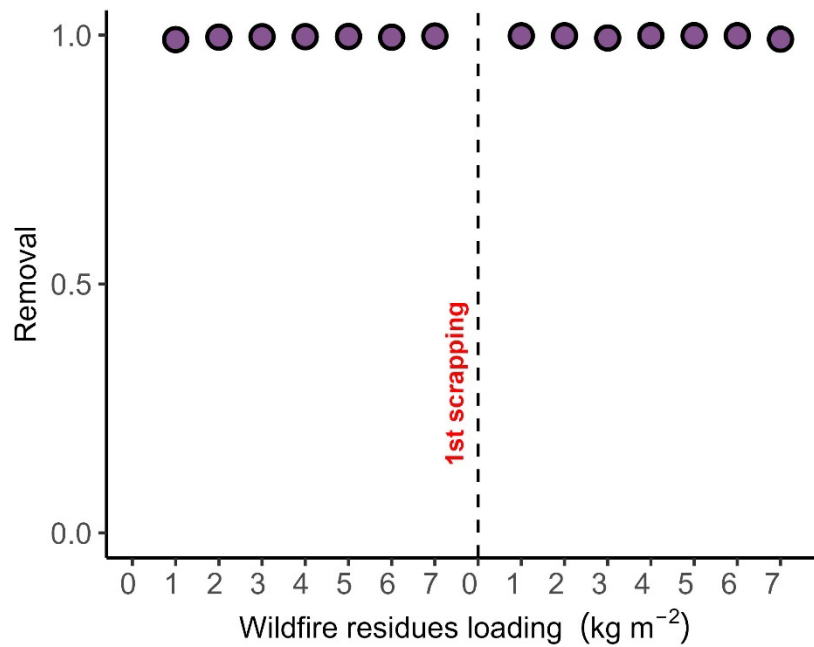


Figure 3-10. Removal of particle concentration (mg L^{-1}) in sand-compost biofilter columns based on wildfire residues loading. Particle concentration of the effluent (mg L^{-1}) which was estimated from the absorbance at 890 nm of samples by using a calibration curve of the absorbance of samples containing a known concentration of compost and wildfire residues particles of the same size range, $< 250 \mu\text{m}$, particle size that could penetrate in the subsurface of the biofilter.

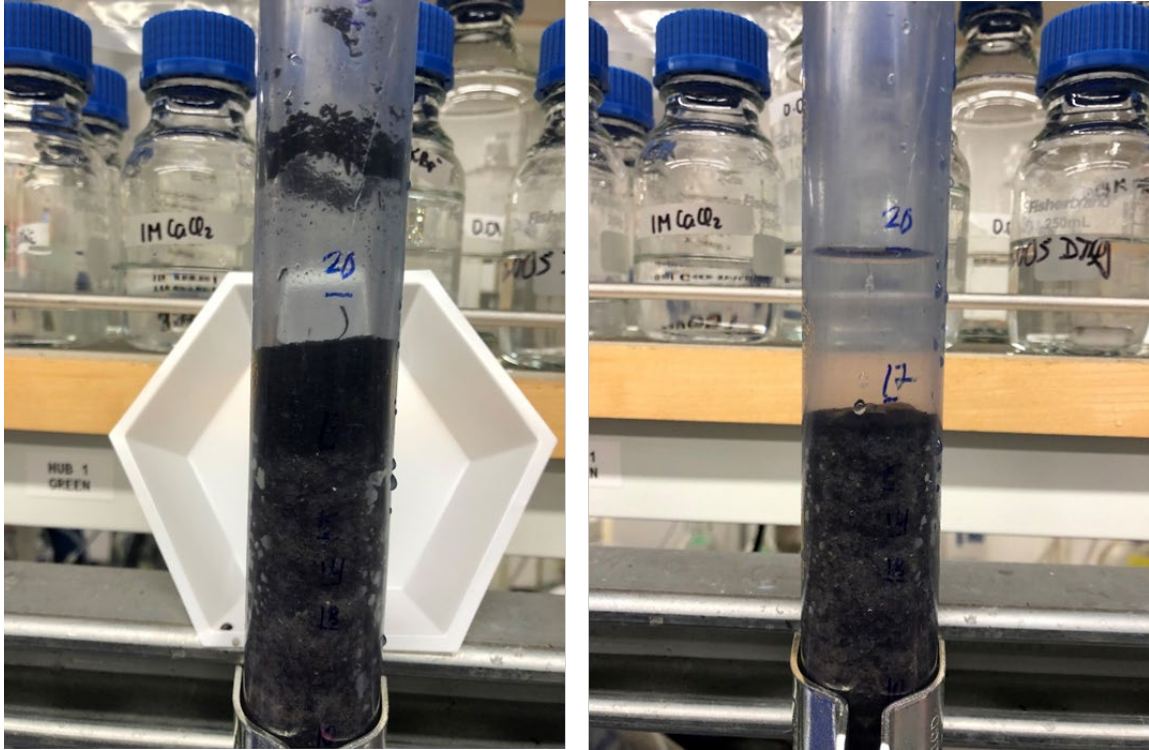


Figure 3-11. Cake layer before 1st scraping (left) and after scraping 100% of the cake layer (right).

3.4.2. Effects of wildfire residues on metals and nutrients removal in stormwater biofilters

Wildfire residues can leach metals to receiving waters (Pinedo-Gonzalez et al., 2017), but it is unclear if the residues could leach metals into the pore water in biofilters or alter the pore water chemistry to affect their metal removal capacity. Our results confirmed that wildfire residue deposition did not change in the removal of metals in compost biofilters with and without wildfire residues (**Figure 3-7**). However, metal removal increased in sand columns indicating that deposited residues increased the removal of metals. We attribute the increase in metal removal in sand columns to an increase in pore water pH (**Figure 3-6**) in the presence of ash in wildfire residues and the limited release of metals into pore water (**Figure 3-12**). An increase in pH could decrease metal solubility and increase metal removal (Blecken et al., 2009). Moreover, our study demonstrates that wildfire residues could release metals when exposed to a solution simulating the root zone (**Figure 3-12**). However, any metals leached from wildfire residues could be adsorbed

on compost due to their metal binding capacity (Lim et al., 2015; Silvertooth et al., 2015; Sun et al., 2020). Adsorption of metals such as Cu and Zn by the compost in the biofilters (**Figure. 3-13**) confirmed the hypothesis. Overall, our results reveal that the deposition of wildfire residues on biofilters would not increase metal risk.

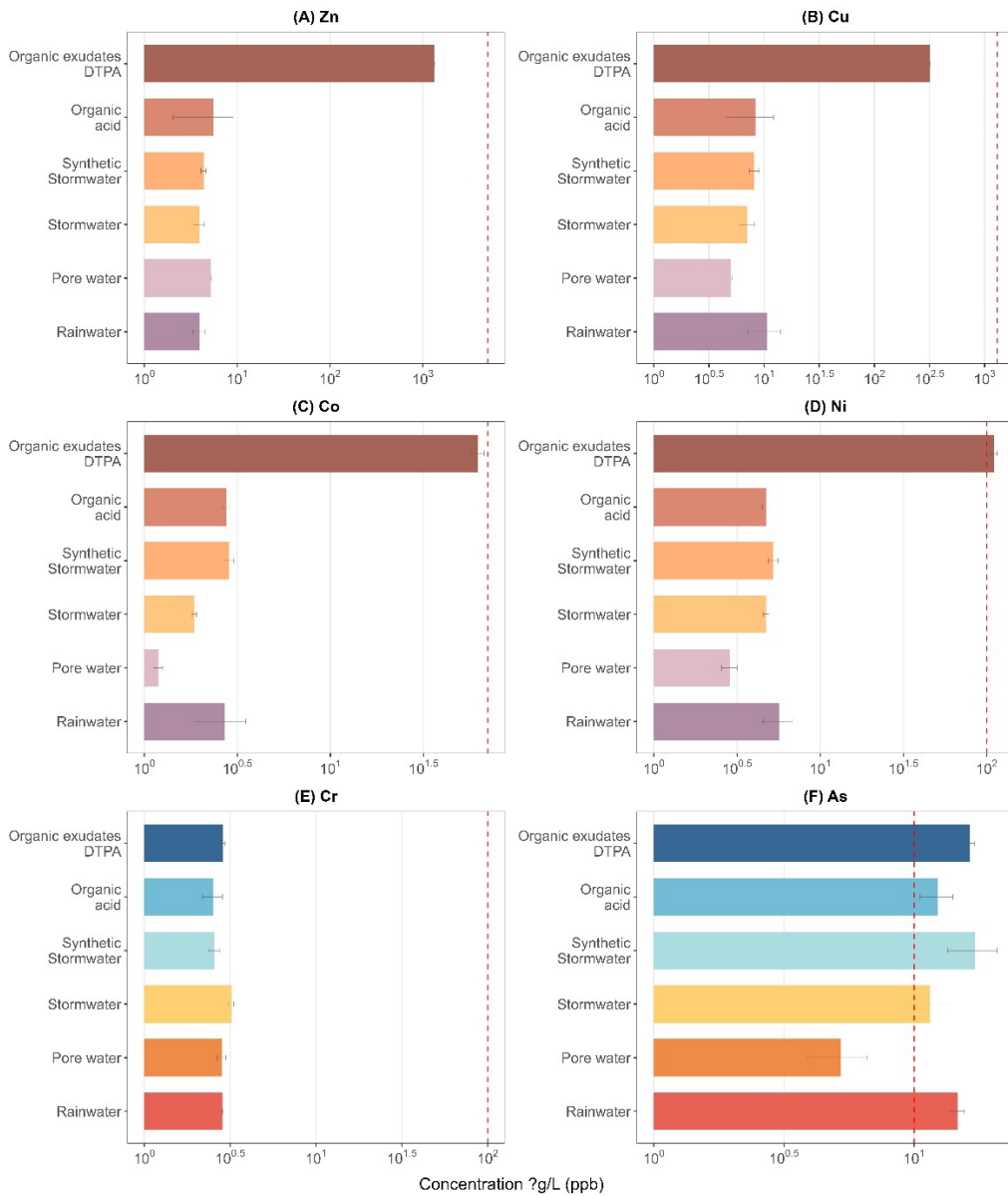


Figure 3-12. Concentration ($\mu\text{g L}^{-1}$) of Zn, Cu, Co, Ni, Cr, and As leached from wildfire residues in 6 different solutions: ultrapure water, natural stormwater, 10 mM NaCl, 10 mM CaCl₂, 10 mM oxalic acid, and 5 mM diethylenetriaminepentaacetic acid (DTPA). The red line represents the Maximum Contaminant

Level (MCL) for drinking water set by the US EPA: Zn (5 ppm), Cu (1.3 ppm), Co (70 ppb), Ni (100ppb), Cr (100 ppb) and As (10 ppb).

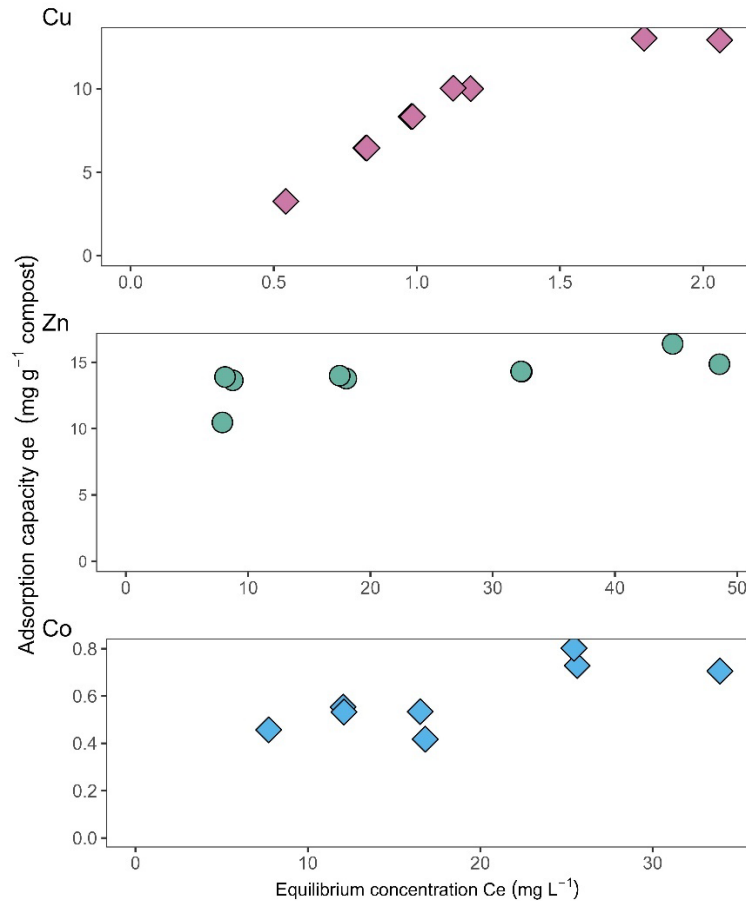


Figure 3-13. Adsorption of Cu, Zn and Co onto compost used in model biofilter media. To examine the metal removal capacity of compost in biofilters, batch sorption experiment was conducted by mixing 0.1 g of compost with a solution containing 0.2 to 50 mg L⁻¹ of six metals: Ni, Rb, Zn, Cu, Co, Cd. Adsorption capacity was estimated by measuring the equilibrium concentration of dissolved metals after 24 h of mixing.

Our study was unable to conclude whether wildfire residues had any significant impact on nutrients removal during stormwater infiltration (**Figure 3-8**). This limitation arose primarily from the initial low removal capacity of the model biofilters used in our study. It is worth noting that these biofilters were deliberately designed to represent conventional biofilters, without specific optimization for nutrient removal. Instead, our objective was to assess the performance of a standard, commonly used biofilter in removing stormwater common pollutants as opposed to emphasizing nutrient removal. As previously mentioned, our model biofilters were unvegetated to

isolate and study the specific pollutant removal mechanisms within the biofilters, while also preventing any alterations in the composition of pore water after the deposition of wildfire residues to eliminate any potential confounding effects of the plants. However, vegetation plays a key role in nutrients removal in biofilters (Fowdar et al., 2021), and the deposition of wildfire residues can impact plant performance, including their ability to absorb water. Additionally, it can influence the microbial community composition, which is associated with processes like denitrification. Future studies should examine the impacts of wildfire residues on the biochemical function of stormwater biofilter specifically on the vegetation and the microbial community in stormwater biofilters. Despite inconclusive results, our study suggests that the deposition of wildfire residues could potentially enhance the removal of nitrate trapped in pore water between two successive infiltration events (**Figure 3-8**). The first flush water represented the stormwater trapped in the biofilters for nearly 15 h between simulated rainfall events, which is sufficient time to decrease nitrate by denitrification (Halaburka et al., 2019), although denitrification was not demonstrated in this study. This result might be attributed to the clogging of biofilters, which could lower oxygen diffusion from the surface to internal pores in biofilters, thus potentially creating anoxic conditions favorable to denitrification. Moreover, our study shows that wildfire residues led to a slight increase in dissolved organic carbon concentration in compost biofilters without affecting the pH (**Figure 3-6**). The absence of pH change could also account for the unaltered phosphate removal capacity of biofilters, possibly due to the buffering capacity of compost in the biofilters neutralizing any OH⁻ released from wildfire ash (Kurola et al., 2011). Furthermore, the addition of wildfire residues may not have provided any extra sorption sites for phosphate removal. Wildfire residues collected in this study contained a negligible amount of aluminum and phosphate (**Table 3-2**). Although the levels of these elements may vary based on the characteristics of the vegetation

and the severity of the wildfire, the presence of these elements in our wildfire residues seemed to be insufficient to significantly enhance phosphate adsorption or leaching. Therefore, it is reasonable to conclude that the wildfire residues would not have altered the phosphate removal capacity of biofilter.

Table 3-2. List of elements (Al, Fe) and nutrients (nitrate, phosphate) in wildfire residues (ratio 1:20) and their concentrations.

Elements name	Concentration (mean ± sd) in $\mu\text{g L}^{-1}$
Aluminum	8.05 ± 0.01
Iron	1.73 ± 0.14

Nutrients name	Concentration (mean ± sd) in mg L^{-1}
Nitrate	1.42 ± 0.26
Phosphate	0.10 ± 0.03

B) – List of metals in natural stormwater collected in Ballona Creek and concentrations in $\mu\text{g L}^{-1}$

Metals name	Concentration (mean ± sd) in $\mu\text{g L}^{-1}$
Lithium	27.5 ± 0.2
Aluminum	1.68 ± 0.08
Strontium	439.3 ± 7.5
Barium	84.3 ± 0.3
Lead	0.0498 ± 0.0008
Iron	9.4 ± 0.3
Cobalt	0.178 ± 0.004
Nickel	1.10 ± 0.02
Copper	3.47 ± 0.06
Zinc	12.6 ± 0.1
Arsenic	2.4 ± 0.1
Cadmium	0.02 ± 0.01
Chromium	1.05 ± 0.0
Manganese	0.3 ± 0.0
Rubidium	2.05 ± 0.03

3.4.3. Effects of deposited wildfire residues on *E. coli* removal

Wildfire residues contain ash and nutrients (Raelison et al., 2023), which can decrease the net removal of *E. coli* potentially by decreasing absorption at high pH resulting from ash dissolution or by supporting the growth of *E. coli* using nutrients leached from wildfire residue

(Valenca et al., 2020). Our study confirmed no such detrimental effect of wildfire residues. The deposition of wildfire residues in both sand and compost columns did not change *E. coli* removal (**Figure 3-9**). The result suggests that deposition of wildfire residues may not have aided the growth of *E. coli* or changed the interaction of *E. coli* with filter media. Sand and compost have low *E. coli* removal capacity due to low sorption sites (Mohanty and Boehm, 2014). Addition of residues did not affect those sorption sites because they were deposited on top of the filters. On the other hand, the deposited residues on the top of the biofilter media could clog the biofilter and increase *E. coli* removal by straining (Bradford et al., 2006). However, our study revealed no significant change in *E. coli* removal, indicating removal by straining did not increase significantly following the deposition of wildfire residues. Deposition of wildfire residues would likely decrease *E. coli* removal if the ash from wildfire residues could increase pH of pore water and increase the electrostatic repulsions (van Voorthuizen et al., 2001). Surprisingly, pH did not increase significantly in pore water following wildfire deposition (**Figure 3-6**), indicating deposition of wildfire residue would not alter the electrostatic interaction. Overall, these results confirm that deposition of wildfire residues on biofilters would have no negative effect on *E. coli* removal.

3.5. Design and policy implications

Given that biofilters are increasingly being built in the same water-scarce areas as we see wildfire occurrence increasing, it is essential to situate biofilters with wildfire impacts and mitigation opportunities in mind. Our study demonstrates that biofilters can help mitigate the long-term negative effects of runoff originated from wildfire-affected areas through the capture of wildfire residues that will otherwise impair downstream water bodies. The laboratory-scale study offers valuable insights through its in-depth investigations and offers significant contributions through potential design considerations in field scale. Future research endeavors should focus on

assessing long-term performance and provide a comprehensive life cycle analysis by considering regional disparities.

This finding is complemented by another study that shows drinking water biofilters can remove dissolved organic carbon originated from wildfire ash and protect drinking water quality (Blackburn et al., 2023). In other words, there is good planning motivation, rather than reason for caution, to build biofilters in wildfire-prone areas. On the other hand, our study findings show that, if not proactively addressed, wildfire-related runoff reduces biofilter infiltration effectiveness by depositing additional material until the loading reaches 2 kg m^{-2} . Thus, knowledge of suspended solid concentration and volume of runoff can be used to predict when a biofilter of specific size will become clogged or require maintenance. Wildfires can thus exacerbate the ongoing operations and maintenance (O&M) challenges faced more broadly by biofilters as a type of decentralized stormwater capture infrastructure without a clear stakeholder responsible for upkeep in many cases (Mothersill et al., 2000; Payne et al., 2015). These combined findings might suggest that biofilter construction is optimally accompanied by routine, maintenance plans, or else much of their potential contribution to mitigating wildfire impacts on water quality will be lost. Most importantly, it is increasingly recognized that O&M can be built into broader public or private landscaping service routines, rather than remaining in the theoretical purview of public works departments or specialized consultants (Beryani et al., 2021). While there is no panacea or replacement for some degree of O&M (Sagrelus et al., 2023), concepts such as zero-additional and more broadly very low-maintenance biofilters also hold promise (Prodanovic et al., 2022).

While sediment removal by scraping—as recommended in this study—typically occurs on an annual or semi-annual basis, the maintenance frequency can increase the overall operational cost of the biofilters. Instead, a sediment trap or pretreatment unit to capture the wildfire residues

could extend the design lifetime of biofilters. It should be noted that biofilters are not the best stormwater Best Management Practices (BMPs) to handle large sediment loads or debris flow after wildfire. Instead, detention ponds and wetlands have a high capacity to capture the debris. Without those large-scale BMPs, biofilters are expected to become clogged immediately after the wildfire. In that case, emergency maintenance is of utmost importance, especially after the first heavy rainfall following a wildfire.

3.6. Conclusions

This study is the first study to examine the potential implication of wildfire residue deposition on two functions of stormwater biofilters: stormwater infiltration and pollutant removal. The results proved that biofilters could remain resilient and stay functional despite the deposition of wildfire residues. The deposition of wildfire residues could clog the biofilter but the scraping of the deposited residue layer could restore its infiltration capacity. The deposited wildfire residues did not alter the removal capacity of compost biofilters for metals and *E. coli* during infiltration of stormwater. This could be attributed to the fact that these deposited residues neither changed the pore water chemistry nor affected the adsorption capacity of filter media. The results suggest that biofilters can effectively remove wildfire residues, and while the deposited residues do impact the infiltration capacity of conventional biofilters, this impact does not extend to the pollutant removal capacity of these biofilters. Although this study examines the short-term removal rate, the biofilters could remain functional despite deposition of wildfire residues and protect water quality downstream until the exhaustion of the media filter, which was not simulated in this study. These results inform management efforts to implement green infrastructure to protect downstream water quality in fire-prone areas.

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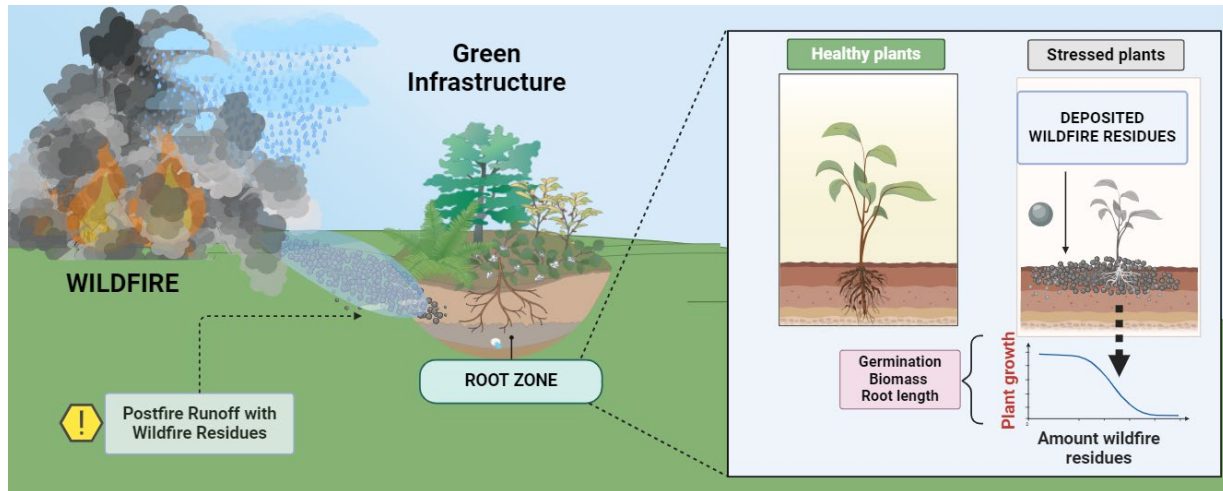
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4. CHAPTER 4 – DEPOSITED WILDFIRE RESIDUES IMPACTS ON PLANT HEALTH IN STORMWATER GREEN INFRASTRUCTURE



Raelison, O.D., Achziger, C., Gallardo, L., Santana, D., Hermsmeyer, L., Belinsky, C., Dayan, C., Choo, J., Nguyen, K., Vilchis, M., Belikov N., Min, S., and Mohanty, S.K. Deposited Wildfire Residues Impacts on Plant Health in Stormwater Green Infrastructure. [In preparation]

Abstract

During postfire rainfall seasons, surface runoff carries wildfire residues including ash, black carbon, and burned soil, and deposits them in downstream surface water and land surfaces, thereby impacting soil and water quality. Thus, installing green infrastructure to intercept the runoff and remove these residues could protect downstream water and soil quality. Most green infrastructure such as biofilters utilize plants to achieve desired functions. However, since wildfire residues contain high levels of toxic pollutants, it is unclear how their deposition might affect plants' functions in green infrastructure. This study examines the impacts of wildfire residues on the germination and early root growth of plants in biofilters using plant mesocosm studies. Natural wildfire residues were deposited in model biofilters with reference soil (for toxicity protocol) and biofilter roadside soil before testing for their effect on germination and plant health. The results revealed that wildfire residues do not appear to impact the germination and growth of plants in stormwater biofilters. However, a more pronounced effect was observed when exposed to 10% wildfire residues instead of 5%, indicating increasing deposition of wildfire residues may have negative effects on plants. Additionally, plants exhibit varying sensitivity to wildfire residues.

