Stormwater Treatment Media for US Navy Constituents of Interest

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Executive Summary

In response to stormwater runoff contaminant concentrations rising above regulatory limits, the Navy has requested research into innovative media that can treat contaminants of interest from stormwater through passive treatment. Currently copper, zinc, and per- and polyfluoroalkyl substances (PFAS) are the focus of Navy stormwater treatment, and in turn this research. Potential media that can be employed to remove these chemicals are provided, including discussion regarding each media's removal mechanisms and observations from peer-reviewed research into what influences their effectiveness. This information will enable the Navy to select the most appropriate and effective media for any installation's stormwater.

1 Introduction

Stormwater treatment has become increasingly important as urbanization in the United States has increased. Urbanization requires additional housing and services for an increasing population, which results in more engineered structures and impervious surfaces built over natural, open landscapes. For example, in the contiguous US between 1982 and 2012, developed land use increased from 72 million acres to 114 million acres. [1] A higher percentage of impervious surfaces significantly reduces the quantity of rainfall that will infiltrate soils and support groundwater recharge, which creates higher volumes of stormwater runoff.[2] For example, the amount of runoff generated is estimated to double when impervious area coverage increases from 0% to 10-20% of total area.[3] Higher volumes of runoff will lead to greater frequency of sidewalk and street flooding if the stormwater is mismanaged.[4] Flooding not only causes damage directly to public and private property, but it also erodes stream channels, impairs fish habitats and it has the potential to threaten public safety through collapsed roadways or drowning incidents. [5], [6] In fact, the 2021 Infrastructure Report Card released by the American Society of Civil Engineers (ASCE) states that between 2004 and 2014, flooding cost US communities $9 billion in property damage and caused 71 deaths, annually. [5]

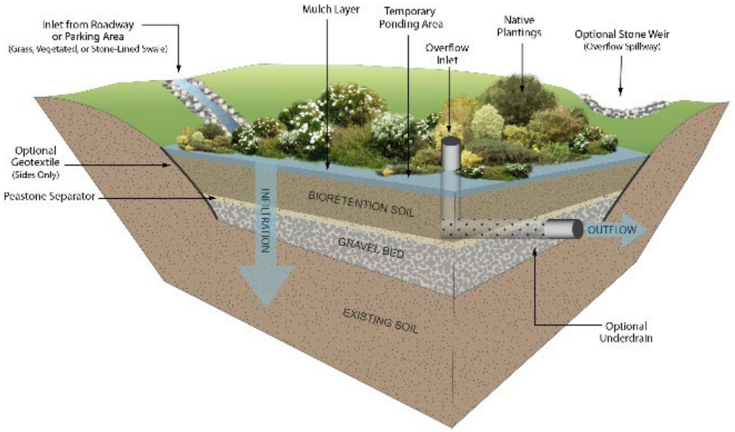

Figure 1. Components of a bioretention LID used to reduce peak flow during storm events [8]

Therefore, to better mitigate flooding impacts, stormwater management infrastructure and stormwater control measures (SCMs) were developed to convey or detain runoff.[4] In the 1940s, SCMs helped to quickly transport runoff from a site to the nearest lake or river by routing the runoff to pipes that would transport it.[4] However, the rapid transport of runoff caused erosion and flooding of downstream water bodies. As a result, future detention basins were designed to reduce the peak flow of specific storm sizes.[4] While these installations were effective in reducing stormwater flow rates, they had limited effectiveness in decreasing runoff volume which led to flooding at downstream locations; therefore, best management practices (BMPs) were developed to further retard and detain stormwater.[4], [7] Common BMPs include infiltration basins, rain gardens, porous pavement, green roofs, constructed wetlands, and grass swales.[4], [7] Generally, these systems are designed for infiltration and have a top layer of plants to provide initial filtering and a microbe growth area, followed by an organic layer (soil, mulch or compost) to support the plant roots, a layer of sand to act as a filter and support hydraulic flow through the BMP, and can even include a gravel layer and pipe to drain the system (**Figure 1**).[4], [8]

Stormwater management becomes more complex when stormwater impacts on water quality are considered. Stormwater runoff is a known pollution source for local waterbodies because of its ability to transport particles and contaminants from engineered surfaces to surface water and groundwater.[2], [9] As runoff volumes increase in response to urbanization, more contaminants are transported from contacted surfaces, which will eventually be deposited in nearby waterbodies.[3], [10] Contaminants transported by the runoff impair the water quality and often exist in concentrations that exceed the US Environmental Protection Agency's (EPA) Water Quality Criteria for aquatic life.[9]–[11] To address stormwater's contribution to water quality impairment, stormwater regulation was added to the National Pollutant Discharge Elimination System (NPDES) program.[4], [12] The NPDES seeks to address water quality issues from a variety of sources, including stormwater.[12] The program covers discharges from municipal, industrial, and construction sources.[12] The NPDES permitting process was intended to be iterative. Therefore, the initial NPDES permits issued required implementation of specific BMPs rather than numeric effluent limits, with the intent that the requirements would be updated if the BMP was ineffective.[13] In more recent years the focus has moved to "clear, specific, and measurable permit requirements and, where feasible, numeric NPDES permit provisions".[13] A 2017 review of MS4 permits provided examples of these types of permit criteria, some using a concentration or load limitation, others citing a percent reduction.[14] The numeric requirements are still not commonplace, and the ones that do exist focus more on sediments, nutrients, and biological pollutants.[14]

Concerns over increased stormwater flow and transport of harmful contaminants are not limited to cities. The US military also has concerns regarding stormwater management as performing its mission and adequate training relies on use of industrial areas, which can have even higher concentrations of contaminants than urban areas.[9] Some military bases also have NPDES stormwater permits and effluent regulations they are striving to meet. For example, in Washington the Navy installations in Kitsap, Everett, and on Whidbey Island all have MS4 permits.[15]–[17] Constituents the Navy has specific interest in include copper and zinc (which are tied to a variety of sources including industrial areas and vehicles),[9], [10], [18] and per- and polyfluoroalkyl substances (PFAS)—which comes from aqueous film forming foam (AFFF, a fire extinguishing agent used largely by the military) as well as a wide variety of common household items[19], as these contaminants are commonly found in stormwater from naval bases. While the native soil, sand, and vegetation of traditional BMPs can successfully detain and slow down stormwater and can retain large particles, they are often ineffective in removing small or dissolved particles, such as heavy metals and PFAS discussed above.[2] As these contaminants become more prevalent, reducing their concentrations in stormwater runoff before they reach downstream water bodies and drinking water sources is becoming a pressing concern.

Passive treatment of runoff contaminants through infiltrating stormwater BMPs using engineered media has proven to be effective in removing contaminants found in stormwater.[2], [20] This report will discuss copper, zinc, and PFAS, providing information on their sources in stormwater runoff, their effects on the ecosystem, and their typical concentration ranges. It will then provide a literature review of conventional and experimental media that can be employed in stormwater

BMPs, how they remove contaminants, and their effectiveness to remove the contaminants of interest. The report will also provide operation and maintenance considerations for the media discussed and a brief discussion of emerging contaminants in stormwater.

2 Constituents of Interest

Because of the varied natural and engineered surfaces stormwater makes contact with, there are a large number of pollutants that can be found in stormwater. The EPA's list of priority pollutants contains 126 pollutants that are regulated under the Clean Water Act.[21] The National Stormwater Quality Database contains data for over 100 constituents.[22] Generally, the contaminants found in stormwater can be classified as solids, nutrients, metals, biological, and trace organics.[2] **Table 1** provides examples of the contaminants in each category. It should be noted that the trace organics classification includes hundreds of chemicals, and more are being detected and identified as analytical instrumentation for aquatic contaminant characterization advances.[23] Many of the known trace organics do not require high concentrations to begin exhibiting toxicities to animals and/or humans.[23] Trace organics likely already exist in stormwater on Navy installations, however knowledge regarding their concentrations, toxicities and prevalence are still being uncovered.[23] For this report, the focus will be on copper, zinc, and PFAS which have been measured in high concentrations at US Navy installations.

Table 1 – Stormwater Contaminant Classifications

Solids	Nutrients	Metals	Biological	Trace Organics
- Sediment - Particulate matter	- Nitrogen - Ammonia - Nitrate - Nitrite - Phosphorous - Orthophosphate	- Arsenic - Cadmium - Chromium - Copper - Lead - Nickel - Zinc	- Bacteria (e.g. fecal coliforms & *E. coli*) - Viruses - Pathogens	- Pesticides - Pharmaceuticals - Personal Care Products - PFAS - Polyaromatic hydrocarbons - Perfluorinated compounds

References: [2], [23]–[26]

2.1 Copper

Copper is a metal that has a variety of uses in the US because of its durability, ductility, conductivity, resistance to corrosion, and antimicrobial properties. Copper is also a key component in its alloys, brass and bronze.[27] Uses of copper and copper alloys include building construction like plumbing, heating, and roofing products; electrical products like electrical wire, lighting, and telecommunications; brake pads and tires; consumer products such as cookware, plastic packaging, and textiles; and manufacturing.[27]–[29]

2.1.1 Sources in the Environment

Copper can enter the environment in the air, in water, or as a deposit onto land, and the sources can be natural or anthropogenic.[27] Natural sources often include any breakdown of the copper that already exists in the earth's crust and in plants, such as erosion of rocks, volcanic eruptions, and decay or burning of plants.[27] Anthropogenic, or human-driven, sources include industrial and manufacturing operations, mining, landfills and sewage, and agriculture.[27] Copper is found both as a particulate and dissolved in stormwater, with the dissolved fraction representing 30-60% of the total copper.[30] In a study by Dean et al. conducted in Baton Rouge, the dissolved fraction of copper was below 0.5 for the majority of the four storm events, and it was below 0.75

the entire study, except for one measurement.[31] Dissolved copper is most likely to be bound to organics or particulate matter; however it can also be in its ionic form (Cu^{2+}).[27], [29], [30], [32] Studies by Dean et al. Gnecco et al. found copper complexed with carbonate or organic matter to be more common than Cu^{2+} in the dissolved fraction of the stormwater.[31], [32] The ionic species will be more mobile and more bioavailable, while particulate bound species are more stable.[31]

Copper in the water cycle comes from weathering and erosion of soils, effluent from wastewater treatment facilities, mining effluent, landfill leachate, agricultural runoff, and stormwater runoff.[27] According to the Toxics Release Inventory (TRI) which tracks release data for a portion of manufacturing facilities in the US, the total on-site release of copper and copper compounds to air, land, and water in 2021 was 156 million pounds.[33] The TRI estimates that 181,000 pounds of copper and its compounds are released to surface water each year and another 123,000 pounds are released to municipal treatment facilities.[27] While the direct release of copper to surface water represents a small portion of total release, it is important to note that the other release areas indirectly contribute to stormwater as copper depositions can be mobilized and transported by stormwater to waterbodies.[10]

