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standard CSF® and soybean hull media have been selected for onsite stormwater treatment BMP testing at the Seattle-Tacoma International airport.

KEYWORDS

NPDES, stormwater, metals, toxicity, filtration, media, BMPs

INTRODUCTION

This paper presents the results of a best management practice (BMP) screening study designed to test the effectiveness of filtration media to reduce metals and potential toxicity of stormwater runoff. This work is a follow up to needs identified by NPDES stormwater sampling, whole effluent toxicity (WET) testing and source tracing conducted in the recent past by the Port of Seattle (the Port) at Seattle-Tacoma International Airport (Port of Seattle 2000, Tobiason et al. 2000). These past studies indicated that stormwater runoff toxicity was associated with zinc from building materials used in certain drainage areas at the airport. Results of this media filtration screening will be used to select media for onsite testing as a stormwater treatment BMP at the airport. This future testing may include long-term performance monitoring to determine filtration media stability, lifecycle capabilities and maintenance intervals.

Though there is considerable volume of literature that evaluates metals and other constituent removal by conventional stormwater BMPs, there are few if any studies that have addressed toxicity as well (ASCE 1999, CWP 2000). Most, if not all stormwater guidelines for BMP performance are based solely on their constituent removal performance on a percentage basis (the difference between influent and effluent on a concentration or load basis). Though this type of metric may be appropriate for some constituents, such as sediments, it may be insufficient to judge performance in abating potential aquatic toxicity of other constituents such as metals.

Others have recently tested a wide variety of organic and other media for wastewater and stormwater treatment, including agricultural waste products such as peanut shells, corn cobs and even kudzu. Most of this work focused on specific adsorption capacities for metals (notably zinc and copper), yet did not examine concurrent toxicity reduction.

In single-pollutant isotherm column tests, Clark et al. (2000) found that low-cost organic media (peat, CSF® leaf compost, and kudzu) had lower copper removal rates than bonechar (a traditional adsorbent), and a cation exchange resin, but had removal rates more favorable than either activated carbon or zeolite. Additionally, their breakthrough tests at lower concentrations of simulated multi-contaminant wastewaters indicated the organic media was capable of removing virtually all the copper. Several USDA researchers used bench-scale column tests to determine the sorption capacities of the many agricultural waste products for a wide variety of heavy metals. They found that acid-extracted soybean hulls (which were tested and reported in this paper) performed the best and were comparable to commercial grade ion exchange resins (Marshall et al. 1999, 2000; Wartelle and Marshall 2000).

Because the material is a readily available waste product and the acid modification process is relatively simple, the soybean hulls promise to be a cost effective alternative to ion exchange

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resins for industrial wastewater. What remains to be determined is if the SBH material would work for stormwater applications, providing desirable performance and physical stability over time and the highly variable flowrates and constituent concentrations associated with stormwater runoff. The leaf compost material tested was developed and patented 10 years ago and has been used and tested in a variety of configurations throughout the country as a stormwater treatment BMP (Stormwater Management 1999). This CSF® media is specially composted from pure deciduous leaf feedstock from the City of Portland Oregon. Performance measurements have focused on removal of target constituents (metals, nutrients, petroleum and sediments).

METHODOLOGY

This study was designed to test the efficiency of several different types of filter media for reducing the concentration of zinc and potential toxicity of simulated stormwater under controlled laboratory conditions. As such, it provided a screening for future field-testing of the media in StormfilterTM units. The filter media tested to date (see Table 1) include both commercially available media and newer "experimental" media.

Table 1. Filter media tested to date

Filter Medium
Deciduous leaf compost (CSF®) ¹
Soy Bean Hulls (SBH) ²
Extra Fine Deciduous leaf compost (XFCSF) 1
Commercial inorganic polyamine "sponge"
Zeolite/Perlite (ZP) ¹

¹ - Filter media provided by Stormwater Management, Inc. of Portland, Oregon.

