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Considerations for evaluating innovative stormwater treatment media for removal of dissolved contaminants of concern with focus on biochar

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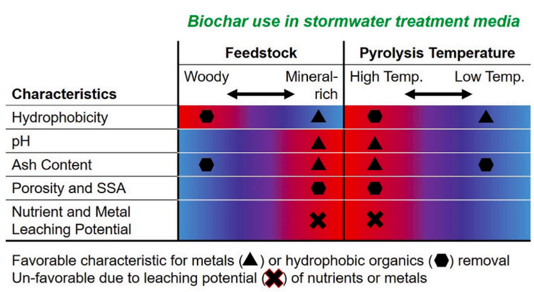
HIGHLIGHTS

- Evaluation strategy for media-based stormwater control measures (SCMs).
- Targeting stormwater contaminants of concern (COC).
- Biochar characteristics and removal potential for COCs.
- Challenges and future considerations for biochar application in SCMs.

GRAPHICAL ABSTRACT



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ABSTRACT

Stormwater from complex land uses is an important contributor of contaminants of concern (COCs) such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), Copper, and Zinc to receiving water bodies. A large portion of these COCs bind to particulate matter in stormwater, which can be removed through filtration by traditional media. However, the remaining dissolved COCs can be significant and require special attention such as engineered treatment measures and media. Biochar is a porous sorbent produced from a variety of organic materials. In the last decade biochar has been gaining attention as a stormwater treatment medium due to low cost compared to activated carbon. However, biochar is not a uniform product and selection of an appropriate biochar for the removal of specific contaminants can be a complex process. Biochars are synthesized from various feedstocks and using different manufacturing approaches, including pyrolysis temperature, impact the biochar properties thus affecting ability to remove stormwater contaminants. The local availability of specific biochar products is another important consideration. An evaluation of proposed stormwater control measure (SCM) media needs to consider the dynamic conditions associated with stormwater and its management, but the passive requirements of the SCM. The media should be able to mitigate flood risks, remove targeted COCs under high flow SCM conditions, and address practical considerations like cost, sourcing, and construction and maintenance. This paper outlines a process for selecting promising candidates for SCM media and evaluating their performance through laboratory tests and field deployment with special attention to unique stormwater considerations.

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1. Introduction

Stormwater runoff from urbanized areas is a major contributor of non-point source pollution. Besides traditional stormwater contaminants such as particulate matter (PM), nitrogen and phosphorus, other contaminants of concern (COC), including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), phenols, pesticides, and heavy metals are often found in stormwater (Lundy et al., 2012; Zgheib et al., 2012). Addressing and removing these pollutants from stormwater can significantly reduce discharged contaminant loads to aquatic bodies and sediments. Stormwater best management practices (BMPs) or stormwater control measures (SCMs) mitigate hydrologic and water quality challenges presented by excess stormwater (Davis et al., 2022). Many SCMs are designed to perform stormwater volume reduction but can also provide some degree of treatment discharge to local water bodies. SCMs frequently use physical sedimentation and filtration as primary mechanisms for removal of PM and will therefore also remove pollutants that are associated with PM. Since PM is a primary target of most SCMs and many pollutants, including COCs, partition primarily to PM, these SCMs can be effective for removal of many pollutants. Dissolved pollutants (which can be present in stormwater or may result from desorption processes from PM trapped in a SCM) represent a greater challenge. However, these dissolved pollutants can be removed in media-based SCMs through sorption mechanisms as the stormwater flows through a reactive media. Media-based SCMs can include bioretention and various reactive media filters.

The removal of stormwater COCs is impacted by the contaminant properties and the characteristics of the medium (Liu et al., 2005). In addition, stormwater systems must be able to handle high and variable stormwater volumes and flows. Non-reactive materials, such as silica sand, are commonly used as a filtration medium for removal of PM (Liu et al., 2005). Other sorptive media have been applied within SCMs to improve dissolved contaminant removal. Some examples of sorptive media include: activated carbon (AC) (Genç-Fuhrman et al., 2007; Liu et al., 2005), biochars, zeolites (Wang et al., 2019), perlite (volcanic rock), vermiculite, mica, kaolinite (Covelo et al., 2007), coal cinder, coal and fly ash (Genç-Fuhrman et al., 2007), iron (Covelo et al., 2007) and aluminum minerals (Genç-Fuhrman et al., 2007), composts (Jang et al., 2007), and ceramsite (Wang et al., 2018).

Due to their high specific surface area, micropore volume, surface charge density and relatively low bulk density (Kookana et al., 2011; Laird et al., 2010), biochar-based materials are of specific interest as a stormwater treatment medium for removal of toxic COCs. Biochar-based media have the potential to enhance the performance of SCMs for removing dissolved pollutants and thus improve the effluent water quality (Ahmad et al., 2014; USEPA, 2014). In addition, biochars have been documented in removal of nutrients, metals, and persistent organic contaminants (i.e., PCBs) from water through physicochemical and/or biological interactions (Beck et al., 2011; Mohanty et al., 2018; Teixidó et al., 2011). Stormwater adsorbents can also provide an opportunity for sequestered hydrophobic organic contaminants to degrade between storm events via chemical and biochemical reactions. However, the media properties that influence the removal of toxic stormwater COCs are also impacted by other variables such as adsorption capacity, particle size distribution, and hydraulic conductivity (Kookana et al., 2011; Laird et al., 2010). These variables lead to a challenge for stormwater practitioners when designing stormwater treatment media for the removal of dissolved pollutants.

The goal of this research is to highlight important criteria for SCM media selection for the removal of COCs from stormwater (Fig. 1). The focus is on biochar as a medium for the removal of toxic COCs, but many of the selection criteria can be applied to other types of media and other contaminants. Various steps in the framework are summarized in Fig. 1 through Boxes 1–5 and details and discussion are provided in the following sections.

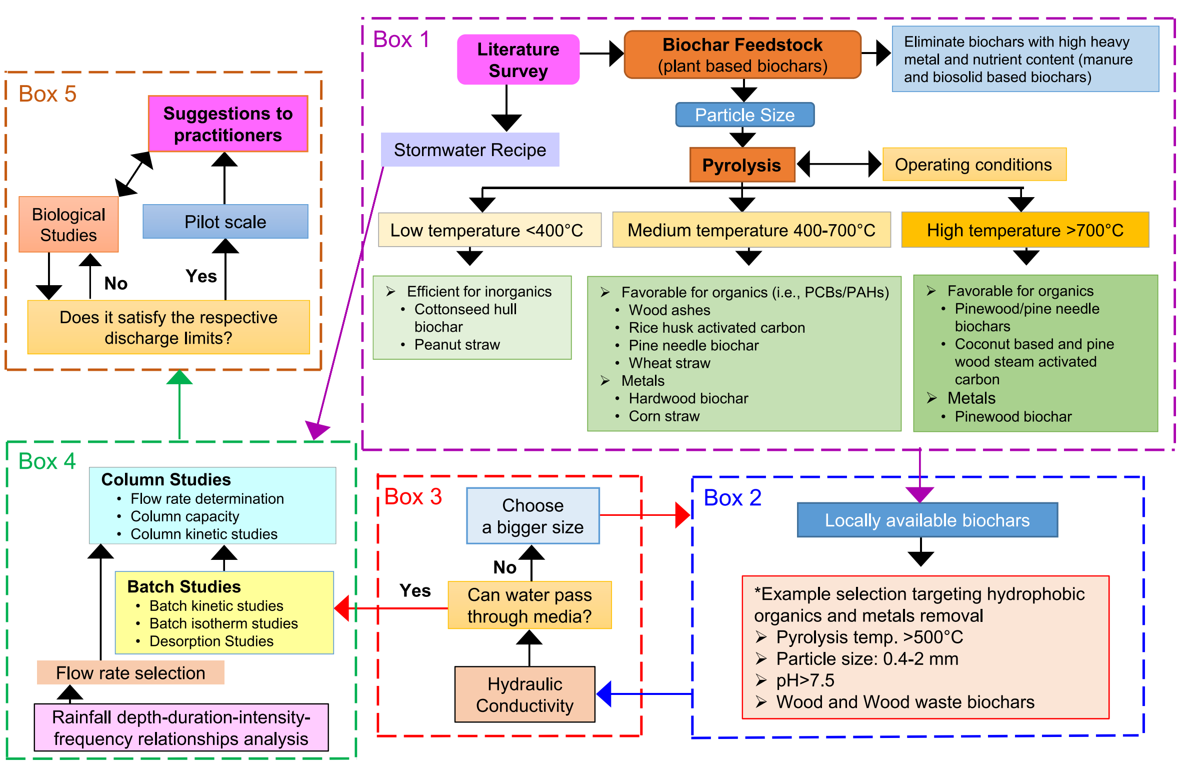

Fig. 1. Evaluation strategy for biochar selection for stormwater treatment. The individual parts are outlined in Boxes 1–5. Box 1: Biochar characteristics and removal potential for COCs. Box 2: Biochar selection and particle size requirement screening; Box 3: Hydraulic conductivity decision; Box 4: Laboratory tests based on local rain fall analysis; Box 5: Effect of biological treatment and pilot scale studies.

2. Criteria for SCM media

Selection of media for removal of dissolved pollutants in stormwater treatment systems is based on several important properties (Fig. 1): 1) *hydraulic conductivity* to provide sufficient flow through the SCM to minimize the risk of flooding, 2) *effective storage volume* in the medium to reduce and delay stormwater effluent flow, 3) *enhanced capacity* for removal of COCs and other pollutants, 4) *rapid kinetics* for pollutant removal, 5) *minimal leaching and/or release* of undesired substances, 6) *long-term stability* of the design, 7) *low cost and sufficient availability* of materials, 8) preferably *locally sourced* to reduce transportation costs and improve sustainability, and 9) *ease of construction*. Depending on the applied SCM approach, ecological factors such as encouraging plant growth, support of beneficial microbial populations, and wildlife habitat may also be important.