There are several sources of copper in stormwater runoff. Copper can derive from building envelopes and roofs as well as debris from vehicles.[10], [18], [27], [34] Brake pads on vehicles are also a known source of copper. It is used as a friction material in the brake pads to minimize squeaking and provide for smooth braking and is approximately 5% by weight of the brake pad. When a vehicle brakes, the pad comes into contact with the rotor and small amounts of the brake pad are deposited on the road. Hwang et al. analyzed heavy metal pollution from vehicles and identified that brake pads account for 15 to 57% of the copper in watersheds in San Francisco and the Puget Sound.[10] In fact, vehicles are estimated to contribute 48% of the copper in stormwater runoff, and while a large part of that can be attributed to brake pads, they aren't the only source of copper on vehicles.[10] The Washington State Department of Ecology (WDOE) performed an analysis of copper sources and release rates in urban runoff, using a 7.2 square mile in Thurston county.[35] They found that brake pads contributed 58.7% of the copper load from the study area and that parking lots, vehicle exhaust, and road wear contributed 6.6%, 2.3%, and 0.53% respectively.[35] Buildings also contributed to the copper load through roofing materials (22.3%), treated lumber (6.2%), and siding materials (2.8%).[35] Davis et al. found that brick and wood siding contributed more copper to runoff than concrete, metal, and vinyl.[36] They also reported high concentrations of copper from commercial roofs, which was assumed to be due to copper sheeting in flashing, trim, and gutters.[36] Their findings were that copper from buildings represents 31% of the total copper load to stormwater runoff and copper from vehicles represents 47%.[36]

Concentrations of copper in our environment have a large variation depending on where they are and their sources. **Table 2** provides a summary of copper concentrations.

Table 2 – Copper Concentrations in the Environment

Location	**Range**	**Mean**	**Reference**
Outdoor Air	0.02-0.79 µg/m^3	NR	[29]
Soils and Sediment	0.001-200,000 ppm	30 ppm	[29]
Ground Water	0.2-98.4 µg/L	NR	[29]
Surface Water	0.02-69,000 µg/L	NR	[29]
Drinking Water	0.009-2,450 µg/L	NR	[29]
Food	0-135 mg/kg	NR	[29]
Stormwater (EPA Urban National Runoff Program)	1-100 µg/L	18.7 µg/L	[27]
Road Dust	69-910 mg/kg	252 mg/kg	[10]
Stormwater	0.3-9,500 µg/L	NR	[2], [10], [22], [30]

NR=Not reported

2.1.2 Harmful Effects

Although copper is an important micronutrient, too much can be harmful. In humans, oral exposure most commonly affects the gastrointestinal and the liver system. Symptoms can include nausea, vomiting, abdominal pain, diarrhea, jaundice, and liver impairment.[27]–[29] Copper has adverse effects on aquatic organisms. For example, lower fish populations and lessened diversity in benthic species has been noted when it is present in water. It can be neurotoxic and damages the sense of smell in fish which reduces their ability to avoid predators.[27], [30] Because of these effects, water quality guidelines have been developed by the EPA for copper concentrations in water.[13] This information is presented in **Table 3**. Numerical effluent requirements for copper are not yet common in NPDES permits.[14] One example that does address copper is from the San Diego Region which provides a stormwater action level of 127 µg/L as well as Total Maximum Daily Loads (TMDLs) for few, specific sub-basins.[37] These permits only cover specific outfalls and point sources which can be controlled for their sites and aren't able to address non-point sources.

Table 3 – EPA Water Quality Criteria for Copper

Criteria Description	**Concentration**	**Reference**
Water Quality Human Health Criteria	1300 µg/L	[27], [38]
Water Quality Aquatic Life Criteria – Acute	4.8 µg/L	[11], [27]
Water Quality Aquatic Life Criteria – Chronic	3.1 µg/L	[11], [27]

2.2 Zinc

Zinc is a metal that naturally occurs in the earth's crust.[39] It is most often used in conjunction with other metals as a protective coating to prevent rust and corrosion or to create metal alloys which can be used for die-casting, electronics, and the US penny.[39], [40] Zinc is also mixed with other elements to create zinc compounds, including zinc sulfide, zinc oxide, zinc sulfate, and zinc chloride. These compounds are used in products such as paints, ceramics, rubber, wood preservation, textiles, and pharmaceutical products. Zinc is a common micronutrient in food.[39]

2.2.1 Sources in the Environment

Zinc can enter the environment through air, water, or land deposits, primarily through anthropogenic sources and less so through natural sources. The most significant anthropogenic sources to the environment are mining operations, metal production, fertilizers, and wood preservatives.[39] The natural sources include particles from weathering and forest fires.[39] Zinc in stormwater will be present in a particulate or a dissolved form. Dean et al. found that the dissolved fraction of zinc ranged from 0.05 up to 0.7, with the fraction being under 0.25 for half of the total duration of the four storms.[31] Hwang et al. reported that the dissolved fraction of zinc in stormwater is generally above 50%.[10] Zn^{2+} is the predominant dissolved species, constituting between 65% and 94% of the total dissolved zinc concentration in both the Dean et al. and Gnecco et al. studies.[31], [32] Zinc will also be more mobile in its ionic form compared to its particulate bound form.[31]

Zinc release to the water cycle comes from urban runoff, mine drainage, and wastewater effluents.[39] According to the TRI, the total on-site release to air, land, and water of zinc and zinc compounds facilities in 2021 was 462 million pounds.[33] Of those releases, TRI estimates that 181,000 pounds of zinc and its compounds are released to surface water each year and another 123,000 pounds are released to municipal treatment facilities.[33]. Similar to copper, zinc releases to air and land contribute indirectly to the concentrations in stormwater, as precipitation or atmospheric deposition removes zinc from the air and stormwater is able to transport it to waterbodies.[39], [41]

The zinc in urban runoff primarily comes from the galvanized metals in the roofs and siding of buildings and a variety of vehicle sources, including tires, brakes, oil leaks, and emissions.[9], [10], [18], [39] The contribution of tires to zinc contamination in stormwater runoff has been of particular interest to researchers. Tires are comprised of 1.5% zinc by weight in the form of zinc oxide (ZnO) which is used to add strength to the rubber, improve resistance to heat and abrasion, and protect the tire from UV light.[10] The average passenger vehicle and heavy-duty vehicle tires lose 4.96 lbs and 19.8 lbs, respectively, of their weight during their lifetime.[10] Estimates based on tire wear rates are that 8,700–10,000 tons of zinc are released each year in the US.[10], [42] The WDOE included analysis of zinc sources and release rates in their stormwater study in Thurston County and found that tire wear accounted for 12.6% of the zinc load in stormwater with other vehicle contributions coming from parking lots (13.4%), brake wear (2%), and vehicle exhaust (0.8%).[35] WDOE also included building materials in their study, noting contributions from siding materials (15.6%), chain-link fencing (4.1%), roofing materials (4%), roof gutters (1.1%), and HVAC (1%).[35] A significant source found by WDOE was moss control, or fungicide application, accounting for 42.8% of the zinc loading to stormwater in the study area.[35] It should be noted that this estimate came from limited data on purchase of these products and application rates in the study area, which may not be representative of a larger study area. The loading estimates from Davis et al. found high concentrations of zinc in runoff from brick, painted wood siding, and galvanized roof material.[35] Siding estimates contributed 58% of the total zinc load, while roofing contributed 7%.[35] In addition, tire wear was estimated to contribute 25% of the total zinc load.[35] This study did not consider zinc loading from fungicides. Both studies align with the estimate from Hwang et al. that tire wear contributes 10-30% of the total zinc load in stormwater.[10] In both studies, zinc loading was an order of magnitude higher than copper loading.[10], [35] A study conducted for the City of San Diego Storm Water Division noted crumb rubber, made from recycled tires and commonly used in synthetic turf, was a significant contributor potentially adding 800 mg/m^2 of synthetic turf each year.[43]

Concentrations of zinc in our environment have a large variation depending on where they are and the sources that contributed. **Table 4** provides a summary of zinc concentrations.

Table 4 – Zinc Concentrations in the Environment

Location	Range	Mean	Reference
Outdoor Air	0.01-0.16 μg/m^3	NR	[40]
Soils and Sediment	5-2,900 ppm	60 ppm	[40]
Surface Water	0.02-1.2 mg/L	NR	[40]
Drinking Water	0.003-2.0 mg/L	NR	[40]
Road Dust	212-1560 mg/kg	252 mg/kg	[10]
Stormwater	0.4-29,000 μg/L	NR	[2], [22], [39], [43]

NR=Not reported

2.2.2 Harmful Effects

Similar to copper, while maintaining appropriate levels of zinc is important for proper health, high levels of zinc exposure can be harmful causing gastrointestinal impacts, including cramps, vomiting, nausea, and diarrhea.[39], [40] Longer term exposure can also cause anemia, pancreas damage, and decrease in HDL cholesterol levels.[39], [41] Long term exposure at lower levels can also inhibit copper absorption and create a copper deficiency.[39] Zinc is also known to be toxic to aquatic life and impair water quality.[9], [10] EPA has established water quality standards for zinc, as presented in **Table 5**. Zinc is one of the toxic pollutants that can be covered in NPDES stormwater permits, but like copper, is not commonly included. For example, of the seven general MS4 permits reviewed in 2017, only one has a numeric limitation for zinc.[14] The San Diego Region permit lists a stormwater action level of 976 μg/L and has a TMDL for one sub-basin.[37] A review of Washington State NPDES permits indicates that none of the municipalities have zinc effluents requirements, however the general industrial permit has a benchmark for zinc concentration, as well as effluent limits for landfills and discharges to impaired waters.[44]

Table 5 – EPA Water Quality Criteria for Zinc

Criteria Description	Concentration	Reference
Water Quality Human Health Criteria	7400 μg/L	[38]
Water Quality Aquatic Life Criteria – Acute (Freshwater, Saltwater)	120 μg/L, 90 μg/L	[11]
Water Quality Aquatic Life Criteria – Chronic (Freshwater, Saltwater)	120 μg/L, 81 μg/L	[11]

2.3 PFAS

Per- and polyfluoroalkyl substances (PFAS) are a group of over 9,000 fully or partially fluorinated hydrocarbon compounds. [19], [45] They are synthetic compounds and do not occur in nature.[19] Their structure has a characteristic carbon backbone with hydrogen atoms either partially or completely replaced by fluorine, creating polyfluoroalkyl substances and perfluoroalkyl substances, respectively.[46] The carbon-fluorine bonds within the fluoroalkyl chain are chemically and thermally stable, and impart high degrees of hydrophobicity to the compounds.[47], [48] The functional group that is attached to the fluoroalkyl chain is hydrophilic and can have a positive or negative charge.[19], [46], [47] An image showing the basic structure of PFAS is provided in **Figure 2**.