Except for the SBH, all media were tested in standard OEM StormfilterTM cartridge units, which contained a 0.07-m³ (2.4 ft³) volume of media. These circular cartridges were fitted in a hydraulic test cell (cube) of 0.19-m³ (50 gal) volume. Because it was available only in smaller quantities, the experimental soybean hull (SBH) medium was tested in a 3000-cm³ wedge-shaped acrylic horizontal flow column, which mimics about a 4% slice of a Stormfilter^{TM®} cartridge volume. See photographs 1-3.

Since zinc was the analyte of interest for this study, filter media performance was evaluated under low, medium, and high influent zinc concentrations. These tests simulated stormwater by using synthetic laboratory water (i.e., standardized water used in toxicity testing) spiked at the three different target zinc concentrations. Testing consisted of passing 360L (95 gal) batches of test water through the filters at flows up to the maximum 1-liter/sec (15gpm) rate recommended by the OEM. To test the effect of varying influent flow rates, the standard CSF® medium was also tested at one-half the design flow rate of 0.5 l/sec (7.5 gpm).

² - The soy bean hulls are an experimental filter medium provided by the U.S. Department of Agriculture, (Marshall et al. 1999; Marshall et al. 2000; Wartelle and Marshall 2000).

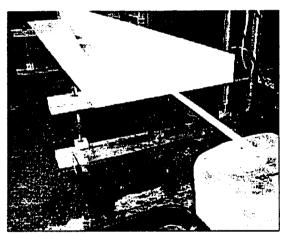
Each target concentration batch was mixed in two dedicated 210L (55 gal) food-grade



polyethylene drums that were drained simultaneously. Continuous flow-composite samples were collected from the effluent from each batch using a flow-splitter device that delivered approximately 3% of the effluent flow to an 18L polyethylene cubitainer. All of the test apparatus material was plastic and was acid washed (10% reagent grade nitric acid), then rinsed with deionized (DI) water prior to collecting samples. Each round of testing ran four batches of test water through the filters, beginning with the control (zero zinc) test water, then progressing to the low, mid and high zinc ranges respectively.

Photograph 1 Overall test setup. Influent test water contained in the blue drums was drained into the StormfilterTM test chamber (gray box on left). Media chamber effluent enters the left side of the flow splitter (white horizontal unit at bottom), and samples were collected at the flow splitter outlet on the right.

The laboratory water was mixed in large volumes to achieve a nominal hardness of 90 mg/l as $CaCO_3$. This lab water was then transferred to the drums and dosed with $ZnCl_2$ to target three ranges of ultimate zinc concentrations: $250 \mu g/l$ (low), $500 \mu g/l$ and $2000 \mu g/l$. Each batch of



test water (two full drums) was allowed to equilibrate for at least 24 hours prior to filtration testing. According to OEM suggestions, each medium was first flushed with at least six volumes of tap water, and then flushed once with DI water prior to beginning the testing program. Then, before and after each concentration series tested, the filters were flushed with one drum of DI water. The filters were also flushed with about 60 L (15 gal) of each respective zinc-spiked batch prior to each batch sampled (to flush out any test water remaining from the previous run).

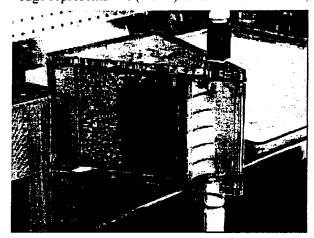
Photograph 2 Flow Splitter close up. Effluent entering narrow head (upper left) gradually spreads over multiple weirs. The custom designed rail/channel splits a continuous fractional flow sample collected in the plastic cubitainer.

The StormfilterTM units are designed to operate in a siphon mode to speed treatment rates above gravity-induced flow rates. Because of this important feature, inflow rates were adjusted during testing to maintain the siphon mode to ensure representative contact times. In general when

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inflows drop below rates sufficient to maintain the siphon, air bubbles rise up inside the cartridge hood, breaking the siphon and acting to clean the outside surfaces of the filtration media. In field installations, this clever design is intended to act as a built-in, self-cleaning step capable of dislodging sediments trapped on the media's surface and allows the sediments to settle at the bottom of vault or other chamber that houses the StormfilterTM cartridge(s).

