Spokane Ponderos

Spokane Ponderosa, a 501c3 non-profit organization, would like to provide comments and an update to the Stormwater Manual for Eastern Washington. We would like to see Ponderosa pine (Pinus Ponderosa) t added to Zone 1 in Bioretention Swale BMP's. Note that the Stormwater Management Manual for Eastern Washington (SMMEW), page 520, lists Pinus Ponderosa as suitable for Zone 2 and notes it is native to upland sites. However Ponderosa pine tolerates flooding very well, and if often found alongside rivers and streams in Eastern Washington. Ponderosa pine along the Spokane River are submerged several feet up their trunk for weeks in the spring, so periods of water filled bioretention swales would help in their growth (see attached photo).

Note that the SMMEW also says this:

Bioretention BMPs are:

l Shallow landscaped depressions with a designed soil mix and plants adapted to the local climate and soil moisture conditions that receive stormwater runoff from small contributing areas;

2 Designed to mimic natural forested conditions, where healthy soil structure and vegetation promote the infiltration, storage, filtration, and slow release of stormwater flows;...

Figure 5.3 shows a hardwood tree in a bioretention swale, we would like to see Ponderosa pine added since they are appropriate.

Ponderosa pine are also drought resistant and should be included in the tree list that currently only has hardwood trees, grasses and other plants that need watering in the summer. This would help cities increase their urban canopy, provide shading once the trees matured, and improve air quality in cities in eastern Washington.

Spokane Ponderosa has also found that adding biochar when seedlings are planted helps the trees retain moisture for their first few years. In addition, studies have found that biochar can trap contaminents (see attachments) and biochar should be considered as a soil additive in bioretention swales.

Thank you for the opportunity to provide comments.

Mike Petersen for Spokane Ponderosa



Biochar: A Renewable Material for Removing Contaminants from Water

> Pusker Regmi, Jose Luis Garcia Moscoso, Doris Hamill^{*}, Sandeep Kumar[#], and Gary Schafran



Department of Civil and Environmental Engineering, Old Dominion University, Norfolk, VA-23529

NASA Langley Research Center, Mail Stop 254, Hampton, VA 23681-2199

> <u>skumar@odu.edu</u> (757) 683-5354

What is Biochar?

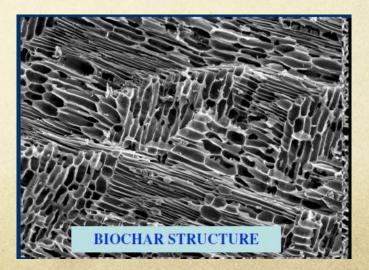
Carbon rich, high energy density solid product resulting from the thermal degradation of biomass. It consists of C, H, O, N, and ash

Essentially a charcoal

Unlike charcoal it is not used as primary fuel

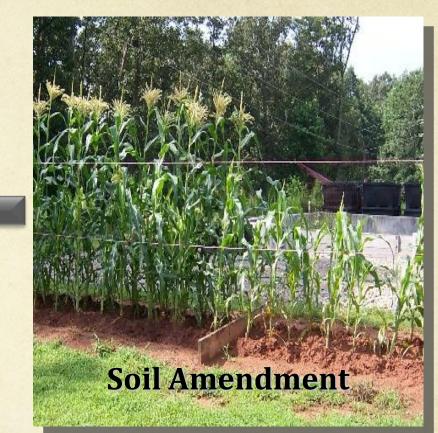
- Highly porous and irregular surface
- □ Its potential as soil amendment was utilized by indigenous people of Amazon





Soil Application

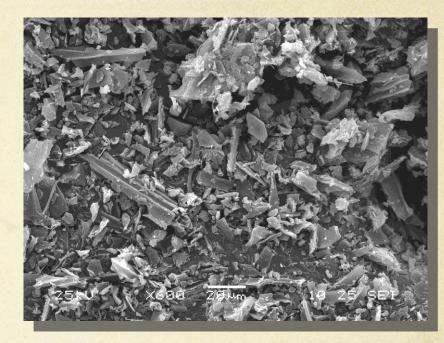
Carbon sequestration



- ✓ Historically, biochar has been used in soil to enhance the plant growth.
- ✓ It helps in improving the water quality.
- The leaching of nutrients from soil, which is one of the cause of ground water pollution is retarded in the presence of biochar

Biochar as Sorbent for Water Treatment

- Porous structure, irregular surface, high surface to volume ratio, and presence of functional group
- Adsorbs both organic pollutants and heavy/trace metals



Biochar can be cost effective alternative to activated carbon

Feedstock for Biochar?

Essentially, all forms of biomass can be converted to biochar.
 Lignocellulosics such as forest thinning, herbaceous grasses, crop residues, manure, and paper sludge are some of the potential feedstock.

Forest Residue

Wood Mill Residue



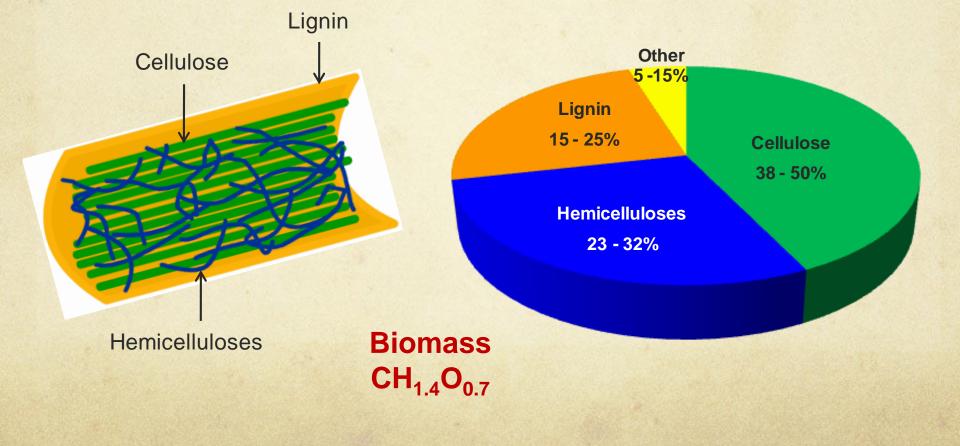
Bark



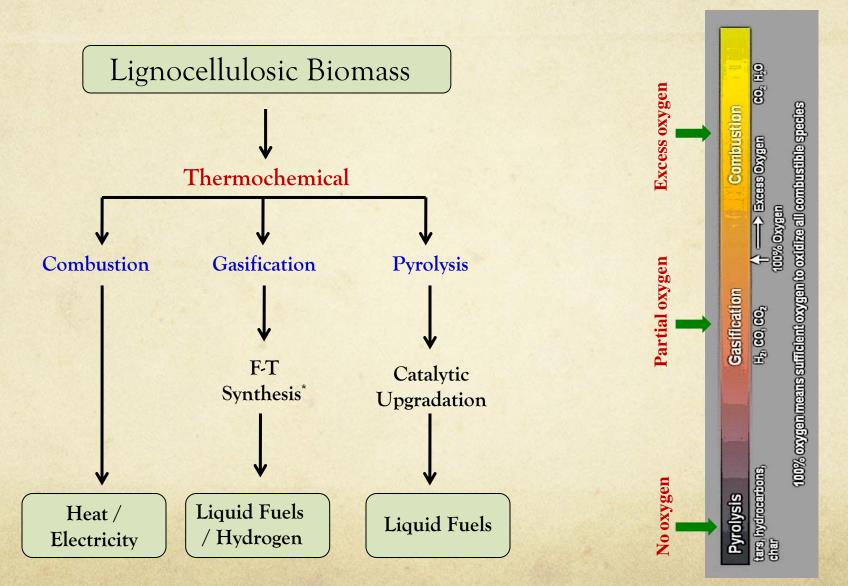
Switchgrass Corn Stover Bagasse Wood chips Image: Corn Stover Image: Corn Stover Image: Corn Stover Image: Corn Stover

Lignocellulosic Biomass

- Renewable organic material
- Non starch based fibrous part of plant material
- □ Major feedstock for achieving 36 BYG of biofuels by 2022 (EISA, 2007)



Thermochemical Conversion of Biomass for Biofuels



A Byproduct from Future Biorefineries

Process	Temperature (°C)	Time	Biochar Yield (%)
Gasification	~ 750	~ 10-20 s	10
Pyrolysis			
Fast	400-700	~ 1 s	12
Moderate	400-700	~ 10-20 s	20
Slow	400-700	~ 5-30 min	35
Hydrothermal Carbonizatio	on 200-350	30-90 min	30-60

Biochar Yield



Oxygen is present in biochar

Biochar (CH_{1.2}O_{0.2})

Temperature

Producing Biochar by Slow Pyrolysis

Combustion



Pyrolysis



Little or no Oxygen

Abundant Oxygen

little or
no heat
little or
no CO₂
H₂O
small
organics
char

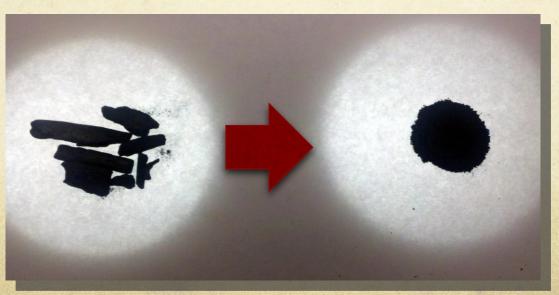
• soot

• ash

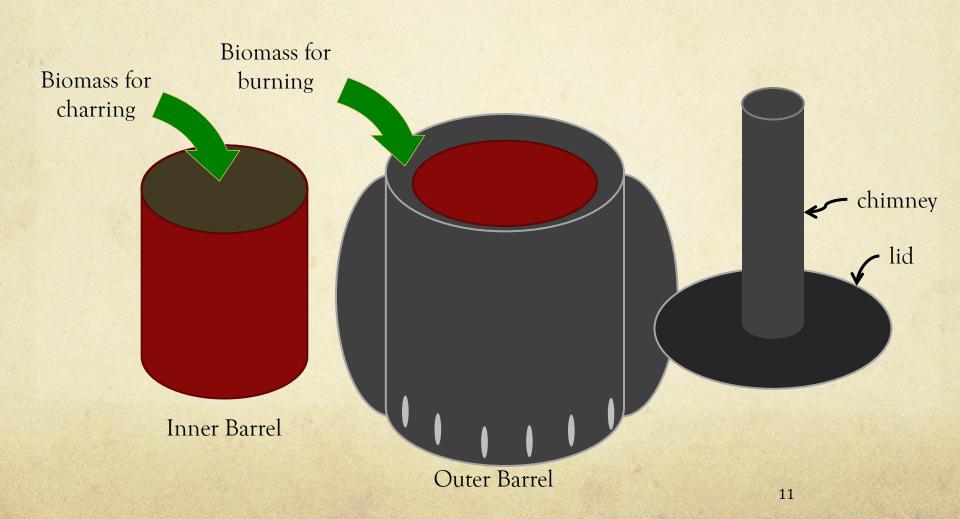
Use combustion to provide heat for pyrolysis

Biochar from Slow Pyrolysis





Two-Barrel Pyrolyzer (Developed by NASA Langley Center)



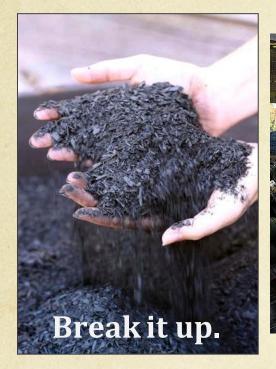
Bluebird Gap Farm, Hampton Event, Nov. 19-20, 2010



City of Hampton, NASA Langley Research Center, and Old Dominion University

Demostration of biochar production via slow pyrolysis and its application in water purification

Using Biochar to Help Plants









Use of Biochar for Water Treatment

Experimental Study with Copper, Cadmium, and Lead Contaminants

Contaminants MCL and their Sources

Trace Metal Contaminants	MCL (mg/L)	Sources
Copper	1.3	Corrosion of household plumbing system, erosion of natural deposits
Cadmium	0.005	Corrosion of galvanized pipes, erosion of natural deposits, discharge from metal refineries, runoff from waste batteries and paints
Lead	0.0	Discharge from steel and pulp mills, erosion of natural deposits, corrosion from household plumbings, erosion of natural deposits