Biochar is a carbonaceous sorbent material produced from biomass feedstock under thermochemical processes such as pyrolysis (slow or fast), hydrothermal carbonization, and gasification. Biochar is an effective material for removal of hydrophobic organic contaminants such as for PCBs (Table 1), PAHs (Table 2) and trace metals particularly Cu and Zn (Table 3). Biochar has the potential to meet many of the described criteria for removal of dissolved COCs from stormwater. The carbon in biochar is recalcitrant with an average half-life of over 100 years (Mohanty et al., 2018), hence, it can last many decades in the SCM environment. Biochar quality and quantity is impacted by the feedstock, the pyrolysis temperature, and the residence time of feedstock within the pyrolysis chamber. The feedstock also determines the elemental content in the final product. The pyrolysis temperature impacts physical and chemical characteristics such as pH, hydrophobicity, particle size and ash content (Tomczyk et al., 2020).

2.1. Biochar characteristics and removal potential for COCs (Box 1 & 2)

Biochar feedstock types and production conditions affect biochar physicochemical properties (Fig. 1), which in turn influence contaminant removal capacity and possible contaminant leaching. Therefore, it is critical to select biochar feedstock based on the stormwater treatment needs. Biochars can be produced from organic materials such as wood waste (wood chips, tree cuttings), industrial by-products (crop residues from the agro-processing industry), municipal waste (newspaper, cardboard, landscaping residues), and non-conventional materials (sewage biosolids, manure and waste bones) (Paz-Ferreiro et al., 2014; Randolph et al., 2017; Tian et al., 2016; Yaashikaa et al., 2020; Zornoza et al., 2016).

Pyrolysis and gasification of these feedstocks produce biochar, while hydrothermal carbonization produces hydrochar (Zhang et al., 2019). Pyrolysis is a thermal decomposition process in an anoxic environment in the temperature range of 300 °C–900 °C; hydrothermal carbonization utilizes a wet feedstock at high temperature (120 °C–260 °C) and pressure (2–10 MPa) (Mohan et al., 2014; Xiang et al., 2020). Different processing methods will result in differences in product characteristics, including the contents of black carbon (Wiedner et al., 2013). Wiedner et al. (2013) showed that biochar has higher black carbon contents (median of 293 BC g C kg^{-1} TOC) than hydrochar (median of 31 BC g C kg^{-1} TOC). In addition, biochar has a higher surface area and larger pore volume than hydrochar (Sun et al., 2014). Thus, biochar is more suitable for stormwater treatment than hydrochar.

Biochar of non-wood origin can contain a reduced amount of aromatic groups but more aliphatic groups, higher ash content and nutrient concentrations compared to wood or plant-derived biochar (Table 4) (Fang et al., 2017; Mukome et al., 2013). Biochar from sewage biosolids can also contain heavy metals (i.e., Cu and Zn) and other contaminants such as pharmaceuticals and personal care products that might be mobilized in a SCM (Paz-Ferreiro et al., 2014). Furthermore, softwood-derived biochar can have a higher pore density and surface area than many hardwood-derived biochar, since softwood is more susceptible to thermal decomposition due to decreased density (Mukome et al., 2013).

Manure-derived biochar has increased levels of nutrients (i.e., N, P, and K) compared to wood-derived biochar. This was shown in a study by Tian et al. (2016), where nutrient release and ammonia ($N–NH_4^+$) sorption of poultry litter was compared with hardwood biochar, thus

Table 1
Characteristics of biochar evaluated prior to media selection for PCB adsorption.

Adsorbent (Geomedia)	Size (diameter) or volume	Surface Area	PCB Congeners/Mix	Study type Contact time & Temp	Maximum Adsorption/ Removal %	Isotherm models & constants	Reference
Pulverized Charcoal (Combustion of Bark)	<150 μm		PCBs: 18, 28, 52, 72, 77, 101, 118, 126, 138, 156, 169	Batch 7 days 20 °C	7.762 mg/g	Langmuir different for all 11 congeners: ∑PCB maximum sorption capacity of Cc, max:106.78 μg/kg; 448-917 × 10^3 μg/kg	Koelmans et al. (2009)
Black Carbon on Sediments *Partitioning			PCBs: 44, 66, 95 PCDDs, and PAHs	Batch 6 months room temperature	>80%, ~90% for all congeners, partition to BC		Lohmann et al. (2005)
Corn Straw Biochar; Activated At 200 °C (BC200) And 700°c (BC700)	0.074–0.45 mm	Raw material (1.32 m^2 g^{-1}), BC200 (1.00 m^2 g^{-1}), BC700 (289 m^2 g^{-1})	PCB 3 (planar, non-ortho), 4 (non-planar, di-ortho), 5 (nonplanar, mono-ortho)	Batch 48 h 20 °C		Freundlich BC200 logK_f:9.58–42.5 (ng/kg) (L/ng)$^{1/n}$; n: 0.9–0.96; R^2: 0.97–0.98 BC700 K_f: 10–39.5; n:0.33–0.43; R^2: 0.94–0.97	Wang et al. (2016)
Wheat Straw and Pine Needle	0.15 mm		PCB-8, PCB-18, PCB-28, PCB-52, PCB-44, PCB-66, PCB-101, and PCB-138	Batch 72 h		Freundlich, R^2 = 98-69%; Log K_f (mg/kg)/(mg/L)^n: 2.7–6.7; n: 0.34–2.2; Log K_d (L kg^{-1}): 3.25, 3.23, 3.08, 4.05 and 4.09 to 4.32, 4.18, 3.99, 4.89 and 5.21 for AC, P350, P550, W350, and W550 respectively at the dissolved concentrations of 2,4,4′-CB	Wang et al. (2013)
Activated Carbon	<75 μm	989 m^2 g^{-1}	PCB 4, 12, 18, 52, 53, 54, 72, 77, 126	Batch 28 days 21-24 °C	10^9–10^{11} ng/kg	Freundlich K_f: 7.53–8.95; 1/n: 0.57–1.08	McDonough et al. (2008)
Enhanced Pinewood Derived Biochar	44–177 μm	358 m^2g^{-1}	PCBs contaminated sediment	Batch 28 days; 20-23 °C	>95% reduction	Freundlich	Gomez-Eyles and Ghosh (2018)

Table 2
Characteristics of biochars evaluated through literature survey for geomedia selection for PAH adsorption.

Adsorbents (Geomedia)	Size/Volume	Surface Area	PAHs	Study Type, Contact Time & Temp	Maximum Adsorption/Removal %	Isotherm Models & Constants	Reference
Powder activated carbon (PAC) anthracite (coal-BP2) based and coconut shells (biomass-CP1) based	BP2 & CP1: 0.54 & 0.97 cm^3/g (average particle size 20 μm, 80% < 45 μm)	BP2& CP1: 1199 & 1158 m^2/g	PAH-16, 30 ± 6 mg/kg; pyrene, 3.8 ± 1.1 mg/kg phenanthrene, anthracene, fluorene, pyrene, benzo(a) pyrene, chrysene, benzo(b) fluoranthene, benzo(k) fluoranthene, benzo(a) anthracene, indeno (1,2,3cd) pyrene, benz (g,h, i) perylene	Batch 30 days 30 °C	Ranging between 69% and 97.5%, highest for anthracene, while lowest for benzo(g,h,i) perylene	Freundlich, Polanyi-Dubinin-Manes Pyrene: Log (K_f):7.2 and 8.15 for anthracite-based AC and coconut shells-based AC, respectively, and their respective n: 0.952 and 1.111 without sediment. With pyrene sorption reduced by factor 5 in coconut shells-based carbon than anthracite-based AC.	Amstaetter et al. (2012)
Granular activated carbon (GAC)	size 3–6 mm, specific volume 1.5 cm^3/g	1000 m^2/g	0.2–10 mg/L PAH napthalene, acenapthene, fluorene, anthracene, pyrene, fluoranthene	Batch 400 min 21 °C	napthalene, acenapthene, fluorene, anthracene, pyrene and fluoranthene: 140, 111, 145, 232, 109 and 93 g/kg respectively.	Langmuir, Freundlich, Redlich Peterson RP model (Napt): A (dm^3/g): 121, B (dm^3/mg): 2.6, g: 0.7	Valderrama et al. (2008)
Pine needle biochar	0.154 mm	0.65–490.8 m^2/g	Ci/Cs: 0.03–0.94 napthalene	Batch 3 days Multiple	136.8 mg/g	Freundlich, Linear Log (K_f): 5.085 L/kg and n: 8.0645, K_d: 1086 mL/g	Chen et al. (2008)
AC/Biochar	20 μm	1199-1158 m^2/g	13.2 ng/L dissolved PAHs	Batch 7 days 30/60 days	56–95% removed by AC and 0–57% by biochar	Freundlich Mean Log (K_f) values for different activated carbon dose: 6.4–9.3 L/ng and for different dose of biochar: 6–8.9 L/ng	Oleszczuk et al. (2012)
Coke-derived porous carbon		562–1904 m^2/g	3.250–6.250 mg/mL PAHs	Batch 18 h 25 °C	>99% for all PAHs at 7 h	Freundlich napthalene, K_f: 146–457.5 mg/kg and n: 0.53–0.71, for fluorene K_f: 35.7–45.6 mg/kg and n:0.49–0.52, phenanthrene K_f:11.7–46.3 mg/kg and n:0.5–0.54, pyrene K_f: 6.2–12.3 mg/kg and n:0.55–0.59	Yuan et al. (2011)
Wood ashes	0.177–0.5 mm		3 mg/L fluorene and 5 mg/L benzo(b)fluoranthene and benzo(g,h,i)perylene fluorene, pyrene, chrysene, benzo(a) anthracene, benzo (b) fluoranthene, benzo(k) fluoranthene, benzo(a) pyrene, dibenz(a,h) anthracene, indeno(1,2,3-cd)pyrene, benzo(g,h,i) perylene	Batch 24 h 25 °C	100% at 800 °C; >99 at 500 °C	Freundlich at 800 °C K_f: 9.4–32.8; n: 1.698–2.564 with acetonitrile	Pérez-Gregorio et al. (2010)
Wood char			pyrene 2.8–112 mg/L phenanthrene, benzo(a) anthracene	Batch 9 days 25 °C	>60%	Freundlich Log(K_f): 4.92–5.66, 4.83–5.13, 5.28–5.88 L/mg for pyrene, phenanthrene, benzo(a)anthracene, respectively; n values: 0.25–1.55, 1.04–1.23, 1.04–1.129.	Wang et al. (2006)
Rice husk activated carbon (RHAC)		446 m^2/g	8 mg/L of each PAH	Batch 1–7 days 28 °C	Pyrene: 104.5 mg/g	Freundlich for napthalene, Redlich Peterson for phenanthrene and Langmuir for pyrene K_f for napthalene is 15.7 L/mg and n is 1.408. For phenanthrene Redlich isotherm constant br is 0.54 and b is 1.4.	Yakout et al. (2013)

Table 3
Characteristics of biochars evaluated prior to geomedia selection for Cu and Zn adsorption.