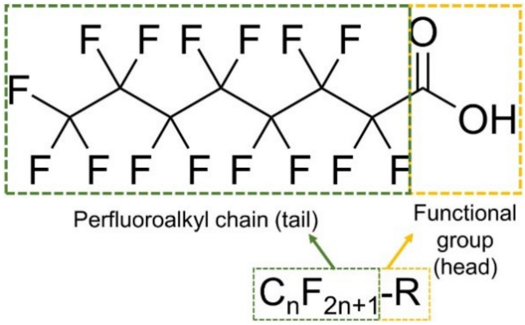

Figure 2. Basic Structure of a perfluoroalkyl substance [49]

PFAS can be generally categorized as perfluoroalkyl acids (PFAAs) or polymeric polyfluoroalkyl precursor compounds. [47] Two types of PFAS that have had the most research and regulatory interest are perfluorosulfonic acids (PFSAs) and perfluorocarboxylic acids (PFCAs).[47] Both are PFAAs and are considered long-chain when they have six or more (PFSA) or seven or more (PFCA) carbon atoms.[46] There are two PFAS that have been the most commonly used and most often detected and, in turn, have the most research available: perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS).[19] Although they are currently the most researched of the PFAS, additional studies are being performed on short-chain (between four and seven carbons) and ultra short-chain (3 or less carbons) PFAS, which are often used as a replacement for long-chain PFAS in commercial manufacturing.[49] **Figure 3** provides an overview of PFAS classifications. The stability and combination of hydrophobicity and hydrophilicity make PFAS useful in a variety of applications, often as a surfactant repelling oil and water.[46], [50] PFAS use began in the 1950s and in the 1960s, 3M and the US Navy developed aqueous film forming foam (AFFF).[51], [52] They found that the addition of PFAS lowered the surface tension, which allowed the AFFF to spread and control fires more efficiently.[51] Other uses for PFAS include adhesives, cosmetics, food packaging, paper products, cookware, stain & water repellants for textiles, coatings, paints, cleaning products, and pesticides.[19], [53] They are also used in the manufacturing of semiconductors, lubricants, chemicals, electronics, and plastic and rubber.[19], [50]

2.3.1 Sources in the Environment

PFAS has been detected in the air, water, and soil around the chemical plants that manufacture and use these substances, as well as in varied distribution around the globe to include isolated areas like the Arctic, suggesting transport through atmospheric deposition.[19], [50] PFAS is stable due to the C–F bonds, has low volatility due to its ionic groups, and is persistent in soil and water.[50] PFAS transport depends on the specific substance composition. Linear PFAS tends to exist in soil, while branched isomers are more prevalent in water.[19] Less hydrophobic short-chain PFAS ($n < 6$) are more commonly found in surface water, while the hydrophobic long-chain PFAS bioaccumulate in fish or are found in sediment.[19] Point sources for PFAS entering the environment include industrial facilities, wastewater treatment plants, landfills, and firefighting training areas.[19], [53] Non-point sources include atmospheric deposition, runoff, precipitation, and breakdown of consumer products (e.g., Teflon coating on cookware entering wastewater).[19]

PFAS can also enter the environment through the degradation of the polymeric precursor compounds.[50] A precursor is a substance that can transform into long-chain PFCAs or PFSAs after being released into the environment.[52] Once they degrade into these forms they are at their most stable and will not naturally degrade any further.[52], [53] This is important to understanding the occurrence of PFAS in the environment; however, further research is required to better understand their degradation pathways.[52] Even PFAS transported as waste from manufacturing processes to wastewater treatment plants, landfills, and incinerators do not fully break down and instead, they remain in their source waters where they can re-enter the environment.[19] Effluent from wastewater treatment plants as well as the biosolid waste generated from sludge processing are also important sources of PFAS to source water.[19] Conventional primary and secondary treatment processes of physical separation and biological nutrient removal are not currently designed to treat PFAS, so the substances either remain in: the wastewater effluent (which exits at outfalls into nearby rivers and lakes); the wastewater that recirculates at the plant and is added to the influent with additional PFAS; or the sludge which is processed and landfilled or applied as a biosolid to land as fertilizer where the PFAS can be transported by stormwater to surface water.[19], [50], [53] As mentioned earlier, AFFF is another well-known contributor to PFAS in source water. The military is the largest consumer of AFFF with release sites including fire training areas, emergency response locations, airports and hangars, and locations where testing, maintenance, and storage of AFFF occurred.[51], [52] The AFFF was most commonly released in liquid form directly into the environment, without any collection or treatment.[51], [52] It is expected that higher concentrations of PFAS will be found in surface and ground water near industrial facilities, military bases, and wastewater effluents.[50]

Concentrations of PFAS found in the environment vary widely. Concentrations for air are generally below 15 pg/m^3 and below 50 ng/L (ppt) for surface water.[54] A summary of ranges of PFOA and PFOS concentrations in various media is provided in **Table 6**. As of August 2017, the Department of Defense (DoD) has identified 401 installations where PFAS release was known or suspected and tested 2,668 ground water wells and 2,542 drinking water systems, finding 90 installations, 1,621 ground water wells, and 36 drinking water systems with PFAS concentrations above 70 parts per trillion (ppt).[50], [55] Section 2.3.2 will explain the significance of this threshold. PFAS concentrations in the measured drinking water systems ranged from 0 to 7,910 ppt and the groundwater monitoring wells ranged up to 10,970,000 ppt across the DoD.[55] The Navy installations measured drinking water systems containing PFAS ranging from 71 to 8100 ppt and groundwater monitoring wells ranging up to 8,000,000 ppt.[55] Anderson et al. reported that PFOS was the most frequently detected of 16 PFAS measured across sampling sites on 10 US military installations. [52] Similar to the DoD report, PFOS was found with concentrations up to 8,970,000 ng/L in surface water and 4,300,000 mg/L in ground water at sites with known AFFF release.[52] In the same study, PFOA was found with concentrations up to 210,000 ng/L in surface water and 250,000 ng/L in ground water. [52] While PFOA was detected less frequently than PFOS, it was still found in 88% or more of the surface and ground water samples. [52]

Table 6 – Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS) Concentrations in the Environment

Location	PFOA Range	PFOS Range	Reference
Outdoor Air	1.22-900,000 pg/m^3	0.46-9.8 pg/m^3	[50]
Dust	2.29-9,818 ng/g	4.56-18,071 ng/g	[50]
Soil	0.00017-140 ppb	0.0002-9700 ppb	[50]
Surface Water	0.1-18,200 ng/L	0.08-51,000 ng/L	[19], [50]
Ground Water	ND-1,836,000 ng/L	19-324,000 ng/L	[19], [50]
Ocean Water	88-192,000 pg/L	8-57,700 pg/L	[50]
Drinking Water	0.0023-100 ppb	NR	[50]
Stormwater	0.51-30.6 ng/L	2.6-42.5 ng/L	[56]–[58]
Road Dust	0.2 ng/kg	0.2-1.4 ng/kg	[59]

NR=Not reported

2.3.2 Harmful Effects

Human exposure to PFAS can occur through water, food (e.g., transfer from packaging), dust, as well as transfer from clothes and carpets treated with PFAS.[50] Exposure to PFAS has been associated with a variety of health impacts including hypertension during pregnancy, increased cholesterol, thyroid disorders, liver damage, decreased antibody production, immunosuppression, and a decreased response to vaccines.[19], [50], [53], [54] Severity depends on exposure duration, frequency, and concentration.[19] In addition, there is a possibility of effects such as breast cancer, ulcerative colitis, asthma, additional risk of infections, diabetes, and developmental impacts, although this evidence is more limited.[53] In 2017 the International Agency for Research on Cancer (IARC) added PFOA to the list of Group 2B agents, meaning that it is possibly carcinogenic to humans due to increased occurrences of kidney and testicular cancer in people with high levels of exposure.[50], [60], [61] Specific impacts to aquatic organisms include mortality, cellular membrane damage, impaired growth, reproductive failure, disruption of hormones, immune and nervous systems, and liver and kidney damage.[53] These negative health impacts may be exacerbated by the fact that PFAS are able to bioaccumulate in humans and animals.[19]

Regulations and guidelines regarding PFAS exposure are continuing to develop. In 2016, the EPA Lifetime Health Advisory (LHA) for PFOA and PFOS combined was 70 ppt.[50], [62] In 2022, the EPA released interim LHAs for PFOA and PFOS, 0.004 ppt and 0.02 ppt, respectively.[62] In March 2023, the draft EPA Primary Drinking Water regulation for PFAS was published which, if approved, will set the limits for PFOA and PFOS at 4 ppt and add a hazard index limit for a combination of four other PFAS.[63] The EPA has also released a draft of their Aquatic Life Water Quality criteria, proposing acute exposure limits of 49 mg/L for PFOA and 3 mg/L for PFOS and chronic exposure limits of 0.094 mg/L for PFOA and 0.0084 mg/L for PFOS.[64] The EPA has not added PFAS effluent limits to their NPDES stormwater permits yet and is working to incorporate it into their industrial and wastewater permits.[65]

3 Stormwater Treatment Media

There are a variety of media that have been used in stormwater BMPs. As discussed previously, early BMPs were focused on managing the flow of stormwater, making hydraulic conductivity a critical factor in BMP design and media selection. As focus has shifted to water quality of stormwater runoff, the media's ability to remove pollutants from stormwater has become important. While their varied physiochemical properties determine their affinity for specific pollutants, most media used in stormwater BMPs relies on similar mechanisms for pollutant removal. These mechanisms commonly include filtration, sedimentation, and sorption and other processes discussed below:[66]–[68]

Filtration occurs when contaminants are trapped in pore spaces between media particles or are strained by the media surface. [34]

Sedimentation occurs when contaminants settle out of solution due to gravitational forces and larger densities and masses than water.[34]

Sorption refers to processes that bind the contaminant to the media which includes adsorption, electrostatic interaction, ion exchange, complexation, precipitation, absorption, and hydrophobic interaction.[34], [66], [68], [69]