Materials

Single ion solution Cu, Cd, and Pb were prepared

Trace Metals	Concentration (mg/L)	Chemical
Copper	40	CuSO ₄ .5H ₂ O
Cadmium	40	$Cd(NO_3)_2.4H_2O$
Lead	40	PbNO ₃

BATCH STUDY

Batch Experiments

- Three metal solutions were treated with 2 g/L, 1 g/L and 0.5 g/L of biochar
- Samples were collected at 30 mins, 1 hr, 2hr, 6 hr, 24hr, 48 hr, and 72 hr

Metal olution

> Biochar

Atomic absorption spectrometer (AAS Hitachi Z-8230) to measure metal contaminants

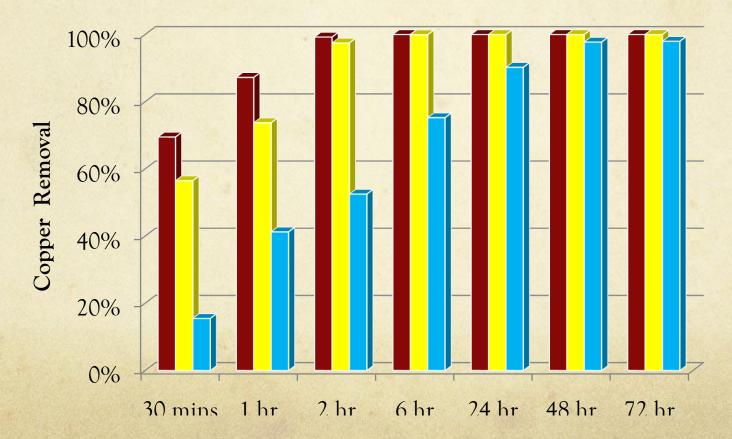


Analysis:

Copper Removal

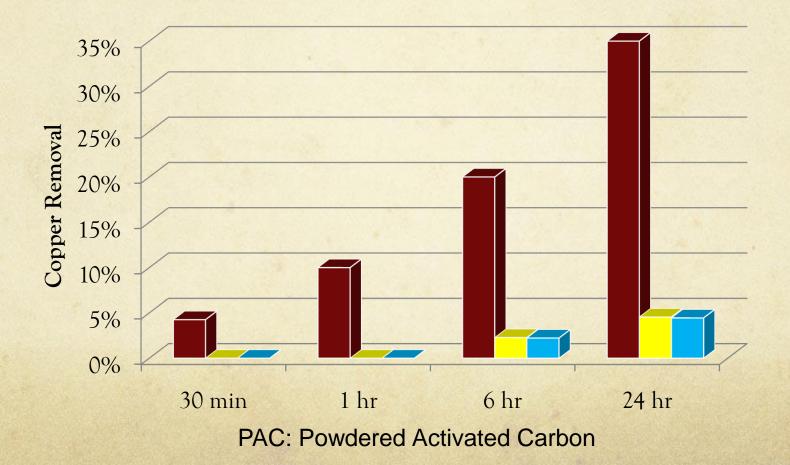
Initial metal conc	pH
40 mg/L	7

■ 2 g/L ■ 1 g/L ■ 0.5 g/L



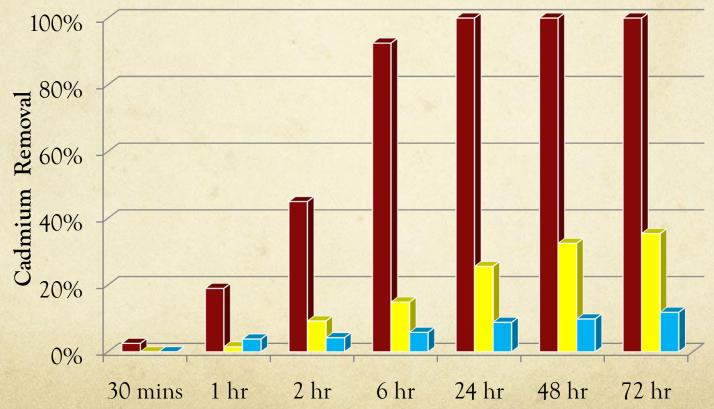
PAC: Copper Removal

	Initial metal conc	pН	
	40 mg/L	5	
■2g	/L <u>1</u> g/L	0.5	o/I

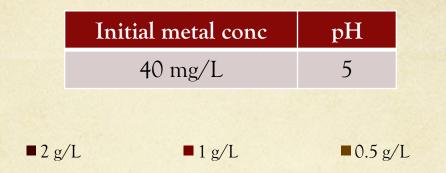


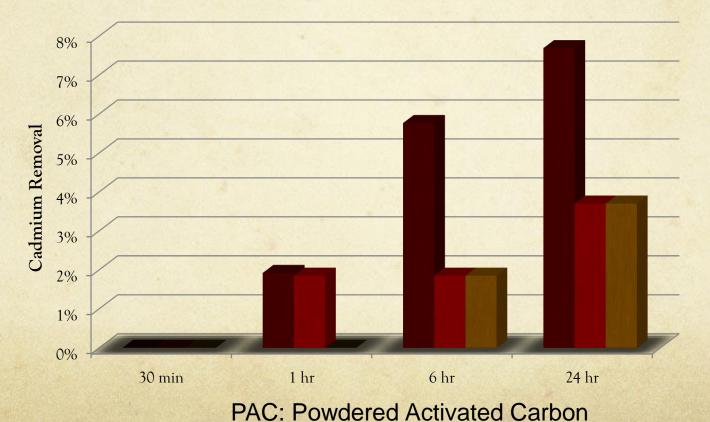
Cadmium Removal

■ 2 g/l ■ 1 g/L ■ 0.5 g/L



PAC: Cadmium Removal

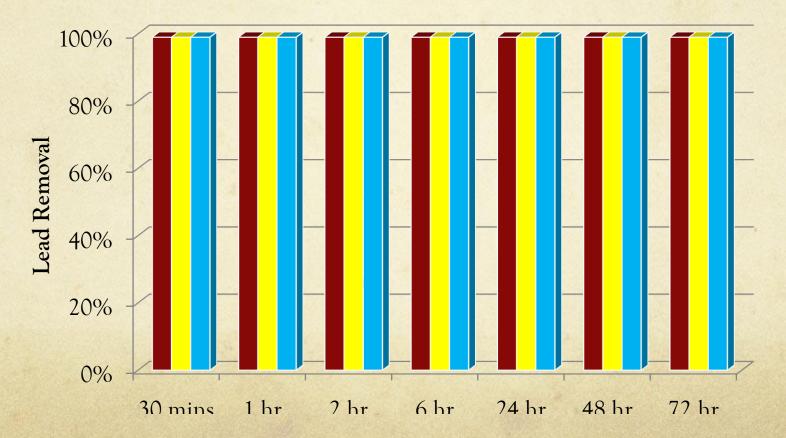




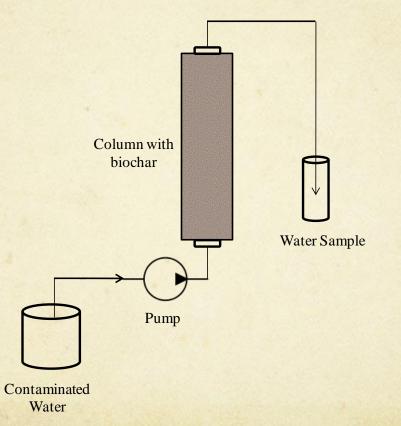
Lead Removal

Initial metal conc	pН
40 mg/L	7

■ 2 g/L ■ 1 g/L ■ 0.5 g/L



COLUMN STUDY



Schematic of column test apparatus

Copper and Lead removal

- Biochar particle size : 0.5 to 1.0 mm
- Measured porosity : 53%
- Volume used in column : 50 ml
- Flow rate for Cu: 2.5 ml/min
- Flow rate for Pb: 3.0 ml/min
- Measurements every 30 min, and 1h after 18 hours of experiment
- Samples analyzed using AAS Hitachi Z-8230

Copper and Lead removal: column study





•2.5 cm diameter columns•50ml of filtering media used

•0.5 – 1.0 mm biochar particles

Copper removal

Time (hours)	C (mg/l)	Time (hours)	C (mg/l)
1	0.0		21.7
	0.0	12	21.7
1.5	0.0	12.5	19.4
2	3.7	14	22.6
2.5	6.6	15	29.1
3	9.8	16	24.8
3.5	13.9	17	22.1
4	12.3	18	14.2
4.5	13.6	19	12.0
5	11.7	20	8.6
5.5	14.6	21	8.1
6	17.4	22	8.9
6.5	17.4	23	8.3
7	13.2	24	6.2
7.5	13.4	25	7.4
8	14.2	26	9.0
8.5	15.1	27	9.4
9	18.4	28	9.9
9.5	20.9	29	7.6
10	22.1	30	10.5
10.5	20.5	31	10.3
11	21.0	Const.	

C/Co = ratio of contaminant removed

C = Concentration measured after filter Co = Initial concentration (40mg/l)

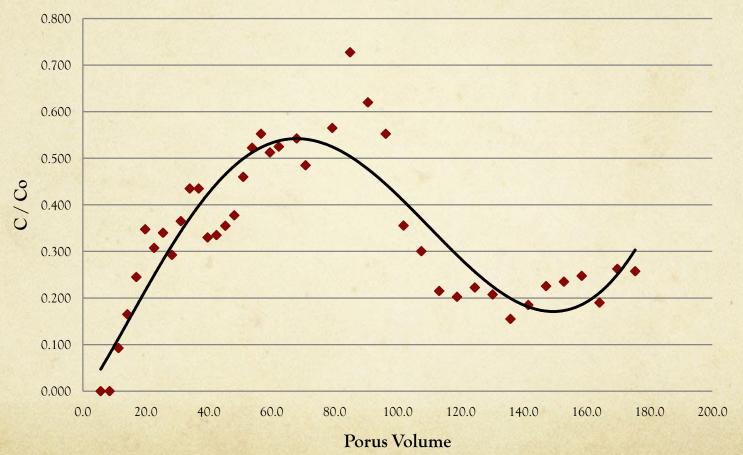
Porus Volume = amount of water that went through the filter porus volume

Filter volume = 50ml
Porosity = 0.53
Porus space = 26.5ml
Flow rate = 2.5 ml/min
pH = 4

Porus volume = (Flow rate * Time) / Porus space

Copper removal

Filter Column Study : Cu removal



Lead removal

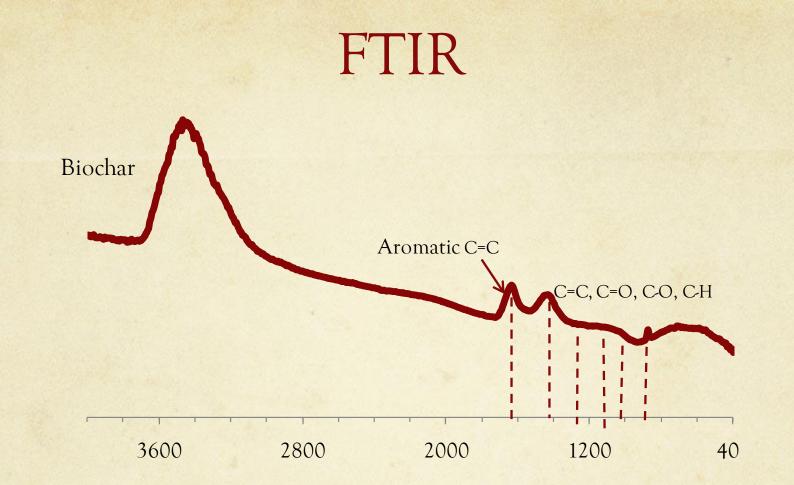
Time (hours)	C (mg/l)
1	0
1.5	0
2	0
2.5	0
3	0
3.5 4	0
4	0
4.5 5	0
5	0
5.5	0
6	0
6.5	0
7	0
7.5	0
8.0	0
8.5	0
9.0	0

After 9 hours of sampling no lead was detected after filtration.