Media	Metals	media size (diameter) or volume	adsorbent surface area	Study type	Contact time & Temp	Removal efficiency or adsorption capacity	Isotherm models & constants	Reference
Wood chips (WC), slag from steel mill (BF, and BOF), drinking water treatment residuals (DWTR), geothite-rich overburden (IRON) and wood chips from landscaper	Cu, Zn, Pb	<1000 um	Not reported	Column and shaker tests	24 h; room temperature	Cu: (WC 93.4%, BF 90.7%, BOF 95.1%, iron 95.5%); Zn: (WC 77.3%, BF 84.5%, BOF 61.1%, iron 79.2%)	Freundlich Not reported	Trenouth and Gharabaghi (2015)
Washed, oxidized, and sodium-replaced AC (AC from coconut shells)	Cu, Cd, Ni	Granular (595–177 µm); Powdered (>75 µm)	PAC (990 m^2/g), AC-W (1364 m^2/g), AC-O (1342 m^2/g), AC-Na (1300 m^2/g)	Batch	2 weeks; room temperature	PAC (142.8 µmol/g), AC-W (180.1 µmol/g), AC-O (107.7 µmol/g), AC-Na (388.2 µmol/g)	Langmuir River water: PAC (q: 142.8 K: 0.005), AC-W (q: 180.1 K: .005) AC-O (q: 107.7 K: 0.009) AC-Na (q: 388.2 K 0.009)	Kim et al. (2012)
Woodchips, biochar-woodchips, straw-woodchips	Cd, Cu, Ni, Pb, Zn (and 6 organics)	Woodchips (2–10 mm); biochar (>0.6 mm)	318 m^2/g	Column studies	11–13 h; not reported	Cu > 80%, no difference between amendments; Zn average 54% (large variability for Zn)	Langmuir and Freundlich Not reported	Ashoori et al. (2019)
Chitosan-combined magnetic biochars (20, 30, 40, and 50% chitosan addition)	Cu (II), Cr (IV)	Not reported	50, 40, 30, 20%, no chitosan (96.91, 104.91, 109.95, 134.68, 337.35 m^2g^{-1})	batch	18 h (equilibrium); temperature not reported	60.6 mg/g for 40 wt %-CMLB	pseudo first and second order 40% CMLB (q: 55.67 mg/g, k_1: 0.00097/min) R^2:0.98	Xiao et al. (2019)
Dairy manure biochar and rice husk biochar	Cu, Zn, Pb, Cd	<0.5 mm	Dairy manure Biochar (5.61 m^2g^{-1}); rice husk biochar (27.8 m^2g^{-1})	batch	8 h; Temperature not reported	Cu-mono 62.4%, Cu-multi 25.6%, Zn-mono 49.4%, Zn-multi 12.3%	Langmuir: Cu-multi (K: 3.01 L/mmol; qmax: 297 mmol/kg, R^2 0.97) Zn-mono (K: 31.4, q_{max}: 496, R^2 0.98 (multi N/A)) Freundlich: Cu-multi (K_f: 203 mmol/kg n: 4.09, R^2: 0.88) Zn-mono (Kf: 457, n: 6.5, R^2: 0.86) (All for DMBC)	Xu et al. (2018)
Synthetic clinoptilolite	Zn, Pb, Cd, Cu	Not measured	Not measured	Batch	240 min; 25 °C	Maximum capacity Cu 33.76 mg/g; Zn 31.47 mg/g	Langmuir: Cu (q_{max}: 33.76 mg/g, b 0.08 L/mg, R^2: 0.99) Zn (q_{max}: 31.74 mg/g, b: 0.074, R^2: 0.99) Freundlich: Cu (n 0.29, K_f: 6.52 L/mg, R^2: 0.95) Zn (n: 0.29, K_f: 5.91, R^2: 0.95)	Y. Li et al., 2017
Modified clinoptilolite (iron and manganese oxides)	Zn (II)	<0.20 mm	27.49–31.36 m^2g^{-1} for both modifications of clinoptilolite	batch	30–240 min; room temperature	max capacity: iron oxyhydroxide 12.84 mg/g; Iron oxyhydroxide and manganese dioxide 22.76 mg/g; manganese dioxied 35.09 mg/g	(MnO_2); langmuir (q: 33.14 mg/g, K_l: 0.17 L/mg, R^2: 0.84) Freundlich (n: 0.23, K_f: 8.78 L/mg, R^2: 0.83)	Hawash et al. (2018)
Sio2 encapsulated zeolite and natural zeolite	Pb, Cu, Zn, Mn	<75 um	Natural zeolite (16.8 m^2g^{-1}) SiO_2 encapsulated zeolite (36.3 m^2g^{-1})	batch	0.5–25 h; room temperature	Zn, at 0.5 g/L 66% removal with SiEQ and 3 g/L 97% removal; Cu, at 0.5 g/L 55% removal, and 3 g/L 98% removal. Competitive adsorption Cu < 40% and Zn < 20%	n/a	Wang et al. (2019)

they are not suitable for stormwater treatment purposes (Mukome et al., 2013). Hardwood biochar also leached less organic and inorganic nutrients than poultry litter biochar. Hardwood biochar pyrolyzed at 500 °C did not release nitrogen (N), whereas hardwood biochar pyrolyzed at 400 °C leached about 0.07 µmol/g of organic N (Tian et al., 2016). In contrast, poultry litter biochar leached high amounts of N, which decreased with decreasing pyrolysis temperature (120–127 µmol/g of N compared to 7.1–8.6 µmol/g of N, when pyrolyzed at 500 °C compared to 400 °C, respectively) (Tian et al., 2016). Mukherjee and Zimmerman (2013) observed that organic N accounted for 60%–80% of

Table 4
Characteristics of biochar based on the feedstock and the temperature of the pyrolysis process.

Feed stock	Pyrolysis Temperature (C)	C%	N %	H%	O%	Molar H/C	Molar O/C	Ash %	pH	Bet Surface Area (m^2/g)	CEC (cmol/kg)	Pore Vol (cm^3/g)	Pore Size (nm)	References
Corn (Maize) Straw	400	57%	1%	3%	39%			22%		4.3				Xing et al. (2018)
	450	57%	1%	3%	39%			24%		5.97				
	500	59%	1%	3%	37%			26%		12.61				
	550	59%	1%	3%	37%			27%		24.38				
	600	60%	1%	2%	36%			28%		29.6				
Apple Tree Branches	300	62%	2%	5%	24%	1.00	0.29	7%	7.5	2.39	18.5	0.00256		Zhao et al. (2017)
	400	71%	2%	4%	15%	0.73	0.18	8%	11.5	7	65	0.00652		
	500	75%	2%	3%	10%	0.47	0.12	10%	11.7	37.2	66.6	0.01241		
	600	80%	1%	3%	7%	0.41	0.06	9%	10.5	108.6	56	0.05854		
Wheat-Straw	400	58%	2%	3%	22%	0.49	0.56	11%	8.2	10	4	0.012	4.6	Gai et al. (2014)
	500	70%	1%	3%	18%	0.35	0.38	11%	8.3	111	5.1	0.09	3.3	
	600	73%	1%	2%	15%	0.22	0.31	12%	9.2	177	1.3	0.11	2.5	
	700	74%	2%	1%	15%	0.92	0.30	15%	9.2	107	0.5	0.058	2.2	
Corn-Straw	400	56%	2%	4%	22%	0.56	0.59	14%	10.2	4	38.3	0.008	8.1	
	500	58%	2%	3%	22%	0.57	0.57	17%	10.4	6	68.6	0.12	2.1	
	600	59%	2%	2%	19%	0.48	0.48	18%	10.4	7	20.1	0.012	6.3	
	700	60%	2%	2%	17%	0.42	0.42	18%	10.4	3	19	0.006	8.2	
Peanut-Shell	400	58%	2%	4%	21%	0.54	0.54	9%	9.3	5	7.2	0.007	5.2	
	500	65%	2%	3%	19%	0.43	0.43	10%	9.4	28	8.5	0.022	3.2	
	600	72%	1%	2%	15%	0.31	0.31	11%	9.6	185	1.2	0.11	2.4	
	700	74%	1%	1%	14%	0.29	0.29	12%	9.9	49	0.3	0.033	2.7	
Safflower Seed Press Cake	400	69%	4%	4%	23%	0.71	0.26	8%	8.2	2.67		0.005		Angın (2013)
	450	70%	4%	3%	22%	0.59	0.24	8%	9.1	3.33		0.0063		
	500	71%	4%	3%	22%	0.50	0.23	9%	9.4	4.23		0.008		
	550	73%	4%	3%	21%	0.44	0.21	9%	9.7	3.78		0.007		
	600	74%	4%	2%	20%	0.38	0.20	9%	9.9	3.41		0.0064		
Corn Stover	300	46%	63%	5%	42%			6%	7.7	3.19		0.0084	10.6	Rafiq et al. (2016)
	400	64%	42%	4%	32%			13%	8.8	3.17		0.0068	8.69	
	500	65%	25%	3%	33%			19%	9.8	4.53		0.0072	6.3	
Wood	300	71%		5%		0.79		50%	5.7	6				Ronsse et al. (2013)
	450	86%		3.5		0.49		1%	6.7	23				
	600	92%		2.3		0.30		1%	9.1	127				
	750	93%		1.1		0.15		1%	10.4					
Straw	300	76%		5		0.79		19%	9.4					
	450	86%		3.5		0.49		23%	10.1	16				
	600	90%		2.1		0.28		25%	11.3	22				
	750	94%		1.2		0.16		26%	11.9					
Green Waste	300	69%		5.4		0.94		7%	8.1					
	450	83%		3.5		0.51		12%	10.0	17				
	600	88%		2		0.27		13%	11.3	46				
	750	93%		1.3		0.16		13%	11.6					
Dry Algae	300	70%		6.9		1.19		56%	7.7					
	450	79%		4		0.61		72%	9.3	14				
	600	83%		2		0.29		73%	11.9	19				
	750	91%		1.4		0.19		76%	12.5					
Bamboo Wood	500	37%	0.51					2%	9.6	107	2.7			Wang et al. (2013)
	700	35%	0.25					3%	9.6	325	1			
Elm Wood	500	46%	0.03					2%	8.0	62.5	1.3			
	700	37%	0.03					2%	9.8	340	0.6			
Rice Straw	500	44%	1.06					32%	10.6	5.12	25			
	700	42%	0.84					33%	11.1	234	21.8			
Wheat Straw	500	52%	0.44					17%	9.3	51.5	27.5			
	700	50%	0.24					19%	10.7	378	14.1			
Maize Straw	500	55%	2.81					26%	10.1	0.36	27			
	700	52%	1.83					31%	11.0	112	27.4			
Rice Husk	500	37%	1.1					38%	9.9	28.6	10.9			
	700	40%	0.93					43%	10.5	195	11.7			
Coconut Shell	500	52%	0.26					7%	10.5	52.8	11.3			
	700	60%	0.25					8%	10.5	394	21.3			
Cottonseed Hulls	200	52%	0.6	6	40.5	1.38	0.59	3%	3.5					Uchimiya et al. (2011)
	350	53%	1.9	4.53	15.7	0.70	0.15	6%	7.0	4.7				
	500	67%	1.5	2.82	7.6	0.39	0.07	8%	10.1					
	650	70%	1.6	1.26	5.9	0.17	0.05	8%	9.9	34				
	800	69%	1.9	0.6	7	0.08	0.06	9%	9.2	322				
Pine Needles	100	51%	0.71	6.15	42.27	1.44	0.62	1%		0.65				Chen et al. (2008)
	200	57%	0.88	5.71	36.31	1.19	0.48	1%		6.22				
	250	61%	0.86	5.54	32.36	1.08	0.40	1%		9.52				
	300	69%	1.08	4.31	25.74	0.75	0.28	2%		19.9				
	400	78%	1.16	2.95	18.04	0.45	0.17	2%		112				
	500	82%	1.11	2.26	14.96	0.33	0.14	3%		236.4				
	600	85%	0.98	1.85	11.81	0.26	0.10	3%		206.7				
	700	86%	1.13	1.28	11.08	0.18	0.10	2%		490.8				
AC		80%	0.67	1.72	17.82	0.26	0.17	0.8%		1036				