> **Adsorption** is a physical process where the contaminant attaches to the outer surface area or the surface area in the pores of the media particle.[69]
>
> **Absorption** refers to the contaminant being captured on the surface of the media and then diffusing into the inner structure or pore spaces of the media.[67]
>
> **Electrostatic interactions** are based on the surface charges of the contaminant and the media. Positive and negative charges will attract and like charges will repel.[66], [69]
>
> **Ion exchange** occurs when the contaminant releases a cation or anion and trades it with a proton or electron from a functional group on the media.[66], [69] The trading of cations and protons is referred to as cation exchange and a media's capacity for this trade is measured

as cation exchange capacity (CEC).[69] A high CEC indicates the media can hold a large amount of cations.[70]

Complexation occurs between the surface functional groups of the media and the contaminant. In this process, the contaminant interacts with the functional group to create a multi-atom structure via covalent bonds or weak interactions (e.g., ionic bonds).[66], [69]

Precipitation occurs when the reaction of the contaminant and a functional group result in the formation of a particulate.[66], [69]

Hydrophobic interaction refers to overlapping of hydrophobic (or water-hating) domains within the contaminant and the media structures. Interactions between these hydrophobic domains will help minimize their interaction with water molecules.[66], [67]

Figure 3 provides a visual representation of these sorption mechanisms. While this figure presents mechanisms specific to contaminant removal by biochar, the mechanism functions the same way regardless of the media being used. Together these mechanisms facilitate the removal of contaminants by the media discussed in this section. The combination of mechanisms and their removal effectiveness will differ with each media. In addition, the removal effectiveness can widely differ due to the varied conditions (experimental set-up, number and concentration of influent stormwater constituents, etc.) of the studies presented in this section. The results of column studies are commonly reported as breakthrough, which is how much of the contaminant was present in the effluent, compared to the influent concentration. Columns that achieved 0% removal (or 100% breakthrough) and 100% removal (or 0% breakthrough) during the experiment have annotations to indicate how quickly breakthrough was achieved for additional context. For media in this section that was studied as an amendment, a weight or volume percentage will be provided if applicable. It should be assumed that the other media in the filter was sand unless otherwise specified.

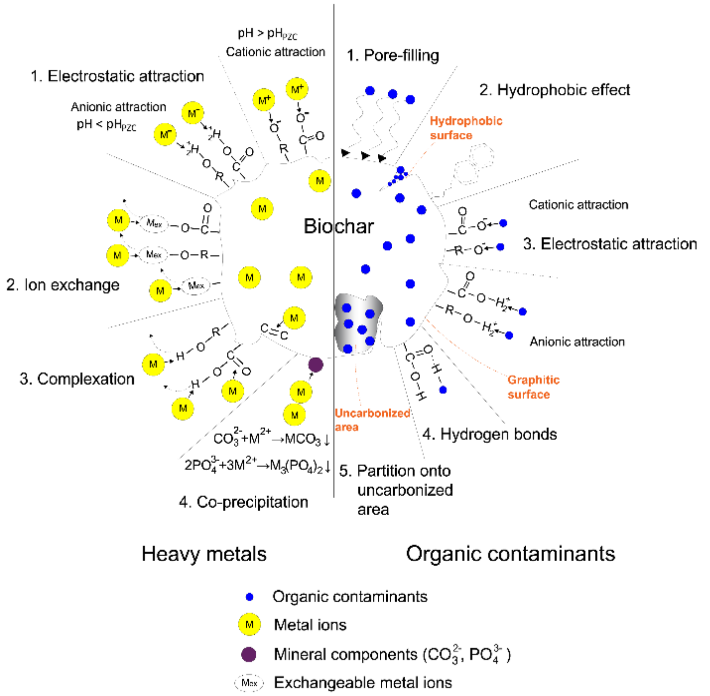

Figure 3. Sorption mechanisms of metals and trace organics on biochar. Similar mechanisms are expected to occur for porous, hydrophobic media or media with properties like biochar [72]

3.1 Field-Ready Medias

For the purposes of this paper, "field-ready" will refer to medias that have been used traditionally in stormwater treatment, are well-researched, and have commercial availability.

3.1.1 Sand

Sand is a silica-based material that comes from the weathering and eroding of rocks.[36], [71] The diameter of the grains ranges between 0.06 mm and 2 mm.[72] Sand is a commonly used media in passive stormwater treatment because of its high hydraulic conductivity which allows for a large amount of stormwater to be conveyed with a relatively small footprint.[2], [73] The hydraulic conductivity of sand found in stormwater treatment studies ranges from 0.3 to 0.69 cm/s[74], [75] and the saturated hydraulic conductivity ranged from 0.08 to 0.28 cm/s[76], [77]. The pollutant removal mechanisms in sand layers are filtration and sedimentation, making it an effective tool for removing solids from stormwater.[2], [73] While sand is considered to be ineffective in removing dissolved contaminants, studies show varied results.[2], [73] A summary of the findings from relevant studies is provided in Table 7.

Table 7 – Stormwater runoff contaminant removal by sand as reported in the literature

Study	**Configuration**	**Stormwater Type**	**Copper (% removed)**	**Zinc (% removed)**	**PFAS (% removed)**
Vu [73]	Column	Synthetic	NI	0%-5%	NI
Ulrich [78]	Column	Synthetic	92%	99%	NI
Barrett [79]	Field	Real	50% (total) 6% (dissolved)	80% (total) 62% (dissolved)	NI
Barrett [80]	Field	Real	14%-59%	35%-87%	NI
Reddy [74]	Batch	Synthetic	5%-43%	43%-58%	NI
Pritchard [75]	Column	Synthetic	35%-85%	25%-85%	PFOA: 0% PFOS: 0%
Ray [76]	Batch	Synthetic	10%-60%	10%-50%	PFOA: 0%-10% PFOS: 0%-15%
	Column		50%-90%	70%-100%	PFOA: 0%-10% PFOS: 0%-40%

NI=Not included in study

Removal mechanisms of the metal contaminants included electrostatic attraction and complexation on the sand surface.[74], [75] It is also possible that removal occurred when dissolved copper or zinc sorbed to sediment that then settled out or was filtered by the media.[79] Influent concentration did not have a significant effect on zinc removal, while increasing concentration did result in lower removal efficiencies of copper.[74] Similarly, the presence of dissolved organic carbon (DOC) affected copper removal, but did not have a significant impact on zinc removal.[76] Speciation also influences how effective heavy metal removal is, as particulate copper and zinc experience higher removal by sand than the dissolved fraction.[79] Sand is ineffective in removing PFAS from stormwater, experiencing rapid breakthrough and can even release effluent concentrations that are higher than the influent if precursors transform during the process. Based on these results, sand can remove some of the copper and zinc load in stormwater, especially if those loads are particulate-bound. However additional materials will be needed to effectively remove the dissolved copper and zinc, and to remove PFAS.

3.1.2 Compost, Mulch, and Woodchips

3.1.2.1 Compost

Compost is a humus material that is formed from the decomposition of organic waste.[81] It is commonly used in stormwater treatment because the high humic content is beneficial for removal and immobilization of metals.[2], [82] In addition, it is low-cost, reduces waste, and improves soil quality.[82] The main removal mechanisms in compost layers are complexation, adsorption, and precipitation for metals and hydrophobic interactions for organic compounds.[2], [83] Adsorption is considered the dominant mechanism for copper.[83] Similar to sand, studies assessing the stormwater treatment capability of compost provide varied results. A summary of the findings from relevant studies is provided in **Table 8**.

Table 8 – Stormwater runoff contaminant removal by compost as reported in the literature

Study	Configuration	Stormwater Type	Copper (% removed)	Zinc (% removed)	PFAS (% removed)
Silvertooth[83]	Column- 100% by vol	Synthetic	>97%	NI	NI
		Real	>90%	0%-100%^{1}	NI
	Field- 100% by vol*	Real	-5%-45% (diss) 5%-50% (total)	34%-58% (diss) 25%-62% (total)	NI
Sun[82]	Column- 5% wt**	Synthetic	93%-100%	89%-100%	NI
Hale[84]	Batch	Synthetic	NI	NI	PFOS: 28%-34%
Borthakur[85]	Column- 30% by vol	Synthetic	NI	NI	PFOA: 74%

NI= Not Included; diss=dissolved

*Includes gravel at top and bottom and geotextile in at compost and gravel interfaces

**Includes sand 90% wt and IOCS 5% wt

^{1}Reached 50% breakthrough after 80% of duration had elapsed, reached 100% breakthrough at the end

Removal of dissolved copper was less than total copper, indicating particulates were removed by filtration.[83] Zinc removal in the column studies of Silvertooth et al. appears to have a wide variance, but it should be noted that removal was 100% until half of the experiment duration had elapsed and did not reach 50% breakthrough until the final fifth of the experiment.[83] Removal of PFAS varied (10%-100%) and was noted to increase with the length of the C-F chain (4-10).[85] Copper removal was impacted by the presence of DOC, which complexes with copper, and lessens sorption capacity, as evidenced by the same column studies and the field studies that followed.[83] This impact was not seen for zinc because it does not have as strong of an affinity for DOC, so it was more easily adsorbed.[83] Compost did not have high remobilization for copper or zinc (<0.74%), however it did release a large amount of DOC.[82] The release of DOC has the potential to remobilize contaminants that were bound to the DOC.[82], [84] It also has the potential to release cations (e.g. calcium) and nutrients (e.g. nitrate and phosphate).[83], [84] While compost demonstrated an ability to remove copper, zinc, and some PFAS from stormwater, the effects of potential leaching from compost should be considered.

3.1.2.2 Mulch

Mulch is another organic media that is used in stormwater treatment. It is generally composed of wood or tree bark, often from waste generated by the lumber and paper industries, and has a high humic content that will interact with aqueous metals to create a strong, stable bond.[70], [86] Similar to compost, the effectiveness for metal removal, as well as being readily available and low-cost, has made them a common addition to stormwater treatment systems.[70] Mulch generally uses ion exchange, adsorption, and electrostatic interactions to remove metals from stormwater.[70], [86] A summary of the findings from relevant studies is provided in **Table 9**.