Experiment is still running

C= 0 even after 48 h

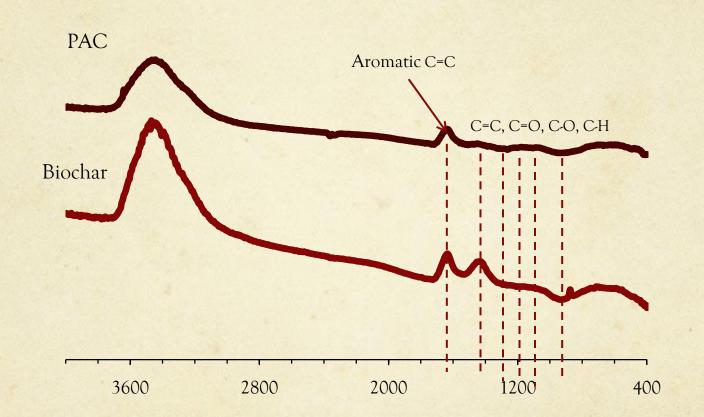
Why biochar worked so well?



• Presence of oxygen containing functional groups such as carboxyl (-COOH), lactone (C=O) and hydroxyl groups

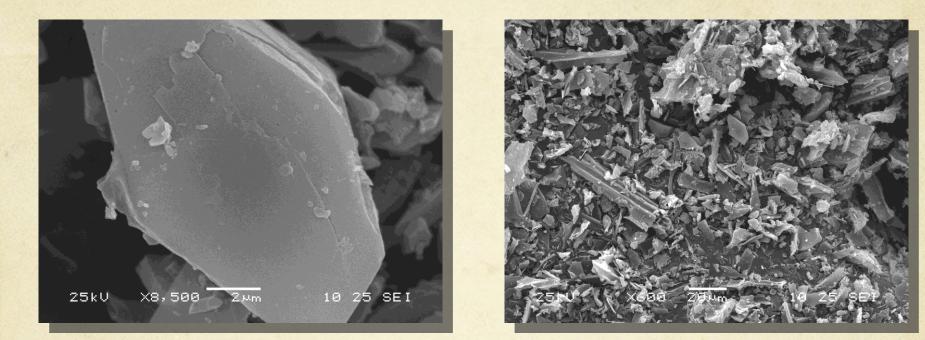
Including Powdered Activated Carbon

(Calgon WPH)



• Lack of oxygen containing functional groups in PAC

Biochar surface



	Biochar	PAC (Calgon WPH)
BET surface area	$70 \text{ m}^2/\text{g}$	$726 \text{ m}^2/\text{g}$

 Irregular surface with high BET surface area (not seen high temperature as in PAC)

Biochar Sorbent Properties

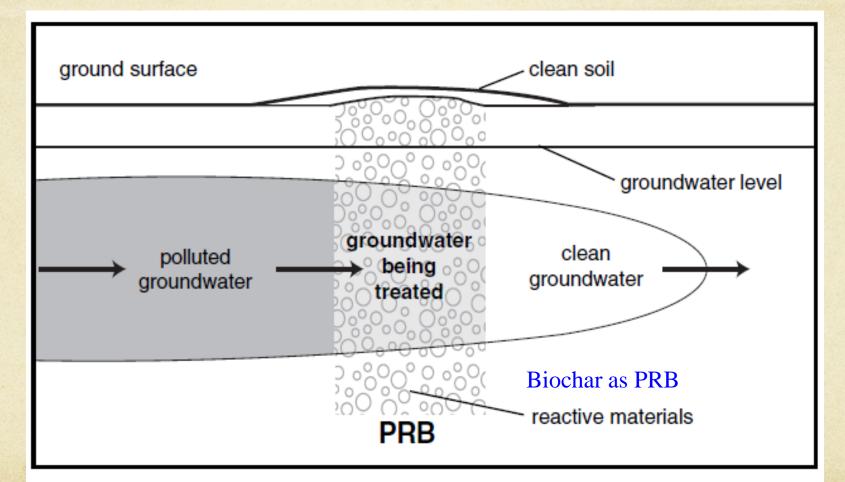
- ✓ The presence of oxygen rich organic compounds on the biochar surfaces adds substantial cation exchange capacity.
- Reported to adsorbs dissolved organic compounds from the soil solution and make them less bioavailable.
- High molecular weight polycyclic aromatic hydrocarbons (PAH) have been reported to be sorbed strongly to biochar surfaces.
- Biochar produced at higher temperature have benefits of high pH, cation exchange capacity, and surface area.
 http://www.biochar-international.org/biochar

Biochar potential applications

Filter water
O Ground water
O Stormwater applications (BMPs)
O Industrial wastewater

Possible Treatment Applications Using Biochar as Sorbent

Biochar as a permeable reactive barrier (PRB) in groundwater treatment



Schematic of groundwater treatment using PRB system. (Source: www.epa.gov/tio/download/citizens/citprb.pdf)

Stormwater Applications

Intercepting storm water flow through the biochar bed

Types of BMPs and proposed biochar application:

i. Infiltration Trenches / Basins:

Proposal: Biochar bed are proposed to be laid over the stones. This may reduce the groundwater contamination by working as a filtration medium.

ii. Detention Basins / Ponds :

Proposal: Lay down a bed of biochar covered with sand / gravel to stop contaminants going to the ground water.

Similar applications of biochar are proposed in (iii) Retention Basins / Ponds (iv) Grassed Swales, and (v) Filter Strips and Buffers types of BMPs around Hampton

Covering the edges of the lawn and garden using biochar, sand and gravel mix

Ref: http://www.hrstorm.org/BMP.shtml

Conclusion

- Small scale community based slow pyrolyzer may be a costeffective option to produce biochar from mixed biomass residue
- Biochar derived from mixed biomass residue can be used as sorbent for water contamination removal and cleaning up waterways
- Trace metal contaminants such as copper, cadmium and lead were almost completely removed by the bichar
- Lead was most amenable to treat with biochar

Even at 0.5 g/L in 30 mins >99% removal was observed

• To understand the amenability of biochar to treat metal several analysis are being performed

Acknowledgement

- Daren Robinson at Hampton's Community Development Department
- Master Gardeners associated with community biochar project at Hampton
- Office of Research at ODU

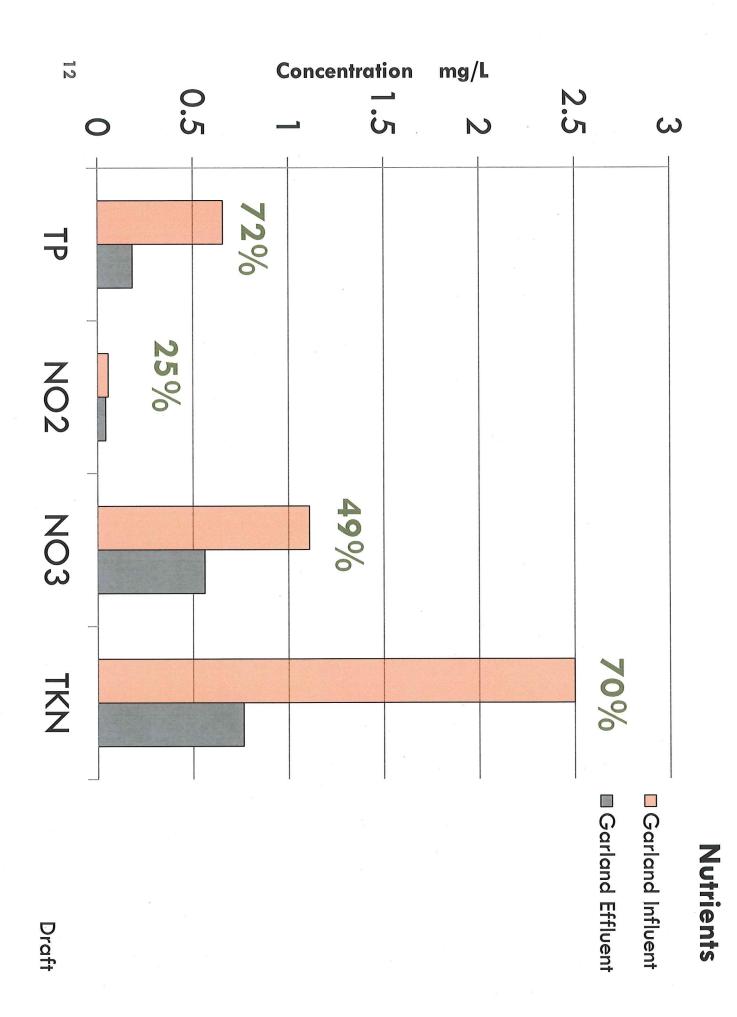
Analytical Results

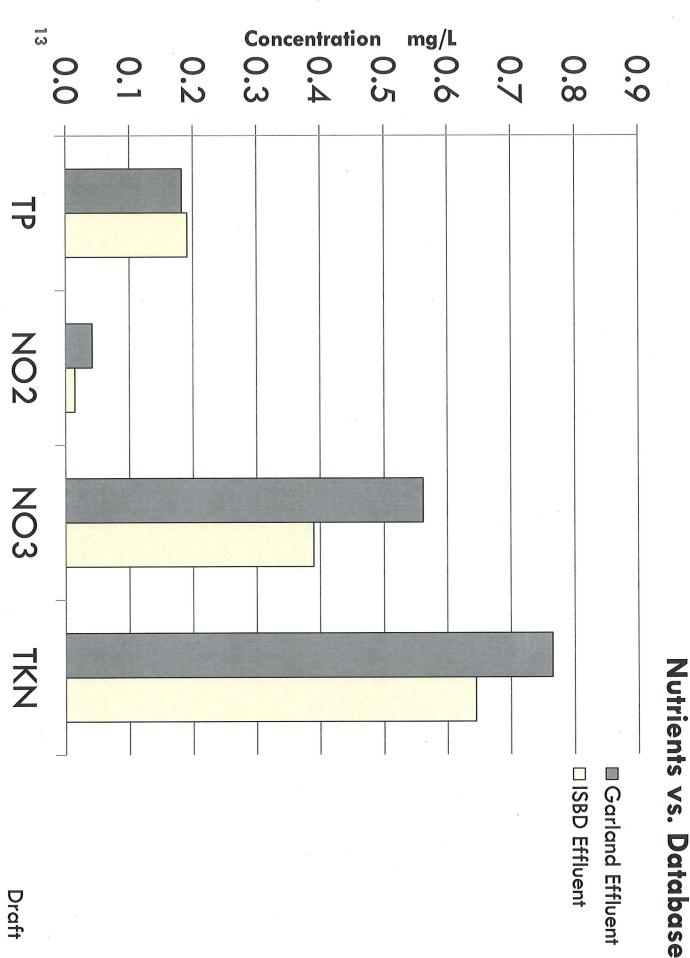


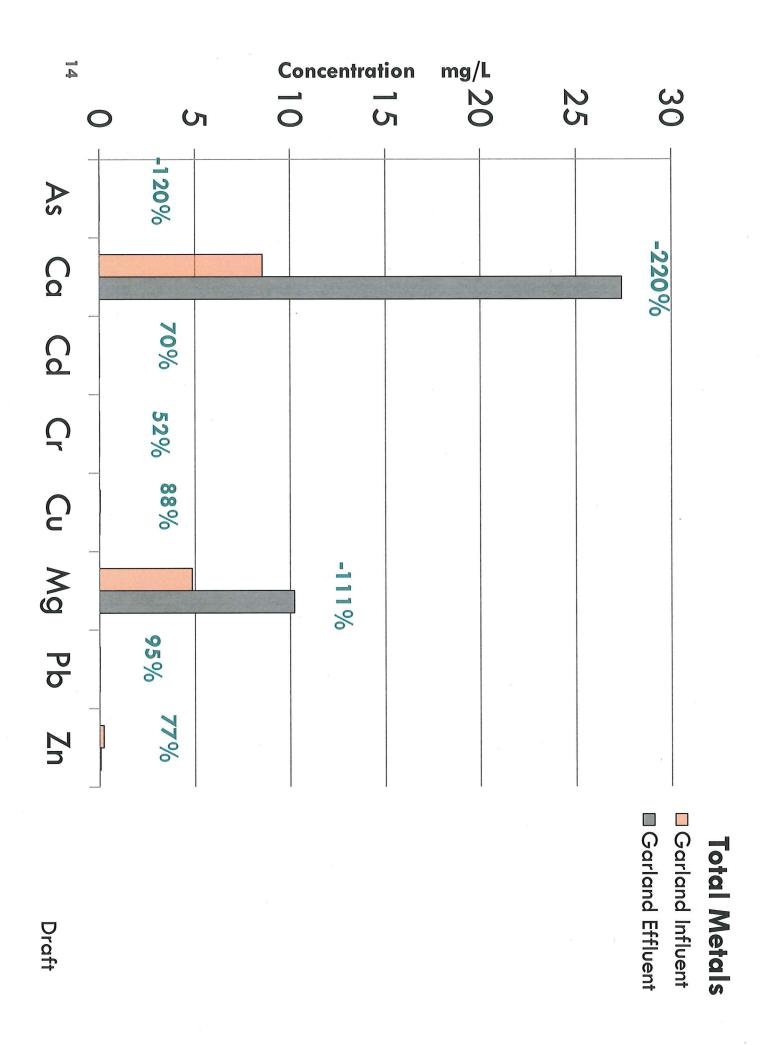
- handout Handout Garland Stormgarden (Water Year 2015-2017)
- 6 sample events
- Constituents analyzed
- Conventionals
- Nutrients
- Total metals
- Diss. metals
- Hardness
- Petroleum
- PCB