total leached N from grass biochar and nitrate (NO_3^-) represented a low fraction of released TN. Cumulative release of N from grass and oak biochar pyrolyzed at 250 °C and 650 °C, respectively, was in the range of 23–635 mg/kg (Mukherjee and Zimmerman, 2013). Sebestyén et al. (2020) showed that crab shell biochar still contains significant N after heat treatment, which made an 8.1% contribution to the surface composition of the biochar, and releases nitrogen-containing heterocycles. Xiong et al. (2022) noted that denitrification of stormwater in a bioretention cell will be poor if the media filler amendment contains a significant amount of N and any release of N by a SCM is problematic in areas prone to eutrophication. Therefore, biochar derived from these sources are not suitable as an SCM medium. Based on the results from previous studies (Tables 1–3), biochar produced from pinewood, pine needle, bamboo, wood, and wood waste (yellow pine and oak wood) are more suitable for stormwater treatment (Chen et al., 2008; Gomez-Eyles and Ghosh, 2018; Mukome et al., 2013; Tian et al., 2016; Wang et al., 2006, 2013).

Biochar retains the pore structure of the feedstock during pyrolysis thus, porosity or pore size distribution in biochar depends on the feedstock type (Lu and Zong, 2018). As a group, biochar derived from plant feedstock have a more porous internal structure, and higher CEC than manure and sewage sludge-derived biochar (Han et al., 2013; Paz-Ferreiro et al., 2014). The firm and physically condensed structure of wood biomass (e.g., pine wood) can increase the stability of the porous structure after pyrolysis (Lau et al., 2017). In contrast, straw biomass has a less dense structure, which can cause the material to break after pyrolysis thus resulting in a compact structure with a non-uniform distribution of vaguely visible pores (Sewu et al., 2017). Micro-morphology of biochar after pyrolysis is shaped by the discharge of volatile constituents at high temperature. By this process, the original structures of straw are disrupted and cause uneven distribution of pores (Hong et al., 2020).

Pyrolysis is the most commonly applied method for biochar production, requiring a high temperature (300–800 °C) under oxygen limited conditions (Lehmann, 2007). The pyrolysis temperature is one of the most important parameters when the biochar properties are designed (Table 4). These properties in turn affect the adsorption of contaminants (Zhao et al., 2018a, 2018b). Increase in pyrolysis temperature results in decreased volatile matter, fewer functional groups, reduced average yield, and fewer hydrogen (H) and oxygen (O) fractions (Guo et al., 2017). This can be illustrated for pine needle biochar: when the temperature of pyrolysis was increased from 400 °C to 700 °C, the porosity of the biochar increased from 0.04 to 0.19 cm^3/g (Li et al., 2017).

Similar increases of hydrophobicity with increased pyrolysis temperature was shown (Table 4) as a result of a high fixed carbon content and reduction of oxygen (Ahmad et al., 2012). Ghani et al. (2013) showed that biochar became thermally stable and more hydrophobic at temperatures >650 °C. Numerous studies have shown that the H:C and O/C ratios of biochar decreased with increasing pyrolysis temperature (Table 4), indicating increasing aromaticity and a lower hydrophilic tendency (Chen et al., 2008). Biochar produced above 400 °C tend to contain more aromatic surface groups, but they are less polar due to the loss of O- and H-containing functional groups (Ahmad et al., 2014). These types of biochar were more efficient in the adsorption of hydrophobic organic COCs due to the increased surface area, surface aromaticity, non-polarity, and micro-pore development (Ahmad et al., 2012; Chun et al., 2004; Mukherjee et al., 2011; Spokas et al., 2012; Suliman et al., 2017). Overall, biochar can be characterized based on the pyrolysis temperature: low (<400 °C), medium (400–700 °C), and high (>700 °C). Biochar produced at lower pyrolysis temperatures are often more favorable for adsorption of heavy metals due to the presence of oxygen-containing surface functional groups. In contrast, biochar produced at high temperatures are more hydrophobic and therefore more effective for adsorption of hydrophobic COCs.

The origin of feedstock can also affect the pH of biochar (Ronsse et al., 2013; Yuan et al., 2011). Biochar produced from wood has on average a pH that is about 2–3 pH units lower than other feedstock produced under similar pyrolysis conditions (Table 4). Biochar pH is also impacted by the pyrolysis temperature (Tomczyk et al., 2020) and the pH increases with an increase in pyrolysis temperature (Gai et al., 2014; Ronsse et al., 2013; Zhao et al., 2017). This is mainly due to the separation of alkali salts from the organic material and formation of carbonates with the increase in pyrolysis temperature above 300 °C (Ding et al., 2014; Yuan et al., 2011).

The capacity for metal removal by biochar is linked to the amount of O-containing functional groups (e.g., carboxyl and hydroxyl) that are present at the biochar surface (Dong et al., 2014). These O-containing functional groups are often negatively charged, which provides binding sites for cations (e.g., Cu^{+2} and Zn^{+2}) and contribute to CEC (Lee et al., 2010). Studies have shown that an increase in pyrolysis temperature from 400 to 700 °C can decrease the CEC (Table 4). This is mainly due to the removal of surface functional groups and the formation of aromatic carbon. Abbas et al. (2018) noted that biochar produced at a pyrolysis temperature <600 °C were effective for adsorption of inorganic contaminants due to electrostatic interactions, precipitation, and ion exchange.

Biochar feedstock and pyrolysis temperature are the two most critical parameters that affect the biochar ash content (Table 4). Compared to non-wood based biochar, wood derived biochar have lower ash content (<7% vs. >50%) (Mukome et al., 2013). Increase in the pyrolysis temperature to 800 °C caused the ash content of biochar derived from sugarcane bagasse to increase 2-3-fold (Hass and Lima, 2018). Tian et al. (2016) also showed that the ash content of poultry litter biochar was 56% and 60%, when produced at 400 °C and 500 °C, respectively. This was significantly higher than 3.2% and 4.2% for hard wood, respectively, produced at the same temperatures. The ash content of biochar plays a critical role in the adsorption of contaminants, especially of phosphate and heavy metal ions such as Cu(II), and Zn(II) (Jiang et al., 2016; Takaya et al., 2016). A high ash content was hypothesized as the reason that Cd(II) and Cu(II) displayed maximum adsorption on sugarcane biochar (Hass and Lima, 2018). Biochar with high ash contents also tend to have higher pH (Table 4), which can reduce the solubility of metals and thus increase the removal (Ippolito et al., 2012; Zhou et al., 2016). The pH of the adsorbent is important in controlling the level of adsorption and desorption of metals and other inorganic pollutants to/from the media. Conversely, higher ash content can reduce the adsorption capacity of organic contaminants by covering the active adsorption sites (Inyang and Dickenson, 2015; Peng et al., 2016).

Ensuring that the media does not substantially change the pH of the stormwater is important for the long-term immobilization of pollutants. The pH of stormwater is typically in the range of 5.5–9.3 (Eriksson et al., 2007; Pamuru et al., 2022). However, this is site-specific depending on local precipitation levels and the characteristics of the land use surrounding the site (e.g., roads, buildings, residential areas, presence of concrete and asphalt etc.). Selection of media that maintains a neutral pH is important for the long-term sequestration of metals in the media. The stormwater pH can also influence the adsorption of organic contaminants, since a change in pH alters the surface charge of the biochar but also changes the properties of COCs (Abbas et al., 2018). Increase in stormwater pH can cause dissociation of carboxyl and phenolic groups from biochar thus increasing the net negative charge on the surface (Xu et al., 2018). The pH of the stormwater will also affect the speciation of organic acids and bases present in the media.