These results suggest that the deposited wildfire residues did not affect the initial germination and growth of plants in green infrastructure, indicating plants in green infrastructure may survive and remain resilient despite the perceived negative impact of burned residues from wildfires.

4.1. Introduction

Wildfires frequency and intensity are increasing during climate change (Abatzoglou et al., 2021; Brown et al., 2023; Dong et al., 2022; Parks and Abatzoglou, 2020). After a wildfire, burned areas exhibit bare soils with remnants of burned residues. These bare soils allow runoff to flow uninhibited carrying wildfire residues to surface water and subsurface soil downstream (Woods and Balfour, 2008). Thus, surface runoff from wildfire-affected areas could have lingering impacts on water quality for years (Cheung and Giardino, 2023; Stein et al., 2012; Thurman et al., 2023). Wildfire residue deposition could also affect the soil quality and vegetation on the land surface because of pollutants they may carry or any change in pore-water water chemistry. For instance, wildfires residues contain heavy metals such as Hg, Cu, Zn, and As (Burton et al., 2016; Cerrato et al., 2016; Lopez et al., 2023), trace elements (Campos et al., 2016), nutrients (Crandall et al., 2021; Sánchez-García et al., 2023), and toxic organic pollutants (Hickenbottom et al., 2023; Li et al., 2023; Wang et al., 2015). The alkalinity of ash can increase soil pH (Plumlee et al., 2007; Raelison et al., 2023), impacting plants and the soil microbial community (Dove et al., 2022; Nelson et al., 2022). Thus, management methods to intercept and remove wildfire residues from runoff could help protect downstream water and soil quality.

Green infrastructure have been implemented in many areas to manage runoff, mainly to reduce flooding while providing water quality benefits by removing sediments and some dissolved pollutants. The same systems could also remove wildfire residues. These nature-based solutions are typically designed with plants atop and a layer of soil or media with high hydraulic conductivity to increase infiltration. In these systems, plants play an important role in helping capture and remove pollutants such as nutrients and other organic pollutants from stormwater. Plant roots help microorganisms to thrive in soils by facilitating various processes: including taking up and

transforming organic forms (Muerdter et al., 2018), providing carbon to microbes (Fang et al., 2021), reducing stormwater volume through the transpiration process (Thom et al., 2020), stabilizing media surface (Muerdter et al., 2018), helping maintain infiltration (Archer et al., 2002; Bartens et al., 2008). Thus, green infrastructure in the region between fire-prone areas and downstream could potentially intercept and remove wildfire residues. Recent laboratory studies have demonstrated the utility of such systems in treating wildfire runoff (Raoelison et al., 2023; Valenca et al., 2020). Results of these studies show that media filters can remove nearly 99% of wildfire residues and most of the deposited wildfire residues accumulate on the top few centimeters of the soil surface in biofilters. Thus, they may affect the pore-water chemistry and composition in the root zone, which could affect the plant health in green infrastructure. For instance, the presence of heavy metals and other contaminants in wildfire residues, along with an increase in pH resulting from ash, as well as the presence of hydrophobic organic carbon, could have detrimental effects on the root zones. Yet, no study to date has examined whether the deposition of wildfire residues has any impact on plant health in green infrastructure. This study aims to evaluate the impact of wildfire residues on the biological functions of biofilters by analyzing plant growth including root length, and aboveground biomass of plant biofilters.

4.2. Materials and methods

4.2.1. Wildfire residues and roadside soil collection

Natural wildfire residues were collected from the Santa Monica Mountains National Recreation Area, USA (34°06'14"N, 118°36'09"W) four weeks after the Palisades Fire, which burned over 4.86 km² between May 14th, 2021, and May 26th, 2021. No recorded rainfall event preceded the wildfire residue collection. The sample was collected from the top 10 cm of the burned soil and was sieved to remove particles larger than 0.83 mm—the maximum size of sand

grain used in filter media—as larger residues are less likely to be carried away long-distance by runoff before their deposition on biofilters downstream and deposition of particles larger than 83 μm would create an additional layer of filter media without clogging. The particle size distribution of wildfire residues was determined using a laser diffraction particle size analyzer (Model L.S. 13 320, Beckman Coulter, Brea, California). Based on the particle size distribution measurement of sieved residues, D10, D50, and D90 of the wildfire residues were 12.0 μm , 42.3 μm , and 172.8 μm , respectively (**Figure 1-1**). In sieve analysis, D10, D50, and D90 represent the particle sizes at which 10%, 50%, and 90% of the particles, by mass, are finer than the specified size, respectively.

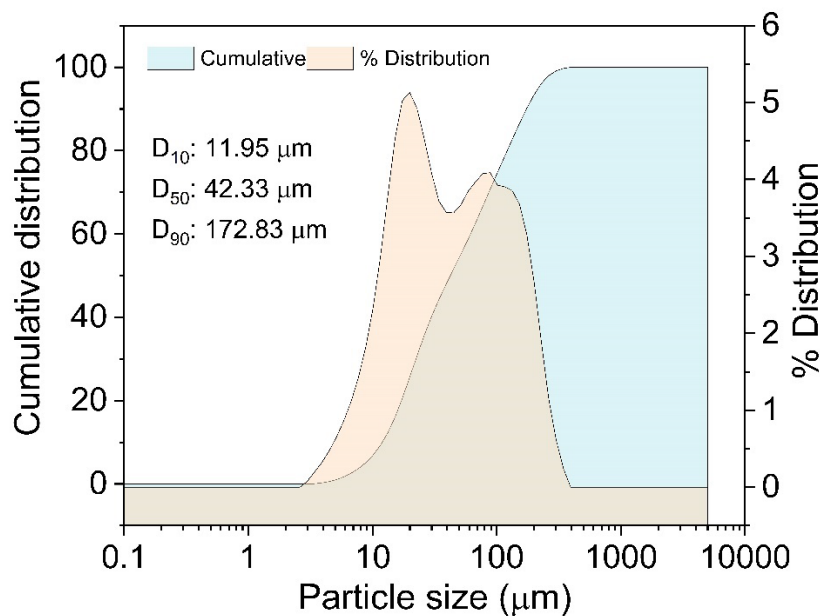


Figure 4-1. Particle size distribution of natural wildfire residues.

Roadside soil was collected from roadside sites in Los Angeles County, CA where green infrastructure are typically implemented to intercept and treat surface runoff. The topsoil layer was cleared of mulch and plant roots, and samples were taken from the subsurface layer up to a depth

of 45 cm. Soil from four different locations within the same site was combined to create a composite sample, which was then sieved to remove gravel (>2mm) and used in our study.

4.2.2. Biofilter soil media preparation

Two types of soils were used in this study: one reference soil provided in the phytotoxicity test and biofilter soil. Stormwater biofilters typically use sand for infiltration purposes, along with an amendment to enhance pollutant removal and support vegetation (Tirpak et al., 2021). In this study, coarse sand (0.59 mm – 0.84 mm, Humboldt Mfg. Co., IL, USA) was mixed with sieved roadside soil at a 7:3 ratio, following the specifications commonly used in biofilters.

4.2.3. Effect of wildfire residues on plant health

To determine the effects of wildfire residues on plant germination and early growth, phytotoxicity tests were performed using the Phytotoxkit (MicroBioTest, Belgium) following the standard procedure ISO 18763:2016. This is a 3-day standardized small-scale bioassay that includes three plant species: the *monocotyledon Sorghum saccharatum* (Sorghum), the *dicotyledons Lepidium sativum* (Garden cress) and *Sinapis alba* (Mustard). By quantifying germination, root growth, and aboveground biomass—all indicators of plant health—we assessed soil toxicity compared to the Organization for Economic Cooperation and Development (OECD) standard soil (reference soil). Bioassays were conducted in triplicate using reference soil and biofilter soil mixed with different amounts of wildfire residues (0%, 5%, and 10% by volume) and three different types of seeds. To understand the toxicity of wildfire residues in soil, the reference soil was used, while to assess the impact of wildfire residues on the biofilter soils, the biofilter soil was used.

Reference soil plates include 9 plates with 100% reference soil (0% wildfire residues), 9 plates with 95% reference soil and 5% wildfire residues, and 9 plates with 90% reference soil and

10% wildfire residues. Biofilter soil plates include 9 plates with 70% sand, 30% roadside soil, and 0% wildfire residues, 9 plates with 70% sand, 25% roadside soil, and 5% wildfire residues, 9 plates with 70% sand, 20% roadside soil, and 10% wildfire residues. This resulted in a total of 54 plates: 27 plates for the reference soil and 27 plates for the biofilter soils.

A water holding capacity test was performed for the two soils without any wildfire residues to determine the amount of water needed for complete hydration of the soil (V_{sat}). The water-holding capacity of soils without wildfire residues was used in all bioassays to isolate the impacts of wildfire residues on water retention and soil moisture. A rapid method to determine the water holding capacity was used. 90 mL of sieved soil was placed in a beaker and filled with 50 milliliters of distilled water, then mixed thoroughly to completely saturate the soil with water. The soil/water mixture was then allowed to reach equilibrium, resulting in a water-saturated soil phase and a layer of water on top, called the supernatant. The supernatant was then placed in a graduated 50 mL cylinder and measured for volume. The water holding capacity (V_{sat}) was calculated using the formula $V_{\text{sat}} = 50 - S$, where S is the volume of supernatant water.

For the germination test, all test plates were first hydrated with a volume of water equivalent to V_{sat} . A black filter paper was placed on each plate, and 10 seeds from the same species were positioned on top of the filter paper. The seeds were arranged in a single row, approximately 1 cm from the middle ridge of the test plate, and spaced equally apart (Figure 4-2). The plates were then placed in an incubator at 25°C for 3 days, in darkness. After 3 days in an incubator, each test plate was individually photographed and documented for measurements of the root length and aboveground biomass. Root length and aboveground biomass were measured with a ruler.



Figure 4-2. A test plate before the incubator with the 10 seeds and the black filter on top of the soil.

4.2.4. *Statistical analysis*

All statistical analysis was conducted using R (version 4.2.1), Matlab, and Adobe Illustrator. Wilcoxon test was performed to assess the statistical differences between the boxplots of samples exposed to wildfire residues and those without and between the reference soil and biofilter soil. Differences were considered significant if the p-value was < 0.05 .

4.3. Results

4.3.1. *Effects of wildfire residues on plant growth in reference soil*

In reference soil, an increase in wildfire residue deposition decreased root length for dicotyledonous plants ($p < 0.05$ for Mustard, $p < 0.001$ for Garden Cress) (**Figure 4-5, Figure 4-6**). However, for monocotyledonous plants, an increase in wildfire residues from 5% to 10% led to a decrease in root length ($p < 0.05$) (**Figure 4-4**). Wildfire residues did not affect the aboveground biomass of monocotyledonous plants ($p > 0.05$) (**Table 4-4**). However, a 5% increase in wildfire residues resulted in an increase in aboveground biomass for both dicotyledonous plants ($p < 0.001$ for Mustard, $p < 0.05$ for Garden Cress), and a 10% increase in wildfire residues further increased aboveground biomass compared to soil without wildfire residues for Dicotyl Mustard ($p < 0.001$) (**Table 4-6**).

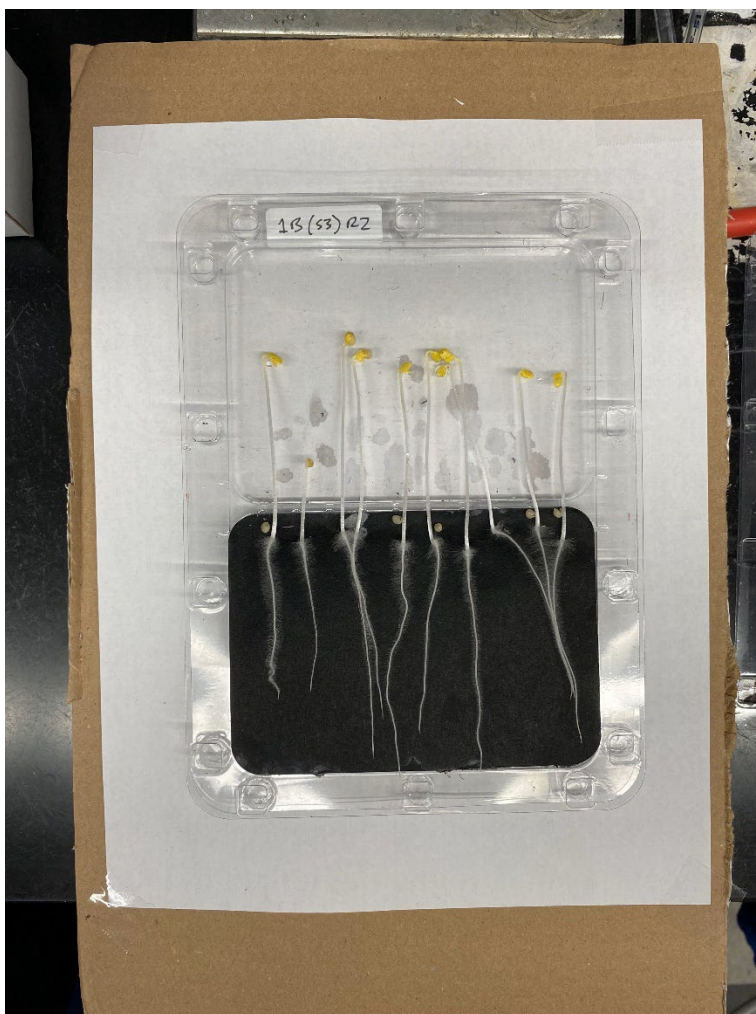


Figure 4-3. A test plate taken out of the incubator was photographed and measured for aboveground biomass and root length.

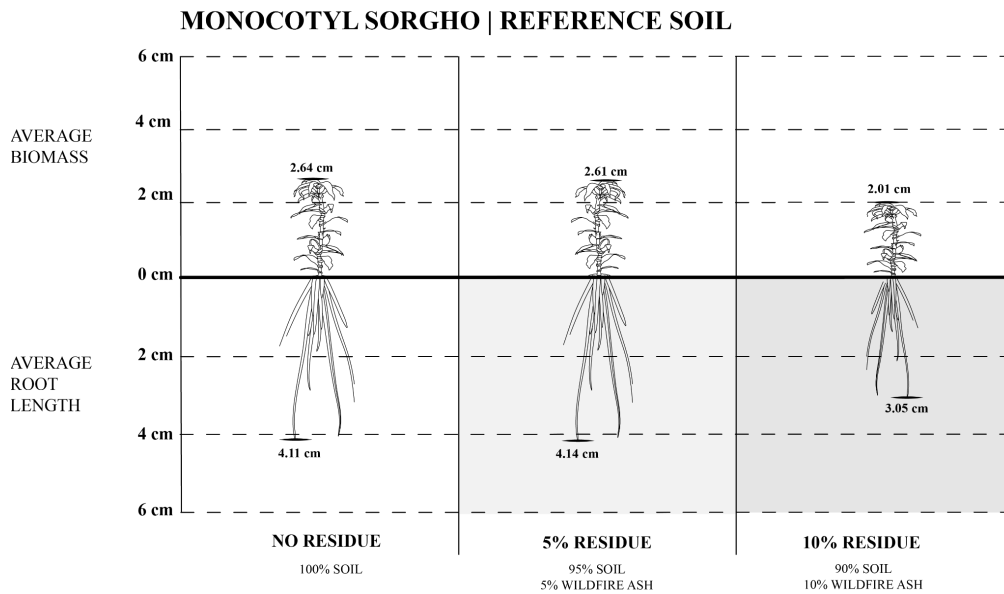


Figure 4-4. Effects of wildfire residues on plant growth of *Monocotyl Sorgho* in reference soil.

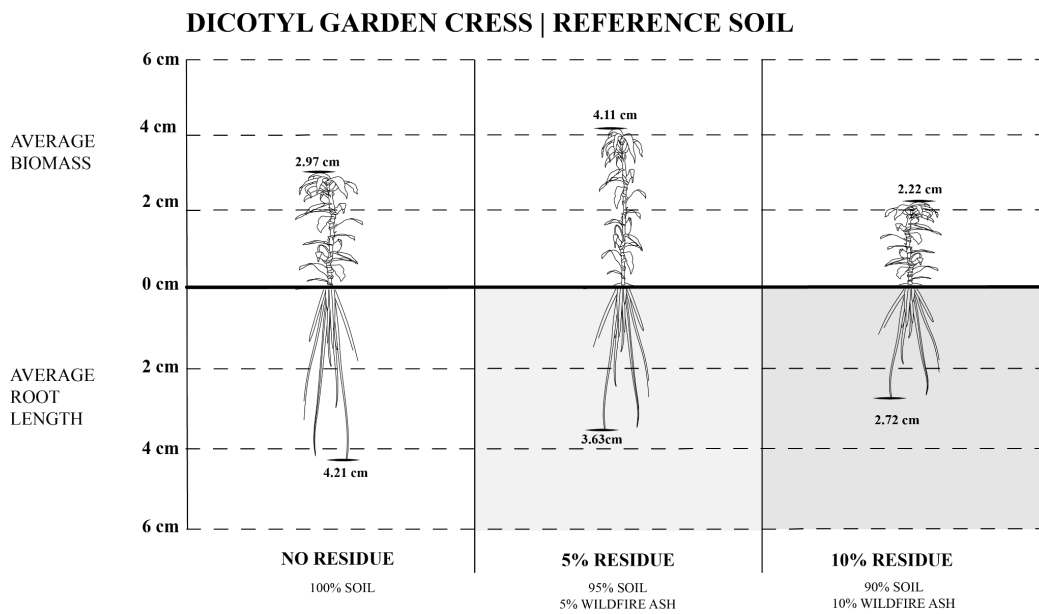


Figure 4-5. Effects of wildfire residues on plant growth of *Dicotyl Garden Cress* in reference soil.

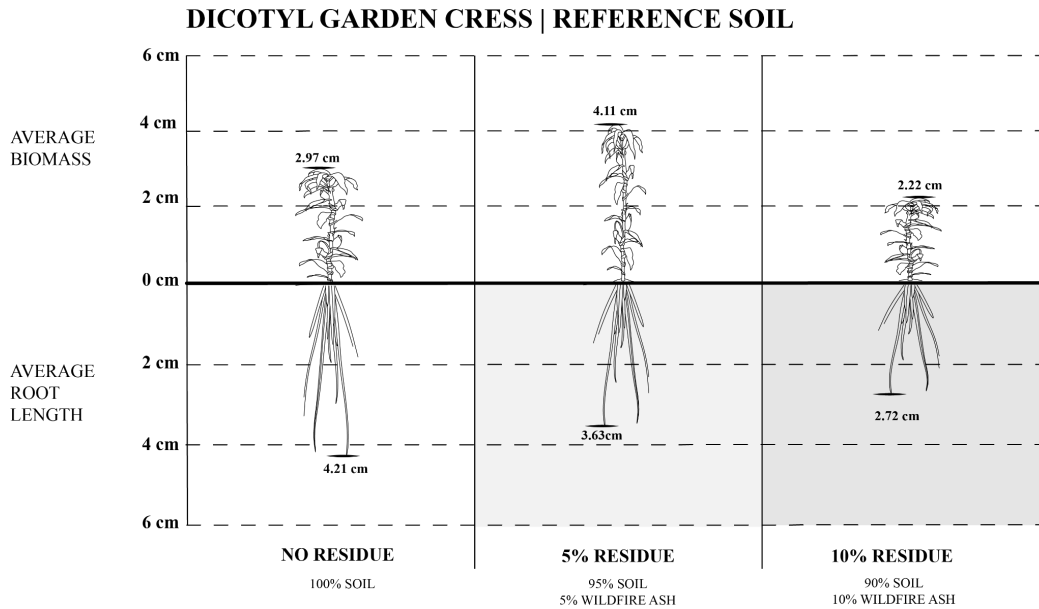


Figure 4-6. Effects of wildfire residues on plant growth of *Dicotyl Mustard* in reference soil.

4.3.2. Effects of wildfire residues on plant growth in biofilter soil

In biofilter soils, wildfire residues did not affect ($p > 0.05$) the root length of both monocot and dicotyledonous plants. There was a notable decrease in root length in biofilter soil with 10% wildfire residues for *Dicotyl Mustard* compared to biofilter soil without wildfire residues ($p < 0.01$) (Table 4-3, Figure 4-9). An increase in wildfire residues from 5% to 10% led to an increase ($p < 0.05$) in aboveground biomass for monocotyledonous plants. However, adding 5% of wildfire residues significantly increased aboveground biomass for dicotyledonous plants ($p < 0.05$) but for dicotyledonous *Garden Cress*, the trend was the opposite as an increase from 5% to 10% in wildfire residues resulted in a decrease in aboveground biomass (Table 4-5).

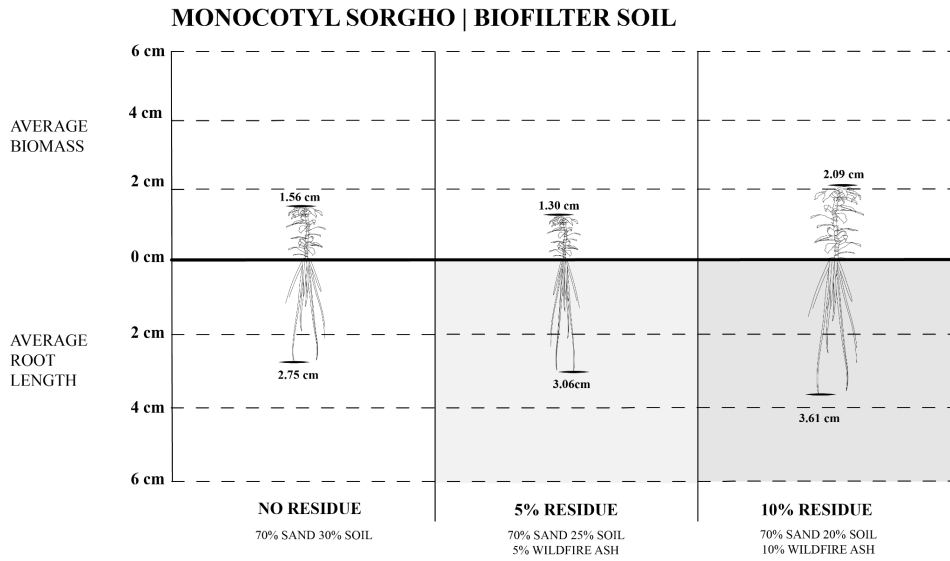


Figure 4-7. Effects of wildfire residues on plant growth of *Monocotyl Sorgho* in biofilter soil

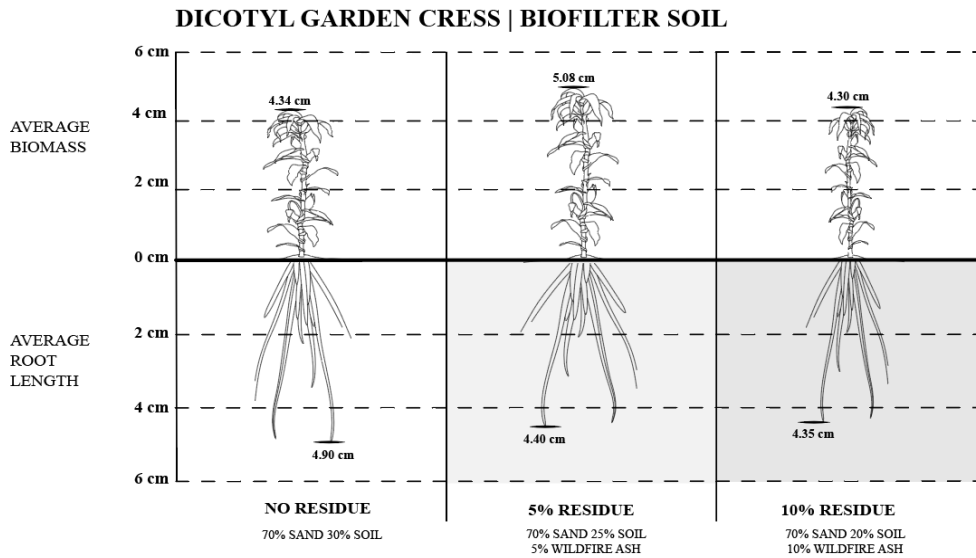


Figure 4-8. Effects of wildfire residues on plant growth of *Dicotyl Garden Cress* in biofilter soil

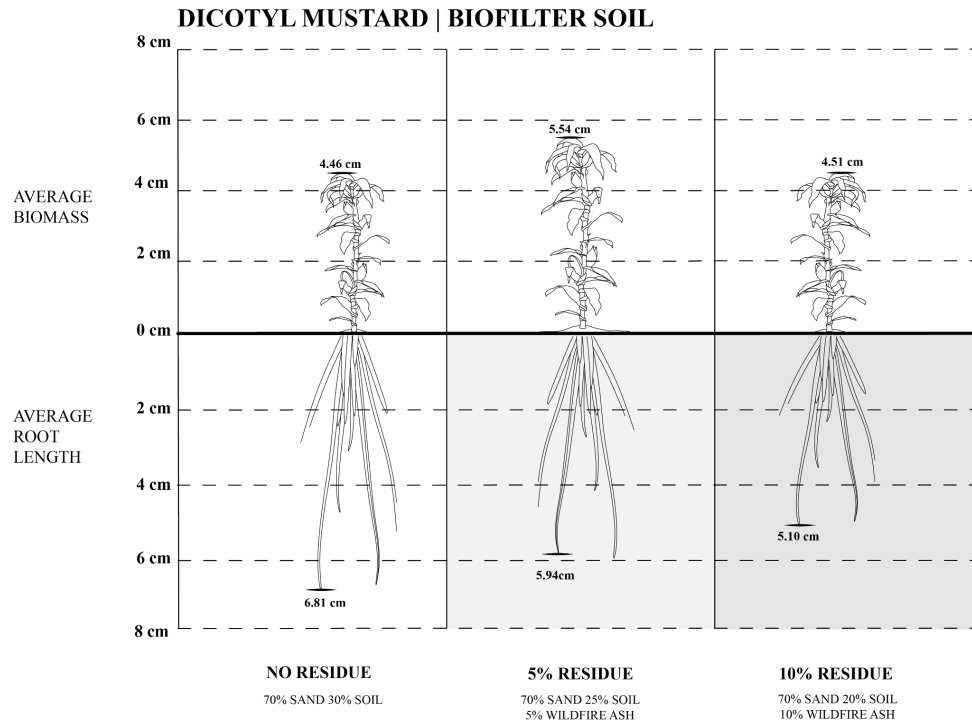


Figure 4-9. Effects of wildfire residues on plant growth of *Dicotyl Mustard* in biofilter soil

4.3.3. Effects of types of soil on root length

Without wildfire residues, the root length of monocot plants was lower in the biofilter soil compared to the reference soil ($p < 0.05$) (Figure 4-10, Table 4-1). Conversely, the root length of dicotyledonous plants, such as Garden Cress, was significantly higher in the biofilter soil ($p < 0.001$) (Figure 4-12, Table 4-3). With 5% wildfire residues, the root length of monocots was lower in the biofilter soil than in the reference soil ($p < 0.05$), whereas it was higher for dicotyledonous plants like Garden Cress ($p < 0.05$) (Figure 4-11, Table 4-2). In the presence of 10% wildfire residues, the root length was higher in the biofilter soil compared to the reference soil ($p < 0.001$) dicotyledonous plants like Garden Cress (Figure 4-11, Table 4-2).