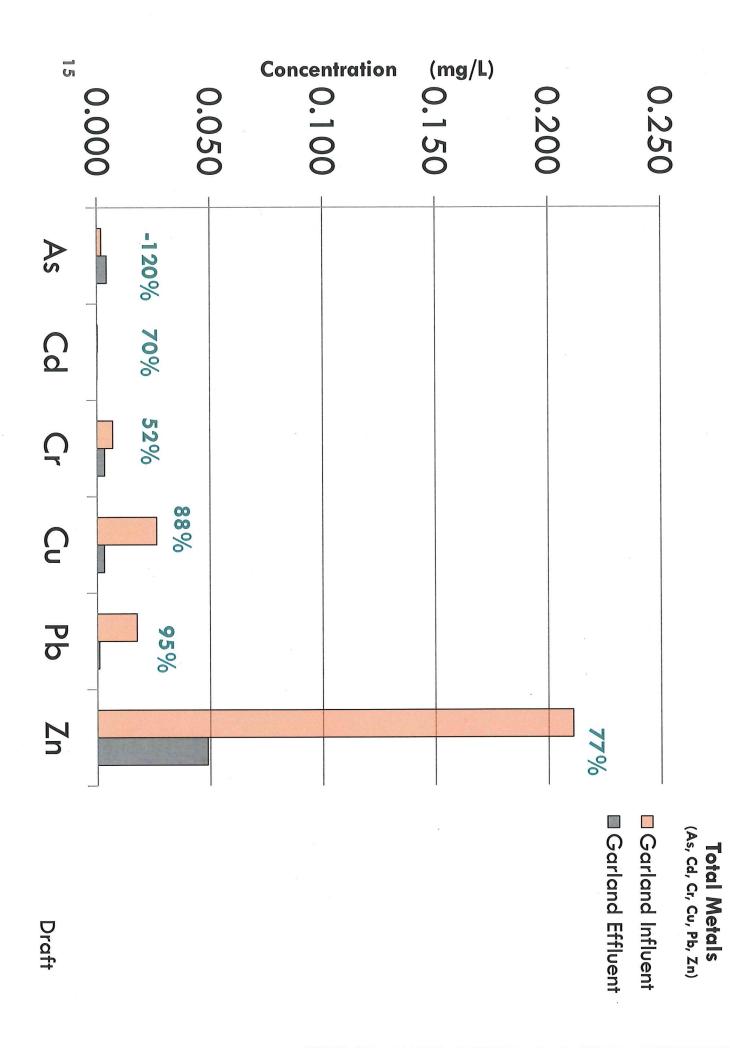


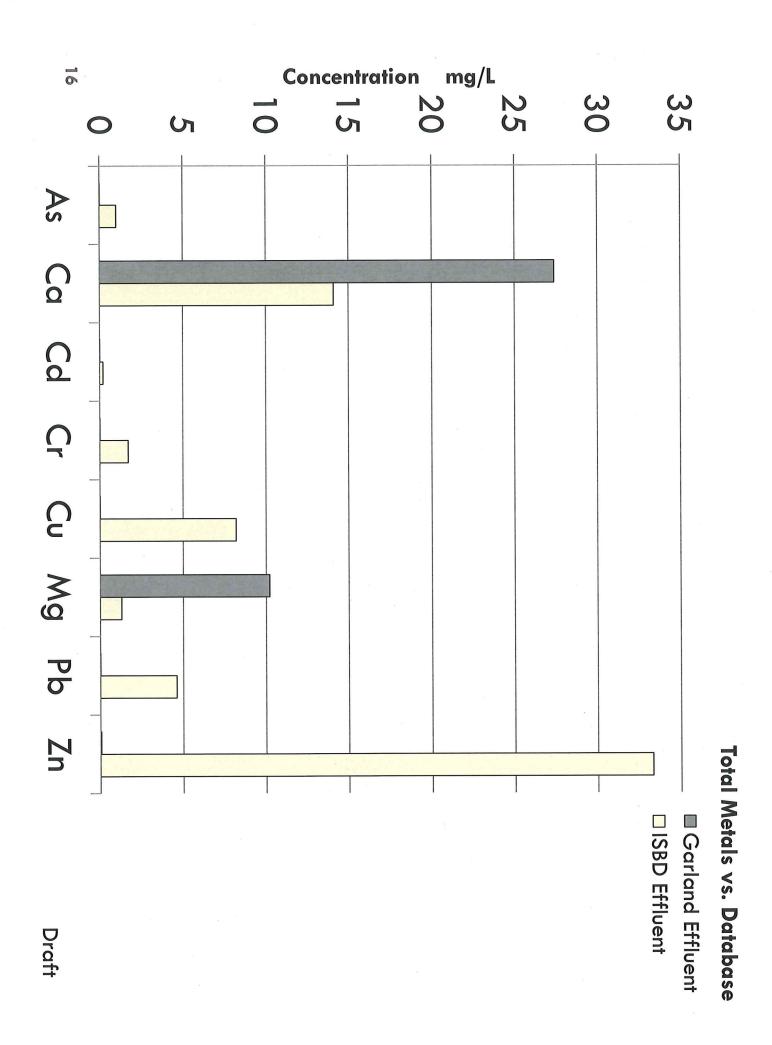
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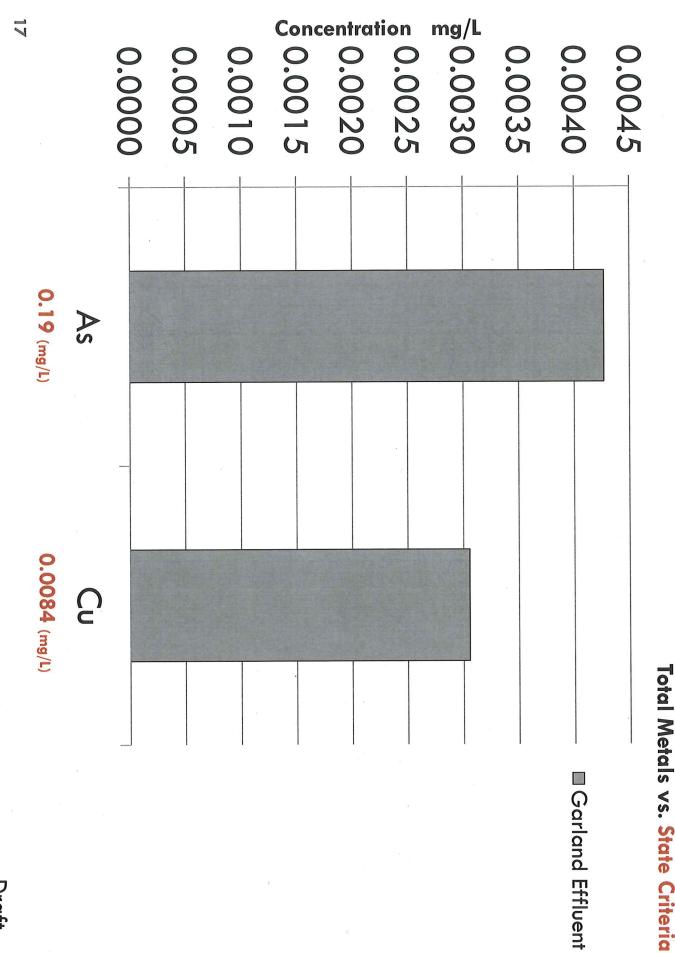