Tests of the SBH medium in the horizontal flow (wedge) column were conducted using the same zinc concentration ranges for the full-scale filter tests, but used scaled flow rates. Since the wedge represents 4% (1 24th) of the full-scale filter, batch volumes and flow rates were scaled



down to 17 liters (4.6 gal) and 0.04 l/sec, respectively. Thus, contact times for the SBH medium would be comparable to the full-scale tests. For this application, test water was mixed and stored in 18-L polyethylene carboys that drained to and from the test column through medical-grade tubing. The test column was constructed from sheet acrylic with PVC pipes and fixtures. Flow from the column was controlled with a PVC ball-valve. Flushing and sampling were conducted in the same manner as the full-scale tests.

Photograph 3 Horizontal flow (wedge) column

Continuous flow composite effluent samples were evaluated for total and dissolved zinc, pH, hardness, dissolved organic carbon (DOC), and acute toxicity with a daphnia (waterflea) species (Ceriodaphnia dubia). Toxicity testing was conducted in an accredited bioassay laboratory using standard U.S. EPA protocols. Table 3 provides a summary of the test conditions. Ceriodaphnia dubia was used as the test species since it is one of the most sensitive to metals' toxicity and is routinely the organism of choice for most bioassay laboratories.

Quality controls for the study included filtration controls and up to three replicate tests at each of the target concentrations. The filtration controls consisted of passing unspiked synthetic laboratory water through each of the filter media under the same test conditions. Both pre- and post- filter control samples were subjected to the same chemical and biological testing described above. Grab samples from each test batch were also analyzed for chemical constituents to verify influent concentrations. Staff used clean techniques during all testing and sampling to minimize metals contamination.

Table 2. Summary of test conditions for the acute Ceriodaphnia dubia bioassay

Parametrix, Inc., Kirkland Washington **Testing Laboratory** WDOE 1998, WQ-R-95-80; USEPA 1993, EPA/600/4-90/027F; **Test Protocols** USEPA 1999, EPA-600/R-98/182 Pre- and post filtered synthetic laboratory water spiked with zinc (as Test Material zinc chloride); stock concentration is 18400 mg/L total zinc. Ceriodaphnia dubia (water flea): ≤ 24 hours at initiation Test Organisms/Age Source of Organisms In-house cultures Nominal Test 0, Post Control, 250, 500, 2000 Concentrations 0, Post Control, 250, 500, 2000, 5000 (SBH only) Reference Toxicant CuSO₄ **Test Duration** 48 hours Control/Dilution Laboratory-prepared synthetic water (80-100 mg/L hardness as Medium CaCO₃) Chemical Data pH and dissolved oxygen for each test concentration and the control (both initial and final solutions); temperature and specific conductivity at test initiation and every 24 hours Mortality (defined as immobility) and reproduction Effect Measured Test Acceptability Control survival ≥90% **Endpoints Reported** Percent Survival

RESULTS AND DISCUSSION

Testing of the different media occurred in phases as results were reviewed and the testing changed accordingly. These changes included eliminating media that proved unfavorable early in the study or making modifications to the filter media as described below. For example, because the post-filter controls had zero daphnid survival, most likely associated with the chemical composition of the medium, further testing of the sponge was ceased. In addition, since initial results for the SBH medium showed a large pH (and hardness) reduction, pH was adjusted in the effluent samples using 0.5 M sodium hydroxide prior to toxicity testing. Furthermore, in-situ pH buffering was also tested by augmenting the SBH media with activated carbon and standard CSF® media. In these tests, about 50% of the wedge test cell volume was filled with buffering media while the remainder was the SBH.

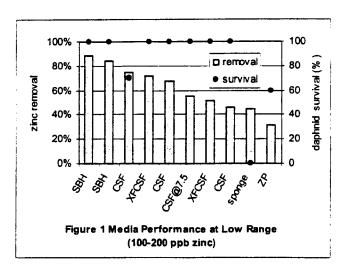
Given the above, Figures 1 to 3 summarize the results of media testing for each of the three target zinc concentrations. To aid interpretation, the percent zinc removal (total recoverable) and the percent daphnid survival are presented on the same figure. Because the analytical results indicated the actual influent zinc concentrations achieved were somewhat variable and lower

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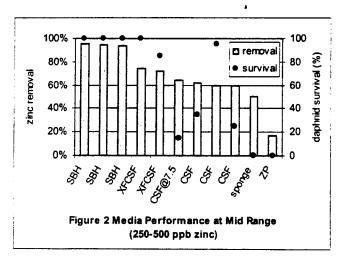
than the targets, the data reported in the figures have low, mid and high ranges indicated rather than nominal influent concentrations. Table 2 contains all test data.