Table 9 – Stormwater runoff contaminant removal by mulch as reported in the literature

Study	**Configuration**	**Stormwater Type**	**Copper (% removed)**	**Zinc (% removed)**	**PFAS (% removed)**
Jang[70]	Batch- hardwood	Synthetic, single metal	69%-72%	61-66%	NI
		Synthetic, multi metal	22%-55%	8%-17%	NI
Ray[86]	Column- hardwood (25%-75% by vol)	Real, spiked	100%	NI	NI
	Column- pine (25%-75% by vol)		66%-96%	NI	NI
	Batch- hardwood		100%	>99%	NI
Ray[87]	Batch- hardwood	Synthetic	0%-87%	43%-81%	NI

NI= Not Included

In the study from Jang et al., the heavy metal sorption was compared between three types of mulch: cypress, hardwood, and pine.[70] The authors expected that a mulch that creates a more neutral pH in the water around it and has a higher CEC will result in mulch retaining more cations.[70] The hardwood mulch had the highest pH (7.43), CEC (42.3 meq/100g), and specific surface area (25-32 m^2/g), so it was not a surprise that it also had the highest sorption capacity.[70] Similarly, Ray et al. found that a higher amount of functional groups, specifically humic acid and fulvic acid, resulted in greater removal of copper by hardwood than by pine.[86] This result indicated that mulch removes copper primarily through ion exchange.[70] A later study by Ray et al. found that removal of copper and zinc by mulch was reduced with lower influent concentrations.[87] In addition, it was noted that copper was more strongly bound to hardwood mulch than zinc, with 2% and 10% desorption, respectively.[87] Results differ regarding how multiple contaminants in stormwater impact removal by hardwood mulch. [70], [86] The multi-metal results from Jang et al. indicate competition for sorption sites amongst the metals, however Ray et al. found that the sorption capacity of hardwood mulch was not impacted by a mixture of metals and organics.[70], [86] Based on these results, mulch is a beneficial addition to a BMP treating stormwater with heavy metals.

3.1.2.3 Woodchips

Woodchips are the by-product of land clearing operations and are readily available and low-cost.[88], [89] Woodchips are used in stormwater treatment, as well as wastewater and agricultural drainage treatment, most commonly for nitrate removal.[2], [90] In addition to biodegradation that occurs for nitrate removal, woodchips use adsorption, ion exchange, and filtration to remove contaminants from stormwater.[88] A summary of the findings from relevant studies is provided in **Table 10**.

Table 10 – Stormwater runoff contaminant removal by woodchips as reported in the literature

Study	**Configuration**	**Stormwater Type**	**Copper (% removed)**	**Zinc (% removed)**	**PFAS (% removed)**
Ashoori[90]	Column*	Synthetic	75%-99%	-13%-78%	NI
Seelsaen[91]	Batch	Synthetic	88%	90%	NI
Teixido[77]	Column**	Synthetic	86%-93%	59%-62%	NI

NI= Not Included

*pre-treated with mixture of sand and 5% wt iron

**pre-treated with mixture of sand and 5% wt iron, then through woodchips, finally through filters that were 50% MnO sand and 50% a sand and 1% wt biochar mixture

The presence of organic polymers like lignin and tannin on the woodchips make it likely that ion exchange is the dominant removal mechanism of woodchips.[91] In addition, the addition of woodchips may contribute to metal removal through precipitation of sulfide metals.[90] Zinc is considered to be highly mobile, making it more difficult to remove from stormwater, which could explain the variability in zinc removal.[90] Using woodchips as a pre-treatment to an infiltration system was beneficial, increasing the removal of both copper and zinc.[77] Like compost, woodchips are likely to release a sizable amount of DOC, potentially over 3000% of the influent DOC concentration in the stormwater runoff.[90], [91] While woodchips demonstrated an ability to remove copper and the potential to remove zinc, the effects of potential leaching should be considered.

3.1.3 Carbonaceous Materials

Carbonaceous materials refers to a group of media that are carbon-based including activated carbon, biochar, carbon nanotubes, and graphene.[69] These media are popular in stormwater treatment because of their high content of organic carbon, large specific surface area, high amount of reactive functional groups, and porous nature.[2], [69] These properties allow them to have high sorption capacities without using a large media mass.[92] Of the carbonaceous materials, activated carbon (AC) and biochar have been studied the most for applications in stormwater treatment.[2] Activated carbon is produced through pyrolysis from a wide variety of materials, including wood, coal, lignite, coconut husks, and peat and then activated with steam, oxygen, or strong acids.[69], [75] Biochar is produced through the pyrolysis or gasification of biomass.[75] Biomass generally comes from wood or waste from agriculture or food industries.[75], [93] Activated carbon has been used in water treatment applications for decades, however biochar has more recently been tested in these applications because it shares many properties with activated carbon, but is less expensive to produce and uses more benign feedstock materials.[94] It should be noted that while biochar is more economical, it does have variations in its properties due to the biomass source and production process.[2], [94] Pyrolysis uses temperatures from 300°C-800°C and a minimal oxygen supply.[94] Gasification uses temperatures in excess of 700°C and oxygen or steam.[94] Generally, a higher process temperature produces biochar with larger surface area and pore volume, higher carbonized fraction, pH, hydrophobicity, and volatile content, and a decrease in cation exchange capacity and functional groups.[93], [94]

The biomass source, or feedstock, can impact the pore structure and pore sizes in biochar.[94] The chemical makeup of the feedstock can also impact the content of volatile matter, ash, and carbon in biochar, as well as its CEC.[93] The sorption capacity of biochar for heavy metals has been demonstrated to increase as the density of oxygen-containing functional groups on the biochar surface increases.[94], [95] Ulrich et al. notes that high-temperature biochar are more hydrophobic which aids in the removal of trace organics, while low-temperature biochar are more hydrophilic which makes them better for removal of metals.[78] The impact of these properties is also reflected in the findings of relevant studies, presented in **Table 11**.

Table 11 – Stormwater runoff contaminant removal by activated carbon and biochar as reported in the literature

Study	Configuration	Stormwater Type	Copper (% removed)	Zinc (% removed)	PFAS (% removed)
Ulrich[78]	Column- biochar (6.7% wt)	Real, spiked	>94%^	>99%^	NI
	Column- GAC (6.7% wt)	Real, spiked	87%	97%	NI
Ashoori[90]	Column- biochar (33% wt)*	Synthetic	89%-95%	28%-80%	NI
Sun[82]	Column- biochar (5% wt)**	Synthetic	80%-100%	52%-100%	NI
Pritchard[75]	Column- biochar (2.4%-3% wt)***	Synthetic	80%-100%	20%-90%	PFOA: 25%-95% PFOS: 55%-98%
	Column- RAC (3.3%-4% wt)****		75%-100%	45%-95%	PFOA: 75%-95% PFOS: 85%-99%
Ray[76]	Batch- biochar	Synthetic	100%	65%-95%	PFOA: 85%-99% PFOS: 55%-99%
	Column- biochar (3% wt)		95%-100%	85%-100%	PFOA: 98%-100% PFOS: 98%-100%

NI= Not Included, GAC= granular activated carbon, RAC= regenerated activated carbon, ^=concentration below limit of detection (1 mg/L)

*pre-treated with mixture of sand and 5% wt iron, biochar in column mixed with woodchips

**includes 5% wt IOCS

***includes two columns: (1) sand and 2.4% wt biochar, and (1) sand, 25.4% wt zeolite, and 3% wt biochar

****includes two columns: (1) sand and 3.3% wt RAC, and (1) sand, 18.4% wt zeolite, and 4% wt RAC

Metals are primarily removed through ion exchange and surface complexation, making surface functional groups on biochar and AC key to their efficient removal.[76] This was supported by Sun et al. who noted that compost outperformed biochar in their study and attributed the difference to compost having a larger amount of oxygen-containing functional groups present than biochar.[82] Both biochar and AC amendments were very effective in removing copper and zinc and provided significant improvements in removal compared to their unamended counterparts.[78], [82], [90] Copper removal efficiency tended to be higher for copper than zinc for biochar and AC.[75], [76], [78], [82], [90] Comparing the two amendment types, Ulrich et al. found that biochar had higher metal removal than GAC while Pritchard et al. found that RAC outperformed biochar.[75], [78] The presence of DOC did not significantly impact the sorption of biochar in the batch or column studies conducted by Ray et al.[76]

Trace organics are primarily removed through electrostatic interaction, hydrophobic interaction, and adsorption, which are governed by the porous nature, high surface area, and hydrophobicity of the media.[76] This is especially true for PFAS, where the hydrophobic interactions between the carbonaceous media and the hydrophobic carbon chain of PFAS have to overcome the electrostatic repulsion between negatively charged media and the negatively charged functional group of PFAS.[75], [76] A longer PFAS carbon chain is more hydrophobic than a shorter carbon chain, which is why biochar and activated carbon tend to remove longer chain PFAS better than shorter chain PFAS.[75] Pritchard et al. noted that biochar removed PFAS better in the beginning of their study, however RAC performed better across the duration of the study.[75] The presence of DOC reduced PFOS removal and had a negligible impact on PFOA removal in batch studies, however in column studies, neither PFOS or PFOA removal was notably impacted.[76]

Due to biochar's ability to retain water, its use often results in lower hydraulic conductivity, which leads to clogging and poor BMP performance.[76] To minimize this impact, biochar is generally used as an amendment to a high hydraulic conductivity media, like sand.[75] Using biochar and AC as media amendments was common in the studies presented in **Table 11**. Even with this consideration, media mixtures with biochar and AC had hydraulic conductivities 6%-91% lower than their unamended counterparts.[75], [76], [90] The highest decrease came from studies using small particle sizes (0.6 mm and 0.1-0.3 mm) for their biochar and AC amendments.[75], [76], [90]

Overall, carbonaceous materials have been shown to improve pollutant removal when added to stormwater BMPs, especially for organic contaminants, and can do so without significantly lowering hydraulic conductivity.[75], [96]

3.1.4 Plants

Plants are commonly the top layer of a bioretention system.[97] Not only do they have an aesthetic benefit, but they also improve hydrological performance by slowing down runoff, preventing washout of media layers, improving hydraulic conductivity, and retaining stormwater.[98], [99] Plants have also demonstrated the ability to uptake and manage pollutants.[98], [99] Using plants and their associated microbes to uptake, immobilize, transform, reduce, and remove contaminants from the environment is referred to as phytoremediation.[98]–[100] A visual representation of these mechanisms is provided in **Figure 4**.

Phytoremediation occurs through different mechanisms than were discussed earlier in this section and include phytoextraction, phytostabilization, phytofiltration, phytovolatilization, and phytodegradation.[98] Phytoextraction refers to the uptake of pollutants by the roots and their translocation and accumulation in the leaves and stalks.[98], [100], [101] Phytostabilization refers to the roots and substrate stabilizing or immobilizing the pollutants, limiting their bioavailability.[98], [100], [101] Phytofiltration refers to the removal of pollutants through sorption.[98] When phytofiltration occurs through plant roots, it is called rhizofiltration.[100], [101] Phytovolatilization refers to the transformation of a contaminant to a modified form and its release via transpiration to the atmosphere.[98], [100], [101] Phytodegradation refers to the degradation and use of organic contaminants by enzymes in the plant tissue.[98], [100], [101]. The numerous plant species each use a select combination of the mechanisms of phytoremediation to uptake a large variety of contaminants, contributing to their removal from stormwater.