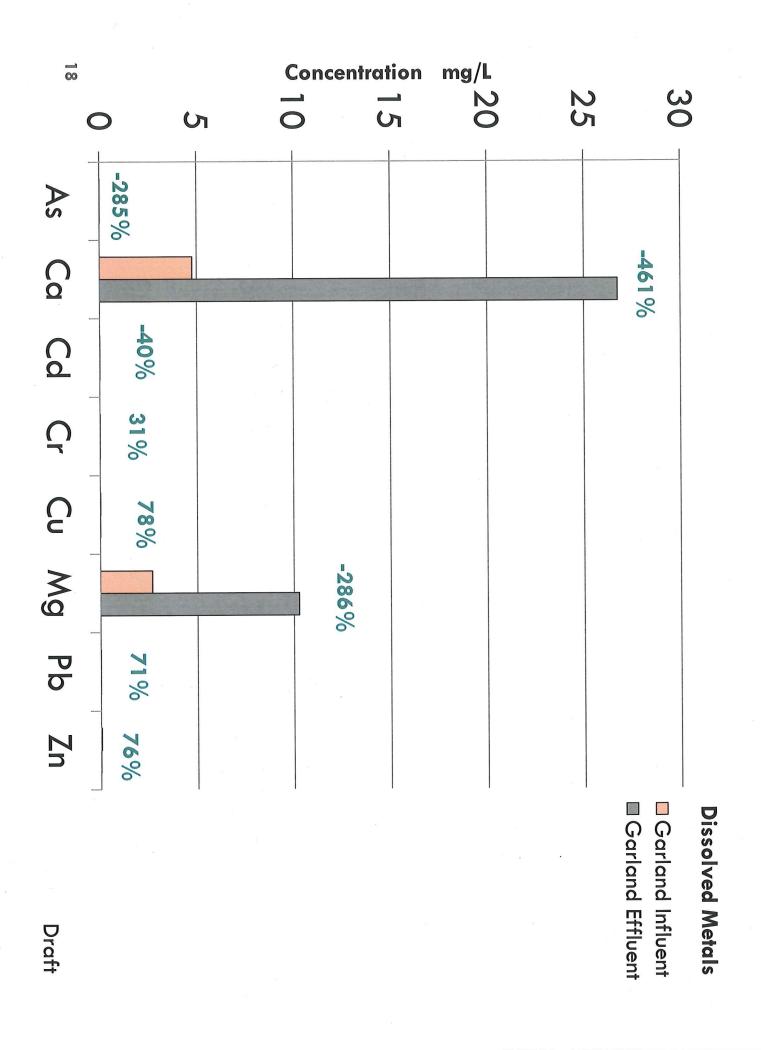


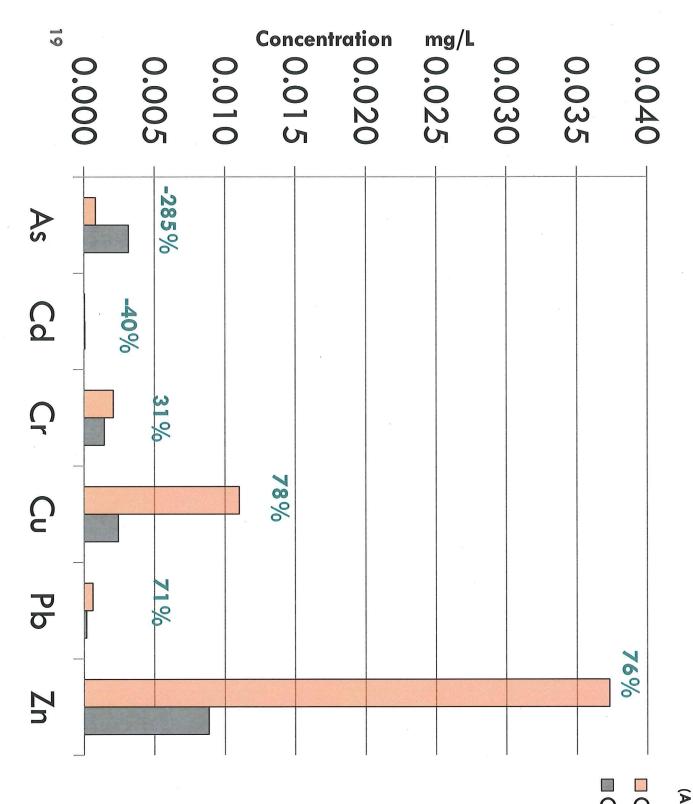






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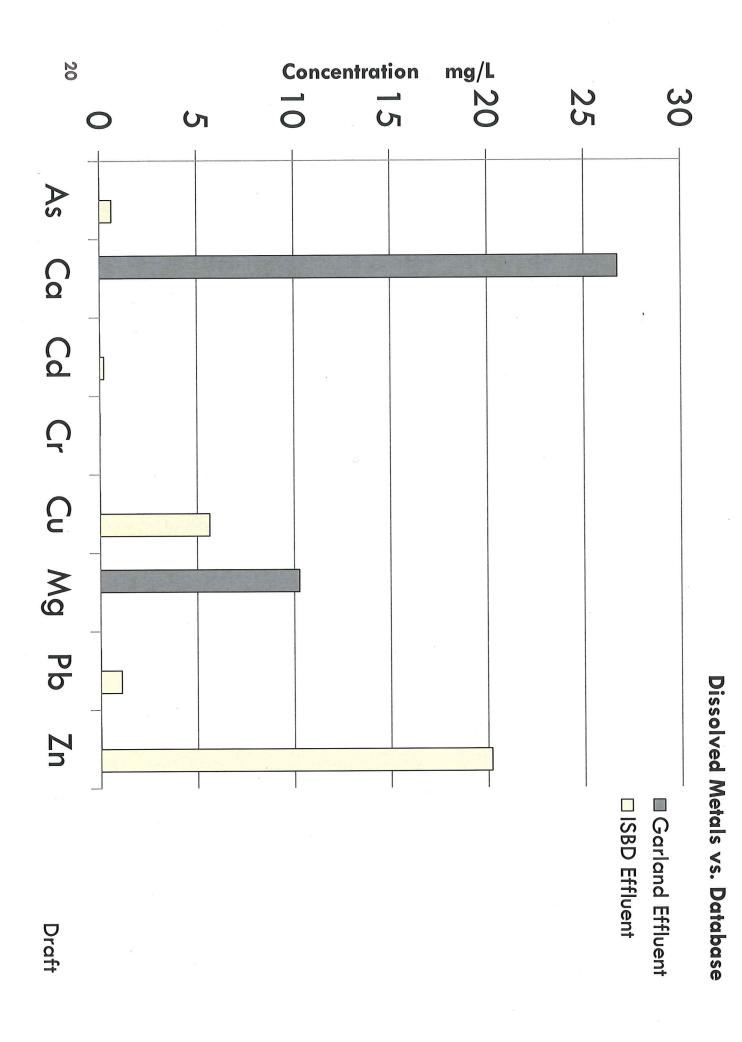


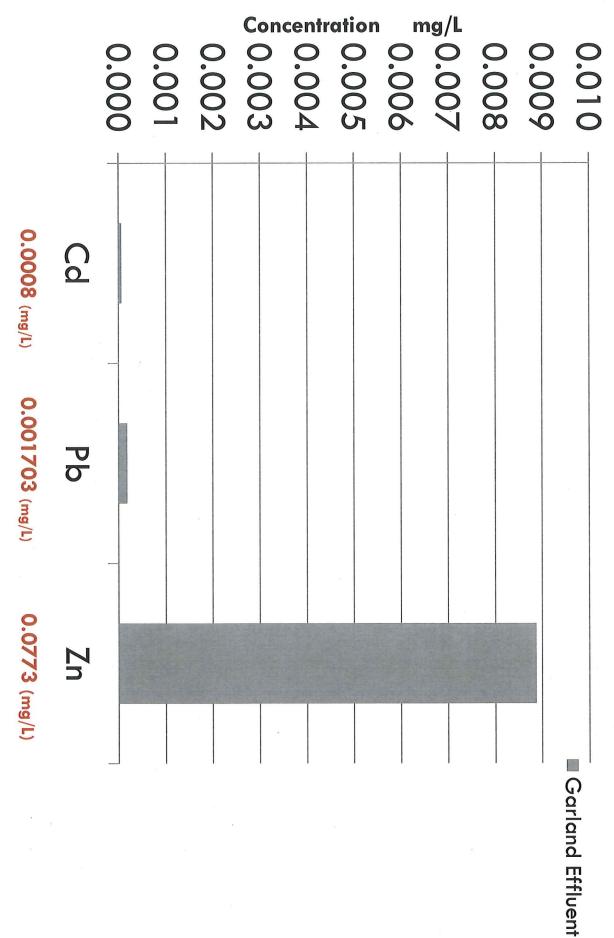


(As, Cd, Cr, Cu, Pb, Zn)

Garland InfluentGarland Effluent

Draft

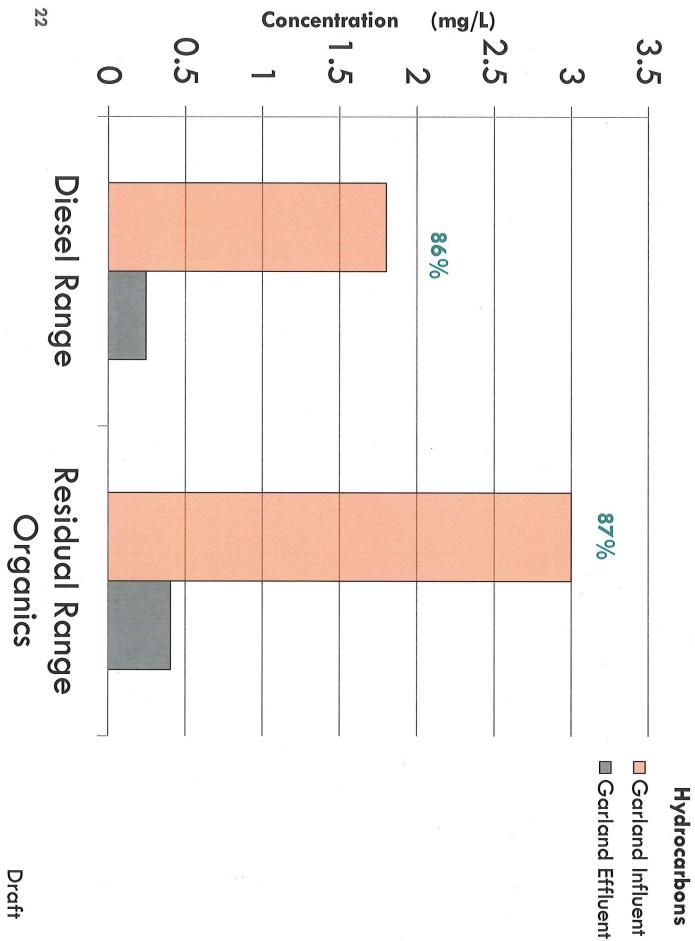


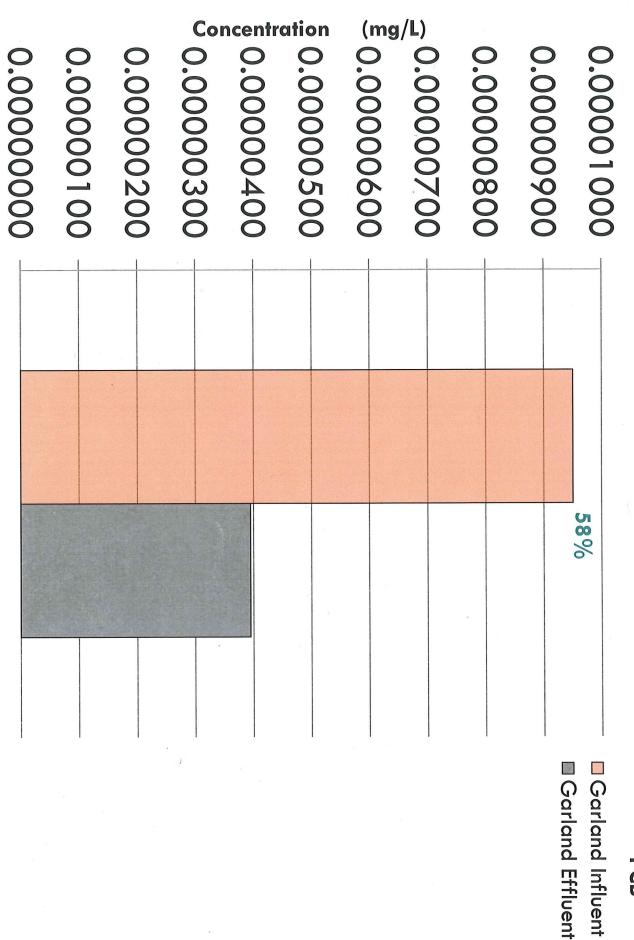


Dissolved Metals vs. Metals TMDL

21

Draft





РСВ

Conclusion

- Monitoring 201 5-2017
- 6 events (small sample size)
- 2015: 3 events
- 2016: 2 events
- 2017: 1 event
- Results
- State criteria
- As below
- Cu exceeded state criteria
- Applicable if directly discharged to surface water

- Metals TMDL
- Cd, Pb, Zn below
- ISBD Effluent Grass Swale
- TP below
- Metals and dissolved metals below
- As, Cd, Cr, Cu, Mg, Pb, Zn
- Ca and Mg could be leaching from biochar
- Continue monitoring
- Next steps

date, much of the material is subjective in nature, and is not, and should not be considered, a certified for definitive source of information that can be relied upon The information and commentary contained in this document is general in nature. Although efforts were made to keep this document's contents accurate and up to 25 509.625.7908 Wastewater Management Adrianne Pearson, Environmental Analyst apearson(@spokanecity.org Thank you! Draft

for any purpose. The information, commentary, and material provided in this document is provided "as is" and for informational and educational purposes only.