Several studies have evaluated the treatment of biochar in an effort to improve the performance as an environmental treatment adsorbent (Tables 1–3). The results showed that biochar derived from hickory wood chips and modified with NaOH showed around 2.5 times greater zinc adsorption capacity than virgin biochar due to increased precipitation and ion exchange (Ding et al., 2016). Wang et al. (2015) produced a novel biochar via slow-pyrolysis of hickory wood pretreated with $KMnO_4$ and evaluated the removal of Cu(II) from an aqueous solution. The results showed that the engineered biochar increased Cu(II) removal approximately 3 times due to pretreatment. In Table 5, an overview of biochar products based on criteria discussed during the decision framework developed in this study is shown.

Finally, an important consideration in the selection of any adsorbent is the cost and availability. The material should be readily available and sourced with a consistent quality according to the desired properties and specifications. Shipping costs will often depend on the local availability of the feedstock, which the shipping challenges and increased costs during the COVID19 pandemic has highlighted. These are important issues for biochar, as many are produced locally with locally available feedstock. Other adsorbents may not be locally produced, and transportation costs could be significant.

In summary, biochar produced through high temperature pyrolysis is more effective for removal of hydrophobic COCs whereas heavy metal removal is favored by biochar produced at lower hydrolysis temperature. Plant-derived biochars tend to have fewer leaching concerns and wood-based products show the best performance. Based on this discussion, Fig. 2 provides an initial screening process for selection of biochars for removal of either heavy metal or hydrophobic organic contaminants. Specific biochars should be individually evaluated for pollutant removal performance. There are benefits related to utilization of locally sourced and produced biochar to ensure reliable supply and to reduce the costs (Fig. 1).

2.2. Media particle size and hydraulic conductivity (Box 3)

The hydraulic characteristics of the media must be compared with the physicochemical treatment characteristics within a media-based SCM. The media size and characteristics will control the flow rate through the media, via a Darcy's law relationship for saturated flow and a van Genuchten relationship for unsaturated flow. Darcy's Law indicates that the saturated hydraulic conductivity and the hydraulic gradient control the flow rate though the media (Erickson et al., 2012). The saturated hydraulic conductivity depends on media porosity, distribution of pore sizes, and tortuosity, and these characteristics can be determined by bulk density and particle size distribution or texture (Hillel, 2004). Compacting of media, i.e., increasing bulk density, can limit the size of the conducting pores and fine particles can often be dislodged and result in clogging of pores (Hillel, 2004). Finer particles lead to greater head loss, lower hydraulic conductivity, and reduced infiltration rates (Kandra et al., 2014). SCMs are generally designed to treat stormwater resulting from rainfalls of up to 3 or more cm/hr. The rainfall becomes runoff after contact with impervious surfaces, and it is subsequently concentrated for treatment for transport into a SCM that is often 10 to 20 times smaller in area compared to the drainage area (Weiss et al., 2007). Therefore, stormwater treatment media will require infiltration/treatment superficial velocities of 30–60 cm/h with a small hydraulic gradient of just over 1 (Funai and Kupec, 2017). This will require that the treatment medium is granular with particle sizes typical of sand and is not compacted.

Wood-based feedstocks generate biochar that are coarser and predominantly xylemic in nature, whereas biochar produced from crop residues (e.g., rye, or maize) and manure offer a finer and more brittle structure (Sohi et al., 2010). Based on the research in this study, the application of coarse-grained parent material and pyrolysis at lower temperatures results in coarser biochar. Therefore, biochar and other adsorbents with particle sizes in the range of 0.4–2.0 mm are recommended for handling common hydraulic loads of stormwater (Kandra et al., 2014). Wood-derived biochars are recommended, as they tend to be coarser than biochar originating from other feedstocks. Some manufacturers market biochar based on different size classes and, while bulk density is an important parameter controlling hydraulic conductivity, it is critical to avoid introduction of fine particles to the medium as well as screen for adequate hydraulic conductivity. Thus, it is suggested to screen new media by particle size due to practicality in purchasing and ability to avoid fine particles and achieve sufficient hydraulic conductivity. Biochar may be added as an amendment to SCM media, thus the addition amount and characteristics of the bulk mixture become important when determining the hydraulic conductivity. Hydraulic conductivity should be determined for specific media and mixtures if it is not already known.

2.3. Adsorption capacity and batch adsorption experiments (Box 4)

Understanding both the capacity and rates for adsorption of COC onto media in SCMs are important for the selection and work towards scale-up and site design. Batch laboratory studies can be employed to determine equilibrium adsorption characteristics of the adsorbent for

Table 5
Selected biochar based on criteria discussed during the decision framework developed in this study.

Biochar #	Distance (km)	feed stock	Pyrolysis Temp (°C)	particle size distribution	Surface Area (m2/g dry)	bulk density (g/cm3)	C%	N%	pH	Ash %	H/C (molar ratio)	Moisture (% wet wt.)	NH4+-N (mg/kg)	NO3-N (mg/kg)	Org-N (mg/kg)	Tot-P (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	EC (EC20 w/w) (dS/m)	Liming (% CaCO3)	Score
BC-1	450	Southern pine	1,000	>2.4mm: 14.1%; 2.4-0.4mm: 48%; <0.4mm: 37.8%	607.9	0.42-0.54 (dry)	85	0.7	8.3	2.9	0.32	67	19	0.45	6636	358	8.8	18.1	0.27	9.1	63
BC-2	2800	Pine wood	550-600	0.4-2.4mm: 8.5%; 2.4-4.8mm: 20%; >4.8 mm: 71%	400		81.7	0.3	8.5	1.2	0.7	5.6	8	41	3177	24	2.4	6	310	5.1	54
BC-3	1100	wood waste diverted from landfill (75%softwood, mostly Southern Yellow Pine and 25% hardwood, mostly Oak)	550-700	2-4 mm: 6%; 4-8 mm: 44.4%; 8-16 mm: 43.5%; 16-25 mm: 5.6%	267	0.19	85.7	0.8	9	4.8	0.39	4.1	3.4	0.9	7975	263	9.3	26	0.203	3.3	52
BC-4	4300	Doug fir and ponderosa pine	850-950	<1 mm: 4.6%; 1-2mm (49.8%); 2-4 mm: 44%; >4mm: 1.8%	456	0.08	83.6	0.9	11	8.7	0.25	27.6	8.4	1.7	9413	725	57.1	113	1.212	11.1	42
BC-5	2800	Pine wood	550	<1 mm: 5.8% 1-2 mm: 8.6%; 2-4 mm: 21.8%; 4-8 mm: 36.1%; >8mm: 27.8%	237	0.09	82.5	0.5	9.1	1.9	0.56	13.6	11.9	0.4	5417	273	3.1	30	0.21	10.5	54
BC-6	2800	Pine wood	550	1-2mm :48.4% 2-4 mm: 47.5%	567	0.08	86.2	0.8	9.4	5.1	0.25	30.5	8.4	1.11	5417	725	66	76.5	1.86	11.1	49

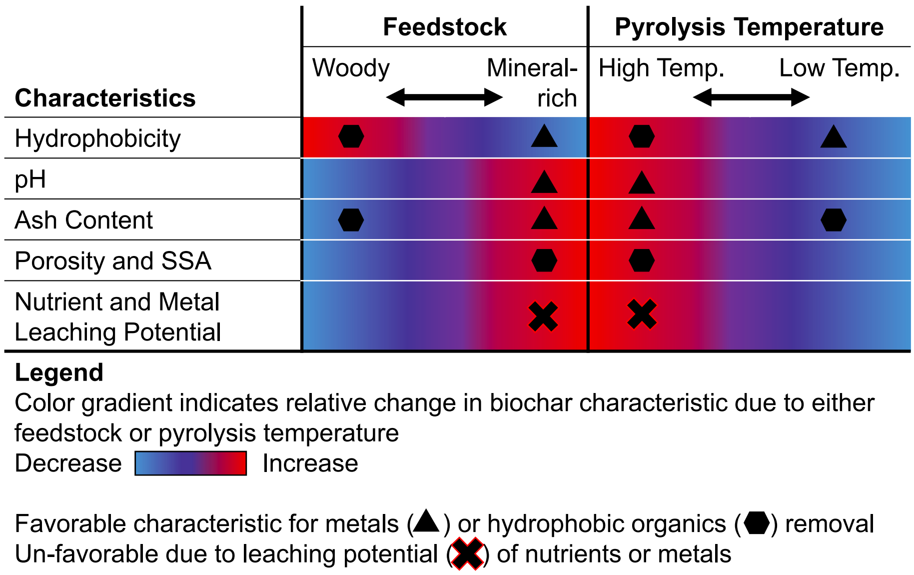

Fig. 2. Initial screening process for selection of biochar. Effect of feedstock and pyrolysis temperature on important characteristics for adsorption of metals and hydrophobic organics.

the specific stormwater chemicals of interest, when suitable materials have been selected based on performance characteristics incl. particle size (Fig. 1). The batch adsorption studies are fast (a few days) thus several adsorbents can be compared, and the results can be used together with isotherm models (Freundlich, Langmuir, linear, others) to evaluate the experimental data under equilibrium conditions (e.g., Yan et al., 2016, Ostrom et al., 2019). Stormwater composition varies depending on the site, precipitation, land use and other aspects most often resulting in pollutant concentrations that are low compared to other polluted waters. Batch studies allow for the determination of media adsorption capacity for specific COC under low-concentration stormwater conditions (Fig. 3). The water chemistry (pH, ionic strength, hardness, alkalinity, natural organic matter) should be properly considered since these impact adsorption. The kinetic tests should be performed in a chemical matrix similar to that expected for stormwater environmental conditions (e.g., pH, temperature, ionic strength). The performance of different adsorbents should be compared at the COC concentration range expected in the stormwater, and not only for the maximum capacity, since this capacity will not be reached under low COC stormwater concentrations and adsorption strength may vary with concentration.