The amount of uptake depends on the species of plant, so choosing the species that exhibits high levels of removal for the contaminant of interest, as well as one that is native to the area, is suitable for the design of the treatment system, is resistant to pests, and is easy to cultivate and harvest is important.[97]–[99], [101] Phytoextraction is one of the main mechanisms used in removal of heavy metals.[98] Ali et al. shares factors that make a plant a suitable choice for phytoextraction including, high biomass and growth rate, a wide and highly branched root system, high accumulation and translocation of the metals of interest, and a tolerance to the effects of metals.[98] Plants that have adapted to naturally survive, grow, and reproduce are referred to as metallophytes.[98], [101] Metallophytes can be classified as excluders (plants that tolerate heavy metals and accumulate them in the roots, limiting translocation to the leaves), accumulators (plants that accumulate heavy metals in their biomass in high concentrations), and indicators (plants that accumulate heavy metals to the concentration found in the substrate).[98], [101] Hyperaccumulators are plants that have uptake and distribution throughout the entire plant to levels far greater than found in the substrate.[98], [101] Finding and employing the

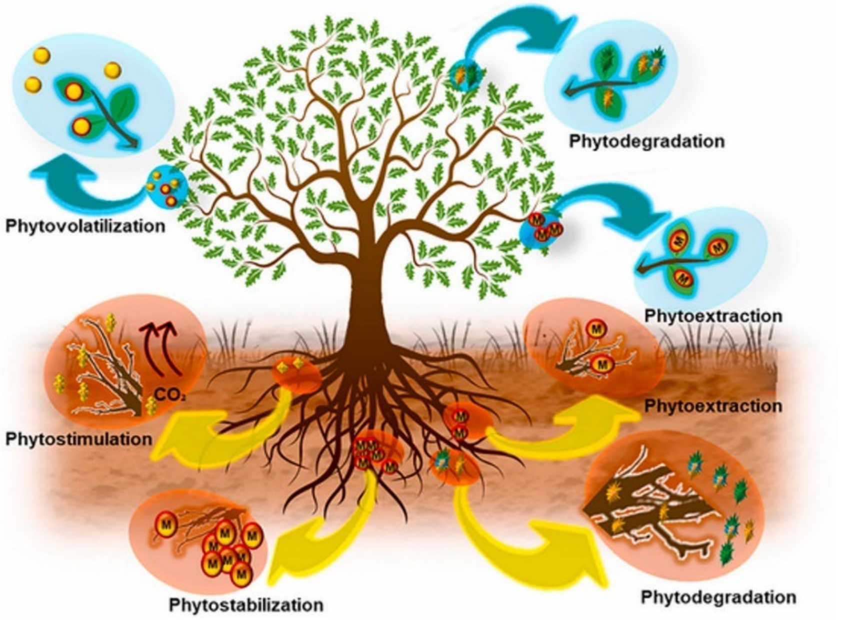

Figure 4. Removal mechanisms of phytoremediation[99]

hyperaccumulators that are effective for the contaminants in the stormwater of interest is key to successful phytoremediation.[98]

There are at least 37 and 18 species of plants that have been identified to be hyperaccumulators of copper and zinc, respectively.[101] Mehmood et al. provides recommended species for phytoremediation of copper and zinc, among other contaminants, and Kafle et al. provides further suggestions of plant species based on phytoremediation mechanism and contaminants.[99], [102] Chu et al. reports that plants in recent studies retained between 0.6% to 30.4% of copper and 1.4% to 21.9% of zinc across various studies and that one study by Sun and Davis saw over 90% of metals removed in the bioretention system, with 2%-11.6% of the removal attributed to plants.[97]

Phytoremediation has also been studied for the removal of PFAS.[100] PFAS enters plants through sorption in the root system.[103] Specifically, plants that are submerged—which would be common in passive treatment as stormwater is captured—predominantly use phytofiltration to remove PFAS, whereas plants that are not submerged engage in phytoextraction.[103] Root systems impact the removal of PFAS as plants with large root surface areas, fast root growth, and thicker taproots experienced higher PFAS uptake.[100], [104] Studies of constructed wetlands have found PFAS removal to range from 50%-96% for the combination of soil and plants.[100], [104] In a study of PFAS uptake by Awad et al., PFOA accumulation in roots was lower than the PFOS accumulation and the PFOA accumulation in the shoots was higher than the PFOS accumulation.[104] This was attributed to PFOS having higher hydrophobicity and interacting more with molecules in the plant roots, which limits its transport into the plant biomass.[104] The three plant species studied provided 5%-53% PFOA removal and 5%-42% PFOS removal was 53%.[104]

It has also been noted that microbes can enhance pollutant removal as well as support plant growth in phytoremediation.[99] Other amendments that can be added to enhance phytoremediation include sugar beet residue, sewage sludge, paper waste, and biochar.[102] Plants are an effective way to increase copper, zinc, and PFAS removal in a stormwater BMP.

3.2 Composite and Emerging Medias

While field-ready medias have the ability to remove pollutants from stormwater, their performance in BMPs can be improved through the inclusion of more reactive engineered media. To address this, researchers have been developing composite media.[2] Composite media combines the properties of two media, often with one coating the other, to create one media that uses the physiochemical properties of both to be more effective in removing multiple contaminants.[2] Some of the most promising composite medias will be discussed in this section. In addition, emerging media that are being researched and not commonly used in stormwater treatment will be presented.

3.2.1 Iron Oxide Composites

Iron is commonly used to enhance contaminant removal from stormwater, as an amendment or as a coating on media like sand and biochar.[23], [66], [74], [105] Iron oxides have large surface areas and surface functional groups that enable heavy metal removal through complexation, precipitation, ion exchange, and adsorption.[74], [106] Results from relevant studies using iron oxide composites are provided in Table 12.

Table 12 – Stormwater runoff contaminant removal by iron oxide composites as reported in the literature

Study	Configuration	Stormwater Type	Copper (% removed)	Zinc (% removed)	PFAS (% removed)
Reddy[74]	Batch	Synthetic	96%-100%	96%-99%	NI
Ernst[106]	Column- GFH	Synthetic	65%-100%	0%-100%[1]	NI
	Column- E33 (100% wt)	Synthetic	20%-100%	0%-100%[2]	NI
	Column- E33* (50% by vol)	Synthetic	45%-100%	0%-100%[3]	NI
	Column- GFH	Real	5%-100%	20%-100%	NI
Liu[105]	Column- IOCS	Synthetic	5%-100%	0%-100%[4]	NI
	Column- IOCS (87% by vol)**	Synthetic	90%-100%	0%-100%[5]	NI
Ma[107]	Column- Magnetite***	Synthetic	NI	NI	PFOA: 63%-64% PFOS: 53%-57%

NI= Not Included, GFH= granular ferric hydroxide, E33=Bayoxide (a granular iron-based media), IOCS= iron-oxide coated sand

*Includes 50% by vol concrete

**Includes 13% by vol crushed cementitious material

***Includes two columns: (1) 50% by vol of gravel and magnetite and (1) 33% by vol gravel and 67% by vol magnetite

[1] Reached 50% breakthrough after 5% duration elapsed and 100% breakthrough after 50% duration elapsed

[2] Reached 50% breakthrough after 5% duration elapsed and 100% breakthrough after 10% duration elapsed

[3] Reached 50% breakthrough after 20% duration elapsed and 100% breakthrough after 50% duration elapsed

[4] Reached 50% breakthrough after 5% duration elapsed and 100% breakthrough after 30% duration elapsed

[5] Reached 50% breakthrough after 20% duration elapsed and 100% breakthrough after 70% duration elapsed

Iron oxide composites are effective in removing copper and zinc from stormwater. Copper removal is inhibited by increased alkalinity and the presence of DOC, while zinc removal is negligibly impacted.[106] Both metals experience increased removal under high runoff pH conditions.[106] This was confirmed when runoff from a highway, with high pH, alkalinity, and DOC concentration, experienced lower copper removal and higher zinc removal than in experiments with synthetic runoff.[106] Liu demonstrated the importance of pH for metal removal when adding a cementitious material layer below the iron-oxide coated sand (IOCS) layer resulted in greatly improved breakthrough curves for copper and zinc.[105] In another study, concrete added upstream of an iron oxide column also increased the pH and improved the breakthrough curve.[106] These materials provide calcite to the treatment system, which raises pH and can contribute to metal sorption through metal-hydroxide precipitation.[106] Ma et al. found that iron oxide can also remove PFAS, providing an additional 31% and 36% removal of PFOS and PFOA, respectively, compared to the unamended columns.[107] The removal was attributed to acetate from PFAS serving as an electron donor to iron, creating a PFAS radical that could more easily be degraded, and to microbial activity in the substrate.[107] Iron oxide composites are an effective media to remove copper, zinc, and PFAS from stormwater.

3.2.2 Manganese Oxide Composites

Manganese (Mn) oxide is an oxidant that naturally occurs in soil.[2], [66] Its use in composite media for stormwater treatment has grown due to its large surface area and negative charge.[106] It can enhance removal of organics through oxidation and adsorption, as well as the removal of metals through complexation and electrostatic interactions.[2], [77], [106] Oxidation is one component of an oxidation reduction reaction, also known as a redox reaction, where electrons are transferred between two compounds.[108] The oxidized compound loses electrons and the reduced compound gains electrons.[108] As indicated earlier, Mn oxide is an oxidant, meaning that it oxides another compound and gains those electrons.[108] Redox reactions degrade the pollutant, making it easier to remove from stormwater.[109], [110] Results from relevant studies are provided in **Table 13**.