Analytic	Analytical Statistical Data	ata								
			No. Contraction	Nutrients	(mg/L)	a contraction	NWTPH-D	NWTPH-Dx (mg/L)		
		TSS	TP	NO2	NO3	TKN	Diesel Range	Range	PCB (mg/L)	
Influent	Mean Median	910.200 132.000	1.412 0.659	0.060 0.056	0.903	3.560 2.500	2.280 1.800	7.000	0.00000951	
	Besidental	070.2071	000	0.010	0.402	2./40	1.43/	7.040	0.0000000	
National	Median	49	0.3	0.0006	606	0.0015	,	ı	'	
Stormwater Quality	Coefficient of variation	1.8	1.1	0.0011	110	0.0011		1	,	
Database	Commercial	5	2			0				
(ver 1.1)	Coefficient of variation	42	1.2	0.0011	011	0.0009	. .		, , , ,	
ISBD: Influent		48.5	0.187	0.0276	0.556	1.21		1	,	
Grass Swale	Median Standard Dev.	28.1 63.2	0.111 0.258	0.012	0.3 0.884	0.704 1.58	1 I	1 1		
				Total N	Aetals (mg/	L), [Detection	on Limit]			
		As	Ca	Cd	Cr.		BW	Pb	Zn	Haraness
Influent	Median	0.0019	8.5600	0.0002	0.0069	0.0264	4.8400	0.0176	0.2110	4]
	Standard Dev.	0.0050	13.8586	0.0010	0.0239	0.1176	6.0581	0.1699	0.9467	59
National	Median Median	0.003	1	0.0005	0.0046	0.012	ī.	0.012	0.073	1
Quality		0.0044		0.0004	0.0014	0.0010	'	0.0017	0.0010	
Database	Commercial Median:	0.0023	1	68UUU U	700	710.0	,	8100	210	
	Coefficient of variation	0.003	•	0.0027	0.0009	0.0015	ı	0.0016	0.0012	
	Mean	3.43	9.58	0.949	6.3	21	1.08	38.8	114	•
Grass Swale	Median	1.78	8.91	0.53	5.2	13	150	8.9	51	ı.
	Standard Dev.	3.7	3.22	1.1	6.62	24.6	3.46	154	168	ı.
		As	Ca	Cd	Dissolved M	Dissolved Metals (mg/L		Pb	Zn	Hardness
	Mean	0.0009	5.2360	0.0000	0.0044	0.0127	3.6220	0.0006	0.0597	28
Influent	Median Standard Dev	0.0008	4.7700	0.0000	0.0021	0.0110	2.6600	0.0006	0.0373	23
		0.0001	2.0000	0.0000	0.0001	0.0000	2.2700	, 0.0001	0.0474	- 1
National	Residental Median	,			-	0.007	r *	£00.0	51500	
Stormwater	Coefficient of variation	•	·	,	•	0.002	,	0.0019	0.0008	,
Database	Commercial									
(ver 1.1)	Coefficient of variation	, ,	, ,	0.00134	0.0006	0.0008		0.0016	0.0014	

ISBD: Influent Median Grass Swale Standard Dev

0.68 3.01

Median Coefficient of

0.00757

5.99

Garland Stormwater Garden with Biochar Amended Soil (Water Year 2015-2017)

		States and		Nutrients	(mg/L)		NWTPH-D	Dx (mg/L)	S. M. LAND SE	
		TSS	TP	NO ₂	NO ₃	TKN	Diseal Range	Range Organics	PCB (mg/L)	
	Mean	61.167	0.205	0.037	0.844	1.255	0.390	0.850	0.00000395	
Effluent	Median	6.500	0.183	0.042	0.562	0.765	0.245	0.405	0.0000395	
	Standard Dev.	109.713	0.109	0.020	0.835	0.979	0.233	0.704	0.00000000	
ICDD: Effluent	Mean	31.100	0.255	0.027	0.657	0.919	-	-	÷	
Grass swale	Median	15.000	0.191	0.015	0.390	0.645	-	-	-	
	Standard Dev.	53.300	0.271	0.053	1.260	0.907	-	-	-	
		1.				tals (mg/L)			1 T	Hardnes
4		As	Ca	Cd	Cr	Cu	Mg	Pb	Zn	naranes
	Mean	0.0050	25.4767	0.0001	0.0040	0.0057	10.3150	0.0032	0.0532	106
Effluent	Median	0.0043	27.4000	0.0001	0.0033	0.0031	10.2100	0.0009	0.0489	110
	Standard Dev.	0.0032	15.6399	0.0000.	0.0035	0.0048	5.2990	0.0041	0.0349	60
ISBD: Effluent	Mean	1.47	20.1	0.26	2.43	10.8	2.61	9.39	45.8	-
Concerne account of the	Median	1	14.1	0.2	1.7	8.2	1.28	4.6	33.3	-
Grass swale	Standard Dev.	1.36	16.8	0.193	2.11	9.03	3.46	16.8	43.6	-

		Station 20	Dissolved Metals (mg/L)								
2		As	Ca	Cd	Cr	Cu	Mg	Pb	Zn	Hardness	
	Mean	0.0043	24.9583	0.0055	0.0018	0.0031	10,1783	0.0002	0.0140	104	
Effluent	Median	0.0032	26.7500	0.0001	0.0014	0.0024	10.2750	0.0002	0.0089	109	
	Standard Dev.	0.0036	16.1800	0.0135	0.0015	0.0018	5.5948	0.0002	0.0158	62	
ISPD: Effluent	Mean	1.17		0.26	-	7.55	-	4.28	26.9	-	
ISBD: Effluent	Median	0.61	-	0.2	-	5.64	-	1.07	20.2	-	
Grass swale	Standard Dev.	1.37	-	0.193	-	6.1	-	7.49	29.1	-	

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Efficacy of biochar to remove Escherichia coli from stormwater under steady and intermittent flow



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ABSTRACT

Biofilters, designed to facilitate the infiltration of stormwater into soil, are generally ineffective in removing bacteria from stormwater, thereby causing pollution of groundwater and receiving surface waters. The bacterial removal capacity of biofilters has been shown to be lower in the presence of natural organic matter (NOM) and during intermittent infiltration of stormwater. To improve the removal of fecal indicator bacteria (Escherichia coli) under these conditions, we amended sand with 5% (by weight) biochar, a carbonaceous geomedia produced by pyrolysis of biomass, and investigated the removal and remobilization of E. coli. Three types of biochar were used to evaluate the role of biochar properties on the removal. Compared to sand, biochar not only retained up to 3 orders of magnitude more E. coli, but also prevented their mobilization during successive intermittent flows. In the presence of NOM, the removal capacity of biochar was lower, but remained higher than sand alone. The improved retention with the biochar amendment is attributed to an increase in the attachment of E. coli at the primary minimum and to an increase in the waterholding capacity of biochar-amended sand, which renders driving forces such as moving air-water interfaces less effective in detaching bacteria from grain surfaces. Biochars with lower volatile matter and polarity appear to be more effective in removing bacteria from stormwater. Overall, our results suggest that a biochar amendment to biofilter media has the potential to effectively remove bacteria from stormwater.

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1. Introduction

As urban areas expand to accommodate growing populations, impervious surfaces replace the natural landscape and impede groundwater infiltration. The result is an overall increase in the net volume and flow rate of stormwater over land (Davis and McCuen, 2005). Consequently, stormwater floods and erodes the urban landscape, and conveys contaminants from the land surface to streams, lakes, and other water bodies (US EPA, 2002).

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To mitigate the adverse impacts of stormwater, city planners are increasingly incorporating green infrastructure or low impact development (LID) into their development projects. Common LID includes the bioretention or biofilter system (US EPA, 2000): a shallow planted area where a native block of soil is replaced with a mixture of sand and compost to promote rapid infiltration of stormwater into the ground. After passing through the infiltration system, water enters the local surficial aquifer. In a biofilter, the filtered water is conveyed back to a surface stormwater conveyance via an underdrain. Henceforth, these two systems will be collectively referred to as biofilters. A review of biofilter performance across the US shows low and inconsistent removal of fecal indicator bacteria (FIB) (Leisenring et al., 2012), key stormwater contaminants responsible for impairment of many of the nation's impaired surface waters (US EPA, 2002). A recent lab-scale study showed that even when fecal bacteria are sequestered by media within a model biofilter, they can be detached from the media and mobilized during intermittent infiltration of stormwater (Mohanty et al., 2013). As a result, biofilters may possibly act as sources of fecal bacteria to infiltrating stormwater. Improvements in biofilter design are needed to address these issues.

To improve the removal of FIB, biofilters have been augmented with various engineered geomedia (Pitt and Clark, 2010), but the performance of these geomedia, particularly those with positive surface charge, is substantially lower in the presence of natural organic matter (NOM) (Torkelson et al., 2012; Mohanty et al., 2013). Moreover, most of the engineered geomedia are selective in removing certain group of contaminants, thereby making them ineffective in treating stormwater that may contain many types of contaminants (Pitt and Clark, 2010). On the other hand, biochar, a carbonaceous geomedia produced by pyrolysis of biomass (Manya, 2012), has potential to remove FIB and NOM in addition to the myriad of contaminants that may be present in stormwater. Previous laboratory column experiments have shown that biochar can effectively remove heavy metals (Park et al., 2011), organic contaminants (Chen et al., 2008), NOM (Kasozi et al., 2010), and nutrients including phosphate (Yao et al., 2011) seeded into deionized water. Two studies have showed that biocharamended sandy soil increased the removal of a model fecal indicator bacterium, Escherichia coli, suspended in deionized water relative to unamended soil (Abit et al., 2012; Bolster and Abit, 2012). While these studies showed that biochar could remove E. coli from seeded deionized water, it is unclear whether the biochar can effectively remove bacteria from a more complex matrix such as stormwater that contains nutrients and natural organic matter (NOM). Moreover, the ability of biochar to sequester attached bacteria during intermittent flow has not been previously investigated.

This study aims to evaluate the efficacy of biochar to remove FIB under complex conditions that typically occur during natural infiltration of stormwater. We hypothesized that augmenting sand media with biochar would increase bacterial removal from a synthetic stormwater, and decrease the mobilization of attached bacteria during intermittent flows relative to sand media alone. To test these hypotheses, we used three types of biochar and a model fecal bacterium: *E.* coli.

2. Experimental methods

2.1. Preparation of sands and biochar

To remove surface impurities, coarse Ottawa sand (0.6-0.85 mm, Fisher Scientific) was treated with 12 M hydrochloric acid and then washed in deionized water until the pH of water became neutral (Lenhart and Saiers, 2002). Three types of biochar made from wood-chips were used: a commercially available biochar obtained from Sonoma Compost Company, CA (referred as Sonoma biochar, henceforth), and two steam-activated biochars produced in the laboratory via pyrolysis of wood chips at 350 and 700 °C, which are referred respectively as low temperature (LT) biochar, and high temperature (HT) biochar henceforth. The sand and biochars were dried at 110 °C overnight, autoclaved (121 °C, 100 kPa, 15 min), and stored in sterile containers prior to use in the column experiments.

2.2. Characterization of biochars

The physical and chemical properties of biochar including surface area, elemental composition (i.e., C, H, O, N, and S), volatile matter, total carbon content, and ash content were analyzed using methods described elsewhere (Novak et al., 2009). Briefly, surface area was estimated by adsorption of nitrogen gas using an automated surface area analyzer (Micromeritics Gemini 2360, GA, USA). The percentage of volatile material, ash content, elemental composition (C, H, O, N, and S) of oven-dried biochar samples were estimated using ASTM D 3172 and 3176 standard methods (ASTM, 2006). We calculated H/C, O/C, and (O + N)/C ratios, which have been used to quantify the content of polar functional groups or polarity index (Chen et al., 2008).

2.3. Synthetic stormwater

Synthetic stormwater was prepared by dissolving 0.75 mM of CaCl₂, 0.075 mM of MgCl₂, 0.33 mM of Na₂SO₄, 1 mM of NaHCO₃, 0.072 mM of NaNO₃, 0.072 mM of NH₄Cl, and 0.016 mM of Na₂HPO₄ in deionized water and then sterilizing the solution using an autoclave (121 °C, 100 kPa, 45 min). This recipe provides an average concentration of major ions in urban stormwater (Grebel et al., 2013). Suwannee River NOM (International Humic Substances Society, MN, USA) was added at 20 mg C L⁻¹ for use in some experiments, as described below. The ionic strength of the stormwater was 4.7 mM. The pH was adjusted to 7.0 ± 0.1 using 1 M HCl or 1 M NaOH. Dissolved organic carbon (DOC) was measure in stormwater with and without NOM using a TOC analyzer (TOC-5000A, Shimadzu Co., Japan).

2.4. Bacteria solution preparation

E. coli K12 (ATCC 10798), a motile, Gram-negative bacterium was prepared following methods outlined elsewhere (Mohanty et al., 2013). Briefly, E. coli were cultured to stationary phase, centrifuged to remove growth media, and suspended in the synthetic stormwater to achieve a concentration of 1.2–1.7 \times 10⁶ colony forming units (CFU)/mL. The E. coli suspension was kept at 4 °C for 16–18 h for E. coli to adapt to stormwater prior to its use in column experiments.