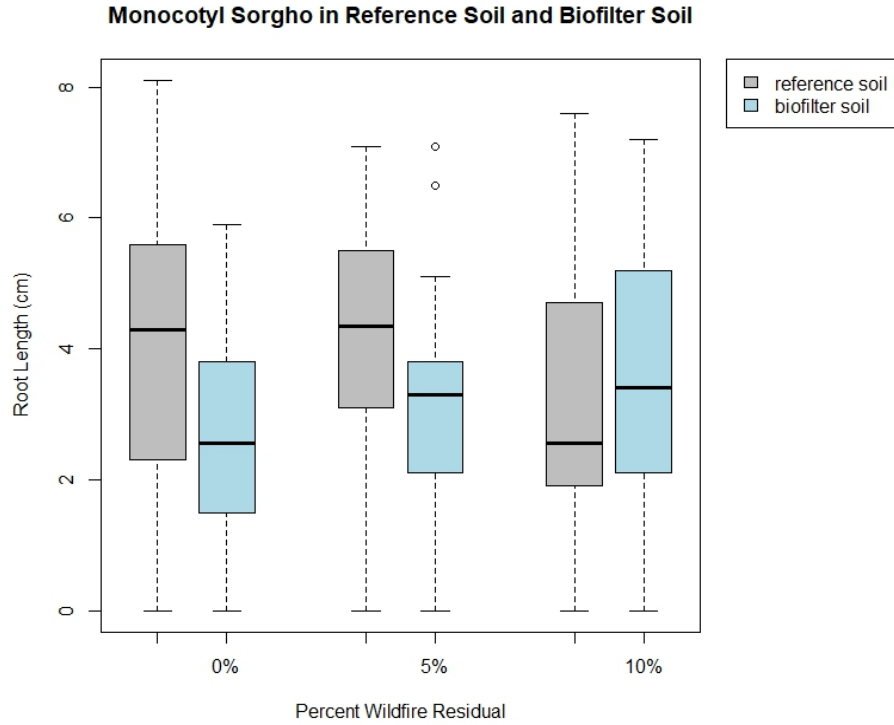


Figure 4-10. Effects of type of soil on root length of *Monocotyl Sorgho* in soils with different amounts of wildfire residues

Table 4-1. P-values of significance for root length of *Monocotyl Sorgho* in both soil types and different amounts of wildfire residues.

<i>p-values</i>	Reference Soil 0%	Reference Soil 5%	Reference Soil 10%	Biofilter Soil 0%	Biofilter Soil 5%	Biofilter Soil 10%
Reference Soil 0%	-	0.9625	0.07163	0.0148	-	-
Reference Soil 5%	-	-	0.03142	-	0.0222	-
Reference Soil 10%	-	-	-	-	-	0.281
Biofilter Soil 0%	-	-	-	-	0.4626	0.07298
Biofilter Soil 5%	-	-	-	-	-	0.2611
Biofilter Soil 10%	-	-	-	-	-	-

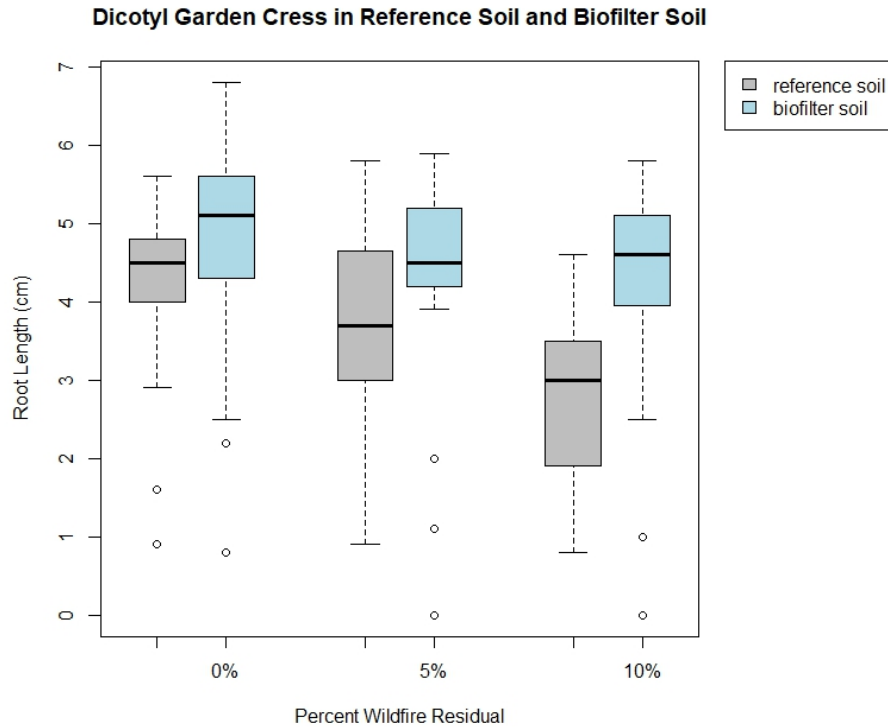


Figure 4-11. Effects of type of soil on root length of *Dicotyl Garden Cress* in soils with different amounts of wildfire residues

Table 4-2. P-values of significance for root length of *Dicotyl Garden Cress* in both soil types and different amounts of wildfire residues

<i>p-values</i>	<i>Reference Soil 0%</i>	<i>Reference Soil 5%</i>	<i>Reference Soil 10%</i>	<i>Biofilter Soil 0%</i>	<i>Biofilter Soil 5%</i>	<i>Biofilter Soil 10%</i>
<i>Reference Soil 0%</i>	-	0.06484	<0.00001	0.02676	-	-
<i>Reference Soil 5%</i>	-	-	0.006714	-	0.02708	-
<i>Reference Soil 10%</i>	-	-	-	-	-	<0.00001
<i>Biofilter Soil 0%</i>	-	-	-	-	0.1413	0.1231
<i>Biofilter Soil 5%</i>	-	-	-	-	-	0.9458
<i>Biofilter Soil 10%</i>	-	-	-	-	-	-

10%						
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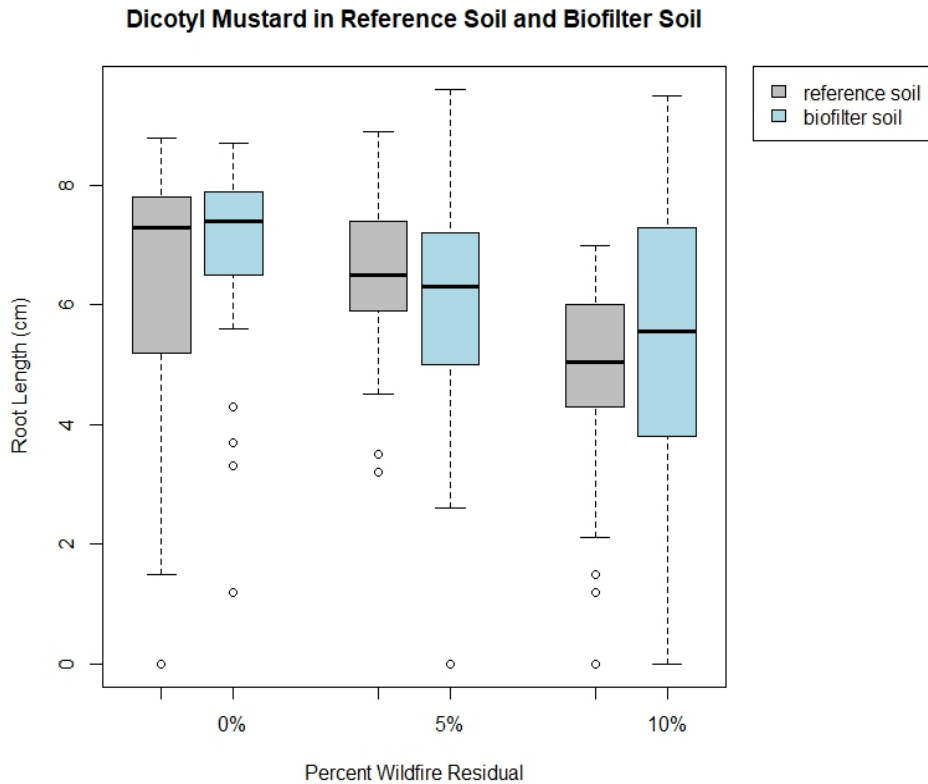


Figure 4-12. Effects of types of soil on root length of *Dicotyl Mustard* in soils with different amounts of wildfire residues

Table 4-3. P-values of significance for root length of *Dicotyl Mustard* in both soil types and different amounts of wildfire residues.

<i>wp-values</i>	<i>Reference Soil 0%</i>	<i>Reference Soil 5%</i>	<i>Reference Soil 10%</i>	<i>Biofilter Soil 0%</i>	<i>Biofilter Soil 5%</i>	<i>Biofilter Soil 10%</i>
<i>Reference Soil 0%</i>	-	0.5903	0.0144	0.2025	-	-
<i>Reference Soil 5%</i>	-	-	0.0002138	-	0.3303	-
<i>Reference Soil 10%</i>	-	-	-	-	-	0.5214
<i>Biofilter Soil</i>	-	-	-	-	0.07859	0.00629

0%						
Biofilter Soil 5%	-	-	-	-	-	0.1877
Biofilter Soil 10%	-	-	-	-	-	-

4.3.4. Effects of types of soil on above-ground biomass

Without wildfire residues, the aboveground biomass of monocot plants was lower in the biofilter soil compared to the reference soil ($p < 0.01$) (**Figure 4-10, Table 4-1**). Conversely, the root length of *dicotyledonous Garden Cress* was significantly higher in the biofilter soil ($p < 0.001$) (**Figure 4-12, Table 4-3**). With 5% wildfire residues, the above-ground biomass of monocots was lower in the biofilter soil than in the reference soil ($p < 0.001$), whereas it was higher ($p < 0.001$) for *dicotyledonous Garden Cress* (**Figure 4-11, Table 4-2**). In the presence of 10% wildfire residues, the above-ground biomass was not affected by soil type ($p > 0.05$), whether biofilter soil or reference soil. However, it increased for *dicotyledonous Garden Cress* ($p < 0.05$) (**Figure 4-11, Table 4-2**).

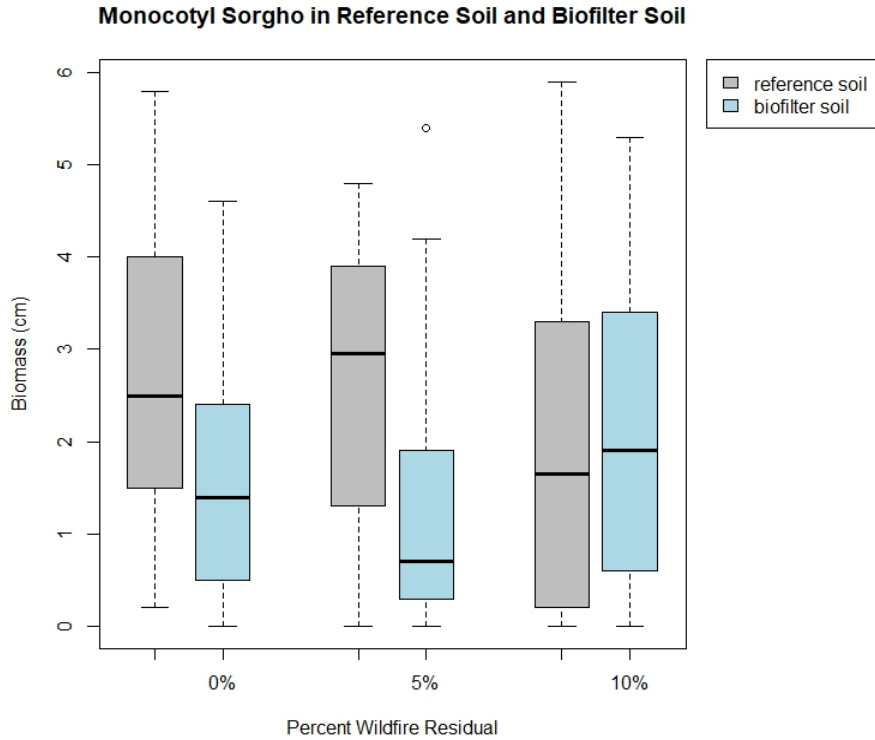


Figure 4-13. Effects of type of soil on above-ground biomass of *Monocotyl Sorgho* in soils with different amounts of wildfire residues

Table 4-4. P-values of significance for above-ground biomass of *Monocotyl Sorgho* in both soil types and different amounts of wildfire residues

<i>p-values</i>	<i>Reference Soil 0%</i>	<i>Reference Soil 5%</i>	<i>Reference Soil 10%</i>	<i>Biofilter Soil 0%</i>	<i>Biofilter Soil 5%</i>	<i>Biofilter Soil 10%</i>
<i>Reference Soil 0%</i>	-	0.9412	0.1833	0.006506	-	-
<i>Reference Soil 5%</i>	-	-	0.1735	-	0.0008717	-
<i>Reference Soil 10%</i>	-	-	-	-	-	0.8654
<i>Biofilter Soil 0%</i>	-	-	-	-	0.4546	0.1669
<i>Biofilter Soil 5%</i>	-	-	-	-	-	0.04413
<i>Biofilter Soil 10%</i>	-	-	-	-	-	-

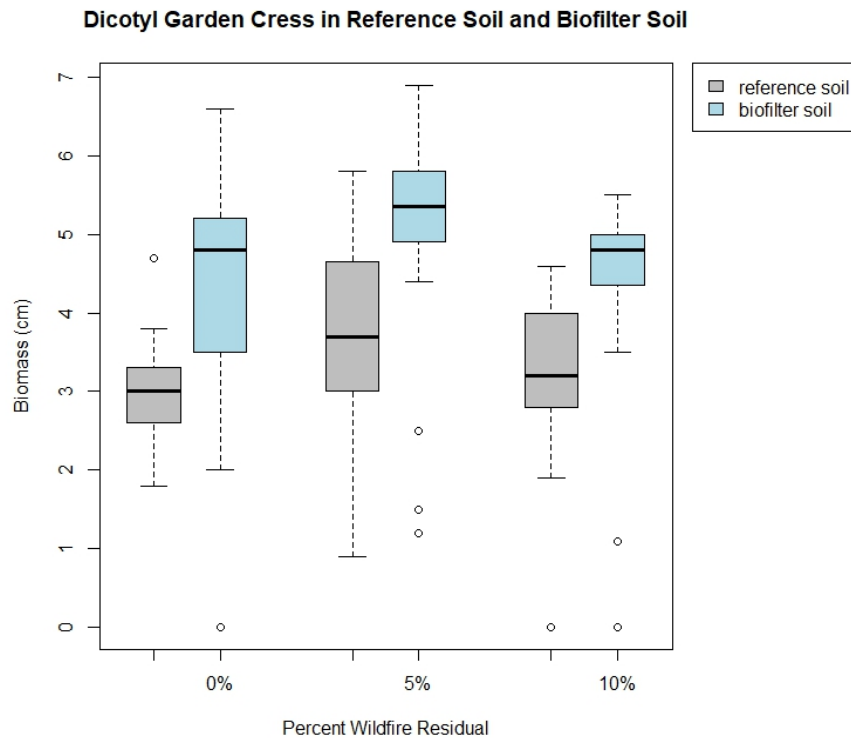


Figure 4-14. Effects of type of soil on aboveground biomass of *Dicotyl Garden Cress* in soils with different amounts of wildfire residues

Table 4-5. P-values of significance for aboveground biomass of *Dicotyl Garden Cress* in both soil types and different amounts of wildfire residues

<i>p-values</i>	<i>Reference Soil 0%</i>	<i>Reference Soil 5%</i>	<i>Reference Soil 10%</i>	<i>Biofilter Soil 0%</i>	<i>Biofilter Soil 5%</i>	<i>Biofilter Soil 10%</i>
<i>Reference Soil 0%</i>	-	0.0194	0.2866	<0.001	-	-
<i>Reference Soil 5%</i>	-	-	0.2171	-	<0.001	-
<i>Reference Soil 10%</i>	-	-	-	-	-	0.0008241
<i>Biofilter Soil 0%</i>	-	-	-	-	0.03655	0.945
<i>Biofilter Soil 5%</i>	-	-	-	-	-	0.02298
<i>Biofilter Soil 10%</i>	-	-	-	-	-	-

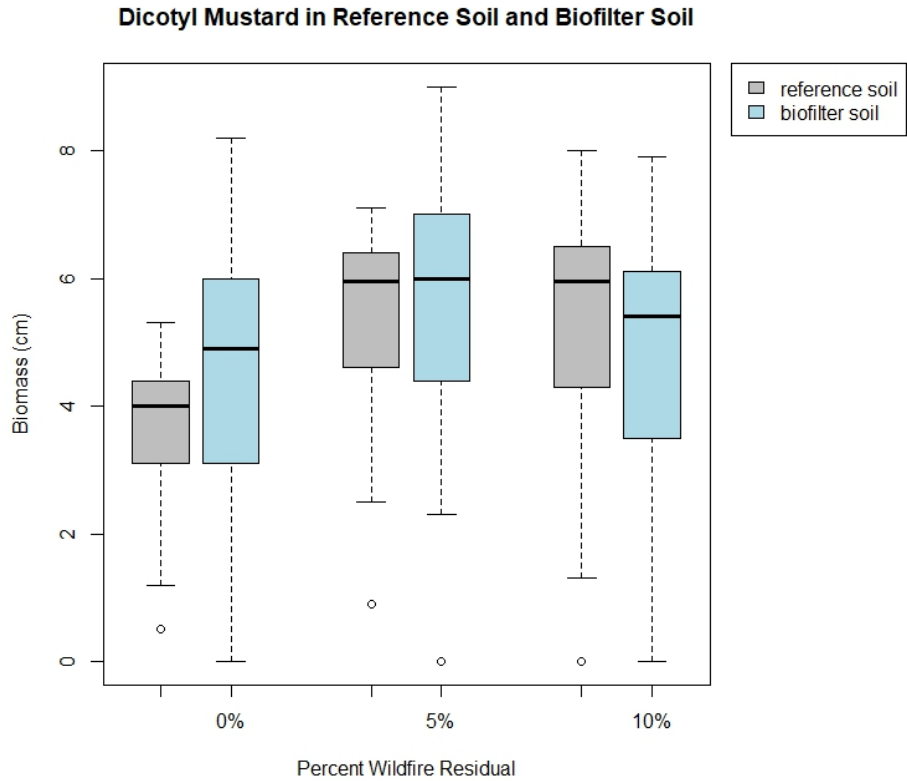


Figure 4-15. Effects of type of soil on aboveground biomass of *Dicotyl Mustard* in soils with different amounts of wildfire residues

Table 4-6. P-values of significance for aboveground biomass of *Dicotyl Mustard* in both soil types and different amounts of wildfire residues

<i>p-values</i>	Reference Soil 0%	Reference Soil 5%	Reference Soil 10%	Biofilter Soil 0%	Biofilter Soil 5%	Biofilter Soil 10%
Reference Soil 0%	-	<0.001	0.0007371	0.05152	-	-
Reference Soil 5%	-	-	0.7517	-	0.7045	-
Reference Soil 10%	-	-	-	-	-	0.2471
Biofilter Soil 0%	-	-	-	-	0.03435	0.9323
Biofilter Soil 5%	-	-	-	-	-	0.08456

<i>Biofilter Soil</i> 10%	-	-	-	-	-	-
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4.4. Discussion

The results of this study demonstrate the effect of deposited wildfire residues on plant health in green infrastructure could vary based on seed type, whether monocot or dicot. Dicots tend to penetrate deeper into the soil, contributing to erosion prevention and forming symbiotic relationships with nitrogen-fixing bacteria. Consequently, they can better support soil microorganisms, enhancing ecosystem resilience. Monocots, on the other hand, typically possess fibrous roots, aiding in soil particle binding and nutrient uptake, thus enhancing moisture retention and plant growth. As most wildfire residues are removed in the top few centimeters of the soil, their effect on roots or plants might be limited based on the root length or distribution. Our results show that an increase in wildfire residues in reference soil led to a decrease in root length for dicot plants, highlighting their sensitivity to wildfire residues. Conversely, an increase in wildfire residues resulted in decreased aboveground biomass, indicating the negative impacts of wildfire on the growth of monocot plants. Therefore, the selection of plant species is crucial to mitigate the potential negative effects of wildfire on plant growth.

In biofilter soil, wildfire residues did not significantly affect root length, indicating the potential resilience of plant biofilters to wildfire residues. However, for some plant species, such as dicotyledonous mustard, a decrease in root length at certain wildfire residue levels suggests a threshold effect of wildfire residues on root growth. As the results often exhibit opposing trends between monocots and dicots, this underscores the importance of tailoring management strategies in biofilter systems.

Without wildfire residues, monocot plants had smaller roots in biofilter soil compared to those in reference soil, while certain dicot species exhibited longer roots in biofilter soil. In the presence of 5% wildfire residues, monocot root length decreased, while dicots exhibited longer root length, indicating the potential resilience of dicots in biofilter environments. In the presence of 10% wildfire residues, both monocot and dicot plants exhibited an increase in root length in biofilter soil, indicating tolerance to higher levels of wildfire residues. In biofilter soil, the aboveground biomass of monocots was decreased, whereas the above-ground biomass of dicots was increased in the presence of wildfire residues, suggesting the resilience of dicots to wildfire residues.

In order to properly apply this study in California, exploring the different plant species that are more efficient for use in biofilter soil could be a future research opportunity. For Southern California biofilters, native plant species have many advantages including their tolerance to dry conditions (Ambrose and Winfrey, 2015) or investigating native Californian plants that are in areas susceptible to wildfires. By replicating the methods of this experiment, it can be possible to analyze the effects of wildfire residue concentration on these native plants that are directly affected by wildfires.