Several studies have evaluated adsorption isotherms for COCs onto biochar (Tables 1–3) (Ahmad et al., 2014; Inyang and Dickenson, 2015; Inyang et al., 2016; Mohanty et al., 2018). For PCBs (Table 1), it was shown that the planarity of PCB congeners can result in different isotherms for the same biochar, whereas non-planar congeners show consistent and improved sorption (Wang et al., 2016). However, at higher pore water concentrations, the planarity of the congeners

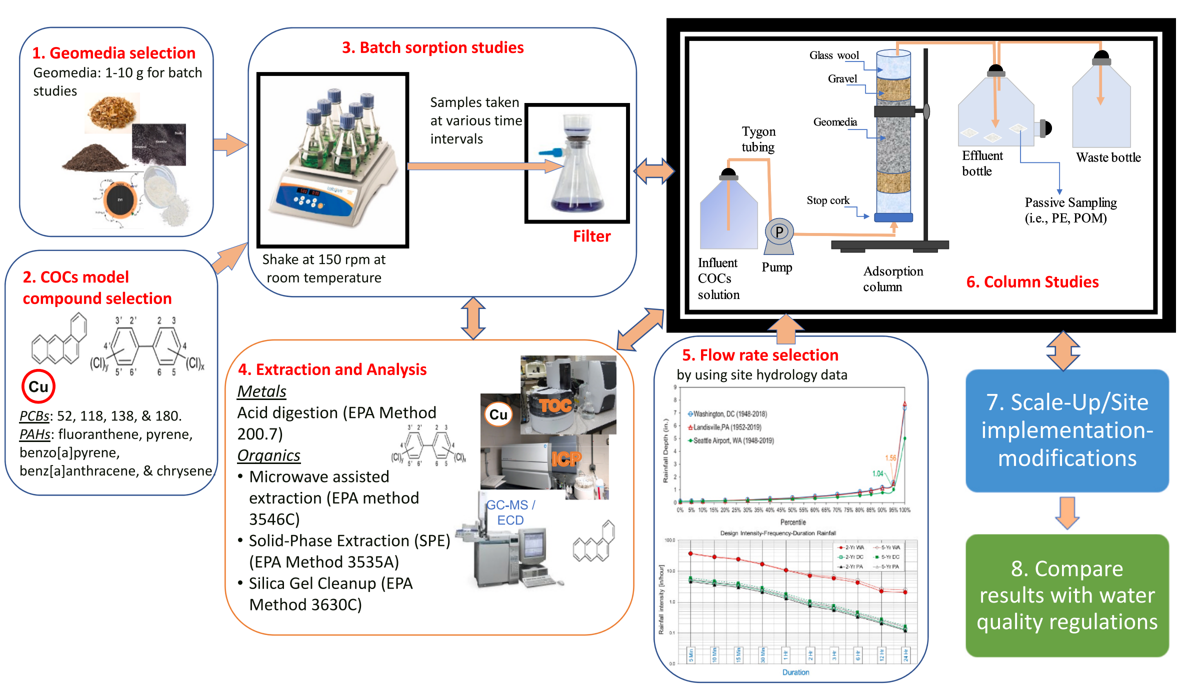

Fig. 3. Experimental approach for biochar selection based on batch and column studies of COC.

becomes less important, and their sorption affinities are near equal (Gomez-Eyles and Ghosh, 2018).

Typically, the maximum adsorption capacities increase with decreasing adsorbent particle size (Tables 1–3), which is attributed to shorter diffusion paths for the contaminants. This allows for deeper penetration of adsorbate into the adsorbent particle. Furthermore, the total external surface area per unit volume for smaller particles is larger.

During batch studies, possible leaching of materials from the adsorbent should also be evaluated. Depending on the adsorbent and its feedstock, leaching of different compounds can occur such as metals (aluminum, iron, heavy metals), nutrients (N, P) and organic matter. The leaching may decrease over time and dynamic leaching characteristics can be investigated using longer-term column studies (Fig. 3).

2.4. Estimating stormwater treatment flow rates, volumes, and durations (Box 4)

To perform batch studies that result in representative results, stormwater flow rates should be selected based on expected flows generated from historical rainfall depth-duration-intensity-frequency relationships for the area of interest since the weather and precipitation characteristics change significantly. Local and regional stormwater regulations also vary and should be included. In this study, precipitation data from three locations were examined: District of Columbia, Mechanicsburg, PA and Tacoma, WA (Tables S1–S3). The impact of the climate/hydrologic differences on stormwater characteristics must also be considered when developing media-based solutions that will be efficient for stormwater runoff conditions. This translates to examining a range of flow rates for media performance. Due to the varying impacts of climate change on weather patterns around the world and in the US, the selection of representative historical precipitation data will become more difficult. A discussion of these changes has not been included in the development of the current decision framework.

Volume of stormwater treated for a specific storm event is commonly defined by a water quality volume, based upon the "first" flush concept and the capture and treatment of an initial runoff volume, without leading to excessive SCM size (Hathaway et al., 2012). First flush of particulate matter is common in urban stormwater runoff situations (Sansalone John and Cristina Chad, 2004). The initial parts of the hydrograph commonly show the highest COC concentrations and incrementally, the COC mass is greater than the corresponding incremental runoff volume (Sansalone and Buchberger, 1997). A first flush is generated as the initial rainfall contacts the land surfaces that contain pollutants that have accumulated on the surfaces since the previous wet weather/wash off event.

The Water Quality Volume (WQV) is a runoff volume based on the amount of impervious cover at a site. Runoff volume criteria are commonly expressed as a depth of rainfall or runoff over the drainage area (e.g., Maryland Stormwater Design Manual, 2009). The stormwater volume that must be captured/managed in the SCM is obtained by multiplying the depth by impervious drainage area. This criterion is specified by the regulating jurisdiction. WQV is specified to size structural control facilities to capture and treat the small/midsize storms up to a maximum runoff depth and the "first flush" of all larger storm events (Hathaway et al., 2012). The Water Quality sizing criterion specifies a treatment volume (depth over drainage area) required to remove the majority of the total stormwater pollution load by intercepting and treating between the 80th and 90th (typically 85th) percentile storm event, which varies from approximately 1.3 cm in arid regions to 3.8 cm in humid regions. The 85th percentile volume has traditionally been considered the point of optimization between pollutant removal ability and cost-effectiveness (Battiata et al., 2010). Capturing and treating a larger fraction of the stormwater runoff would remove decreasing amounts of pollutant and require much larger SCM sizes thus increasing the cost for relatively little benefit.

In the US, Section 438 of the Energy Independence and Security Act of 2007 requires the use of the 95% annual daily storm event as a SCM design requirement (USEPA, 2009). This is the annual 95th percentile of average daily precipitation depth, which is determined using long-term daily precipitation records from the National Oceanic and Atmospheric Administration (https://www.weather.gov/marfc/DailyPrecipitation). A statistical comparison of precipitation data, based on historical records of precipitation for the three locations in the United States used in this study can be found in Tables 6–8. For this analysis, approximately 95%, 86% and 85% of the total rainfall volume occurred (Fig. 4) in storms of 2.5 cm or less plus the first 2.5 cm of rainfall from all larger storms for Washington, D.C., Landsville, PA and Seattle Airport, WA. Differences in rainfall characteristics became clear when comparing the number of rainy days (≥0.25 cm) to the number of days with large rain events (≥2.54 cm) (Table 6). From a SCM perspective it is important

Table 6
Presentation of location and rainfall data for PA, DC and WA.

State	PA	DC	WA
Station	Landisville 2 NW	National Arboretum	Seattle Tacoma International Airport
Latitude	40.11903	38.9133	47.4444
Longitude	−76.4265	−76.97	−122.3138
Elevation (ft)	109.7	15.2	112.8
Rainfall data collection start date	4/1/52	8/1/48	1/1/48
Rainfall data collection end date	2/12/19	12/31/18	2/12/19
Total number of years data collected	66.62	68.40	71.12
Min Rainfall (in.)	0.00	0.00	0.00
Max Rainfall (in.)	7.74	7.37	5.02
Avg. Rainfall (in./day)	0.12	0.12	0.11
Avg. Rainfall (in/yr)	41.48	42.85	38.83
Rainfall depth from the 95th percentile storm event (in)	1.52	1.56	1.04
Total rainfall from the 85th percentile storm event (in)	0.79	0.97	0.65
Cumulative rainfall depth (%) or yearly volume % of total storms collected when ≤ 1 inch plus the first inch of rainfall from all larger storms collected over 67, 68, and 71 years for each location obtained from Figs. S1–S3	85.6%	85.2%	94.5%
The average number of days with precipitation ≥ 0.1 inch (per year)	75 (20% of all storm events)	73 (20% of all storm events)	94 (26% of all storm events)
The average number days with precipitation ≥ 1 inch (per year)	10 (3% of all storm events)	11 (3% of all storm events)	5 (1% of all storm events)
The average number of days with precipitation ≤ 1 inch (per year)	350 (96% of all storm events)	352 (96% of all storm events)	360 (99% of all storm events)

Table 7
Rainfall Depth-Duration-Intensity-Frequency values for durations of 5-min to 5760-min (96-hr) with 2-year return frequencies for Tacoma, Washington, Mechanicsburg, PA and Navy Yard, DC, (Data from Tables A1–A3 for flow rate selection) (NOAA-NWS, 2019).

Location	Tacoma, Washington		Mechanicsburg, PA		Navy Yard, DC	
Frequency	2-yr		2-yr		2-yr	
Duration min (hr)	Depth (in)	Intensity in/hr	Depth (in)	Intensity in/hr	Depth (in)	Intensity in/hr
5	0.13	1.53	0.38	4.57	0.43	5.1
10	0.20	1.19	0.61	3.64	0.68	4.07
15	0.25	1.00	0.76	3.04	0.85	3.42
30	0.35	0.69	1.05	2.1	1.18	2.36
60 (1-hr)	0.44	0.44	1.31	1.31	1.48	1.48
120 (2-hr)	0.59	0.29	1.52	0.76	1.71	0.86
180 (3-hr)	0.73	0.24	1.65	0.55	1.83	0.61
360 (6-hr)	1.06	0.18	2.03	0.34	2.23	0.37
720 (12-hr)	1.12	0.09	2.47	0.21	2.68	0.22
1440 (24-hr)	2.06	0.09	2.9	0.12	3.12	0.13
2880 (48-hr)	4.00	0.08	3.35	0.07	3.63	0.08
4320 (72-hr)	4.50	0.06	3.56	0.05	3.83	0.05
5760 (96-hr)	6.00	0.06	3.77	0.04	4.03	0.04

In general, intensity = (60 * depth (in))/duration (hr).