2.5. Biofilter experiment

Sand and a mixture of sand and each type of biochar (5% w/w) were dry-packed in glass chromatography columns (Kontes, 15 cm length, 2.5 cm diameter). Dry-packing was chosen over wet-packing as biochar floats during wet-packing, preventing uniform distribution. After packing, biochar occupied ~22% of the space inside the column, which was calculated by subtracting the volume (ratio of sand weight to bulk density of sand) occupied by the sands in the biochar and sand mixture from the total column volume. Hereafter, these columns are referred to as 'sand' and 'biochar' columns even though the biochar column also contains sand (95% by weight or 78% by media volume). To condition the geomedia, 1 L of deionized water (~33 pore volume) followed by 150 mL (~5 PV) of synthetic sterile stormwater (either with or without NOM, depending on experiment) were flushed upward through packed geomedia. Upward flows displace air from most pores between geomedia grains within column. The relative saturation of each column was estimated by measuring the weight of the column before and after packing with dry and saturated geomedia at different stages of experiments. The pore volume was estimated by subtracting the weight of dry-packed column from completely saturated column.

The column experiments were conducted in two phases: (1) attachment phase and (2) mobilization phase. During the attachment phase, 90 mL (3 PV) of the stormwater -bacterial suspension were injected at 0.1 cm min⁻¹ (~0.5 mL min⁻¹) through each column from the bottom (upward flow). Subsequently, 90 mL (3 PV) of sterile stormwater was injected to remove bacteria from pore water. Any bacteria remaining in the column were assumed to be attached at interfaces within the column. The next phase, the mobilization phase, examined if attached bacteria can be detached during intermittent flow. During this phase, the pump was stopped for 0.5 h, and the columns were overturned and pore water was drained by gravity. The column was overturned to maintain the water flow direction relative to the media during draining as would occur in the field. Following the pause, the drained column was overturned again, to maintain the flow direction, and 60-80 mL of sterile synthetic stormwater was pumped upward through the column. These draining and wetting steps were repeated twice. The experiments took approximately 12 h. We used upward flow in order to minimize preferential flow, which could affect the net removal capacity of geomedia during intermittent flow (Mohanty et al., 2013).

Infiltration experiments were repeated with sand and LT biochar, increasing the pause interval to 21 h to investigate if longer intervals between infiltrations would have any impact on bacteria remobilization. The experiments continued over 3 days after the injection of *E. coli*. A total of forty column experiments were conducted to examine the effect of biochar types, pause duration, and NOM on the attachment and mobilization of *E. coli*. Experiments involving a 0.5-h pause used 24 columns – eight combinations of geomedia (four types) and stormwater (with and without NOM) each run in

triplicate. Experiments involving a 21 h-pause used a total of 16 columns where four replicate columns tested two types of geomedia (sand and LT biochar) and stormwater with and without NOM.

2.6. Sample collection and measurements

Column effluent was collected in 10-mL fractions using an automated fraction collector (Model CF1, Spectrum Chromatography). The bacterial concentration in the effluent was quantified by spread plating techniques and reported as colony forming unit (CFU) per mL of effluent. Each sample was enumerated in duplicate at three decimal dilutions using tryptic soy agar (TSA, Difco, Fisher Scientific). Concentrations calculated using plates with between 30 and 300 CFU were averaged to obtain a concentration. This technique of measuring *E. coli* directly rather than using a surrogate measurement, like turbidity, was chosen as culture-based measures of *E. coli* are used to assess water impairment in practice.

The persistence of *E*. coli in the stormwater feed solution (with and without NOM) was tested by incubating the feed solutions inoculated with *E*. coli in triplicate (15 mL centrifuge tube) at room temperature (~23 °C) for 4 days. To examine the persistence of *E*. coli in the presence of biochar and sand, we repeated the incubation tests adding biochar and sand to the feed solution also in triplicate (Supplementary Material). The concentration of *E*. coli was monitored daily using the same technique as for the effluent samples – spread plating on TSA. In addition, the experiments without geomedia were repeated to estimate cell counts using a hemocytometer and microscope (method details in Supplementary Material).

2.7. Data analysis

The log-removal of *E*. coli from stormwater during the attachment phase was calculated and is referred to as removal capacity. The number of attached bacteria in the column was calculated using a mass balance, assuming bacteria behave conservatively in the column.

To identify statistically significant differences between the removal capacities and the fraction of attached bacteria mobilized from sand and biochar columns under different experimental conditions, analysis of variance (ANOVA) was performed using Turkey's HSD test. All statistical analyses were formed using SPSS Statistics (v.20, IBM, NY, USA). Differences were considered significant at p < 0.05.

3. Results

3.1. Characterization of biochars

The physical and chemical properties of the three biochars varied (Table 1). Sonoma biochar had approximately five times more surface area than the other two biochars. Dry biochar was composed of fixed carbon (72–81%), ash (12.2–15.4%), and volatile matter (6–16%). The ash contents of all biochars were similar, but the fixed carbon and volatile matter varied among biochars. Sonoma biochar contained 1.8 and 2.7 times more volatile matter than LT and HT biochar, respectively. The fixed

Biochar ID	Surface area ^b	Volatile matter				omposi [.] y wt. ba				Atomic 1	ratios
	$m^2 g^{-1}$	(%)	Ash	С	Н	0	Ν	S	H/C	O/C	(O + N)/C
Sonoma	326.2 ± 5.9	16.03	12.22	78.88	0.69	7.77	0.4	0.043	0.009	0.098	0.104
LT	65.9 ± 1.2	8.73	15.36	80.67	0.71	2.23	1.02	0.009	0.009	0.028	0.040
HT	64.9 ± 6.5	5.95	12.74	84.38	0.59	1.49	0.78	0.019	0.007	0.018	0.027

^b Surface area was measured in triplicate.

carbon fraction of HT biochar (81%) was higher than Sonoma biochar (72%) and LT biochars (76%). The (O + N)/C ratio or polarity index was greater in Sonoma biochar compared to other two biochars.

3.2. Attachment of E. coli on sand and biochar

During application of bacteria-laden stormwater without NOM, E. coli concentrations in biochar column effluent were ~2 orders of magnitude smaller than concentrations in the effluent of the sand columns (p < 0.05, Fig. 1 or Figure S1). The LT biochar column removed significantly more E. coli than Sonoma biochar (mean difference = $0.7 \log_{10} p < 0.05$), but there was no other significant difference between removal capacities between other biochars. The presence of NOM in stormwater significantly lowered the removal capacity of the biochars relative to experiments without NOM; the removal capacities reduced by 2.4, 2.5, and 1.2 logs for LT, HT, and Sonoma biochars, respectively (p < 0.05). NOM had no impact (p = 0.22) on the removal capacity of sand. Removal capacities of the LT, HT, and Sonoma biochars in the presence of NOM were significantly higher than those in sand by 1.0, 0.6, and 0.9 log units (p < 0.05) (Table 2).

3.3. Detachment of E. coli during intermittent flows

During each pause, 48–53% of pore water was drained by gravity from the sand columns, whereas only 8–18% drained from biochar-amended sand columns. After rewetting, nearly 95% of pores were refilled with infiltrating stormwater in all columns.

During intermittent flow separated by 0.5-h pauses, attached bacteria were mobilized from the sand and biochar columns (Table 2). The concentration of E. coli in the column effluent during the intermittent flow events varied from below detection limit to as high as 2×10^6 CFU/mL. The concentration of E. coli was typically high at the start of infiltration and decreased as infiltration continued. The fraction of attached bacteria mobilized from the biochar columns was significantly lower than that from sand columns (p < 0.05). Combining data from experiments with and without NOM, two intermittent flow events mobilized on average 19% of attached E. coli from sand columns, but mobilized only 1%, 1%, and 3% of attached E. coli from LT biochar, HT biochar, and Sonoma biochar, respectively. Without NOM, intermittent flows mobilized 14.7% of E. coli attached to sand columns, which further increased to 24.3% in the presence of NOM, but the difference was not statistically significant (p = 0.14). Intermittent flows

released 0.001–0.2% of *E*. coli attached to biochar without NOM. In the presence of NOM, mobilization from biochar columns was significantly higher than in the case without NOM (2–5% higher, p < 0.05). The fraction mobilized during intermittent flow did not significantly vary with biochar types (p > 0.87). In all experiments with 0.5-h pause, the total fraction mobilized during the second infiltration mobilized 58% (on average) fewer *E*. coli than the first infiltration (Fig. 1).

3.4. Effect of interval between intermittent flows on the detachment of E. coli

A 21-h pause did not change the moisture content of the columns compared to the 0.5-h pause. However, the longer pause affected the mobilization of *E*. coli from sand columns (Table 2). Without NOM, an increase in pause duration from 0.5 h to 21 h caused a net decrease in the fraction of *E*. coli mobilized from sand from 15% to 8% (p < 0.05, Fig. 2). With NOM, the longer pause duration increased the total fraction of *E*. coli mobilized from sand during intermittent flows from 24% to 83% (p < 0.05). The longer pause duration decreased the mobilization of *E*. coli from biochar, but not significantly (p > 0.05).

The mobilization of *E*. coli in successive intermittent flows depends on the media type (biochar or sand) and NOM concentration. During the 21 h pause experiments in sand columns, the second intermittent flow mobilized 27% fewer *E*. coli than first intermittent flow without NOM, but mobilized 69% more *E*. coli in presence of 20 mg C L⁻¹ NOM. In biochar columns, however, the second intermittent flow mobilized 65% fewer *E*. coli than the first intermittent flow irrespective of NOM concentration in the stormwater.

3.5. Persistence of bacteria in stormwater matrix

Monitoring of influent stormwater seeded with *E*. coli suggested their growth over 4 days (Fig. 3 and S2). The growth rate (average \pm standard deviation) of *E*. coli in stormwater with NOM was 1.2 (\pm 0.3) d⁻¹, which decreased to 0.5 (\pm 0.2) d⁻¹ in stormwater without NOM. The DOC content of synthetic stormwater with and without NOM was 1.5 and 21.2 mg/L.

We repeated the growth experiment adding biochar or sand to the stormwater. In the presence of sand, bacterial concentrations in the aqueous phase increased over five days, but the concentration of bacteria in the presence of biochar decreased below the detection limit within one day and remained undetected through out the experiment (Figure S3).

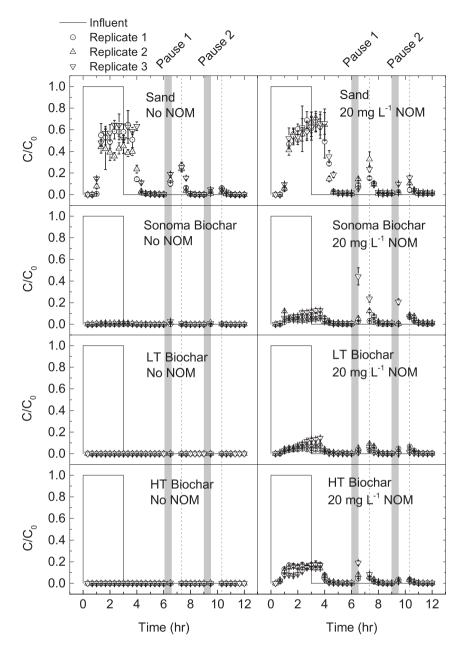


Fig. 1 – Transport and mobilization of *E*. coli through sand and biochar columns with and without NOM. The influent concentration was approximately 1.3 (\pm 0.2) \times 10⁶ CFU/mL. The gray area indicates the 0.5 h pause during which the column was drained, and the dashed lines indicate the timing of the first samples after the pause. The error bar indicates one standard deviation of measurements. The figure in log-scale is provided in the supplementary materials (Figure S1).

4. Discussion

4.1. Effect of biochar amendment on attachment of E. coli

Biochar-augmented sand columns removed 1 to 3 orders of magnitude more *E*. coli compared to sand during saturated flow. This indicates that even in a complex stormwater matrix, biochar has strong potential to remove waterborne bacteria. The increase in bacterial attachment may be due to the overall increase in attachment sites in the biochar columns. Biochar is highly porous relative to sand, thus the surface area of biochar is at least 5 orders of magnitude larger than sand; sand has a typical surface area of 0.01 m² g⁻¹. Addition of 5% biochar by weight increased the net surface area available for adsorption by a factor of 360 in columns amended with LT or HT biochar and a factor of 1790 in the columns amended with Sonoma biochar. However, the actual surface area available for bacterial attachment could be smaller because the estimated values include the internal surface area of pores within biochar that may not be accessible to bacteria.