4.5. Conclusions

This study examined the effects of wildfire residues on plant growth in biofilters. The results revealed that the effects of wildfire residues on root length and aboveground biomass depended on the type of seeds and the soil composition. However, wildfire residues did not appear to impact the germination and growth of plants in stormwater biofilters. In general, the effect was prominent when exposed to 10% wildfire residues instead of 5%, indicating increasing in deposition quantity may have a negative effect on plants. The soil type seemed to have a more

significant effect on the above-ground biomass. The seed that fared the best in higher concentrations of wildfire residues was *dicotyl garden cress*, indicating different plants may have different sensitivity to wildfire residues. Overall, these findings underscore the importance of considering plant species composition, wildfire residue levels, and soil types in biofilter systems to enhance their effectiveness in mitigating the impacts of wildfires on plant growth and ecosystem functioning.

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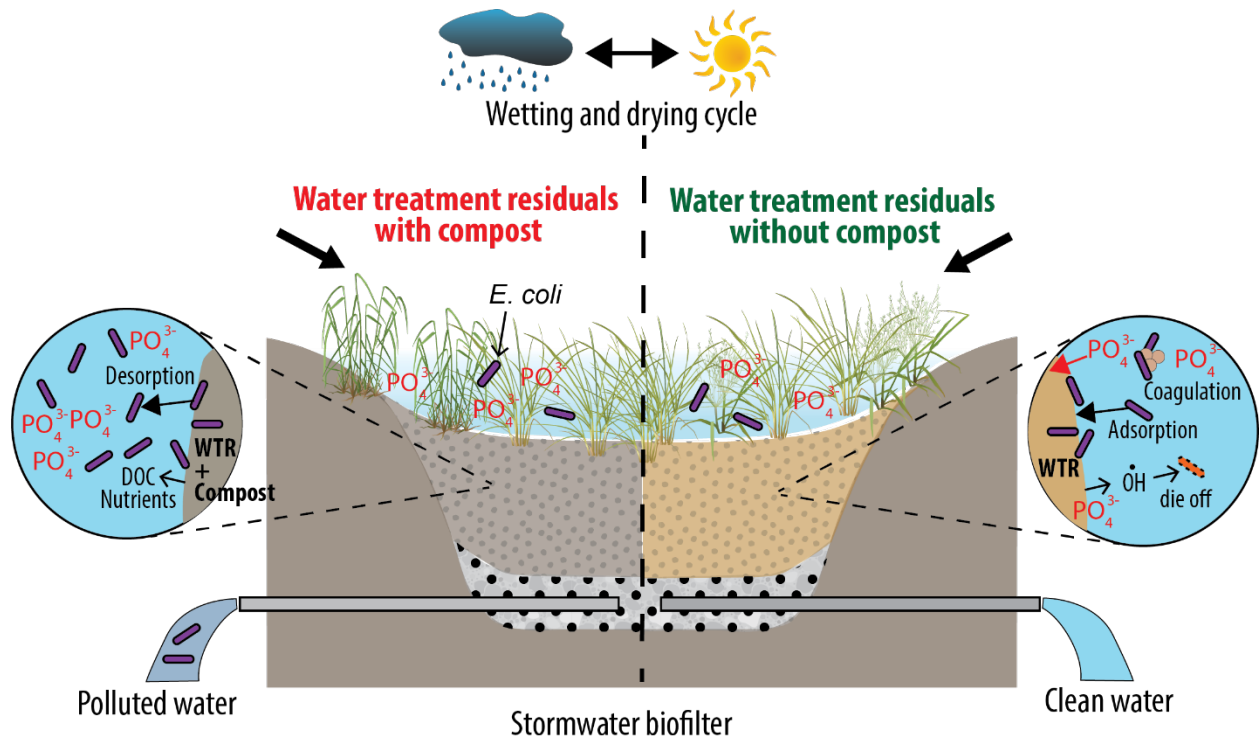
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5. CHAPTER 5 – COMPOST DECREASES BACTERIAL AND PHOSPHATE REMOVAL CAPACITY OF DRINKING WATER TREATMENT RESIDUALS IN STORMWATER BIOFILTERS



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Raelison, O.D., Das, T., Guyett, K., Visweswaran, A., Spallone, S., Ramos, R., Merrifield, R., Pierce, G., and Mohanty, S.K. (2023) Compost decreases bacterial and phosphate removal capacity of drinking water treatment residuals in stormwater biofilters. *Science of The Total Environment*. 166635. <https://doi.org/10.1016/j.scitotenv.2023.166635>

Abstract

Drinking water treatment residuals (WTR), a waste-derived product, are often recommended to use as an amendment in stormwater biofilters to enhance their capacity to remove phosphate and microbial pollutants. However, their efficacy has been assumed to remain high in the presence of compost, one of the most common amendments used in biofilters. This study tests the validity of that assumption by comparing the removal capacities of WTR-amended biofilters with and without the presence of compost. Our results show that amending sand with WTR increased *E. coli* removal by at least 1-log, but the addition of compost in the sand-WTR media lowered the removal capacity by 13%. Similarly, the addition of WTR to sand improved phosphate removal to nearly 1177%, but the removal decreased slightly by 8% when adding compost to the media. The results confirmed that dissolved organic carbon (DOC) leached from the compost could compete for adsorption sites for bacteria and phosphate, thereby lowering the capacity based on the amount of DOC adsorbed on WTR. Collectively, these results indicate that the stormwater treatment industry should avoid mixing compost with WTR to get the maximum benefits of WTR for bacterial removal and improve the performance lifetime of WTR-amended biofilters.

5.1. Introduction

Urban areas, where more than 70% of the world's population is projected to live by 2050, are increasingly water-stressed due to an increase in demand and a lack of water resources to meet the demand (Flörke et al., 2018; He et al., 2021). Climate change and the resulting uncertainty with the hydrological cycle further exacerbate this issue (Li et al., 2022; Taylor et al., 2013). To alleviate this concern, most cities are now implementing green infrastructure such as biofilters to restore the hydrological balance. Conventional biofilters are typically designed by replacing a section of subsurface soil with a mixture of sand and compost (Tirpak et al., 2021). While this design is adequate to increase infiltration and recharge groundwater, it is not adequate to remove pollutants such as pathogens and nutrients (Ghavanloughajar et al., 2021; Kranner et al., 2019; Valenca et al., 2021c). Fecal bacteria such as *E. coli* an indicator of pathogens in stormwater runoff are found to be the leading cause of surface water impairment (US EPA, 2017). Similarly, nutrients such as phosphate are difficult to remove by using sand and compost (Chahal et al., 2016). Therefore, it is important to evaluate the best design or biofilter media mixture that could remove these pollutants from surface water.

To increase *E. coli* and phosphate removal, conventional biofilter media are often mixed with engineered amendments including biochar, activated carbon, and zeolite (Grebel et al., 2013; Mohanty et al., 2018; Tirpak et al., 2021). However, these amendments are relatively expensive to produce and may not be available in all cities, thereby adding transportation costs to the overall project. Thus, most practitioners end up not using any amendments. In contrast to engineered amendments, waste-derived amendments such as drinking water treatment residuals (WTR) can be locally available in all cities where drinking water treatment plants are located. The WTR are produced in the coagulation and flocculation chambers, where aluminum or ferric salts are added

to create flocs and settle them to the bottom with the formation of aluminum and iron oxides. These iron or aluminum oxides have more positive surface charged sites compared to conventional biofilter media, thereby providing stronger adsorption sites for the adsorption of *E. coli* and phosphate (Babatunde et al., 2009; Wallace et al., 2023; Xu et al., 2019). However, it is not clear how much WTR is sufficient to provide the maximum adsorption capacity.

Numerous studies have examined the potential of WTR for the removal of phosphate (Ali and Pickering, 2023; Ament et al., 2022, 2021; Guo et al., 2015; Hsieh et al., 2007; Liu et al., 2014; Lucas and Greenway, 2010; O'Neill and Davis, 2012; Palmer et al., 2013; Poor et al., 2019; Qiu et al., 2019; Sidhu et al., 2021; Wang et al., 2021; Yan et al., 2017) but far fewer studies have examined the potential of WTR to remove *E. coli* from stormwater (Xu et al., 2019; Zoski et al., 2013). All those studies confirmed a variable removal capacity of WTR, but the cause of variable removal is unknown (Ippolito et al., 2011). While a few studies were conducted in fields (Ali and Pickering, 2023; Ament et al., 2022), the majority of the studies were conducted in controlled laboratory conditions (Ament et al., 2021; Zoski et al., 2013). The high removal obtained in lab studies is often not matched with the results of the field study, indicating laboratory study may not fully account for the complexities of field conditions such as the presence of other amendments to support plant growth. For instance, no study to date has examined whether or how the presence of compost or mulch, the most commonly used amendments in conventional biofilters (Tirpak et al., 2021), would affect the pollutant removal capacity of WTR. Consequently, WTR capacity has been assumed to remain high despite mixing with compost in the field (Xu et al., 2020). This might not be the case in practice, potentially because of the interaction of compost, particularly dissolved organic carbon released from compost, with the amendment surface. For instance, other iron media such as iron filling and iron oxide-coated sands are shown to be affected by the presence of

compost (Ghavanloughajar et al., 2021; Mohanty et al., 2013). As metals are present in stormwater, some studies have shown a high capacity of WTR to remove heavy metals such as Cu, Cd, Pb (Deng et al., 2016; Lim et al., 2015; Na Nagara et al., 2022; Soleimanifar et al., 2016; Wang et al., 2021) but it is unknown if the mixture compost-WTR may leach metals. Thus, it is important to evaluate how compost may affect WTR's capacity to remove stormwater pollutants—a research gap with practical implications on stormwater biofilter design that has not been explored to date.

The objectives of this study are to quantify the optimum amount of WTR needed to achieve high *E. coli* and phosphate removal and to examine whether and how the presence of compost could affect the ability of WTR to remove *E. coli* and phosphate. The dissolved organic carbon (DOC) leached from compost can compete with phosphate or nitrate (both anions) and *E. coli* (which has a phospholipid surface) for adsorption sites on water treatment residuals (WTR), particularly the positively charged surface sites. We hypothesize that the presence of compost would decrease WTR capacity to remove both pollutants. To test the hypothesis, the removal capacities of sand filters amended with different WTR fractions were measured, and the removal capacities of WTR-sand filters with and without compost were compared. The result provides insights into how the compost interaction with WTR affects their pollutant removal capacity and informs the practical knowledge of when and how to use WTR to get the maximum benefits.

5.2. Materials and Methods

5.2.1. Collection of natural stormwater

Natural stormwater was collected from Ballona Creek in Los Angeles, CA (34° 00'32" N, 118° 23'3" W) following the method elsewhere (Valenca et al., 2020). The urban creek receives both dry- and wet-weather runoff from a 318 km² urban area with 82% developed and 61% impervious surface. Water quality parameters such as pH, electrical conductivity, and DOC of

stormwater were measured to ensure the stormwater quality did not fluctuate significantly between experiments. Before the experiment, the stormwater was autoclaved and spiked with nitrate (10 mg L⁻¹), phosphate (1 mg L⁻¹), and *E. Coli* ($1.79 \pm 0.18 \times 10^5$ CFU mL⁻¹) to prepare the influent solution for injection into the biofilters. These desired final concentrations are within the expected range concentrations of nitrate, phosphate, and *E. coli* in urban Stormwater reported in International BMP Database (Tirpak et al., 2021) and used in experimental studies (Grebel et al., 2013) so that the result can be applied in most places.

In this study, nutrients and *E. coli* were chosen because they are most difficult to remove in stormwater treatment systems (Tirpak et al., 2021). However, in natural stormwater, other pollutants such as metals and metalloids coexist with nutrients and pathogens. We did not examine metal removal by WTR or compost, which has been extensively examined before (Kranz et al., 2022; Soleimanifar et al., 2016). The mechanism of the removal of metals, which are cations, is different from that of nutrients (anions) or pathogens. Furthermore, the use of metals in the same stormwater matrix would have affected the viability of *E. coli* due to metal toxicity and affect the results.

5.2.2. Collection of drinking water treatment residuals and compost

We used garden compost (Whitter Fertilizer, CA, USA) and drinking water treatment residuals as amendments in our biofilters. The drinking water treatment residuals (WTR) were collected from the Long Beach Groundwater Treatment Plant, California, USA, in August 2022 at the bottom of the sludge basin where the most concentrated solids have accumulated (**Figure 5-1**). The groundwater treatment plant provides 65% of the potable water in Long Beach from local groundwater where the remaining 35% was supplied through purchased, imported surface water. The groundwater from an aquifer of the central basin of Los Angeles is pumped from active wells

around Long Beach and Lakewood areas and treated by flocculation, sedimentation, and inactivation. In the flocculation basin, ferric chloride and a polymer blend as coagulant chemicals were added to settle sludge in the sedimentation basins overnight, which were collected and discharged directly to the sewer. WTR were collected from the bottom of the sludge basin, transported in 5-gallon polyethylene buckets, and dewatered under sunlight until dryness (<5% water) for 4 days by spreading them out on a plastic tray on a rooftop (**Figure 5-1**). Compost and WTR were first sieved to remove particles larger than 0.83 mm to limit their size, similar to the coarse sand.



Figure 5-1. (left) Collection of the drinking water treatment residuals in the Groundwater treatment plant in Long Beach. (right) drying process of the drinking water treatment residuals on the roof in August 2022.

5.2.3. Characterization of drinking water treatment residuals and compost

Batch leaching experiments were conducted to examine the leachate composition from WTR and compost. Briefly, 2 g of WTR or compost were mixed in 40 mL of deionized water in a 50-mL centrifuge tube using a wrist-action shaker (Burrel Scientific) for 24 h, which is sufficient to achieve equilibrium. The leachate was centrifuged (5000 rpm for 15 min) to remove suspended particles, and the supernatant was filtered through a 0.45 μm PES syringe filter before analyzing

for pH, EC, UV₂₅₄, DOC using a Total Organic Carbon Analyzer (TOC-L, Shimadzu), and phosphate using the Hach Spectrophotometer model DR 280 (TNT 8048; Hach, Loveland, Colorado), and Fe and Al using inductively coupled plasma optical emission spectroscopy (ICP-OES). The results were reported in Supplementary Material (**Table 5-1**).

Table 5-1. Physicochemical properties of the WTR and compost

Properties	Compost	Drinking water treatment residuals (WTR)
pH	7.70 ± 0.01	7.1 ± 0.1
EC (µS cm ⁻¹)	2173 ± 135	143 ± 15
UV ₂₅₄ nm	3.945 ± 0.001	0.21 ± 0.02
DOC (mg L ⁻¹)	199.4 ± 11.3	6.6 ± 0.8
Fe (mg L ⁻¹)	1.14 ± 0.06	0.070 ± 0.001
Al (mg L ⁻¹)	1.40 ± 0.05	0.15 ± 0.02
Phosphate (mg L ⁻¹)	25.2 ± 1.2	0.04 ± 0.01

5.2.4. Preparation of biofilter media mixture

Conventional biofilters typically use nearly 70% or more sand by volume to increase infiltration and organic amendments such as compost up to 30 % by volume to enhance pollutant removal and support the vegetation atop (Tirpak et al., 2021). Compost and drinking water treatment residuals as amendments were mixed with coarse sand (0.59 mm – 0.84 mm, Humboldt Mfg. Co., IL, USA) to create different media mixtures.

To quantify the optimum amount of WTR to be used in biofilters for pathogen and phosphate removal, sand was mixed with different volume fractions of WTR: 0%, 10%, 20%, 30%, and 40%. To compare the effects of compost on the WTR removal capacity, two WTR-sand mixtures were prepared with the same amount of WTR but with and without compost. The mixture without compost contained 80% sand and 20% WTR, and the mixture with compost contained 70% sand, 20% WTR, and 10% compost. The percentage of WTR 20% and compost 10% was chosen because this study adhered to the maximum amendment limit of 30% in biofilter design

(Tirpak et al., 2021). The selection of 20% WTR and 10% compost based on initial optimization results to ensure long-term performance while minimizing the need for frequent replacement and prevent rapid exhaustion while maintaining effective pollutant removal.

5.2.5. Packing and characterization of biofilter media

In this study, model biofilters without plants were used to isolate the pollutant removal by WTR without any interference from other confounding factors created by the vegetation layer and root zone. The model biofilters were designed by packing the different mixtures in transparent polyvinyl chloride columns (2.54 cm ID x 30 cm length) following the method elsewhere (Borthakur et al., 2022b; Ghavanloughajar et al., 2020). Small columns were used in this study to simulate 1-D transport and compare the effect of amendment types and fractions on the performance of media filters (Borthakur et al., 2022b; Mohanty et al., 2014). However, small column studies often do not predict the behavior of pollutant removal at large-scale levels as it does not account for soil heterogeneity. Consequently, the applicability of our results to larger biofilter systems is limited. Nevertheless, the experimental design is adequate to compare the adsorption capacity of different amendments in flow-through conditions simulating ideal conditions in the field. Moreover, we assumed that the preferential flow near the wall perimeter or the wall effect is assumed to have negligible effects on solute transport in this study because the ratio of the diameter of the column and grain size in our study is nearly 290, which is well above the threshold 50 (Mehta and Hawley, 1969). Columns were packed with the sand-WTR mixture for each WTR concentration to estimate the optimum amount of WTR needed to remove the pollutants. To examine the effects of compost on the WTR pollutant removal capacity, additional columns were packed with the media mixture containing 70% sand, 20% WTR, and 10% compost. To ensure uniform packing, the media mixture was added incrementally in the column until the

net length of the filter media layer became 15 cm as described in a previous study (Borthakur et al., 2021). Triplicate columns were used per media mixture type (**Figure 5-2**). In some cases, WTR and compost can be added in layer configuration with the compost layer on the top to support plant growth (Ulrich et al., 2017). In that case, leachate from compost could also interact with underneath the WTR layer. Thus, the result of a layered system could differ from a mixed amendment system.

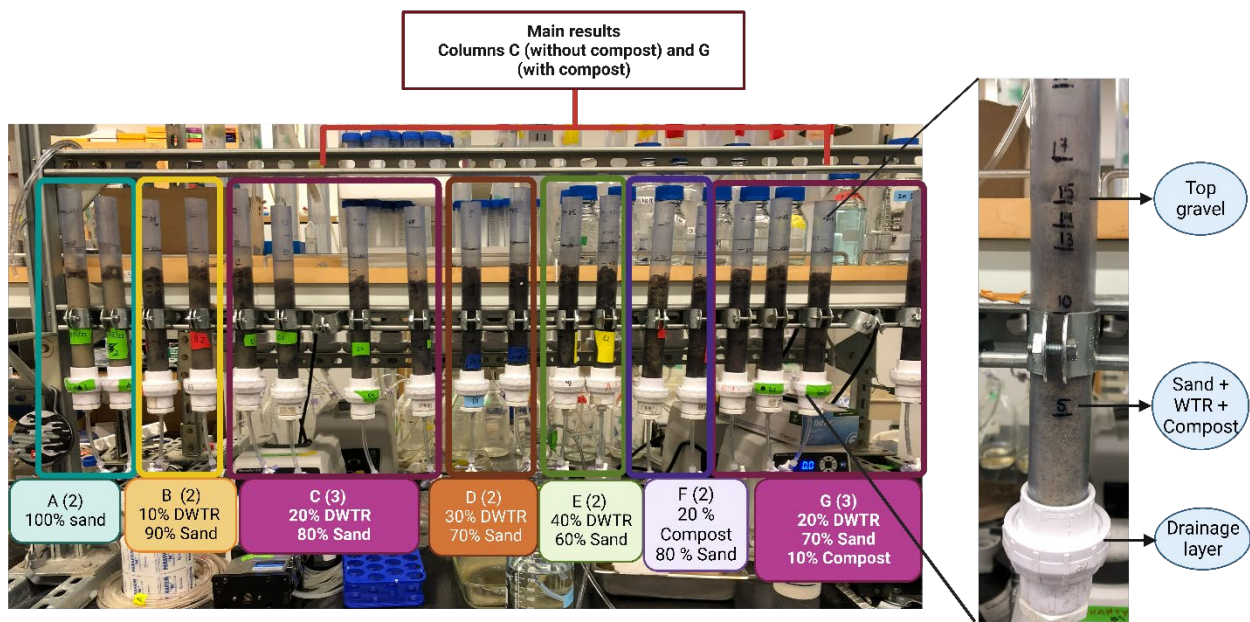


Figure 5-2. Experimental set-up of the biofilters columns with a zoomed-in column configuration.

To ensure consistency in packing, each type of column was characterized for saturated pore volume (PV), bulk density, and porosity. The hydraulic conductivity was measured using a falling head method (Ghavanloughajar et al., 2020). The bulk density of filter media was measured by dividing the weight of the media by the volume they occupied in the column, and the pore volume was estimated based on the weight difference between the dry columns and completely saturated columns (Borthakur et al., 2022a). The hydraulic characteristics of filter media are summarized in **Tables 5-2 and 5-3**. The bulk density and porosity of biofilters with different amendment mixtures

were used to explain if changes in these physical parameters affected pollutant removal. Using a pore volume of 24.5 mL and a flow rate of 0.6 mL/min, the hydraulic retention time (HRT) was estimated to be approximately 41 minutes.

Table 5-2. Hydraulic properties of the sand-WTR columns to quantify the optimum amount of WTR for E. coli and phosphate removal.

Media composition	Hydraulic conductivity cm s⁻¹	Bulk density (g cm⁻³)	Pore volume (mL)
0% WTR + 100% Sand	0.035 ± 0.005	1.73 ± 0.24	25.75 ± 1.34
10% WTR + 90% Sand	0.022 ± 0.002	1.74 ± 0.27	25.90 ± 1.56
20% WTR + 80% Sand	0.014 ± 0.001	1.54 ± 0.01	22.77 ± 1.27
30% WTR + 70% Sand	0.002 ± 0.0003	1.61 ± 0.14	26.45 ± 9.40
40% WTR + 60% Sand	0.003 ± 0.0005	1.59 ± 0.03	21.85 ± 1.77

Table 5-3. Hydraulic properties of the sand-WTR columns to test the removal capacity of WTR with and without compost.

Media composition	Hydraulic conductivity (cm s⁻¹)	Bulk density (g cm⁻³)	Pore volume (mL)
0% WTR + 100% Sand	0.035 ± 0.005	1.73 ± 0.24	25.75 ± 1.34
20% WTR + 80% Sand	0.014 ± 0.001	1.54 ± 0.01	22.77 ± 1.27
20% WTR + 10% Compost+ 70% Sand	0.005 ± 0.001	1.46 ± 0.02	20.87 ± 1.42

5.2.6. *Change in WTR surface properties with exposure to compost leachate*

To quantify the amount of DOC adsorbed on WTR from compost leachate, batch adsorption experiments were conducted using 2 g of sieved WTR (<45 µm) was mixed with 40 mL of 10 mM NaCl with or without DOC leached from compost for 24 hours using a wrist-action shaker (Burrel Scientific). The solution was centrifuged (5000 rpm for 15 min) to remove suspended particles, and the supernatant was filtered through a 0.45 µm PES syringe filter before

analyzing for DOC using a Total Organic Carbon Analyzer (TOC-L, Shimadzu). Batch studies provide a quantitative measurement of how WTR surfaces could retain DOC. However, it is important to note that extrapolating these batch study results to design field-scale biofilters has limitations due to the disparities between the two designs. Nevertheless, the findings of our study still hold scientific value as they contribute to a qualitative understanding of how DOC affects the surface properties of WTR.

To measure the change in surface charge of WTR after the exposure to compost leachate, WTR was first exposed to the dissolved organic carbon (DOC) present in compost leachate before measuring their surface charge using Zetapals (Brookhaven Instruments, NY) following a method described in a previous study (Ghavanloughajar et al., 2021). Briefly, 2 g of sieved WTR (<45 μm) was mixed with 40 mL of 10 mM NaCl with or without DOC leached from compost for 24 hours. The WTR suspension was centrifuged (6123 G-force for 5 min), and the pellets were resuspended in 40 mL of 10 mM NaCl. The suspension containing 1 μm was isolated after gravity settling of the suspension containing all WTR fractions and used for surface charge measurement. The pH of the suspension was adjusted using HCl or NaOH between 2.5 to 8, and the zeta potential of samples was measured against the pH of the solution to estimate how the point of zero charges would shift in the presence of DOC leached from compost. The supernatant of the compost leachate without and with WTR was measured for pH, EC, UV_{254} absorbance and DOC (**Table 5-4**).

Table 5-4. Properties of DOC without and with WTR.

Properties	DOC without WTR	DOC with WTR
pH	7.52 ± 0.04	7.56 ± 0.09
EC ($\mu\text{S}/\text{cm}$)	1896 ± 16	1925 ± 12
UV 254 nm	4.0109 ± 0.0002	4.0098 ± 0.0003
DOC (mg/L)	178.9 ± 22.7	99.5 ± 7.3

5.2.7. *Estimating removal capacity of drinking water treatment residuals with and without compost*

To simulate rainfall and infiltration of stormwater runoff in biofilters in a natural environment, contaminated stormwater was intermittently applied on the top of biofilters. For each wetting event, a total of 6 PV of contaminated stormwater was applied on the columns at 6.4 cm h⁻¹ for 4 h, followed by a drying event when the pore water in columns was drained by gravity and dried for 20 h at room temperature (22 °C). The infiltration rate through media filters depends on the stormwater loading rate, which is a function of the catchment area and rainfall intensity. However, the maximum infiltration rate through a media filter is typically controlled by the hydraulic conductivity of filter media. The infiltration rate chosen here simulates the typical infiltration rate desired in urban biofilters (4 – 20 cm h⁻¹) (Tirpak et al., 2021). The dry-wet cycle was repeated four times to simulate intermittent infiltration events and inject a sufficient amount of stormwater to compare the removal capacities of filter media with different types of amendments. However, four cycles are not sufficient to examine the long-term removal rate, which can be influenced by the exhaustion of the adsorption capacity of WTRs with DOC present in stormwater and clogging.