Table 13 – Stormwater runoff contaminant removal by manganese oxide composites as reported in the literature

Study	**Configuration**	**Stormwater Type**	**Copper (% removed)**	**Zinc (% removed)**	**PFAS (% removed)**
Ernst[106]	Column- MnO_2	Synthetic	0%-100%[1]	0%-100%[2]	NI
Liu[105]	Column- MOCS	Synthetic	10%-100%	0%-100%[3]	NI
	Column- MOPM		0%-100%[4]	0%-100%[5]	NI
	Column- MOCM		65%-100%	45%-100%	NI
Teixido[77]	Column- MOCS (50% by vol)*	Synthetic	81%-88%	56%-60%	NI
Charbonnet[110]	Batch	Synthetic	100% (no DOC) 48% (w/ DOC)	52% (no DOC) 69% (w/ DOC)	NI
	Column- MOCS		95%-100% (no DOC) 10%-90% (w/ DOC)	0%-95% (no DOC) 0%-75% (w/ DOC)	NI

NI= Not Included, MnO_2=granular material with manganese dioxide coating, MOCS=manganese oxide coated sand, MOPM=manganese oxide coated polymeric media, MOCM=manganese coated cementitious material

* pre-treated with mixture of sand and 5% wt iron, then through filters that were 50% MnO sand and 50% a sand and 1% wt biochar mixture

[1] Reached 50% breakthrough after 5% duration elapsed and 100% breakthrough after 55% duration elapsed

[2] Reached 50% breakthrough after 5% duration elapsed and 100% breakthrough after 30% duration elapsed

[3] Reached 50% breakthrough after 5% duration elapsed and 100% breakthrough after 15% duration elapsed

[4] Reached 50% breakthrough after 55% duration elapsed and 100% breakthrough after 60% duration elapsed

[5] Reached 50% breakthrough after 20% duration elapsed and 100% breakthrough after 25% duration elapsed

Metal removal in the above studies was attributed to electrostatic interactions, adsorption, complexation, and precipitation.[77], [105], [110] The importance of electrostatic interactions was shown through better performance of Mn oxide composites that had a lower point of zero charge or were in a higher pH stormwater, both of which resulted in a more negative surface charge.[105], [110] Liu found that copper was better removed than zinc, likely because copper was present in both particulate and dissolved forms which could be removed through complexation and filtration, while zinc was mostly present in a dissolved form, which could only be removed by complexation.[105] Similarly, the manganese coated cementitious material (MOCM) had the best performance of the Mn oxide composites studied by Liu because the media employed adsorption with the Mn oxide coating and precipitation/filtration with the cementitious media.[105] The MnO_2 studied by Ernst et al. did not perform as well as the granular ferric hydroxide (GFH) (**Table 12**), experiencing breakthrough much earlier.[106] The Mn oxide had a lower capacity for both copper and zinc than the iron oxide, which was likely due to the iron oxide having a ten-fold higher specific surface area.[106] Teixido et al. found that the MnO and biochar amended columns (**Table 13**) removed 5% more copper and 20% more zinc than the control columns.[77] The best performance in the study was from the amended and pretreated columns (**Table 12**), which removed 5% more copper and 2% more zinc than the amended columns without woodchip pre-treatment(Table 13).[77]

The density of Mn oxide coating was reduced during some experiments, which was not able to be reversed with regeneration.[77], [110] The reactivity of the Mn oxide coating was also reduced during the experiments due to the presence of DOC, which reduced the manganese to Mn^{2+} that competed with the metals for sorption sites.[77], [110] The reactivity of the coating was able to be restored using MnO^{-}_{4} to return the oxidation state to pre-treatment levels[77], or by using hydrochloric acid to desorb nearly all of the adsorbed copper and zinc.[110] A biochar layer ahead of a Mn oxide composite would remove DOC and improve performance.[77], [110] The presence of DOC had an impact on metal removal, especially for copper.[110] This was likely due to the Mn^{2+} competition already mentioned, as well as DOC complexing with metals, making them unavailable for complexation.[110] Manganese oxide composites can remove copper and zinc from stormwater and should be studied to determine efficiency of PFAS removal.

3.2.3 Polymer Composites

Polymer is a broad term that refers to chemical compounds of linked monomers, which are atoms or molecules.[111], [112] Natural polymers include cellulose, pectin, gelatin, and collagen.[113] Synthetic polymers include polyvinyl chloride, polystyrene, polyethylene, and polyester.[111], [114], [115] They have been used in water and wastewater treatment to adsorb contaminants, as coagulants and flocculants to encourage the formation of flocs, in ion exchange resins, and in membrane filtration.[2], [113] Their functional groups are able to remove a variety of contaminants from water and because they can be synthesized inexpensively, they are an appealing option for stormwater treatment.[2] Often coated on clay surfaces, the polymers create a positively charged surface and add hydrophobic domains to the net negative surface charge and hydrophilic of the clay particle. This surface modification enhances the removal of trace organics and organic matter, alone or complexed with other contaminants.[2], [76] Primary removal mechanisms of polymer composite media include ion exchange, hydrophobic interactions, and electrostatic interactions.[76] Two polymers that have been studied in stormwater treatment applications are poly(diallyldimethylammonium) chloride, referred to as PDADMAC, and protonated poly(4-vinylpyridine-co-styrene, referred to as PVPcoS.[76] Ray et al synthesized composites with PDADMAC and PVPcoS on montmorillonite clays, and Borthakur et al synthesized a composite in situ, by running synthetic stormwater spiked with PDADMAC through an existing biofilter with a sand and compost mixture.[76], [85] The results of these studies are provided in **Table 14**

Table 14 – Contaminant Removal by Polymer Composites

Study	Configuration	Stormwater Type	Copper (% removed)	Zinc (% removed)	PFAS (% removed)
Ray[76]	Batch- PDADMAC	Synthetic	90%-98%	45%-70%	PFOA: 10%-100% PFOS: 40%-100%
	Column- PDADMAC (3% wt)		75%-90%	70%-90%	PFOA: 0%-10% PFOS: 0%-15%
	Batch- PVPcoS		90%-100%	10%-70%	PFOA: 5%-100% PFOS: 50%-100%
	Column- PVPcoS (3% wt)		80%-95%	75%-100%	PFOA: 0%-100%[1] PFOS: 60%-100%
Borthakur[85]	Column*	Real	NI	NI	PFOA: 98% Other PFAS: 85%-95%

NI=Not included

*Includes 70% by volume sand, 30% by volume compost, and 10 g/L PDADMAC applied through stormwater

[1] Reached 50% breakthrough after 15% duration elapsed and 100% breakthrough after 65% duration elapsed

Metals removal primarily occurred during ion exchange with surface functional groups on the composite media and complexation with the clay.[76] PVPcoS provided greater metals removal than PDADMAC.[76] PFAS removal occurred through electrostatic interactions of the contaminant functional group with PDADMAC and through hydrophobic interactions of the C–F chain with PVPcoS.[76], [85] The electrostatic interactions resulted in greater removal for shorter chain PFAS than for longer chain PFAS.[85] The addition of DOC to stormwater resulted in a decrease in PFAS removal due to DOC competition for sorption sites (>90% was removed for both clay composites without DOC, <70% was removed with DOC present).[76] The impact of DOC on metals removal was not as significant, with minimal changes in copper removal for both polymer composites and minimal and a small increase in zinc removal, for PDADMAC and PVPcoS, respectively.[76] Hydraulic conductivity of polymer composite columns was comparable or slightly better than unamended columns, and was significantly higher than biochar amended columns, indicating clogging would not be increased with the addition of polymer to biofilter media.[76], [85] PDADMAC successfully replenished removal capacity of the sand/compost biofilter and did not degrade under intermittent flow conditions, suggesting polymer composite media can have a functional lifetime of many years without needing to be replaced.[85] Polymer composites are an effective media for removing copper, zinc, and PFAS.

3.2.4 Crab Shell

Crab shell, sourced from food industry waste, has been studied as a potential sorbent media for stormwater treatment.[116] Crab shells contain calcium carbonate and chitin, which together facilitate removal of copper and zinc through precipitation.[106], [116] The results from Vijayaraghavan et al. are shown in **Table 15**.

Table 15 – Contaminant Removal by Crab Shells

Study	Configuration	Stormwater Type	Copper (% removed)	Zinc (% removed)	PFAS (% removed)
Vijayaraghavan[116]	Batch	Synthetic	93%	100%	NI
	Column		99.3%	99.8%	NI

NI= Not Included

The calcium carbonate within the crab shells binds with metals which initiates the precipitation of metal carbonates.[116] The formed carbonates are then adsorbed by the chitin in the crab shell.[116] Increases in effluent pH were observed, likely due to the disassociation of calcium carbonate and the subsequent reaction of carbonate and water to form bicarbonate and hydroxide.[116] While the heavy metal removal by crab shells was significant, it was also noted that large quantities of calcium and magnesium leached during the study.[116] Crab shells are an effective media for copper and zinc removal, however the pH change and ion leaching need to be considered.

3.2.5 Foam Glass

In a study by Lee et al., foam glass media created from waste glass and a foaming agent was used as the filtration media in an upflow column experiment.[117] Foam glass is highly porous and was expected to remove particulates well.[117] The column used two layers of foam glass media as a replacement for traditional sand filter media.[117] A summary of the results are presented in **Table 16**.

Table 16 – Contaminant Removal by Foam Glass

Study	Configuration	Stormwater Type	Copper (% removed)	Zinc (% removed)
Lee[117]	Column	Synthetic	Particulate: 69%-74% Dissolved: 5%-11%	Particulate: 74%-83% Dissolved: 9%-14%

The particulate fraction of each contaminant was well removed and the dissolved fraction was minimally removed, similar to sand.[117] Examination of the media surface revealed that the contaminant was primarily angular particles which were retained in the pores of the foam glass, confirming that filtration was the primary removal mechanism.[117] Foam glass is an effective media for particulate copper and zinc removal, however the dissolved fraction will require additional media for removal.

4 Emerging Contaminants - Microplastics

Plastic has become a dominant material in a wide variety of products because it is lightweight, durable, and inexpensive to produce.[118] Plastic debris comes from littering, tire wear particles, solid waste, roads, and atmospheric deposition.[119] Left in the environment, these particles can break down into smaller particles, called microplastics (MPs).[119], [120] Microplastics are fragments, fibers, and granules from plastic debris that are greater than 1 μm and under 5 mm in length.[118]–[121] MPs can also come directly from consumer products, like cosmetics, coatings, cleaning products and medicines, in the form of capsules, pellets, fibers, and microbeads, or they come from larger plastic debris as previously mentioned.[118], [121], [122]

Microplastics can be ingested, inhaled, and absorbed by the skin.[122] Potential human health effects from exposure to MPs include lung inflammation, respiratory disease, liver effects, cardiovascular disease, allergies, and digestive issues.[122], [123] Health effects to aquatic organisms include inflammation, tissue damage, reduced feeding, development issues and reduced growth, and impaired reproduction.[124], [125] In addition, MPs can transport harmful chemicals, called secondary toxins, including heavy metals, pesticides, antibiotics, polyaromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs), along with their toxicity.[123] Research into the acute mortality of adult coho salmon has identified 6PPD-quinone, a transformation product of 6PPD found in tire wear microparticles, as the primary toxicant.[126] Further research will be required to determine the full effects of microplastic exposure.

Stormwater is a known transport mechanism for MPs, especially for debris on the road like tire wear particles.[120], [127] In fact, a study of the Charleston Harbor in South Carolina reported that 90% of the MPs present in the harbor were tire wear particles from local highways.[127] In a study by Werbowski et al. microplastics concentrations ranged from 1.1 particles/L to 24.6 particles/L in stormwater samples from the San Francisco area.[120] Among these particles, rubbery fragments and fibers were the most common types.[120] The concentration of microplastics has been found to have a positive correlation with industrial land use and percent impervious land area.[120] As discussed earlier, secondary toxins like heavy metals can be present on MPs in stormwater.[119], [123] For example, MPs that have been photodegraded – which is expected after prolonged exposure to the environment – have been shown to be capable of transporting 2.4 µg – 21.7 µg of heavy metals per gram of MPs.[119], [127] Copper and zinc are of interest to the Navy due to their prevalence, and based on these findings, it is likely that there is a high concentration of microplastics present in stormwater runoff from Navy installations as well.