Table 2 — Log removal of applied E. coli in columns packed with sand and different types of biochar during injection of contaminated stormwater, and the percentage of attached bacteria mobilized during two intermittent flows with 0.5-h and 21-h intervals.

Geomedia	Log rei	noval ^a	Bacteria mobilized (%) ^b						
	w/o NOM	w/NOM	0.5-h	Pause	21-h I	Pause			
			w/o NOM	w/NOM	w/o NOM	w/NOM			
Sand	0.29 ± 0.09	0.21 ± 0.01	14.7 ± 5.5	24.3 ± 7.2	8.0 ± 1.3	77.6 ± 17.3			
LT biochar	3.62 ± 0.27	1.18 ± 0.22	0.01 ± 0.01	2.29 ± 1.08	0.003 ± 0.002	0.074 ± 0.032			
HT biochar	3.28 ± 0.52	0.83 ± 0.05	0.02 ± 0.02	2.56 ± 0.40	-	-			
Sonoma biochar	2.32 ± 0.32	1.16 ± 0.20	0.11 ± 0.09	5.17 ± 2.69	_	_			

^a Log removal of *E*. coli during their injection; log removal is calculated by taking negative logarithm of the ratio of effluent and influent concentration.

^b 100 times ratio of total E. coli eluted during two intermittent flows and total E. coli attached before intermittent flows.

Another explanation for the effectiveness of biochar on the removal of E. coli from stormwater is that E. coli may bind more efficiently to biochar than sand, possibly due to an increase in overall attractive forces between the bacteria surface and grain surfaces. According to Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Malte, 1999), an E. coli cell may experience a combination of attractive van der Waal forces and repulsive electrostatic forces when it comes into close proximity to grains. Under unfavorable attachment conditions (where the bacterium and grain are of the same net charge), most E. coli are likely to attach to sand or biochar at the secondary minimum (Redman et al., 2004), although some fraction may attach at the primary minimum near rough grain surfaces and wedge pore spaces (Torkzaban et al., 2008). Non-DLVO forces from hydrophobic and steric interactions may also influence the attachment of bacteria on sand and biochar (Chen and Walker, 2012). For attachment to occur, E. coli must overcome electrostatic repulsion between negatively charged surfaces of E. coli, biochar, and sand (Table S1), which increases with increasing pH of solution (Hayashi et al., 2001). Because biochar increases the pH of pore water (Novak et al., 2009), the electrostatic repulsion is expected to be greater in biochar than sand. (The pH of effluent from our biochar columns was ~9 while from the sand columns it was ~7.5, data not shown). However, bacterial retention in the biochar

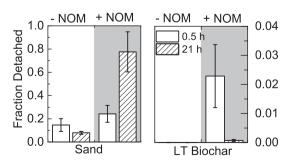


Fig. 2 – Fraction of attached E. coli mobilized from sand (left) and LT biochar columns (right) in stormwater with and without NOM during two intermittent flows. The gray background represents results from experiment with NOM. The error bar indicates one standard deviation of results obtained from four replicate column experiments. Note that the scale of y-axis is magnified for LT biochar.

columns was greater than in the sand columns, suggesting attachment on biochar may occur as a result of the non-DLVO forces including hydrophobic attraction. Hydrophobic attraction is expected to be much greater between bacteria and biochar than bacteria and sand due to the high organic carbon content of biochar (Abit et al., 2012). Addition of 5% biochar to the sand column increased the net fixed organic carbon by 4%. Thus, biochar may retain E. coli at the primary minimum due to the increased hydrophobic interactions (van Loosdrecht et al., 1987). Previous column studies demonstrated an increase in E. coli retention upon biochar addition to a sandy soil, and retention occurred primarily near the inlet of the columns, suggesting straining at intra- or inter-pores could also contribute to E. coli removal (Abit et al., 2012; Bolster and Abit, 2012).

The attachment of other indicator organisms and pathogens to biochar could differ from E. coli because of a difference in their surface characteristics (Abit et al., 2014). For instance, Abit et al. (2012) observed that removal of different E. coli isolates by biochar could vary. Camesano and Logan (1998)

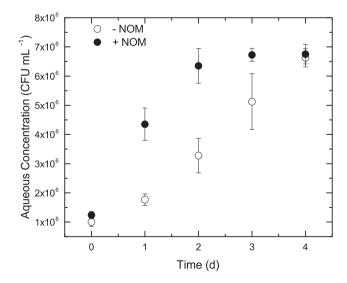


Fig. 3 – Growth of E. coli in stormwater at room temperature (23 °C) with and without 20 mg C L^{-1} NOM. The error bars indicate one standard deviation of triplicate experiments.

found that motile bacteria, compared to non-motile bacteria, were less likely attached to sand in column experiments, particularly at low flow velocity and low ionic strength. Additional research should explore the ability of biochar to remove different health-relevant organisms including pathogenic bacteria and viruses.

The concentration of bacteria in the influent could also affect their net removal in columns. Haznedaroglu et al. (2009) observed that the removal capacity of *E. coli* in sand columns was not a function of influent concentration when it was below 10⁷ CFU/mL, but the removal capacity decreased when the influent concentration was increased to 10⁸ CFU/mL. The decrease in removal capacity at higher influent concentration was attributed to exhaustion of favorable attachment sites on sands. Because biochar has so many potential attachment sites, they may not be similarly exhausted. The influent concentrations used in our study are high relative to those expected in actual stormwater (Grebel et al., 2013). However, future work should explore more fully the effect influent concentration has on geomedia removal capacity.

4.2. Effect of biochar amendment on mobilization of E. coli

E. coli attached to interfaces in both biochar and sand columns were mobilized during intermittent flow; however, the mobilized fraction was smaller in biochar-amended columns compared to unamended columns. This suggests that a biochar amendment may minimize the mobilization of sequestered bacteria from a biofilter, thereby improving its overall removal efficiency. Bacteria mobilization during intermittent flow has been attributed to several processes that may occur during draining and rewetting: an increase in shear forces at the grain boundary (DeNovio et al., 2004), scouring by a propagating air-water interface (Saiers et al., 2003), and reduction of capillary forces on bacterial cell (Crist et al., 2004). The observed reduction of E. coli mobilization from the biochar columns may be explained by bacterial attachment at the primary minimum promoted by hydrophobic forces (Abit et al., 2012) and increased water-holding capacity or decreased intrusion of air during gravitational drainage. A stronger bacterial attachment between E. coli and biochar compared to sand could decrease the likelihood of bacterial mobilization from biochar surface. Furthermore, during gravity drainage, pores within and in between biochar particles could retain water by capillary pressure (Abel et al., 2013). A decrease in water drainage could reduce the movement of air-water interfaces in biochar columns, which could further decrease bacterial mobilization during intermittent flow (DeNovio et al., 2004).

4.3. Effect of NOM on attachment and detachment of E. coli

NOM is present in natural waters and may be particularly high and variable in stormwater. Thus, it is important to understand the effect of NOM on bacteria removal. The removal of *E*. coli from stormwater in the sand and biochar columns was lower in the presence of NOM. The lower removal is attributed to competition of NOM for attachment sites and an increase in electrostatic repulsion between grain and cell surfaces after adsorption of NOM (Foppen et al., 2008). In previous studies (Foppen et al., 2006; Mohanty et al., 2013), NOM reduced the removal capacity of a mixture of sand and iron-oxide coated sand to a value similar to that of unamended sand, thereby eliminating all benefits of geomedia amendment. However, in this study under similar conditions, removal capacities of biochar-amended columns were 0.6-1 log higher than the capacity of unamended columns in the presence of NOM. Biochar amendment also reduced the remobilization of attached E. coli during intermittent flows of stormwater with NOM. Under similar conditions, more than 50% of attached E. coli were mobilized from iron oxide coated sand (Mohanty et al., 2013). Collectively, results of these studies indicate that carbonaceous geomedia such as biochar may be more effective than geomedia with positive surface charge in removing bacteria from NOM-laden stormwater.

4.4. Effect of flow interval durations on the detachment of E. coli

During a wet season, the duration between two consecutive storm events may vary from less than an hour to a few days or longer, which could affect the mobilization of bacteria sequestered in the filter media. In the sand columns without NOM, intermittent flows with 21-h interval mobilized fewer bacteria than intermittent flow with 0.5-h interval. In the sand columns with NOM, intermittent flows with longer interval mobilized more bacteria, indicating growth of E. coli or a changing condition within the column that render attached cells more susceptible to mobilization as the column ages in presence of NOM. It appears that the former process can at least partially explain the observed phenomenon. We found that E. coli appears to grow in the artificial stormwater matrix with and without NOM, and the growth rate in stormwater with NOM is approximately two times faster than in stormwater without NOM. Within 24 h of growth, the concentration of E. coli increased 4 fold in the presence of NOM. If E. coli in the column grow at the same rate as E. coli in the stormwater suspension, then a 21 h-pause would be long enough to replenish or regenerate E. coli in sand columns with NOM compared with the regeneration during 0.5 h-pause. Mobilization of E. coli from biochar columns, however, did not change significantly when the interval between intermittent flows was increased from 0.5 h to 21 h, which indicates that biochar could have sequestered bacteria that may have grown. The batch study confirmed that biochar either prevented the growth of E. coli or removed them from stormwater despite their growth. Further study is needed to examine the persistence of attached bacteria using a visualization technique (Crist et al., 2004). Nevertheless, the ability of biochar to potentially preventing the growing cells from passing through biofilter media renders it attractive for their use in biofilters.

4.5. Effect of biochar types on removal of E. coli

A previous study showed that bacterial removal capacity of different biochars varied by several orders of magnitude and the removal capacity depended on biochar preparation conditions including pyrolysis temperature and feedstock origin (Abit et al., 2012). It is important to know which property of biochar correlates well to high bacterial removal so that a screening method to select the most effective biochar can be developed. Although Sonoma biochar had five times more surface area than LT and HT biochar, the removal capacity of Sonoma biochar was one order of magnitude less than the removal capacities of the other biochars. This indicates that increase in surface area alone does not explain the removal of bacteria by biochar. Comparing the properties of biochar with their removal capacity, it appears the biochars with the lowest polar surface or greatest hydrophobicity and lowest volatile matter had the highest E. coli removal capacities. Biochar pores smaller than bacteria size may not be available for bacterial attachment. Some of the larger pores can be blocked by the volatile matter, decreasing the attachment of bacteria (Chen et al., 2012). Biochar containing a higher O/C, N/C or (O + N)/C ratio is expected to be more interactive with polar compounds (Wang et al., 2007) or less interactive with hydrophobic surface such as bacteria surface (Kingshott et al., 2003). An increase in atomic ratio (O/C, N/C) also indicates increases in polar groups known to reduce bacterial attachment on geomedia (Kingshott et al., 2003). These surface properties, however, can change as biochar ages (Uchimiya et al., 2010). Moreover, a long-term exposure to environmental conditions is likely to lead to biofilm growth (Luo et al., 2013), which in turn could affect its capacity to remove bacteria.

5. Conclusions

This study demonstrated that amending sand with biochar improved the removal of bacteria from stormwater during intermittent infiltration of stormwater, thereby making it attractive for use in biofilters or biorentention systems. Because biochar is less expensive than other available engineered geomedia and can be produced locally from biowaste, a large scale application of biochar is economically viable (Lehmann and Joseph, 2009). The following are the major conclusions of this study:

- Biochar-amended sand removed more *E*. coli from stormwater than quartz sand.
- Intermittent infiltration of stormwater remobilized *E*. coli attached to sand and the mobilization was higher with an increase in NOM.
- Compared to sand, biochar had lower mobilization of E. coli during intermittent flows.
- An increase in interval duration between rainfalls had contrasting effect on *E. coli* mobilization in presence of NOM: while mobilization increased in sand columns, it did not change in biochar columns.
- The increase in overall removal of *E*. coli by biochar is attributed to stronger attachment of *E*. coli at biochar surfaces and higher water-holding capacity of biochar amended sand.
- Biochar with low volatile matter and polarity was most effective in removing *E. coli*.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2014.05.026.

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