During each wetting cycle, the effluent samples were collected in two fractions: the first PV eluted during the infiltration event and the last PV before the ending of the infiltration event. The first PV represents old water from the previous rainfall where trapped *E. coli* could either grow or die off depending on the conditions in the biofilters (Ghavanloughajar et al., 2021; Valenca et al., 2021b). This first-flush effluent could also contain the *E. coli* detached and remobilized from biofilters during the passing of air-water interfaces at the onset of the wetting cycle (Mohanty et al., 2013). To examine if the presence of compost or WTR could proliferate or inhibit *E. coli*

growth during the drying period, the growth-die-off index (GDI) was estimated using the following equation (Ghavanloughajar et al., 2021):

$$GDI = -\log \frac{C_2^{i-1}/C_0^{i-1}}{C_1^i/C_0^i}$$

where C_0 , C_1 , and C_2 represent *E. coli* concentration in the influent, first flush, and last sample of the injection, respectively, and i and $i-1$ represent the current injection and previous injection, respectively. Positive GDI indicates that *E. coli* grow during the drying period, and negative GDI indicates *E. coli* die off during the drying period. The concentration of *E. coli* in the last PV was used to estimate the steady-state removal capacity of the biofilters as a typical breakthrough occurs within 2 PV of the injection (Mohanty et al., 2013). The *E. coli* removal capacity of the biofilters was calculated as $-\log (C/C_0)$, where C and C_0 represent the *E. coli* concentration in the effluent and influent water, respectively.

To estimate phosphate removal, the effluent was analyzed after the application of 6 PV of contaminated stormwater per day. The removal capacity of biofilters was calculated by using the equation: $1 - (C_e/C_i)$; where C_e and C_i represent the concentration in the effluent and influent, respectively. The percent change in removal by the addition of WTR or compost compared to the control was calculated by multiplying 100 with the ratio of the net change in the removal by adding WTR or compost and the removal in the control.

5.2.8. Effluent water quality analysis and leaching

The effluent was analyzed for *E. coli* using agar plates (Valenca et al., 2020). Phosphate concentrations were measured using the Hach Spectrophotometer model DR 280 (TNT 8048; Hach, Loveland, Colorado). Effluent sub-samples were filtered through a 0.45 μm PES syringe filter (Cytiva Whatman™ Uniflo) to remove any suspended solids and were measured for pH using

an ion-selective electrode (model #9107BN, Fisher Scientific), dissolved organic carbon using a Total Organic Carbon Analyzer (TOC-L, Shimadzu), and UV₂₅₄ absorbance using a spectrophotometer (Lambda 365, PerkinElmer), and metals – Fe and Al - using inductively-coupled plasma optical emission spectroscopy (ICP-OES). We did not monitor redox potential assuming oxic condition in the media filter. The short HRT (~41 min) indicates that oxygenated stormwater would quickly replace pore water, thereby maintaining oxic conditions during infiltration events. However, the conditions in the media filter could become anoxic if the pore water remains stagnant for more than weeks (Berger et al., 2019), which was not the case in this study. Thus, we did not expect redox to play a critical role in this study due to the experimental design.

5.2.9. Statistical analysis

All statistical analysis was conducted using R (version 4.2.1). The Wilcoxon test was performed to compare the means of two independent sample groups with and without compost. Differences were considered significant if the p-value < 0.05.

5.3. Results

5.3.1. Effect of compost leachate on surface charge on WTR

Adsorption of DOC from compost leachate on WTR decreased the net positive charge sites or increased the net negative surface sites based on the pH of pore water (**Figure 5-3**). The DOC leached from compost could adsorb on the WTR surface through electrostatic attraction and surface deposition. The result of our batch adsorption experiments reveals that about 45 % of available DOC adsorbed onto the WTR surface (**Table 5-4**). At stormwater pH 7.7, the net surface charge on WTR was negative, which became more negative after the adsorption of DOC (**Figure**

5-4). The point of zero charges for WTR was ~4.4, which decreased to ~3.6 after the adsorption of DOC from compost leachate.

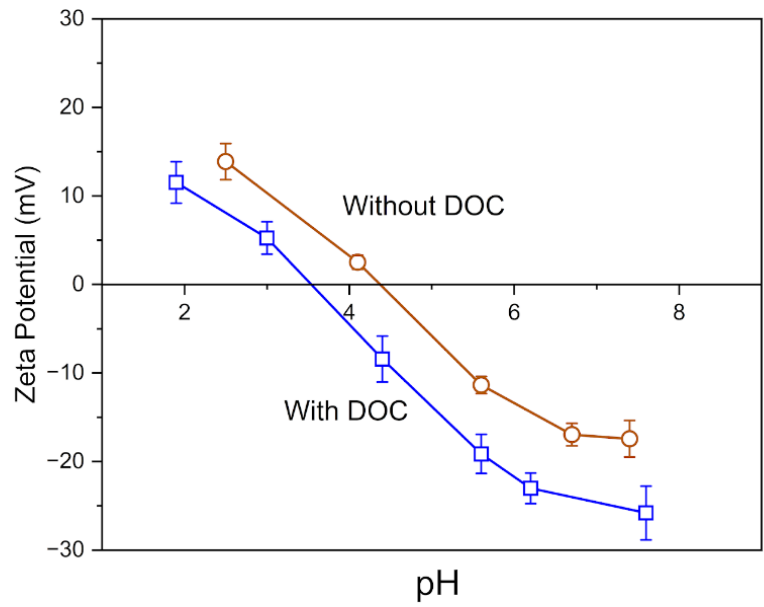


Figure 5-3. Zeta potential of WTR with and without exposure to DOC present in compost leachate.

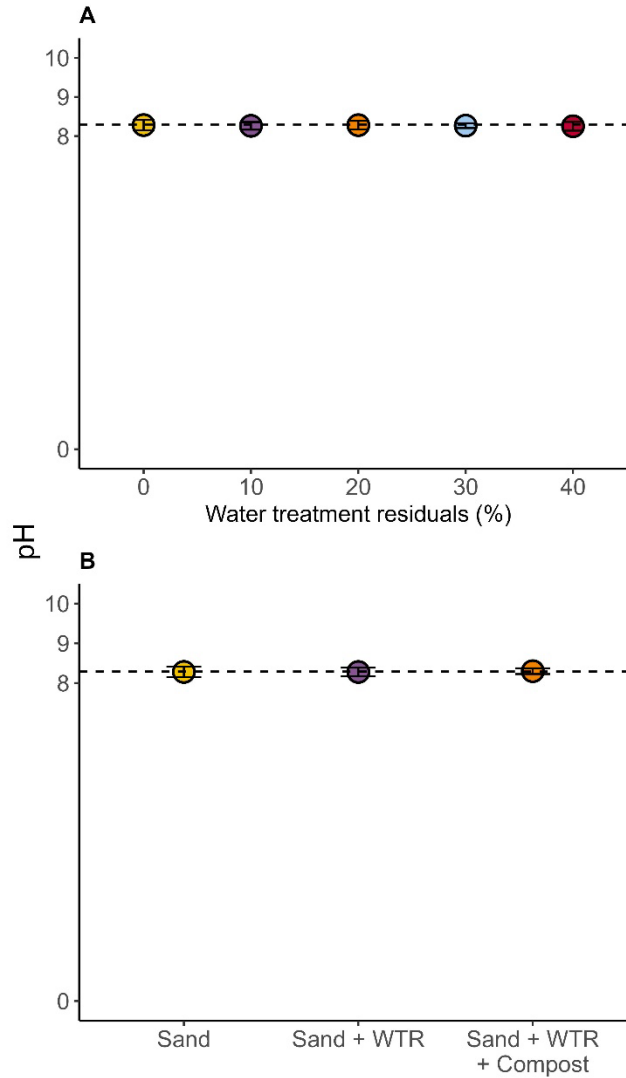


Figure 5-4. pH based on (A) the volume fraction of WTR in sand filters and (B) before and after the addition of compost to sand and WTR mixture. The dashed line represents the pH of the influent concentration.

5.3.2. Optimal amount of WTR for *E. coli* removal

E. coli removal increased with increases in WTR fraction in biofilter media (**Figure 5-5**). However, the removal peaked at 30% of WTR, and any more addition of WTR decreased *E. coli* removal. On average, the log removal capacity of sand columns was 0.34, which increased by approximately 2 orders of magnitude to a log removal of 2.03 when 30% of WTR by volume was added to the sand. Based on the slope of the regression line, each 10% increment of WTR fraction in the sand could increase the log *E. coli* removal by 0.5, but the benefits would not increase

beyond 30% WTR. A similar removal rate in all four injections indicates that the clean-bed removal capacity did not influence overall removal capacity based on all four injections. The consistent removal efficiency in four injection events enabled a comparison of removal capacities with different filter media combinations.

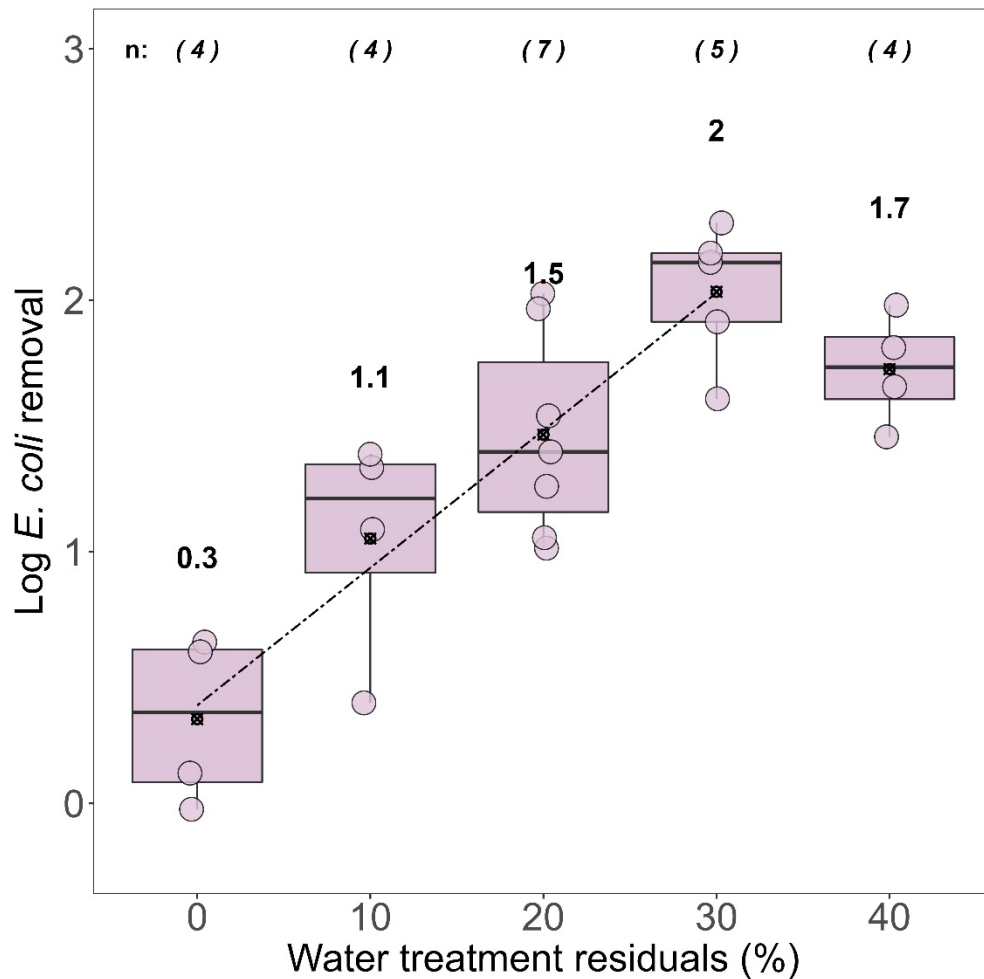


Figure 5-5. Removal of *E. coli* in sand filters amended with different volume fractions of water treatment residuals. The two-dashed line represents the regression equation fitting the *E. coli* removal at different fractions of WTR in sand filters ($R^2 = 0.99$). The mean log removal was noted above each box. Hydraulic retention time in this column was approximately 41 min. The numbers between parenthesis and above each boxplot represent the “n-values” used to create each boxplot analysis.

5.3.3. Optimal amount of WTR for phosphate removal

Phosphate removal increased with the fraction of WTR in sand filters, but the increase in removal was nonlinear with respect to WTR added (Figure 5-6). Increasing the WTR volume from

0% to 10% increased phosphate removal by 1126 % but increasing its amount beyond 10% did not result in a similar high increase in phosphate removal. Increasing the WTR fraction from 10 to 20% increased phosphate removal from 93.46% to 97.31%, and any further increase in WTR fraction did not result in a significant increase in the phosphate removal capacities of sand filters.

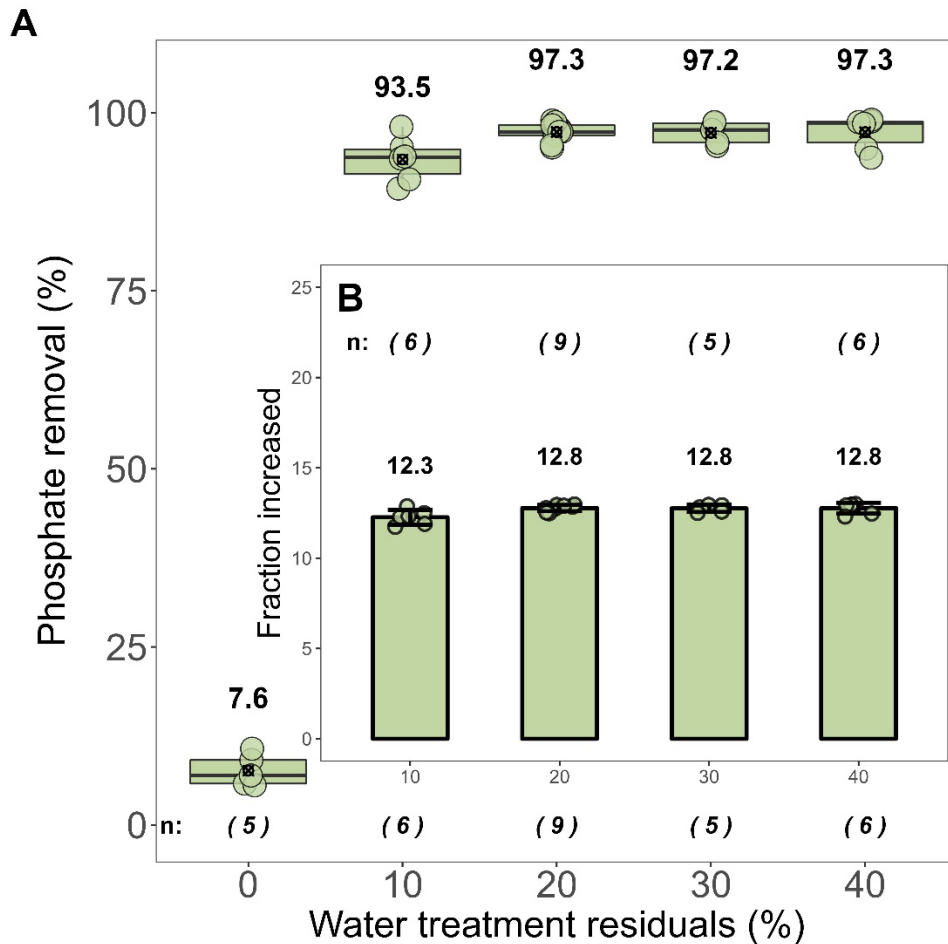


Figure 5-6. A) Increase in phosphate removal based on the volume fraction of water treatment residuals in sand filters. B) The fraction increase in removal occurred due to addition of a specific volume of WTR compared to the reference (0 % WTR). The error bar represents the standard deviation of the dataset. Hydraulic retention time in this column was approximately 41 min. The numbers between parenthesis and below or above each boxplot represent the “n-values” used to create each boxplot analysis.

5.3.4. Effects of compost on *E. coli* removal capacity of WTR

The presence of compost decreased WTR's ability to remove *E. coli* in sand biofilters (Figure 5-7). The sand-only filter had a limited log *E. coli* removal capacity of 0.29 and adding

20% of WTR to sand significantly ($p < 0.001$) increased the log removal to 1.44. However, adding 10% of compost in the mixture of sand-WTR significantly ($p < 0.05$) decreased the log removal to 0.94—a net decrease in removal by 13%.

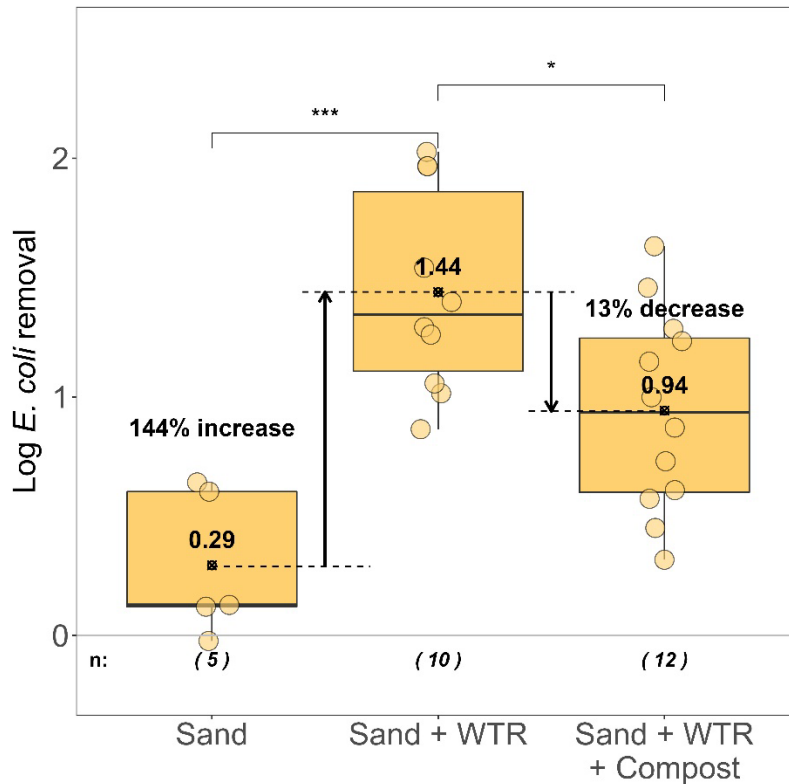


Figure 5-7. Removal of *E. coli* before and after the addition of compost to sand and WTR mixture. The sand columns contain 100 % sand; the Sand + WTR columns contain 80 % sand and 20 % WTR; and the Sand + WTR + Compost columns contain 70 % sand, 20 % DWTR, and 10 % compost by volume. * and *** represent a p-value < 0.05 and < 0.001 , respectively. Hydraulic retention time in this column was approximately 41 min. The numbers between parenthesis and below each boxplot represent the “n-values” used to create each boxplot analysis.

The addition of WTR and compost to sand filters did not significantly change *E. coli* concentration in the pore water during the period between infiltration events (**Figure 5-8**). The sand, sand-WTR, and sand-WTR-compost filters exhibited a net negative growth die-off index, indicating *E. coli* were mostly removed from the trapped pore water either by adsorption or die-

off during the no-flow period. The addition of compost did not contribute to the increase or the growth of *E. coli* in the pore water.

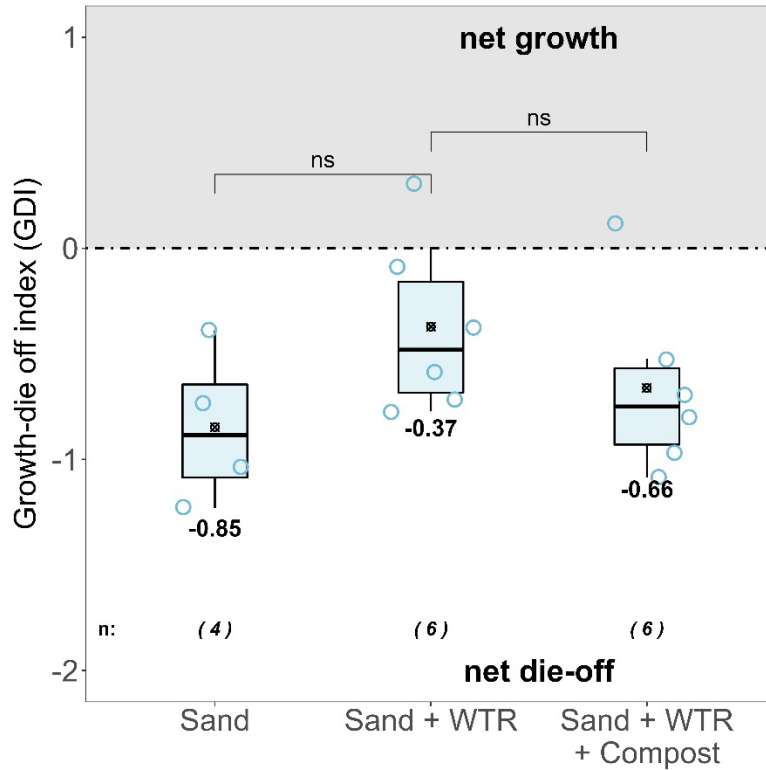


Figure 5-8. Growth-die-off index of sand filters containing WTR and compost. The sand columns contain 100 % sand, the Sand + WTR columns contain 80 % sand and 20 % WTR, and the Sand + WTR + Compost columns contain 70 % sand, 20 % WTR, and 10 % compost by volume. Positive GDI values (shaded area) represent the net growth of bacteria during flow interruption, while negative GDI values represent net die-off or removal of bacteria. ns means a non-significant difference between the groups. The black dot represents the mean value of the dataset. Hydraulic retention time in this column was approximately 41 min. The numbers between the parenthesis and below each boxplot represent the “n-values” used to create each boxplot analysis.

5.3.5. Effects of compost on phosphate removal capacity of WTR

The addition of compost decreased the phosphate removal capacity of WTR in sand filters (Figure 5-9). The addition of 20% WTR in sand biofilters significantly ($p < 0.001$) increased the phosphate removal in sand biofilters by a factor of 11.8 from 7.6% (without WTR) to 97.3% (with 20% WTR). However, adding compost to the filter media significantly ($p < 0.01$) decreased the

phosphate removal from 97.3% to 89.7%. The removal capacity of sand-WTR filters without and with compost was respectively 15.3 and 14.1 times higher than the removal capacity of sand filters.

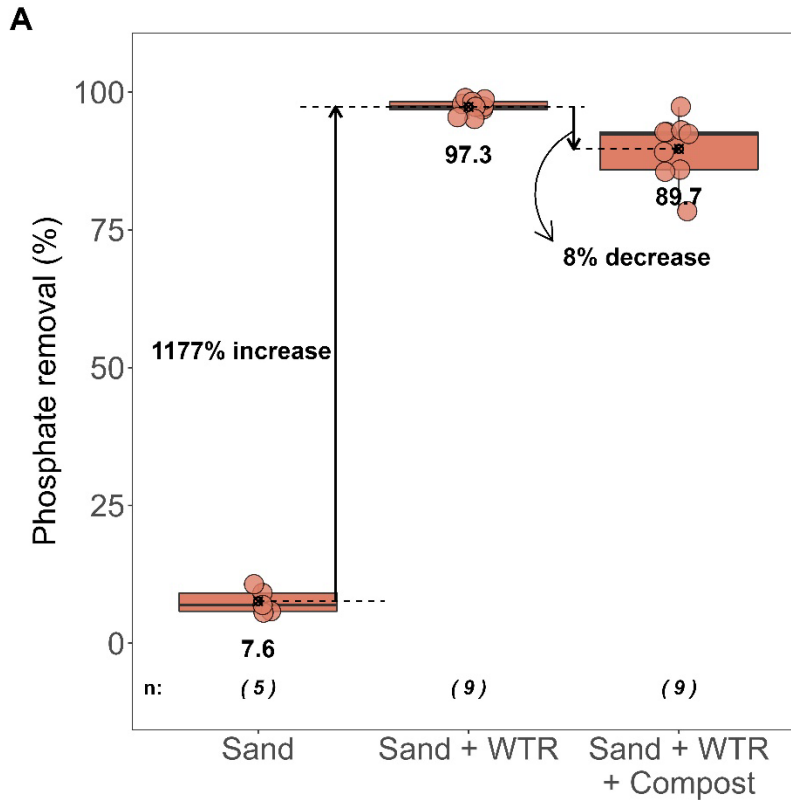


Figure 5-9. Phosphate removal capacity of sand filters, sand filters amended with 20 % WTR (by volume), and sand filters amended with 20 % WTR and 10 % compost. ** means p-value < 0.01, *** means p-value < 0.001. Hydraulic retention time in this column was approximately 41 min. The numbers between the parenthesis and below each boxplot represent the “n-values” used to create each boxplot analysis.