Table 8
Selected rainfall durations for flow rate selection for SCM studies.

Duration (h)	Intensity (in/h)	Intensity (in/h)	Flow rate (cm/h)
	East coast	West coast	
1	1.4	**1.4**	71.7
12	0.2	**0.44**	**22.5**
24	0.12	**0.1**	5.1

how many times per year a rainfall event of given magnitude can be expected to occur. This information is needed to determine the storage volume, a design volume the SCM must safely hold and treat (USEPA, 2009).

The above estimation of stormwater flows is important if the media batch studies will be followed by column studies to evaluate dynamics situations in a representative way. For column studies, site conditions will determine water quality volumes and rainfall/runoff intensities. Depths and intensities must then be multiplied by an appropriate parameter to account to the ratio of drainage are to SCM surface area. This value could be somewhere between about 8 and 30 (Weiss et al., 2007). A multiplier of 20 has been frequently used (Yan et al., 2018).

2.5. Adsorption capacity, rates, and column adsorption experiments (Box 4)

Based on batch study results, the most promising adsorbents can be selected for more rigorous column studies to determine their adsorption capacity/lifetime, removal efficiency, and mass transport limitations for COCs. Column operation allows for more realistic treatment conditions than batch studies. Contact time in field SCMs is controlled by the depth of the treatment media and the flow velocity through the media (which depends on media size and hydraulic gradient). Small column studies (i.e., 2.5–5.0 cm internal diameter and 20–50 cm length) can be carried out by filling the column with a predetermined amount of a selected biochar. The amount of the adsorbent can be estimated from the batch isotherm data or by using existing isotherm data derived from published literature for the contaminant of interest (Tables 1–3). The adsorbent alone may be added to the columns, or it can be mixed with an inert material (e.g., silica sand) at ratios as low as 1% adsorbent. Lower ratios would be used to promote a shorter breakthrough time for experimental convenience. A synthetic stormwater made with COCs mixtures of a collected stormwater is pumped at constant flow rate designed to maintain desired media contact times. The flow rate/hydraulic loading can be estimated based on required infiltration rates for the climatic area under consideration (Fig. 3) as described below.

A stormwater column study may be expected to last several months. Effluent samples are periodically collected, and the performance of the column adsorption is evaluated in terms of a breakthrough curve (Fig. 3). The loading behavior of COCs in a fixed bed column is stated in term of C_t/C_0 (effluent concentration/input concentration) with respect to time for a particular bed height, flow rate, and initial concentration of COCs. These measurements would continue until reaching breakthrough (the appearance of a non-zero column effluent concentration or a concentration over a specified limit), and ideally exhaustion (column effluent concentration equal to the influent concentration), during this time. The time required for breakthrough and the shape of the breakthrough curves are important elements for assessing the dynamic response of an adsorption system (Malkoc and Nuhoglu, 2006). Sampling intervals might be large initially and become smaller as breakthrough is approached. At breakthrough, the capacity of the adsorbent is determined at the stormwater COC concentration, based on the total mass uptake of the COC and the mass of adsorbent used. The lifetime of the adsorbent is estimated based on the depth (volume) of water treated. Higher pollutant concentrations should *not* be used to force faster breakthrough, since this can change the isotherms due to changes in kinetics. The higher concentration changes the adsorption capacity of the adsorbent and negates any correlation back to use of the adsorbent at the lower concentration. A higher flow rate can be used to force a faster breakthrough, with consideration of mass transfer limitations at higher rates.

In separate experiments the removal dynamics of COC as a function of flow rate/contact time can be evaluated to determine the necessary contact time for removal of COCs (Yan et al., 2017, 2018) and assess the mass transfer limitations in the porous media columns. Therefore, column studies are performed with different flow rates (Fig. 3). Steady state COC removal is evaluated after passage of at least three bed volumes of synthetic stormwater for contact times ranging from approximately 5 to 200 min. As the contact time decreases, the concentration of the COC exiting the column will be increased because adsorption can occur.

As previously described, stormwater runoff is highly dynamic thus steady state column operation can provide information on media capacity and mass transport limitations. Changes in flow rates and/or pollutant concentrations during a column experiment will provide more realistic results at the expense of more complex and time-consuming studies. In addition, to assess the impact of dry/drained/wet conditions (real field situations) on the efficiency and capacity of media as

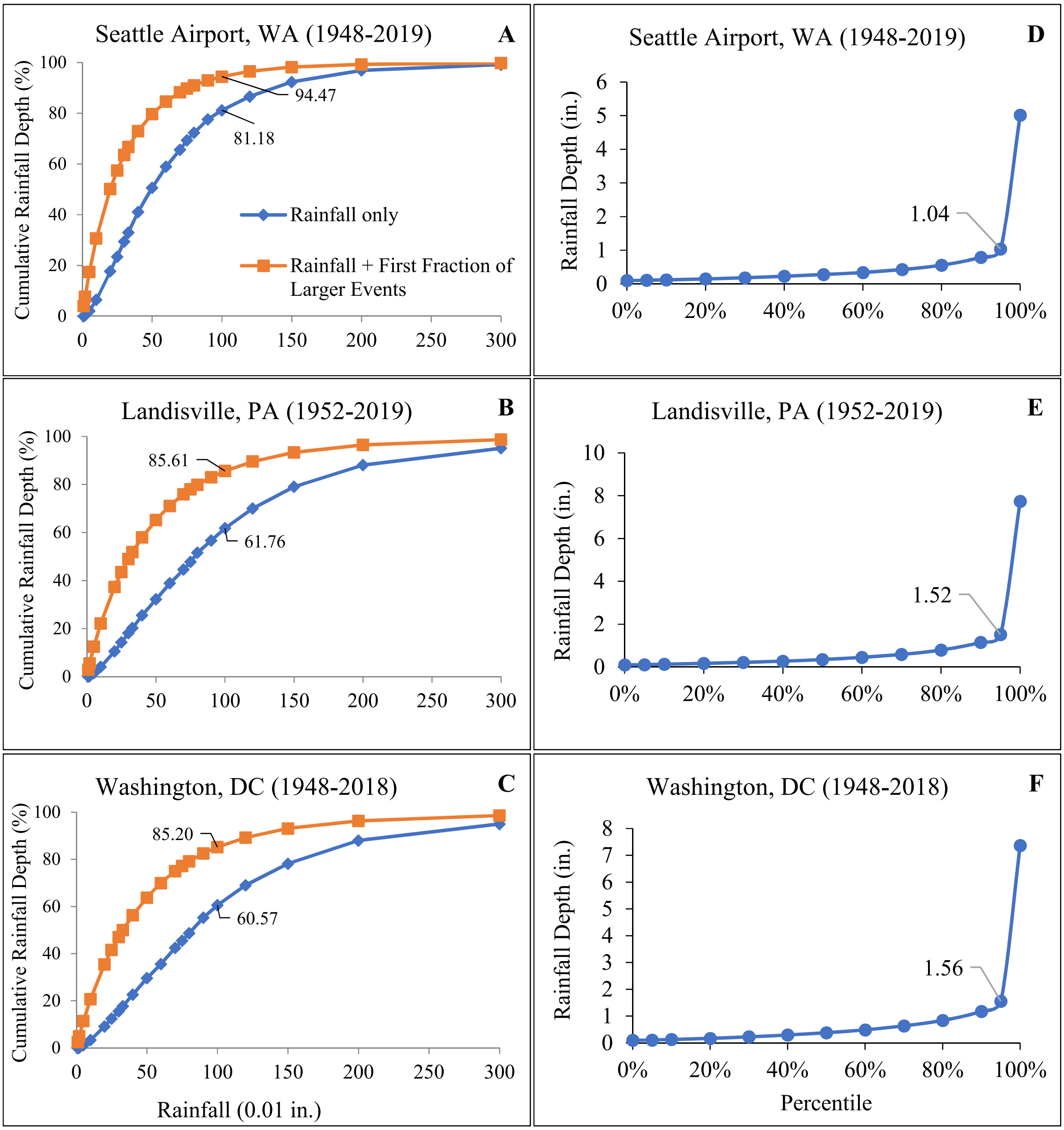

Fig. 4. Cumulative rainfall depth from 71, 67, and 68 years of data at Seattle Airport, WA (A), Landsville, PA (B), and Washington, DC (C), and Rainfall depth from the 95th percentile storm event for Seattle Airport, WA (D), Landsville, PA (E), and Washington, DC (F).

well as desorption of COCs, columns can be prepared that can be charged with stormwater for several hours and then allowed to subsequently drain for several days. These types of studies can provide information about pollutant transformations (chemical and biological) during drying periods in SCMs.

The stability of COCs in post-treatment media can be assessed through a series of fate studies such as desorption (leaching) of COCs, since leaching can result in treatment failure and COC breakthrough. The desorption studies are designed to evaluate the mass of adsorbed COC subsequently available for leaching into clean water in contact with the biochar. Concurrently, biotransformation of organic COCs and mobility of metals can be assessed through the loss of COC mass over time on biochar or other media in biologically active study systems.

Column adsorption data have traditionally been presented based on the treated water volume as 'empty bed volumes'. With stormwater, a more accurate reference can be depth of water treated, which corresponds to stormwater depth. With drainage area information highlighted, treated stormwater depth can be correlated to rainfall and then (using annual rainfall information) to years of operation for the media. From this predicted lifetime, mass of required media may either be scaled up or down accordingly to meet a desired lifetime. Ideally, these experiments will lead to selection of media that has a high capacity and stability for the targeted COC in order to reduce the need for maintenance and extend the lifetime of the SCM, i.e., media with a documented long time (large volume treated) until breakthrough.