Studies regarding the removal of microplastics often consider the effectiveness of the infiltration system as a whole, rather than comparing various media. MPs are a type of suspended solid and are primarily removed via filtration, the same mechanism as total suspended solids (TSS).[128] Recent studies of infiltration systems show MP removal efficiency ranges from 84%-96%.[129] A bioretention cell composed of mulch, soil, and vegetation in Canada produced an 89% reduction in microplastics.[128] In case studies of a rain garden with a mix of sandy loam, clay, and compost as its media, the microplastic concentration was reduced 85%-98%.[120], [130] A filtration system in Sweden was built with sand and biochar filters side by side receiving stormwater after screening and coarse filtration occurred.[131] Across three storm events, the sand portion removed 96% of the influent MPs and the biochar portion removed 93%.[129] Across these studies, it was noted that characteristics, such as size and shape, of the MPs in the stormwater impacted removal efficiency.[129] Larger particles were better removed than smaller particles and fragments were better removed than fibers, which are narrow and can flow through pores.[120], [129], [131] Even with these differences, infiltration systems employing media discussed in Section 3 including sand, compost, mulch, vegetation, and biochar are an effective method for removing microplastics from stormwater.

5 Operation and Maintenance Considerations

Choosing the appropriate media mixture does not guarantee a BMP will be effective, but considering operational and maintenance aspects during design and implementing a maintenance plan can improve the effectiveness and lifespan of a BMP. The sand filters studied by Barrett et al required approximately 49 hours of maintenance each year.[79] Maintenance for these filters consisted of inspections, media maintenance, debris removal, structural repairs, pump replacement, and dewatering.[79] These maintenance efforts are not limited to sand filters and reflect some of the most common considerations across a variety of SCMs: clogging and inspection and cleaning of outlet structures.[34], [75]–[77], [132]

Clogging, a common occurrence in poorly maintained SCMs, comes from accumulation of sediments and pollutants on the media particles.[75], [132] A clogged SCM indicates low hydraulic conductivity and low infiltration rate, making it less effective for pollutant removal and shortening its useful life.[76], [130]–[132] Media selection can impact this: smaller pore sizes capture more suspended solids, but they also clog more easily, which should be considered in design of an

SCM.[131] Similarly larger sized particles can improve hydraulic conductivity, but will sacrifice some contaminant removal.[76]

Clogging can be reduced by including a pretreatment stage to remove larger contaminants from the stormwater, by replacing, tilling, or covering the top layer of soil, or with regeneration/bioremediation.[73], [97], [130], [132] Pretreatment, like a forebay, has been shown to remove solids and heavy metals from stormwater, lessening the load the filter media receives and increasing the media's useful life.[97] Estimates of media lifetime through modeling based on anticipated contaminant loads and media capacities can indicate the required frequency of media replacement or regeneration.[73], [97] Regeneration is beneficial when the sorption capacity of the treatment media has been exhausted, which is expected over time after repeated sorption cycles.[69] Regeneration of carbon-based materials can be facilitated with acid or alkali solutions, restoring 50%-95% of their sorption capacity.[110] There is also evidence that electro-regeneration of organic removal capacity of carbon-based materials can be effective, restoring up to 90% of the capacity.[133] To be cost-effective, regeneration needs to be performed in situ, which is often done by adding a chemical that will coat the existing media.[85] Borthakur et al. studied the potential for PFAS-exhausted sand and compost to be regenerated in situ with PDADMAC and found that the PDADMAC restored PFAS removal to 85%-100%.[85] The authors also found that PDADMAC was not easily degraded and it did not increase clogging, which had been a concern.[85] Regeneration feasibility can be impacted by the regeneration method and BMP design.[110] Clogging can also be a concern for the inlet and outlet structures of an SCM which can be blocked with debris that prevents stormwater flow and elevates water levels.[132] Not only will elevated water levels harm vegetation, but if they rise enough, they can top the treatment system and release stormwater without any treatment.[132] Regular inspections and cleaning should be included in the maintenance plan to reduce this risk.[132]

Choosing vegetation for an SCM can impact the maintenance requirements. During establishment, it needs to be monitored so that dead plantings can be removed, replanting can occur, and weeds or less desirable plants don't grow.[132] Constructed wetlands discussed by Blecken et al saw that the arrival of vegetation that attracts mosquitoes was correlated with an increase in mosquito population.[132] To minimize this risk, vegetation like Pontedaria cordata and Sagittaria latifolia are used because they grow quickly (and will outcompete the less desired species) and they repel mosquitoes.[132] As discussed earlier, hyperaccumulators have a high capacity to remove heavy metals from stormwater. Their inclusion, especially for species that remove multiple metals, can lower maintenance costs compared to planting a variety of species to capture each contaminant.[97] Lifespan of the SCM can be increased by harvesting, if the contaminant is predominantly in the foliage, or replanting if it accumulates in the roots.[34], [97], [132] Although this process avoids the risk or re-release from plant decay to the SCM, care must be taken during the disposal process to ensure contaminants aren't released back into the environment during that process.[132]

Successful operation of the SCM will require inspections to find any areas in need of care and reasonable access for the maintenance team as well as any equipment they may need.[132] Inspections should be conducted regularly to ensure proper functioning and should include key structures, vegetation, particle accumulation, infiltration rate, rodent or pest damage, and environmental damage.[132] Planning for inspections and maintenance upfront will help to ensure efficient operation of the SCM and to fully realize its water quality and safety benefits.[132]

6 Conclusion

Stormwater management can be a challenge, balancing traditional water quantity concerns with the more recent focus on water quality. This challenge is only compounded by the seemingly infinite contaminants that can be present in stormwater, some of which are resistant to degradation and removal. Copper, zinc, and PFAS have all been found in stormwater at concentrations well above recommended water quality and health advisory limits and have impacts ranging from gastrointestinal distress to neurotoxicity and mortality. The NPDES permitting process sets stormwater treatment standards across the country, including Navy installations. Passive treatment methods offer a cost-effective method to improve stormwater quality and there are a wide variety of media that can be employed in these systems. Traditional media like sand, compost, mulch, woodchips, activated carbon, biochar, and vegetation can provide contaminant removal, as can more innovative media like composites with iron oxide, manganese, and polymers, as well as crab shells and foam glass. The removal efficiency ranges and keys to efficient removal of copper, zinc, and PFAS are discussed in Section 3 and summarized in the technical matrix in Appendix A. While relevant studies regarding the removal of trace organics by the media discussed in this report have not been included, the composite and more reactive media do show potential to be able to remove them. In order to select the correct media, a characterization of the site’s stormwater is critical and should include concentrations of constituents of interest and DOC as well as metal speciation and concentrations of contaminants with the potential to compete with copper and zinc. A combination of media, in layers or mixed, will provide the best results for removal of copper, zinc, and PFAS, as well as future contaminants of interest.

Appendix A: Technical Matrix

Media	**Copper (% Removal)**	**Zinc (% Removal)**	**PFAS (% Removal)**	**Keys to Efficient Removal**	**Reference**
Sand	5%-92%	0%-100%	PFOA: 0%-10% PFOS: 0%-40%	SW: Larger particulate fraction and less DOC improves metal removal.	Section 3.1.1 &Table 7 [73]–[76], [78]–[80]
Compost	-5%-100%	0%-100%	PFOA: 74% PFOS: 28%-34%	SW: Larger particulate fraction and less DOC improves metal removal. Longer chain length improves PFAS removal.	Section 3.1.2 & Table 8 [82]–[85]
Mulch	0%-100%	8%-99%	No Data	Media: High CEC, high humic acid and fulvic acid content, and high specific surface area improve metal removal. SW: Neutral pH improves metal removal. Presence of multiple metals lessens individual metal removal.	Section 3.1.2 & Table 9 [70], [86], [87]
Woodchips	75%-99%	-13%-90%	No Data	Media: Presence of organic polymers and functional groups improves metal removal.	Section 3.1.2 & Table 10 [77], [90], [91]
Activated Carbon	75%-100%	45%-97%	PFOA: 75%-95% PFOS: 85%-99%	Media: Increased functional groups, especially oxygen-containing groups, improve metal removal. High porosity, high specific surface area, and high hydrophobicity improve PFAS removal. SW: Longer chain length improves PFAS removal. Presence of DOC can lower PFAS removal.	Section 3.1.3 & Table 11 [75], [78]
Biochar	80%-100%	20%-100%	PFOA: 20%-100% PFOS: 55%-100%		Section 3.1.3 & Table 11 [75], [76], [78], [82], [90]

Plants	0.6%-30.4%	2%-11.6%	PFOA: 45% 77%-82% w/ soil PFOS: 53% 90%-95% w/ soil	Media: Choosing hyperaccumulators for the contaminant of interest and plants with high translocation factor, high growth rate (biomass for metals and roots for PFAS), wide and branched root system with large surface area, thicker taproots, and that are native to the area, resistant to pests, and easy to cultivate will improve contaminant removal.	Section 3.1.4 [97], [104]
Iron Oxide Composite	5%-100%	0%-100%	PFOA: 63%-64% PFOS: 53%-57%	SW: Higher alkalinity and DOC will decrease copper removal. Higher pH will increase copper and zinc removal.	Section 3.2.1 & Table 12 [74], [105]–[107]
Manganese Oxide Composite	0%-100%	0-100%	No Data	Media: A lower point of zero charge and higher specific surface area will improve metal removal. Carbonaceous pretreatment media (like biochar) will increase metal removal. SW: Higher pH and higher particulate fraction will improve metal removal. Higher DOC will decrease metal removal.	Section 3.2.2 & Table 13 [77], [105], [106], [110]
Polymer Composite	75%-100%	10%-100%	PFOA: 0%-100% PFOS: 0%-100%	Media: Increased surface functional groups will improve metal and PFAS removal. SW: Presence of DOC can decrease PFAS removal.	Section 3.2.3 & Table 14 [76], [85]
Crab Shell	93%-99%	100%	No Data	SW: pH control required to help limit calcium and magnesium desorption.	Section 3.2.4 & Table 15 [116]
Foam Glass	5%-74%	9%-83%	No Data	SW: Higher particulate fraction will increase metal removal.	Section 3.2.5 & Table 16 [117]

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