5.3.6. Effects of WTR and compost on the leaching of Fe, Al, and DOC

Metals and DOC concentrations were leached from WTR-amended filter media, but the concentration was not significantly different from that leached from the sand column, indicating the addition of WTR would not increase the concentration of Fe and Al in the effluent (**Figure 5-10**). Similarly, the addition of compost to WTR did not significantly change the concentration of Fe, Al, and DOC in the effluent (**Figure 5-11**). Collectively the results indicate that the addition of WTR initially would leach DOC and metals, but not sufficiently high to exceed the downstream water quality.

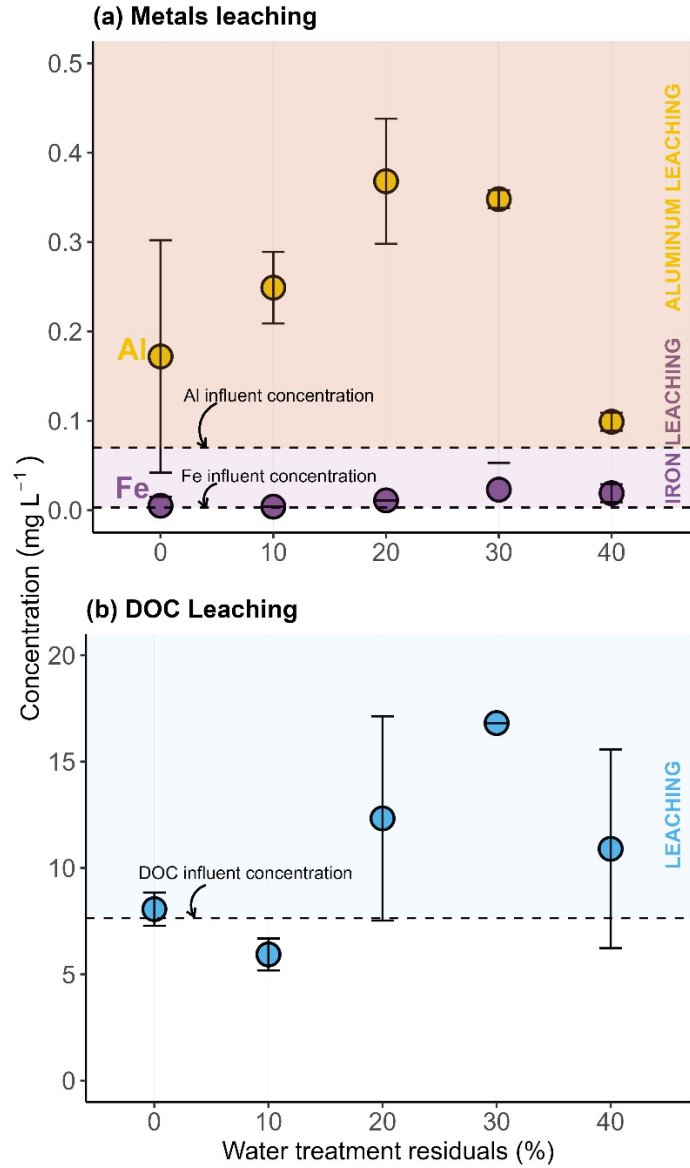


Figure 5-10. Leaching concentration of (a) metals – Al and Fe - and (b) DOC in the effluent samples of the columns with different volume fractions of water treatment residuals. The dashed line represents the influent concentration. The colored area above the dashed line means that leaching occurred.

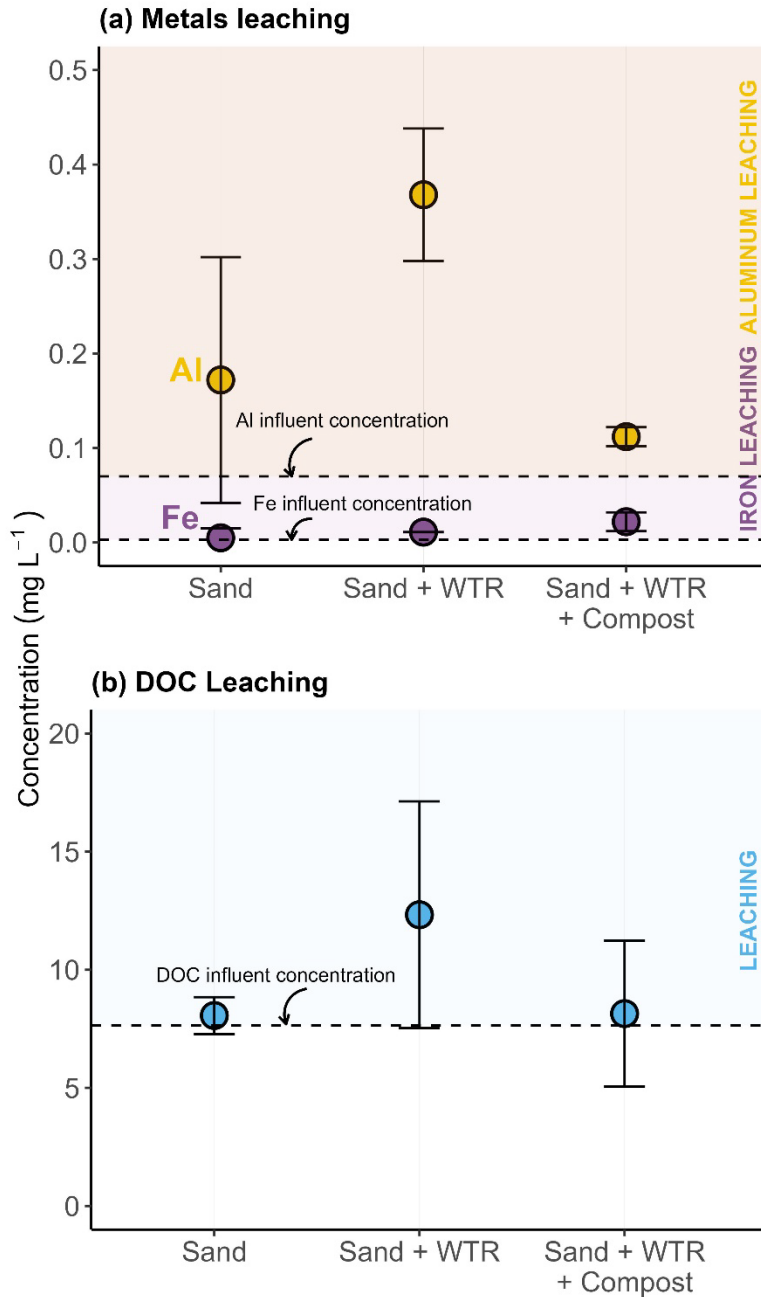


Figure 5-11. Leaching concentration of (a) metals – Al and Fe - and (b) DOC in the effluent samples of the columns before and after the addition of compost to sand and WTR mixture. The sand columns contain 100 % sand; the Sand + WTR columns contain 80 % sand and 20 % WTR; and the Sand + WTR + Compost columns contain 70 % sand, 20 % DWTR, and 10 % compost by volume. The dashed line represents the influent concentration. The colored area above the dashed line means that leaching occurred.

5.4. Discussion

5.4.1. *E. coli* removal in WTR-amended biofilters

Pathogens in stormwater runoff are the leading cause of surface water impairments (US EPA, 2017), and they are most difficult to remove in conventional biofilter media without the addition of expensive engineered amendments (Mohanty et al., 2014; Valenca et al., 2021a). Our results show that the addition of an inexpensive and waste-derived amendment such as WTR could increase *E. coli* removal and that 30% WTR was the maximum amount one should add to maximize *E. coli* removal (**Figure 5-5**). An increase in removal with an increase in WTR fraction is attributed to an increase in the adsorption sites contributed by iron oxides present in WTR. As ferric chloride is used in the treatment plant as a coagulant, iron oxides are formed during coagulation and settled as sludge. A difference in the removal capacity of sand filters without and with WTR can be explained in terms of Derjaguin–Landau, and Verwey–Overbeek (DLVO) theory. DLVO theory accounts for (a) van der Waals force, which depends on the surface area and molecular structures, and (b) electrostatic interaction, which depends on surface charges on bacteria and the filter media surfaces (Hermansson, 1999). Other forces, such as hydrophobic and steric interactions, may also influence the attachment of bacteria filter media (Chen and Walker, 2012). The DLVO profile of sand and bacteria has a potential barrier that prevents a direct attachment of bacteria as both have a net negative surface charge (Bolster et al., 2001). Under electrostatic repulsion between negatively charged surfaces, bacteria can attach to the secondary minimum (Tufenkji and Elimelech, 2004). However, the barrier disappears when the surface of the filter media becomes net positive, which is the case for WTR. The result is consistent with other studies that used iron-based amendments to remove microbial pollutants (Abudalo et al., 2005; Mohanty et al., 2013; Xu et al., 2019; Zoski et al., 2013).

Our study showed that an increase in WTR fraction increased *E. coli* removal, and the optimum volume fraction of WTR in biofilters was 30%. The *E. coli* removal is expected to increase with increases in WTR fraction due to an increase in the number of reactive surfaces for bacterial attachment. However, a decrease in *E. coli* removal was observed when the WTR fraction increased from 30 to 40%. The bulk density and porosity (**Table 5-1**) of the column did not change drastically, with an increase in WTR to 40%. The constant hydraulic conductivity of all columns suggests a limited contribution of changes in pore size distribution on *E. coli* removal in columns with different amounts of WTR. However, the analysis of Al and Fe in leachate revealed a significant decrease in Al concentration when the WTR fraction increased from 30 to 40%, possibly due to precipitation (**Figure 5-10**). High concentrations of dissolved Fe and Al in pore water could alter the surface charge of *E. coli* and enhance the removal of *E. coli* by coagulation (Delaire et al., 2015). Thus, we speculated that a decrease in *E. coli* removal could be a result of a decrease in dissolved Al in the pore water. Nevertheless, the result has practical implications for determining how much WTR can be added to biofilters without reducing the advantage of WTR.

5.4.2. Phosphate removal in WTR-amended biofilters

In most biofilters, enhanced removal of phosphate is typically achieved by adding iron amendments such as iron filings (Erickson et al., 2012), iron-amended sand (Chiew et al., 2009), and WTR (Ali and Pickering, 2023; Hsieh et al., 2007; O'Neill and Davis, 2012). Our study confirmed the result of the previous studies that WTR can be efficient at removing phosphate (**Figure 5-6**). In addition, our result provided the optimum amount (~10-20%) of WTR needed to achieve the goal. Among all amendments, waste-derived amendments such as WTR could reduce the design cost because of their availability in cities where drinking water treatment plants are operated. Phosphate is removed mostly by sorption (Baken et al., 2016; Loganathan et al., 2014)

and ion exchange or surface complexation (Wan et al., 2020). Unlike sand, WTR has net positive surface sites that could attract anions such as phosphate. In particular, phosphate forms inner-sphere complexation through ligand exchange on the surface of iron oxides or hydroxides in the WTR (Loganathan et al., 2014; Wan et al., 2020; Wu et al., 2020). Our study showed any increase in the volume of WTR beyond 10% would not proportionally increase phosphate removal. This is confirmed by another study that shows that a mixed layer of 90% sand and 10% of WTR (5% by total media volume) is enough to provide phosphate removal of 97.5% in bioretention systems for long-term (Ament et al., 2021). Therefore, a higher amount of WTR may not be needed if phosphate is the only pollutant of concern. However, the WTR residue quality could vary based on drinking water treatment design, process operation, and source water quality. Thus, the amount of WTR needed to achieve the removal objective could change based on WTR quality.

5.4.3. Effects of compost on *E. coli* removal capacity of WTR

Compost is widely used in a biofilter to improve vegetation establishment as it supplies nutrients and conserves moisture. Yet, their interaction with other amendments, such as WTR, is rarely studied, despite the potential of compost to decrease the adsorption capacity of amendments (Mohanty and Boehm, 2014). Our study confirmed that the addition of compost to WTR-amended biofilters could significantly reduce *E. coli* removal by 13% (**Figure 5-7**). This behavior of WTR could be attributed to the alteration of the surface charge of WTR after DOC sorption. Zeta potential measurement of WTR with and without compost exposure confirmed this hypothesis (**Figure 5-3**). *E. coli* removal capacity of WTR could also decrease because of the competition of negatively charged DOC and bacteria for positively charged attachment sites (Li et al., 2010; Yang et al., 2012), blocking of adsorption site with large size DOC molecules (Foppen et al., 2008), and change in hydrophobicity of the bacteria through DOC sorption (Chen et al., 2011; Tanneru and

Chellam, 2012). The DOC is expected to leach continuously from compost and interact with WTR. Thus, aging of WTR in the presence of compost could further decrease *E. coli* removal capacity. Thus, field studies with aged WTR should be used in future studies to confirm this hypothesis. Nevertheless, our results indicate that mixing compost with WTR should not be recommended in sites where pathogens are the primary pollutant of concern in stormwater. In that case, biochar could be used as an alternative to compost as the amount of DOC leached would be significantly lower than that of compost and could also support plant growth by conserving moisture and supplying nutrients (Mohanty et al., 2018). However, it should be noted that compost provides many other biological benefits, including nutrients for plants and bioavailable DOC for enhanced denitrification. Thus, eliminating compost can reduce the functionality of biofilters. Thus, the design objective of the biofilter should be taken into account for making the decision on whether or not to use compost along with WTR in stormwater biofilters.

5.4.4. Effects of compost on phosphate removal capacity of WTR

Our results indicate that DOC leached from compost decreased the phosphate removal capacity of WTR by 8% (**Figure 5-9**). Phosphate removal is dependent on the amendment's surface properties and porewater chemistry (Xu et al., 2020), and the addition of compost altered both in the biofilters. Compost leaches DOC into pore water, resulting in the adsorption of DOC on WTR, which increases the negative surface charge on WTR. Zeta potential measurement confirmed this hypothesis (**Figure 5-3**). As both DOC and phosphate bind with the same sites (Ding et al., 2021; Li et al., 2020), competition between DOC and phosphate for available adsorption sites could decrease the overall phosphate removal. While DOC can sterically hinder the adsorption sites for bacteria, DOC may not block the same sites from phosphate due to the smaller molecular size of phosphate compared to DOC. However, DOC could substantially reduce

the adsorption of phosphate when DOC concentration is relatively higher than phosphate concentration (Li et al., 2021). Our results reveal that the presence of WTR did not promote DOC leaching from compost but instead increased the adsorption of DOC leached due to the iron and iron and aluminum contained in the WTR that bind with the DOC from compost (**Table 5-4**), DOC leaching from a WTR-compost biofilter was lower than that from a WTR-only biofilter (**Figure 1-11**). As a result, phosphate removal was lower because fewer attachment sites are available for phosphate with an elevated DOC concentration in pore water. This has critical implications in stormwater as typical phosphate concentration in stormwater is less than 1 mg L^{-1} , whereas DOC concentration could be $10\text{-}100 \text{ mg L}^{-1}$ (Grebel et al., 2013). Although our study indicates that DOC strongly interferes with phosphate removal in biofilter systems, the decrease is not substantial. As compost also provides other biological functions, the choice of using or not using compost may ultimately depend on the design objective of biofilters and the types of pollutants that are required to be removed. If the addition of compost and WTR could not help meeting the discharge limit for phosphate, then the removal of compost as an amendment could help meet the design goal.

5.4.5. Design implications

The results of this study provide insight into how to best use WTR in stormwater biofilters in conjunction with other amendments, such as compost, in order to maximize the removal of *E. coli* and phosphate. The results can be applied to other pollutants that exhibit similar adsorption behaviors on positively charged amendments, such as WTR. For instance, WTR addition could enhance the removal of negatively charged organic contaminants, including Polycyclic Aromatic Hydrocarbons (PAHs) and Per- and Polyfluoroalkyl Substances (PFAS), through electrostatic interaction (Xu et al., 2020; Zhang et al., 2021). Our results confirmed that the addition of compost decreased phosphate removal but still maintained removal exceeding 85%, indicating that the

compost and WTR mix could still have sufficient capacity to remove metalloids such as arsenate and chromate. Our study also shows that the addition of 30% WTR is sufficient to provide maximum adsorption capacity. At such high concentrations, WTR could release Fe and Al, which could adversely affect the plants in biofilters. However, our study demonstrates that the concentration of Al and Fe in leachate did not exceed the toxic threshold, suggesting that WTR may not pose any additional toxicity to plant growth. However, future studies should evaluate the effect of WTR on plant health in biofilters.

Although the results of the study provide insights into any change in the performance of WTR-amended media filters in the presence of compost, the performance of media filters in the field conditions could differ due to changes in climate conditions. For instance, characteristics of dry-wet cycles or drying durations in field conditions could significantly differ from those used in our study, and the resulting changes in biofilter could affect the microbial community, plant health, and hydraulic behavior of media filters. For instance, a lack of moisture during a long drying period could inhibit microbial activity and slow down compost decay (Alcala Jr. et al., 2009). Furthermore, a prolonged wetting period could create a reducing environment in the pore water, which could increase iron dissolution from WTR. Thus, future studies could examine these long-term effects of climate variability on the performance of WTR-amended filter media.

5.5. Conclusions

To improve pollutant removal, amendments are typically mixed and added to stormwater biofilters without accounting for their interactive effect. This study examines for the first time the effects of compost, the most common conventional biofilter media amendment, on the capacity of water treatment residuals (WTR), a waste-derived amendment, to remove *E. coli* and phosphate from contaminated stormwater. The results proved that adding WTR could increase biofilters'

capacity to remove *E. coli* and phosphate. The optimal amount of WTR required for maximum *E. coli* removal depended on the composition of the WTR, including the fraction of metal oxides and the amount of organic matter present. Additionally, the presence of compost in the system reduced the biofilters' performance for *E. coli* and phosphate removal. The result was attributed to a net decrease in attachment sites or alteration of attachment sites by adsorption of dissolved organic carbon leached from compost. DOC adsorption was confirmed to increase the net negative surface charge or decrease the net positive surface charges on WTR. The presence of compost did not contribute to the growth of *E. coli* in biofilters, indicating a decrease in *E. coli* removal was mainly because of the exhaustion of attachment sites. These results indicate that compost should not be mixed with WTR in order to utilize the maximum benefits of WTR. Thus, this study not only provides practical knowledge of when and how WTR should be applied but also shows mechanistic insight into how WTR may interact with other conventional media, such as compost or mulch, that may already be present in the biofilters.

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6. CHAPTER 6 – INNOVATIVE COHORT-BASED RESEARCH EXPERIENCE: FOSTERING SCIENCE IDENTITY AND STEM ENGAGEMENT TO PROMOTE STEM RETENTION

Raelison, O.D., Dixie, K., Mohanty, S.K. Innovative Cohort-Based Research Experience: Fostering Science Identity and STEM Engagement to Promote STEM Retention. [In preparation]

Abstract

The United States invests millions of dollars to support science, technology, engineering, and mathematics (STEM). Yet, the US lags in STEM education and fails to retain students in STEM with 1 in 2 first-year students dropping out of STEM majors due to negative learning experiences arising from large classrooms and a lack of interaction with professors and peers. A lack of science identity is mainly found among underrepresented minorities explaining the diversity gap in STEM. We hypothesize that improving students' science identity or their ability to portray themselves as scientists and STEM engagement through hands-on research experience could improve their learning experience and later influence their decisions to choose STEM as a career. To evaluate the impact of cohort-oriented research on improving science identity and STEM engagement, the education study was conducted in the Spring quarters of 2022 and 2023 in the "Green Infrastructure" class in Civil and Environmental Engineering at UCLA. As the course includes a group project, two cohorts each year were examined to conduct a hands-on laboratory project. Quantitative and qualitative data were collected from surveys, laboratory observation, focus group interviews, and grades. Results revealed that the research experience increases self-efficacy, helps develop a sense of community, enhances students' interest, and increases STEM persistence. This method could be adopted in other classes in Environmental Engineering or related disciplines to enhance student engagement and retention of minorities in STEM education.

6.1. Introduction

The US education systems struggle to attract and retain students in science, technology, engineering, and mathematics (STEM) fields, resulting in shortages of STEM professionals (Hawthorne, 2022) in the era of the rapid growth of STEM jobs (National Science Foundation, 2019). This highlights an urgent need to bolster STEM education to maintain global competitiveness. Actively recruiting talented individuals from underrepresented minority (URM) groups not only helps meet the demand for STEM professionals but also reduces diversity gaps in STEM fields (National Academies of Sciences, Engineering, and Medicine, 2011). However, the attrition rate in STEM, particularly in engineering, exceeds that of other fields of study with nearly 50% of first-year students changing or dropping out of STEM majors (Malcom and Feder, 2016). The high dropout rate is often attributed to negative learning experiences arising from poor quality of teaching (Emberley et al., 2024; Judson et al., 2015; Kamen and Leri, 2019) and a lack of interaction between professors and peers (Coman et al., 2020; Polmear et al., 2024; Samuelson and Litzler, 2016). Therefore, improving the quality of student learning is crucial to fostering STEM persistence, especially as challenges in URM retention continue to arise.

The quality of student's learning can be improved by adopting comprehensive strategies to enhance students' science identity—their ability to portray themselves as scientists. A strong science identity is associated with improved academic performance and increased interest in science (Merolla and Serpe, 2013; Piatt et al., 2019). Strengthening science identity has been shown to increase the likelihood of students pursuing and persisting in STEM fields, thus promoting STEM resilience (Ross et al., 2021; Schinske et al., 2016). Science identity is driven by both extrinsic and intrinsic attitudinal factors, a sense of community, and the ability to connect

classroom learning with real-world science (Archer et al., 2010; Aschbacher et al., 2010; Carlone and Johnson, 2007; Vincent-Ruz and Schunn, 2018).

This study aims to test the hypothesis that implementing strategies that contribute significantly to the key factors driving science identity and student interest would promote STEM retention. STEM retention refers to preventing dropout and ensuring students persist in STEM education and careers. By incorporating these strategies, the study will assess their impact on improving student learning, self-efficacy, sense of belonging, and interest in science. *First*, enhancing intrinsic motivation, particularly in engineering requires increasing self-efficacy among students. Engineering culture, which tends to emphasize a fixed mindset, creates a negative learning experience marked by high pressure, anxiety, and stress, and where the fear of making mistakes is prevalent (Deters et al., 2024; Emberley et al., 2024; Jensen and Cross, 2021). Developing self-efficacy helps students develop a growth mindset where they perceive mistakes and failures as opportunities for growth rather than setbacks. Their ability to persist in the face of challenges. This shift in perspective can support and sustain interest and engagement in STEM fields. *Second*, nurturing a sense of belonging is crucial for creating a supportive learning community in engineering. Sense of belonging is defined by how accepted, respected, and valued students feel. Studies have shown the beneficial role of a learning community in creating a positive and supportive environment and improving STEM retention (Alcéna-Stiner and Markowitz, 2020; Brownell et al., 2012). Research highlights the importance of a sense of belonging for developing persistence and improving retention in engineering (Fletcher et al., 2023; Ong et al., 2020; Patrick et al., 2023; Polmear et al., 2024). Peer interaction is the primary contributor to a sense of belonging, and the lack of in-person interaction can decrease students' academic performance, particularly among minority students (Fletcher et al., 2023). *Third*, students often struggle to

connect theoretical concepts with real-life applications (Behrendt and Franklin, 2014). Many studies have shown the beneficial role of research and experiential learning, in helping students develop these connections while fostering a sense of belonging through student collaboration and critical thinking (Hefferan et al., 2002; Kamen and Leri, 2019; Sidebottom, 2020; VanMeter-Adams et al., 2014). Laboratory experience can become a key component of fostering science identity by positively influencing student attitudes (Simmons et al., 2008) and integrating knowledge, thereby strengthening their interest in science (VanMeter-Adams et al., 2014).

While many studies have focused on Course-based Undergraduate Research Experiences (CUREs) and the benefits of laboratory research experience (Harris et al., 2021; Kolon and Mabrouk, 2022; Mraz-Craig et al., 2018; Scarborough et al., 2022; Shortlidge et al., 2016), no study has evaluated the impact of a cohort-based research experience on fostering all the factors that drive science identity, increasing student interest, and simultaneously maximizing a strong sense of community. We hypothesize that by combining research experience with a strong sense of community, cohort-based research can increase self-efficacy, enhance the learning experience, help develop a sense of community, and enhance students' interest in pursuing engineering. To test the hypothesis, we engaged a cohort of undergraduate students from different majors with little to no prior research experience. They were given the opportunity to learn the research process from start to finish—from identifying a problem to producing a research article. This education research study investigates three learning outcomes for students participating in a cohort-based research experience. (1) Develop the confidence to identify and apply specific scientific concepts in the laboratory setting, thus enhancing self-efficacy in scientific experimentation and problem-solving. (2) Develop a sense of community with other students participating in the laboratory experiment. (3) Articulate their interest and engagement in science and career goals.