2.6. Stormwater treatment through mesocosm studies (Box 5)

Larger column or mesocosm laboratory test systems can be used to provide more realistic performance data (e.g., Davis et al., 2001, 2003;

Bratieres et al., 2008; O'Neill and Davis, 2012; McManus and Davis, 2020). These systems will have depths that approach that of field-scale systems (up to 1.2 m) and surface areas of around 0.2 up to 1.0 m^2. Such study systems should be constructed as a field system using the media recommendations determined from previous studies. This would include needed inclusion and layering of media and stabilizing components such as sand but could also include vegetation. Vegetation would have to be selected to fit the climate and other constraints of the sites (Read et al., 2008). However, the complexity that plants add to the study system often results in vegetation being applied as the last step to confirm that sufficient treatment takes place in the presence of vegetation. The systems can be gravity-fed with stormwater at appropriate "storm" sizes and intervals to evaluate water and pollutant mass balances. Stormwater volumes (depths) would be applied to match those in the field and water would be allowed to collect and pool if conditions permit. Samples can be collected at the discharge point of the mesocosm, along with discharge flow rates and volume. These systems are often left to drain for several days thus mimicking natural events and the storm event would be repeated. Such experimentation can last for several months to collect reliable, representative, and adequate data.

Effluent concentrations can be represented dynamically as they vary with time during a storm event, or they can be composited as an Event Mean Concentration (EMC), the total event mass per total event volume (Davis et al., 2022). If influent concentrations are varied, EMCs can be used to represent these COC concentrations also. At the end of the mesocosm study, the media can be evaluated for accumulated COC and other environmental parameters of interest. COC are expected to accumulate from the top down in a media-based SCM and this accumulation can be demonstrated in post-experiment destructive testing (e.g., Blecken et al., 2009b).

2.7. Field studies (Box 5)

Once media, configurations, and other parameters are selected, full-scale design and design of field SCMs can proceed (Fig. 3). Monitoring of the field SCM should be considered prior to design and implementation with the SCM having a single inlet point and outlet point. Flows into and leaving the system could be monitored using a flow measurement devise, such as a weir or flume (e.g., Hunt et al., 2006; Li and Davis, 2009; Trowsdale and Simcock, 2011; Li and Davis, 2014). Collection of volume-weighted samples should be done throughout the storm event so that the EMC can be measured. Protocols for sample collection, retrieval, storage, preservation, analysis, and reporting should be maintained (Fig. 3). At a minimum, rainfall data should be collected at the site, but additional weather data may prove helpful in explaining the overall performance of the SCM. A sufficient number of storms should be monitored to provide a statistically reliable determination of the performance of the SCM. This could require from one to three years of field monitoring and data. As in mesocosm studies, samples of media can be collected and analyzed to determine pollutant fate, estimate pollutant penetration into the media, strength of pollutant affiliation, and pollutant mass balances (e.g., Li and Davis, 2008; Komlos and Traver, 2012; Jones and Davis, 2013). Maintenance requirements and system lifetime estimate can be derived from these data.

2.8. Effect of biological treatment and COC transformation (5)

Assessment of the potential for biodegradation of organic COCs and mobility of metals can be performed at all of the design phases outlined in this study: batch, column and field studies with increasing complexity (e.g. Huang et al., 2018; Xiang et al., 2019). The in-situ potential for biodegradation/transformation of COCs can occur in the laboratory phases by examining the used media in the presence of known microbial cultures that can biodegrade captured organic COCs (LeFevre et al., 2012). As stated earlier, most hydrophobic COCs are bound to PM and hence the ability of microorganisms to degrade PM-bound COCs can be tested by evaluating the SCM media samples containing COCs with an enrichment of the bacteria containing known biodegradation pathways. The change in composition of COCs at predetermined time intervals is monitored and compared to the microbial community composition, their function, their abundance, and who is viable in treatment media. This information will provide insights into development of maintenance procedures for the field SCM, since presence of biodegradation of organic COCs can extend the lifetime of the SCM.

3. Challenges with use of biochar in stormwater treatment media

In addition to the considerations outlined in this evaluation strategy, numerous other challenges are related to biochar application in SCMs. Although biochar has been widely applied as a soil amendment, it has not yet reached the level of commercialization as some other prevalent adsorbents, like activated carbon. As a result, it can be difficult to find biochar with consistent quality and specifications. Furthermore, many biochar manufacturers may not pre-size their product, which limits its use in SCMs, due to the need to limit fine particles in media-based SCMs in order to meet hydraulic conductivity requirements and prevent clogging. Standardization and commercialization of this industry is necessary to provide a consistent quality product for practical and widespread implementation.

Contaminant leaching is an important consideration, as some biochars may act as both a source and sink for various constituents. Some feedstock and pyrolysis temperatures may contribute to the potential for leaching of nutrients and heavy metals, for example municipal wastes or biosolids feedstocks and high pyrolysis temperatures. Colloidal particulates from biochar may also pose a risk as contaminants have the potential to be co-transported with fine or nano particles (Swaren et al., 2022). Finally, biochar-derived dissolved organic matter (DOM) poses a potential risk for mobilization of constituents like Cu, which has a high affinity for DOM (Huang et al., 2019). Contaminant leaching either directly from biochar or because of co-transport of colloids or biochar-derived DOM causing mobility of COCs should be evaluated prior to implementation.

In a study using machine learning to predict heavy metal immobilization by biochar (Palansooriya et al., 2022), N content of biochar and biochar application rate were found to be the most important factors for heavy metal immobilization in soils. Thus, application rates of biochar should be further investigated for media-based SCMs. Many laboratory studies have investigated impacts of different biochar feedstocks and operating conditions on contaminant removal performance, but studies examining different media mixtures are lacking. This is especially important because the type of soil/medium can affect biochar adsorption performance. Several studies have correlated SCM media depth with heavy metal removal, where the top 10 cm of media accumulate the bulk of the particulate and dissolved heavy metals load (Blecken et al., 2009a; Hatt et al., 2008; Jones and Davis, 2013). Theoretically, increasing biochar amount will increase COC removal, however other factors like hydraulic conductivity and practical factors like cost will need to be considered in determining a biochar application rate.

Many long-term challenges related to the use of biochar in stormwater treatment are not yet understood. Aging and weathering of biochar poses a potential risk, as this may cause biochar to breakdown into finer particles which can cause clogging of media or colloidal transport of COCs; microbiological weathering may release adsorbed COCs back into the environment. Physical weathering is primarily caused by slaking, or physically breaking down into finer pieces due to wetting and drying periods, and is dominant in biochars produced at low temperatures with high O% (Zhong et al., 2020). Some laboratory studies have documented effects of artificial weathering (dry-wet and freeze-thaw cycles) of biochars and found a reduced alkalinity in weathered biochars (Xu et al., 2018). They attributed this effect to an increase in oxygen-containing functional groups, production of carbonates, and breakdown of aromatic moieties. Biochemical weathering may occur in the field, through microbial-mediated biochemical processes. During these processes, aromatic carbon moieties can be oxidized, which then form new surface functional groups (Mao et al., 2012). Eventually, highly weathered (>1000 years) biochar can release benzene polycarboxylic acids (Mia et al., 2017). The increase in oxygen-containing functional groups may improve immobilization of some COCs like heavy metals, however the process of aging and weathering may differ for different biochars in different media mixes and climates. While the weathering and aging of biochar in soils has been investigated, the effects of weathering on contaminant immobilization lacks thorough investigation.

Finally, the sustainability of biochar use is a necessary consideration. It is well known that biochar production is lower cost and lower energy input compared to activated carbons. Regeneration of biochar is a possibility, and a challenge for sustainability purposes. Some studies have shown that biochar can be regenerated and perform adequately after multiple regenerations (Wei et al., 2019). These materials also have the potential to be recovered or regenerated for reuse, although regulatory and economic incentive may be lacking for this to be a viable option in stormwater treatment systems. Currently, maintenance of media-based SCMs involves raking and removal of the top layer of media as this contains the bulk accumulation of COCs. Consistent local availability of feedstock is an important consideration for sustainability. Additionally, pyrolysis is the most common production method for biochar production, however other processes like hydrothermal liquefaction may have lower global warming potential (Kumar et al., 2020). Thus, different biochar production methods should be investigated for this purpose.

4. Conclusions

Addressing environmental and ecological challenges of stormwater from complex lands will require specialized SCM and media compositions. Many different materials are possible candidates for use as COC treatment media. Biochar is a promising product, and the properties are affected by the type of the feedstock and pyrolysis temperature. These variations result in biochar products with a wide range of physical and chemical characteristics such as surface area, pore volume, ash and carbon content, pH, CEC, and leachable constituents. High pyrolysis temperature results in biochar with high specific surface area, porosity, ash content, and pH, but with low CEC values. Biochar produced from manure, biosolids, or solid waste feedstocks show lower surface areas, carbon content, and high CEC and nutrients contents compared to plant or wood-based biochar even at higher pyrolysis temperatures. Screening biochar for optimal removal of a targeted COC is important, but evaluation for use in SCM media should consider practical use and dynamic processes.

A stormwater treatment medium should be able to handle stormwater flow rates typical of the sites of interest. With information about the stormwater site and weather data, laboratory studies can be designed that provide information about estimated field designs and operational lifetimes. Scaled up mesocosm studies provide more realistic performance information under controlled conditions. Field scale monitoring and research will require years of study due to the variable conditions of storm events that a SCM will experience. Many laboratory studies have examined biochar feedstock, operating conditions, and even engineered biochars for pollutant removal optimization, however there is a lack of pilot-scale and field studies examining biochar as a stormwater treatment medium. Several key considerations for use of biochar in media-based SCMs are outlined in this paper, including the importance for scale up evaluation due to conditions that can be difficult to mimic in the laboratory.

It is suggested that tradeoff among concurrent efficiency outcomes of pollutants of interest and impacts of stormwater flow rates on system performance can be minimized by employing layers of media in SCMs. Different pollutants may be most efficiently removed by different types of media. Therefore, a possible solution is the development of different treatment modules based on treatment of stormwater characteristics from the site of interest, where local conditions (intensity, contaminant load, duration, and periodicity) influencing the dynamics of the contaminant loadings will be considered. Future research should consider configuration design and addition amount in evaluations of SCM media.

CRediT author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2022.135753.

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