6.2. Materials and Methods

6.2.1. Implementation plan: Background on the class and the research opportunity

The study was conducted as part of the "Green Infrastructure" course at the University of California, Los Angeles (UCLA), offered each spring quarter by the Department of Civil and Environmental Engineering. This course primarily enrolls undergraduate students, with a total of approximately 80 students per quarter, including both undergraduate and graduate students. In this class, a group project counts toward 50% of their final grade. Typically, students in this course conduct a literature review on a chosen topic for their group project or design conceptual study implementing green infrastructure at a site for water quantity and quality benefits. In contrast, a group of students – “the cohort” – was given the opportunity to undertake a research project in a laboratory environment. The cohort was guided through the entire research process, including conducting a literature review, formulating research questions and hypotheses, designing experiments, collecting and analyzing data, and writing a final report.

To ensure consistency, the 2022 and 2023 cohorts worked on the same research topic and research questions. The research topic was directly related to the course content on “Green Infrastructure” and was aligned with the research interests of the principal investigator. While the specific scientific results of their projects may vary due to differences in hypotheses, this study focuses on educational and social aspects for a comprehensive understanding of the student cohorts' learning experiences and approaches, rather than on the scientific outcomes of the projects. This consistent topic selection enables the integration of data from both years, allowing conclusions and observations to be drawn across different cohorts. This approach ensured that all participants faced the same challenges and obstacles to evaluate their performance uniformly.

6.2.2. *Participant sampling*

Each year, a group of students was selected from the class to form a cohort, comprising undergraduate students from diverse backgrounds, majors, and academic years, preferably with little to no prior research experience. The target number of participants for each cohort was estimated to be approximately 10, aligning with the typical group size for class projects. At the beginning of the quarter, the principal investigator of this study announced the research opportunity and explained its nature as part of an education study. Then an application form was distributed among all students to ensure they did not feel pressured to participate during the intervention in class. The application form served to remind students about the research opportunity and outlined the eligibility criteria and preferences. To meet the target number, interested application forms were screened and only those meeting specific criteria were chosen to participate in the hands-on laboratory project, forming the cohort. In Spring 2022, 8 students were selected, and in Spring 2023, 11 students were selected, resulting in a total of 19 participants (n=19) for this study.

6.2.3. *Inclusion and Exclusion criteria*

This study was designed to promote greater participation of underrepresented minorities in STEM disciplines to enhance the representation of marginalized groups in STEM. To achieve this, our inclusion criteria encompassed ethnicity to prioritize students from underrepresented minorities and underserved populations, such as Black/African American, American Indian/Alaskan Native, Native Hawaiian, other Native Pacific Islander, Hispanic/Latinx communities, and as well as women. Furthermore, our selection process gave preference to students without prior research experience. This intentional approach enabled us to assess their potential and ability to conduct research and collaborate effectively, particularly when

encountering challenges during the research process. Despite prioritizing these criteria, each application was thoroughly reviewed to ensure the formation of the most diverse student cohort possible.

One of the objectives of this study is to enhance retention in STEM education, specifically focusing on increasing the number of students who continue their STEM studies from one academic year to the next and aspire to pursue graduate school. To achieve this, only undergraduate students enrolled were considered. Consequently, graduate students were ineligible to participate in this study. This exclusion criterion ensures a clear focus on the undergraduate student's interest and persistence in science relevant to our research objectives.

6.2.4. *Data collection*

The assessment strategy for this study used both quantitative and qualitative methods to comprehensively evaluate student academic performance, sense of community, and interest and engagement in science. Quantitative assessments included midterm, quiz, and final grades to measure academic performance. Additionally, hands-on laboratory experiments conducted during the course were observed and evaluated. Quantitative data was also collected through 5 surveys administered at multiple points: a pre-survey for the entire class at the beginning of the quarter, a pre-survey for the cohort before starting any research experience, a post-survey for the cohort at the end of the research experience, and another post-survey for both the cohort and the entire class at the end of the quarter. Another post-survey was sent one year later for the cohort. These surveys included Likert-scale, multiple-choice, and open-ended questions to gather detailed feedback and obtain both quantitative and qualitative data.

Qualitative assessments involved focus group interviews conducted at the end of the study, providing in-depth insights into student experiences. The focus-group interviews were conducted

in a closed room where conversations could not be heard by others so that participants feel comfortable providing information in this manner to maintain privacy in the research settings. Additionally, students' final presentations offered a qualitative evaluation of their learning outcomes and research experiences. This integrated assessment approach ensured a thorough and nuanced evaluation of both academic achievements and experiential learning. Students were expected to give informed consent. Any information that is obtained in this study and that can identify the participant remained confidential. Privacy was also maintained for all the activities. Confidentiality was maintained by means of coding identity so that they remain anonymous in any data analysis and all data will be presented in aggregate.

6.2.5. *Alignment table*

In this study, three learning outcomes were examined. Students were expected to:

1. Develop the confidence to identify and apply specific scientific concepts in the laboratory setting, thus enhancing self-efficacy in scientific experimentation and problem-solving
2. Develop a sense of community with other students participating in the laboratory experiment
3. Articulate their interest and engagement in science as well as career goals

For the first learning outcome, quantitative data was collected via pre- and post-surveys to assess students' ability to gain confidence in performing and conducting research, final presentations, and reports. For the second learning outcome, qualitative data was collected through observation of student interactions, focus group interviews, and open-ended survey questions. Quantitative data were obtained from post-surveys to determine the percentage of students expressing a sense of belonging.

To address the third learning outcome, quantitative data was collected via pre- and post-surveys to assess students' ability to define career goals and their decisions regarding graduate school. Qualitative data was obtained from post-surveys and focus group interviews to analyze reasons for STEM interest. Additionally, qualitative data was gathered during laboratory experiences to assess student participation in questioning. The pre-survey also included a demographics section to ensure a diverse participant pool. A follow-up post-survey was conducted after one year to determine the number of STEM undergraduates pursuing graduate school.

Table 6-1. Alignment table presenting the various components of assessment aligned with the learning outcomes.

Learning Outcomes	Assessments tools
Develop the confidence to identify and apply specific scientific concepts in the laboratory setting, thus enhancing self-efficacy in scientific experimentation and problem-solving	<ul style="list-style-type: none"> • Survey (Likert scale, multiple-choice, true-false questions) • Final report • Final presentation
Develop a sense of community with other students participating in the lab experiment	<ul style="list-style-type: none"> • Survey (Likert scale, multiple-choice, true-false questions) • Lab observation • Final presentation
Articulate their interest and engagement in science as well as career goals	<ul style="list-style-type: none"> • Survey (Likert scales, multiple-choice, true-false questions) • Final report • Lab observation • Final presentation

6.2.6. Timeline

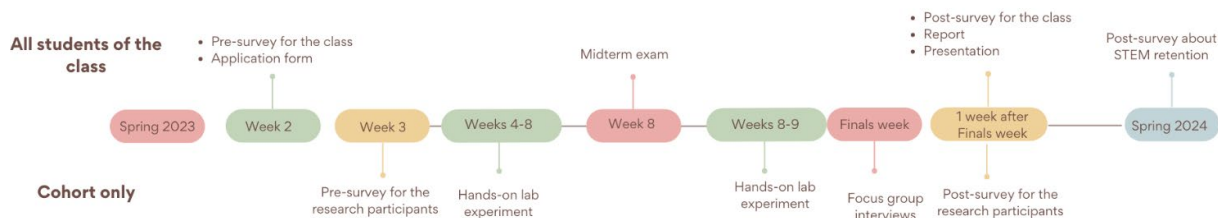


Figure 6-1. Timeline of the second cohort during the Spring quarter of the 2022-2023 academic year (12 weeks).

6.2.7. Data and statistical analysis

All statistical analyses were conducted using R (version 4.2.1). The Wilcoxon test will be employed to compare the means of two independent sample groups—participants and non-participant students. Differences were deemed significant if the p-value was less than 0.05. The sample size of participants in this study was 19, while the sample size of non-participants comprised of other undergraduate students in the class was 47.

6.3. Results

6.3.1. Diversity of the cohorts

The pre-survey data from both cohorts show significant diversity, with 50% consisting of underrepresented minority students (**Figure 6-2, Figure 6-3**). The cohort comprises students with diverse majors, predominantly in engineering but also spanning other fields (**Figure 6-2**). Females represent the majority of the cohort at 68.4%. Academically, the majority are in their 3rd year (57.9%), followed by 4th-year students (36.8%). While white students constitute around 30% of the cohort, there is significant representation from Hispanic and Asian-Other backgrounds, each comprising 21%. Notably, 31.6% of the cohort consists of transfer students and an equal proportion are first-generation college students. This variety of majors, genders, academic years, ethnicities,

transfer, and first-generation college identifications underscores the diverse backgrounds and experiences within the cohort, essential for comprehensive analysis of study outcomes.

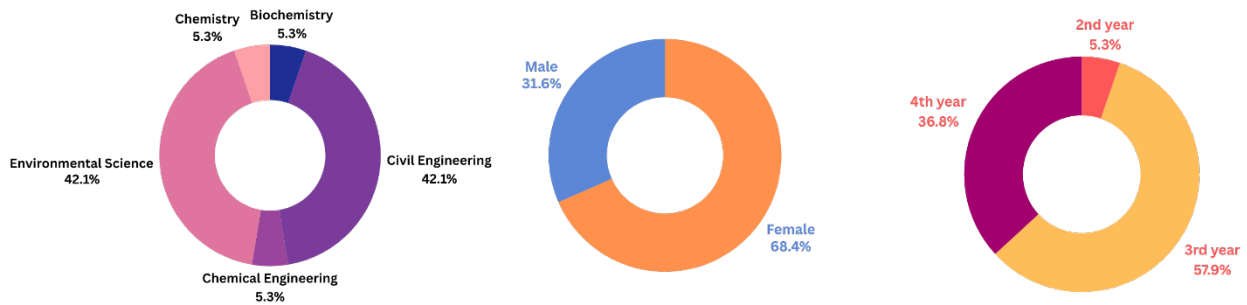


Figure 6-2. Distribution of majors, gender, and academic year among combined cohorts. Data were collected from the pre-survey of the two combined cohorts, capturing students' majors, their gender, and their academic year at the time of the class. The donut pie charts present the percentage distribution among the cohorts' members (n=19).

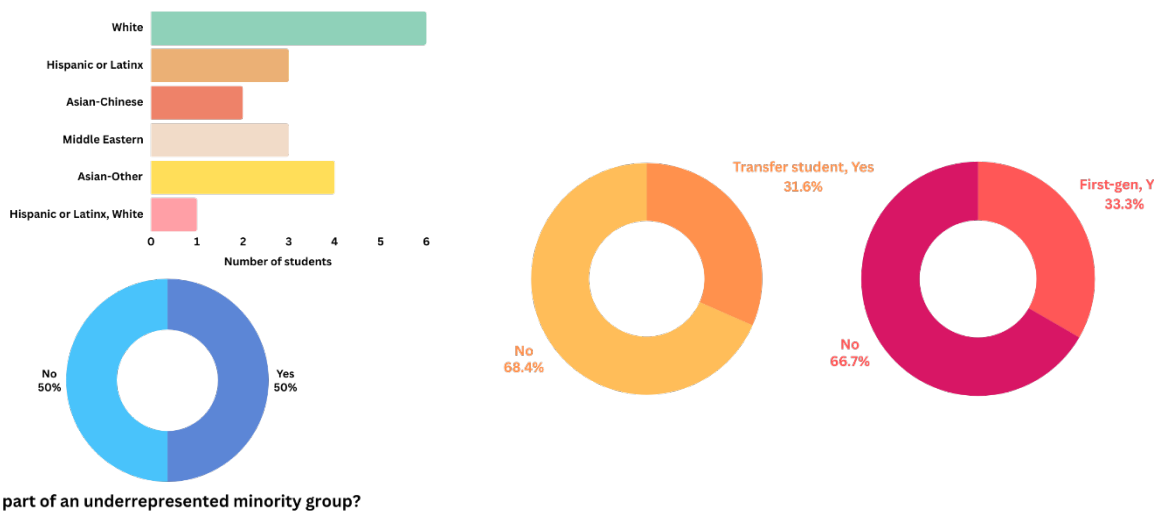


Figure 6-3. Distribution of ethnicity, transfer status, and first-generation college status among combined cohorts. Data were collected from the pre-survey of the two cohorts, capturing students' ethnicity, transfer student status, and first-generation college status. The donut pie chart presents the percentage distribution among the cohorts' members, while the bar chart indicates the number of students in each ethnic category (n=19).

6.3.2. The cohort-based research experience fosters science identity by increasing self-efficacy

The research experience has significantly increased students' belief in their ability to successfully perform research and understand the class (**Figure 6-4**). After the research opportunity, the students demonstrated a better understanding of the main topic of the class, with an increase from 53% "Strongly Agree" or "Agree" to 94%. Concerning the class concepts, all students (100%) expressed confidence in their understanding of the concepts learned, indicating that the cohort-based research experience helped them better grasp the class concepts and make connections to real-life applications in the lab. This was also confirmed by the students during the focus-group interview (**Figure 6-8**). Moreover, students predominantly responded with agreement or strong agreement to all questions related to the research process and their ability to perform lab work, indicating a notable gain in confidence in research following the experience. These high self-perceptions signify the emergence of a strong science identity among students, underscoring their new competence in both science and research.

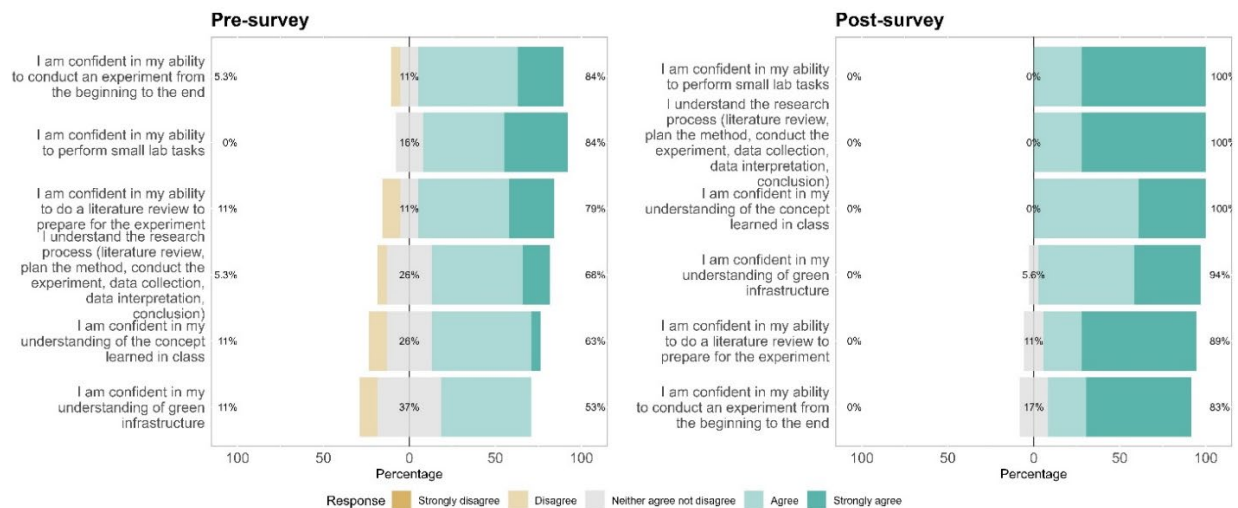


Figure 6-4. Comparison of Linkert survey responses from pre- and post-surveys. Data related to self-efficacy were collected (n=19).

6.3.3. The cohort-based research experience fosters science identity by enhancing learning experience

The cohort-based research appears to enhance the learning experience and academic performance compared to students who did not engage in hands-on lab work (**Figure 6-5**). While only 85% of students in the non-cohort group reported a better understanding of the class due to group projects, all students (100%) in the cohort affirmed, with over 50% strongly affirming, that the project helped them better understand the class. Furthermore, 79% of non-cohort students believe that the group project helped them perform academically better, resulting in a better final grade, with 4% disagreeing. In comparison, 89% of cohort students believe, with half of them strongly believing, that they performed better academically, resulting in a better final grade, thanks to the research experience. Additionally, by the end of the class, 94% of cohort students found their group supportive, with 5% expressing neither agreement nor disagreement. In contrast, only 85% of non-cohort students found their group supportive, with 4% disagreeing and 11% expressing neutrality. This underscores how the research experience cultivates a more supportive, cohesive, and collaborative group dynamic, which also explains why almost 100% of cohort students strongly recommend that new students engage in the research project.

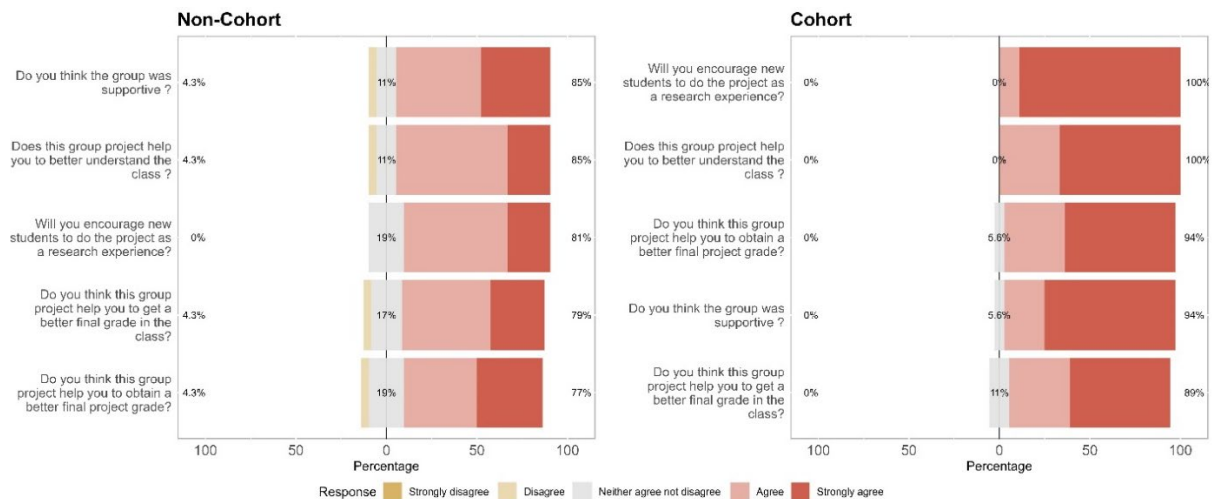


Figure 6-5. Comparison of post-survey data from Likert surveys regarding the impact of the group project on academic performance and the classroom learning environment, distinguishing between the non-cohort (n=47) and cohort (n=19) groups. The left plot represents the non-cohort group, while the right plot represents the cohort group.

6.3.4. *The cohort-based research experience fosters science identity by developing a sense of belonging*

The cohort-based research experience helps develop a sense of community among the students (**Figure 6-6**). Comparing perceptions before and after the experience, initially, 64% of students agreed, with 9% disagreeing and 27% expressing no opinion, that they had a positive and supportive group dynamic. However, after the experience, 100% of students agreed, with approximately 75% strongly agreeing that the group was very positive and supportive. Regarding the classroom environment, there was a noticeable shift in perception, with the number of students believing the environment to be supportive and positive increasing from 73% to 91%. Particularly, they seem to enjoy peer interaction, with 100% of students feeling a sense of community within the group, compared to less than 50% before the project began.

At the start of the class, 27% of cohort students felt isolated or marginalized in the classroom, a sentiment that completely dissipated after the research experience, with no student feeling alone or marginalized. In the group project, initially, 27% of students expressed neutrality,

while 72% disagreed with feeling isolated and marginalized. However, by the conclusion of the project, 100% of students disagreed with feeling alone or marginalized in the group, a sentiment shared by all cohort students.

Additionally, students not only felt a sense of belonging in the class but also found the research opportunity to be “fun” and highly “collaborative” (Figure 6-7), affirming their appreciation for and enjoyment of working in groups, as supported by the focus-group interview (Figure 6-8). The post-survey revealed unanimous agreement among students regarding the significant importance of the cohort/community aspect in their study. During focus group discussions, students expressed gratitude for their peers, recognizing the support they provide, especially in alleviating pressure during lab work and boosting confidence through collaborative problem-solving (Figure 6-8). These findings underscore the benefits of community and the transformative impact of fostering a sense of belonging in the learning experience.

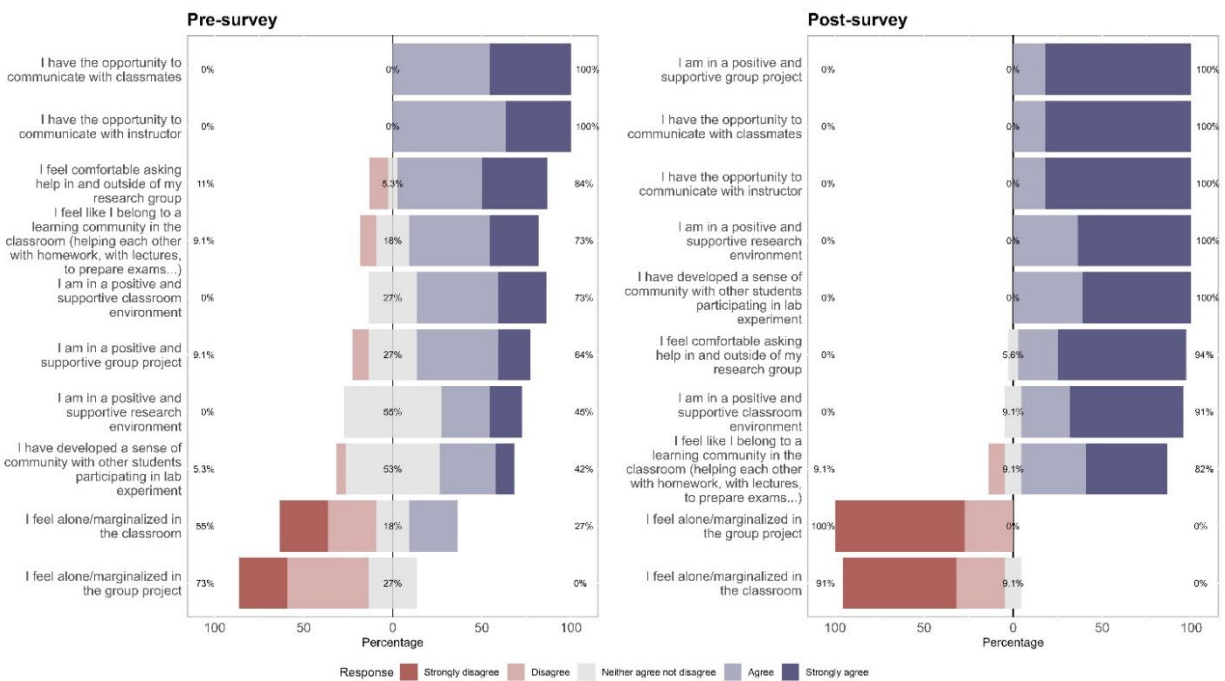


Figure 6-6. Comparison of Likert survey responses from pre- and post-surveys, focusing on the group project, including environment and sense of belonging (n=11).



Figure 6-7. Word clouds describing the research experience according to the combined cohorts. This visual representation of word data is depicted in different sizes. The bigger and bolder the word appears, the more often the word is mentioned by the students and the more important it is. Data collected from post-survey where students were asked to describe in 3 words the research experience. n=50.

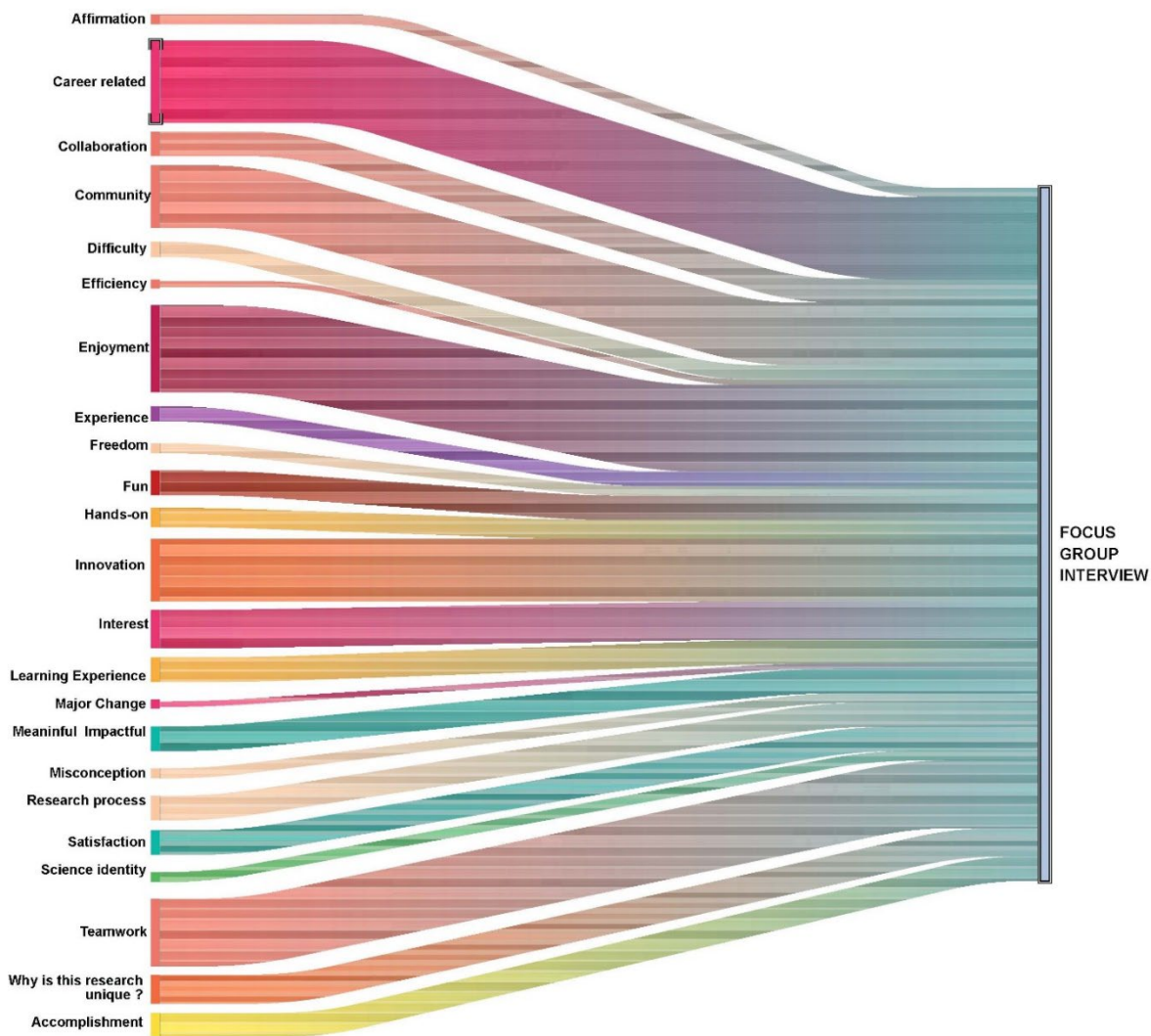


Figure 6-8. Sankey diagram illustrating key themes emerging from the focus group interview. The varying width of the streams represents the frequency of each theme, conveying the importance and weight of various aspects discussed during the interviews. Streams with the same color represent similar ideas, highlighting the connections between related themes.

6.3.5. *The cohort-based research experience increases interest in science*

The cohort-based research experience enhances students' clarity in articulating their career aspirations and intention to pursue further education in STEM (**Figure 6-9**). Nearly 100% of students strongly agree, up from 95%, about having a strong interest in STEM after the research project. Initially, 18% of cohort students expressed disagreement regarding feeling confident in their field, and 64% expressed agreement. After the research group, 91% of students felt more

confident. Similarly, while only 82% initially felt they were contributing to knowledge and impacting the world, all students strongly agreed about the impact they were making following the research group. Before the group project, 21% of cohort students expressed no intention to continue research, a number which decreased to 11% post-project. In the focus-group interview (Figure 6-8) and the 1-year follow-up survey, most students indicated they may consider returning to graduate school after gaining industry experience, and that the research experience strengthened their interest in environmental engineering and sustainability. Others mentioned realizing they may actually prefer lab work over fieldwork. These findings significantly contribute to overall STEM engagement.

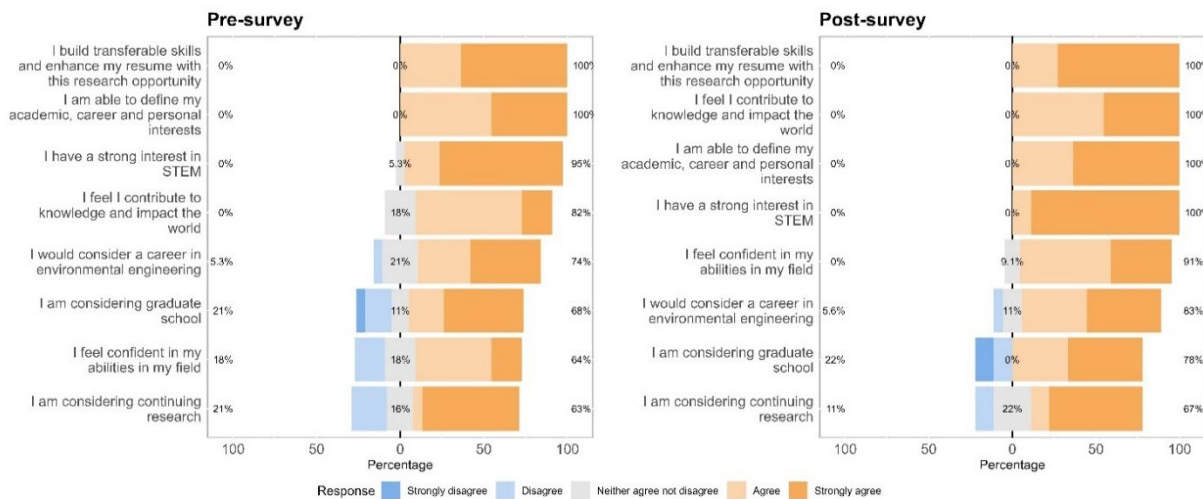


Figure 6-9. Comparison of Likert survey responses from pre-and post-surveys, focusing on STEM persistence, including career goals, graduate school intentions, and interest in engineering and research fields (n=19).

6.3.6. The cohort-based research experience enhances STEM persistence

The cohort-based research experience may have influenced the decision-making for graduate school (Figure 6-10) for 33% of the students participating in the project. In contrast, those who did not participate in the research project only stated that 11% of them were influenced

by the group project to decide on graduate school. This highlights the importance of enhancing STEM persistence through innovative research opportunities.

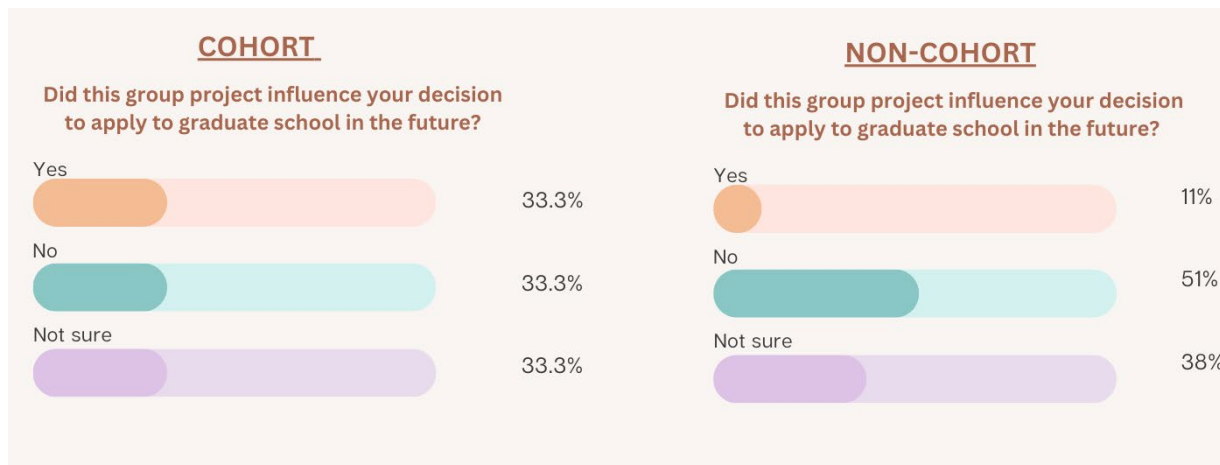


Figure 6-10. Linkert surveys from post-surveys data. Data collected from the 1-year follow-up post-survey from the cohort students (n=19) and post-survey for the class for the non-cohort students (n=47).

6.4. Discussion

Science identity is driven by both extrinsic and intrinsic attitudinal factors, a sense of community, and the ability to connect classroom learning with real-world science (Archer et al., 2010; Aschbacher et al., 2010; Carlone and Johnson, 2007; Vincent-Ruz and Schunn, 2018). Intrinsic attitudinal factors are internal beliefs and attitudes that could influence motivation. (Rittmayer and Beier, 2009). As an intrinsic attitudinal factor, self-efficacy would influence motivation and persistence in science, which would rekindle science curiosity (Simon et al., 2015). Therefore, our results (**Figure 6-4**) reveal that the cohort-based research experience can highly increase self-efficacy, thereby fostering science identity.

Moreover, a sense of belonging can reinforce extrinsic attitudinal factors, which include encouragement or feedback from peers. As results show that the cohort-based research opportunity increases a sense of belonging (**Figure 6-6**), the research experience contributes to bolstering science identity through an increased sense of community. Finally, the last factor that drives

science identity is connecting classroom learning with real-world science. The research opportunity has also shown that the method could help better understand concepts in class (**Figure 6-5**) and that students can successfully apply what they learned in class in practical settings (**Figure 6-4**). Therefore, the cohort-based research opportunity by contributing to all of these fosters scientific identity.

Moreover, results show that the research opportunity increases interest in science (**Figure 6-6**). As STEM engagement includes the level of motivation and commitment, if the students develop a strong science identity and sustained interest in science, they would be more likely to remain in STEM by engaging or pursuing STEM careers. Therefore, research opportunity seems to both contribute to increased science identity and increased interest in science, resulting in an increase in STEM engagement. On the other hand, a strong science identity and a high interest in science can also lead to higher retention rates in STEM disciplines. Thus, research opportunity could also contribute to STEM persistence, which was actually proven by the results in the 1-year follow-up study where 33% applied to graduate school because of this research opportunity vs 11% for those who did not (**Figure 6-10**). The research opportunity has increased students' interest in science, increased their confidence (self-efficacy), and strengthened their science identity, all of which are critical components of STEM engagement and are foundational for STEM retention.

Based on the group interview, there are three common ways for undergraduate students to gain research experience: research-involved classes, undergraduate research programs, and lab classes. In all these methods, undergraduates typically assist graduate students with ongoing projects or follow predefined instructions provided in the class. As a result, students often understand the overall goals of the project but may not see the final results or outcomes, particularly in lab-based classes.

In contrast, the research opportunity provided in this study was distinct because students conducted their own work rather than assisting others. This autonomy increased their motivation and interest. The cohort of students appreciated this research experience for being more personal and significant. They were involved in thinking, designing, and analyzing their projects, which allowed them to understand the rationale behind their choices and enjoy the process of exploring the "why" and "how."

Compared to their previous experiences, the students found this opportunity more enjoyable because it encouraged them to come up with solutions on the spot and innovate. They particularly valued the creative freedom in the research process, especially the creativity involved in data analysis (**Figure 6-8**). Similarly, studies have shown the importance of creative freedom in research as a factor of persistence in engineering (Atwood and Pretz, 2016; Zhou et al., 2023).

Overall, this research opportunity significantly enhanced the students' learning experience. It fostered a sense of personal involvement and creativity that students found more enjoyable, engaging, and unique compared to their prior research experiences.

6.5. Limitations and research opportunities

This study was successfully conducted in an Environmental Engineering class, but it could be applied to any STEM class. According to a post-survey, students from both the cohort and the class recommended incorporating such research experiences into other STEM classes (**Figure 6-12**). Although 80% of students in each cohort received an A and 20% received an A⁻ in the class, there was no significant improvement in the midterm and final grades between the cohort and the non-cohort groups. However, the final grades for the cohort of 2023 did show an increase compared to the non-cohort students (**Figure 6-12**). This discrepancy is likely because the class lasted 12 weeks, with the midterm occurring in week 7, around the same time as the lab work.

Therefore, the benefits of the research experience may not have been fully realized until the final grade, explaining why at least one cohort performed better than the non-cohort group.

All students enjoyed the experience, and seeing the results and the entire project come together at the end was rewarding and satisfying for them. However, feedback indicated that a 12-week quarter might be too short, especially when students need to complete data collection and analysis early on. For universities on a quarter system, it is crucial to start lab work very early to allow sufficient time for feedback and paper revisions. Additionally, creating small cohort groups can ensure full commitment and responsibility from all students, potentially increasing student participation. Finally, it is essential to implement a recruitment process. When students are highly motivated, they contribute more effectively to teamwork. Therefore, ensuring that students are selected through a thorough application process can enhance the overall success of the research experience.

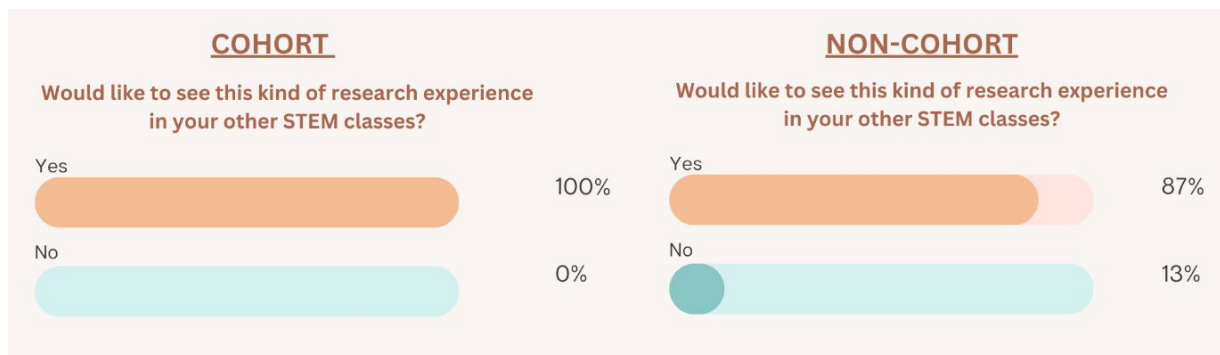


Figure 6-11. Data collected from the 1-year follow-up post-survey for the cohort (n=19) and post-survey after the class for the non-cohort (n=47).

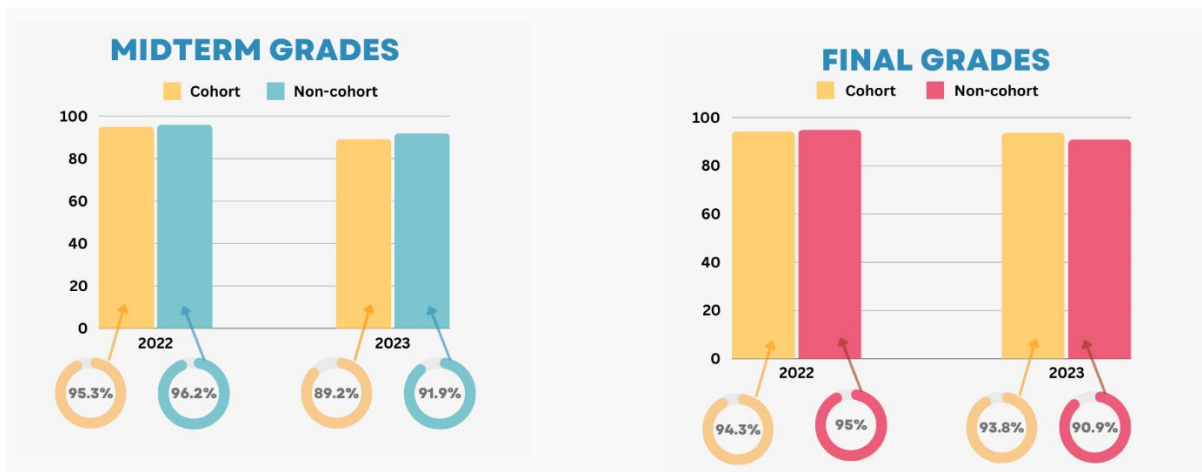


Figure 6-12. Midterm and Final grades from the 2022 and 2023 cohorts. n=19

6.6. Conclusion

The research opportunity provided in this study significantly enhances students' STEM engagement by increasing self-efficacy, sense of belonging, and interest in science, all of which are crucial factors fostering science identity. Moreover, the positive and supportive environment created by the cohort with a greater sense of community helps sustain engagement and motivation, thus improving STEM engagement and potentially improving long-term retention in the STEM field. By engaging in hands-on activities, students work in small cohorts to learn the whole research process from beginning to end. They not only build confidence in their abilities to understand and conduct scientific research but also develop a stronger identity within their group and in the classroom. As the research process is challenging and sometimes tedious, this experience has helped develop a greater sense of belonging within the group and ignited a deeper interest in pursuing scientific endeavors. These findings suggest that providing unique and immersive research opportunities is a powerful approach to enriching science education and promoting sustained student engagement in science.

6.7. Institutional Review Board Statement

The study was conducted in accordance with federal, state, local, and institutional regulations and approved by the Institutional Review Board at the University of California, Los Angeles (IRB#23-000465, certified “Exempt” on 4 May 2023).

6.8. References

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7. CHAPTER 7 – CONCLUSIONS AND RECOMMENDATIONS

7.1. Conclusions

Wildfires Impact on Water Quality: A comprehensive analysis of pre-and post-fire water quality data from 44 studies reveals that wildfires can significantly increase pollutant concentrations by two orders of magnitude but the extent to which concentrations increase varies with contaminant type, flow rate, time lag between fire and sampling, and burned areas. Nutrient levels peak within the first year after a fire and return to baseline within two years. In contrast, concentrations of heavy metals such as Pb, Cu, and Zn are highest a year after the fire. The mean concentration of PAHs increases four months post-wildfire, particularly for heavier PAHs, but remains within regulatory limits in most cases within a year following a wildfire. The study also reveals a lack of consistency in data collection and reporting, especially since most studies did not report first-flush concentration after a wildfire.

Impact of Wildfire Residues Deposition on Biofilters Functions: This study is the first to examine the potential implications of wildfire residue deposition on the physical, chemical, and biological functions of stormwater biofilters. These functions include stormwater infiltration, pollutant removal, and plant health, respectively. The results proved that biofilters can remain resilient and functional despite the deposition of wildfire residues. The deposition of wildfire residues could clog the biofilter, but the scraping of the deposited residue layer can restore its infiltration capacity. The deposited wildfire residues did not alter the removal capacity of compost biofilters for metals and *E. coli* during infiltration of stormwater. Additionally, wildfire residues did not appear to impact the germination and growth of plants in stormwater biofilters but the effects of wildfire residues on root length and aboveground biomass depends on the type of seeds and the soil composition. In general, the effect was prominent when exposed to 10% wildfire

residues instead of 5%, indicating increasing in deposition quantity may have a negative effect on plants. The plants exhibit different sensitivity to wildfire residues. Overall, the results suggest that biofilters can effectively remove wildfire residues. While the deposited residues do impact the infiltration capacity of conventional biofilters, this impact does not extend to the pollutant removal capacity or the plant functionality of these biofilters.

Design of Wildfire-Resilient Stormwater Biofilters: To improve pollutant removal, amendments are typically mixed and added to stormwater biofilters without accounting for their interactive effect. This study examines for the first time the effects of compost, the most common conventional biofilter media amendment, on the capacity of water treatment residuals (WTR), a waste-derived amendment, to remove pollutants from contaminated stormwater. The results proved that adding WTR could increase biofilters' capacity to remove wildfire-associated contaminants including *E. coli* and phosphate. Additionally, the presence of compost in the system reduced the biofilters' performance for *E. coli* and phosphate removal. These results indicate that compost should not be mixed with WTR in order to utilize the maximum benefits of WTR when implementing stormwater biofilters in wildfire-prone areas.

Innovative Cohort-Based Research Opportunity: By integrating my dissertation research into an educational initiative, this study reveals the benefits of combining a cohort-based learning community with a comprehensive research experience. Over 2 years, I formed a cohort of 10 students from diverse engineering majors and backgrounds, preferably those with limited prior research experience. These cohorts were guided through the entire research process, from hypothesis formation to publication. This approach effectively enhances their understanding of theoretical concepts learned in class through practical application and promotes STEM engagement by increasing self-efficacy, and interest in science, all of which are crucial factors

fostering science identity. Moreover, the positive and supportive environment created by the cohort with a greater sense of community helps sustain engagement and motivation, thus improving STEM engagement and potentially improving long-term retention in the STEM field. For all, this experience also increases their interest in environmental engineering and sustainability. These findings suggest that engaging students in unique and immersive research opportunities is a powerful approach to enriching science education and promoting sustained student engagement in science.

7.2. Recommendations for future studies

Water Monitoring Efforts After Wildfires: Chapter 2 underscores the urgent need for enhanced international water monitoring networks to gather essential data. Such data are crucial for developing effective watershed management strategies to protect water resources in fire-prone areas. Future studies should focus on the following recommendations:

- **Sampling Protocols:** It is essential to record the pH of water during the first flush, as this is when the impact is most severe. Extensive monitoring and reporting of these parameters could help mechanistically link changes in pH with factors such as fire severity, climate, topography, soil type, vegetation, and the time lag between the fire and sampling.
- **High-Frequency Data Collection:** Future sampling protocols should prioritize collecting first flush water samples after wildfires and obtaining high-frequency temporal data at locations both near and beyond the hazard area. This approach will provide a more comprehensive understanding of the temporal dynamics of water quality changes following wildfires.
- **Long-Term Monitoring of Organic Micropollutants:** It is recommended that future studies monitor Polycyclic Aromatic Hydrocarbon (PAH) concentrations for more than one year

to determine if levels exceed safety limits over time. Additionally, monitoring other organic micropollutants is crucial to assess their long-term impact on water quality.

- **Dissolved Nutrients:** Future research should include the reporting of dissolved nitrogen and phosphorus species, such as nitrate, ammonium, and orthophosphate. This information is vital for understanding the nutrient dynamics in post-fire runoff and their potential effects on aquatic ecosystems.

Impact of Wildfires on Mercury Fate and Transport: Wildfires result in the re-emission of some mercury to the atmosphere and the hydrologic mobilization of Hg (II) in both dissolved and particulate forms to neighboring riparian zones, wetlands, and downgradient lakes where Hg (II) can be converted to neurotoxic methylmercury. The transport of dissolved Hg (II) was observed to be strongly correlated to DOC concentration. However, Chapter 2 shows that most studies did not report supporting data such as pH, DOC, and particulate matter, all of which can affect the speciation of metals in water. DOC quality is particularly important to bind metals such as mercury, whose concentration typically increases after a fire. The results in Chapter 2 also show that Total Suspended Solids (TSS) concentration increased up to 3 order magnitude post-fire, but particulate-bound Hg (II) was observed to significantly increase due to wildfires because of elevated TSS levels. Therefore, future studies should focus on identifying the combined effects of increased mobilization of mercury and the release of nutrients and chemicals that could accept electrons to facilitate the formation of methylmercury in water bodies and its uptake in aquatic food webs.

Disinfection Byproduct Formation in Stormwater Biofilters: Most wildfire residues are deposited in surface water reservoirs such as lakes or ponds that are used as sources of drinking water. Chapter 2 highlights the increase of Dissolved Organic Carbon (DOC) concentration in

surface water after a wildfire. However, high concentrations of DOC in water sources can form toxic Disinfection Byproducts (DBPs) by reacting with disinfectants during water treatment. Adding green infrastructure could treat the post-fire runoff and potentially decrease DBP formation in the water during drinking water treatment. However, whether and how green infrastructure can affect DBP formation potential in the water after treatment has not been evaluated. Future research should examine how the design of stormwater biofilters could affect DBP formation potential in the effluent, especially regarding amendment choice.

Shift In Stormwater Biofilter Microbiome Following the Deposition of Wildfire Residues: Post-fire runoff can carry wildfire residues and deposit them on stormwater biofilters. Chapter 3 proves that wildfire residues accumulate on the top of the biofilter. Wildfire residues can release toxic heavy metals, high levels of nutrients, and organic carbon that can alter the biochemical processes of the root zones. Chapter 4 also shows that plants have varying sensitivity to wildfire residues. Therefore, future studies should examine the impacts of wildfire residues on the microbial communities of biofilters.

Moreover, despite inconclusive results on nitrate, Chapter 3 shows that deposition of wildfire residues could potentially enhance the removal of nitrate trapped in pore water between two successive rainfall events. The first flush water represented the stormwater trapped in the biofilters for nearly 15 h between simulated rainfall events, which is sufficient time to decrease nitrate by denitrification. This result might be attributed to the clogging of biofilters presented in Chapter 3, which could lower oxygen diffusion from the surface to internal pores in biofilters, thus potentially creating anoxic conditions favorable to denitrification. Future research should examine how the accumulation of deposited wildfire residues on top of biofilters as well as potential

alterations in the microbial community caused by wildfire residues impact microbially mediated biochemical processes such as denitrification.

To conclude, all these recommendations aim to enhance our understanding of the impacts of wildfires on water quality and inform the development of strategies and solutions to mitigate these effects. Implementing comprehensive monitoring and focused research efforts will help develop more effective watershed management practices that protect water resources in wildfire-prone areas. Ultimately, these efforts will contribute to protecting both the environment and public health from the adverse effects of wildfire-contaminated water.