Overall, the CSF® and SBH media provided the most promising results. Compared to the CSF® and SBH, results for the zeolite/perlite and sponge media were poor, therefore, further testing of these two was ceased. Results for the initial round of CSF® tested at one-half the design flow rate were comparable to the standard flow rate, therefore only one round of the low flow rate testing was conducted. Two rounds of testing the XFCSF showed only modest improvements in zinc removal compared with results for the standard CSF®.

The first round of CSF® had substantial turbidity from unstabilized media and negative zinc removal (Zn addition) at the mid and high range tests. Because the effluent from this first round exhibited low dissolved fractions (27% and 39% dissolved zinc at the mid and high ranges, respectively), the data suggested that the particulates causing the turbidity contained substantial sorbed zinc. Therefore, for the first round of CSF® testing, the zinc removal based on the dissolved fraction better represents performance (62% and 24% removal at the mid and high



ranges, respectively). Furthermore, these rates are comparable with both total recoverable and dissolved zinc removal in the two subsequent rounds of CSF® testing. Thus, figures 2 and 3 contain the removal rates for dissolved zinc for the first round, and total recoverable zinc for the final 2 rounds of standard CSF® media testing.



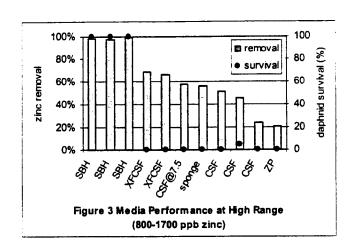
The SBH effluent zinc concentrations remained consistently low throughout all ranges tested. During 9 of 10 tests over a wide range of influent concentrations, zinc concentrations in the SBH effluent ranged from 13 µg/l to 29 µg/l, averaging 20 µg/l. The highest zinc in SBH effluent was 48 µg/l resulting from the 4.4 mg/l influent, representing 99% removal. Effluent zinc concentrations for the other media generally increased with increasing influent concentrations. Therefore, overall zinc removal was inconsistent and decreased with increasing influent

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concentration for media other than the SBH. Except for the sponge media, daphnid survival correlated well with effluent zinc concentrations. Inferred LC50s approximated expected LC50s of about 150 µg/l zinc.

In general, the organic media added between 3 to 35 ppm DOC, while the mineral medium (zeolite/perlite) added less than 0.5 ppm DOC. The sponge in particular contributed about 25 ppm DOC over all zinc ranges tested. In contrast, DOC imparted by the other organic media (2-7 ppm for the CSF® and 10 ppm or more for the SBH) dropped during successive tests.

Hardness was relatively unchanged by all media except the sponge and the SBH, which reduced hardness by 21% to 48%. The CSF® media increased hardness by only a few percent. In contrast, the SBH media consistently removed about 60 to 80 ppm hardness from the influent, resulting in about a 70 to 80% decrease overall. The sponge media also removed hardness, but less so than the SBH media. This reduction in hardness is likely due to the high affinity these two media have for divalent metals like calcium and magnesium, in addition to zinc.



Despite the pre-test flushing procedure used, almost all media generated suspended solids during initial control and low-range zinc test water passage, indicating that a certain fraction of the media volume, though low, escaped. Turbidity as well as the higher DOC in effluent samples indicated this fact. Perhaps smaller screen sizes in the StormfilterTM cartridges would be in order.

Quality Control

Three levels of QC sampling showed acceptable results indicating effective sampling procedures and representative data. Effluent zinc in controls for each medium varied by only a few ppb from influent control concentrations except for the SBH medium, which appeared to add from 14 to 37 ppb zinc, mostly in particulate form. In the influent controls, zinc ranged from <5ppb to a maximum of 24 ppb, pH ranged from 7.0 to 7.4, hardness ranged from 74 to 96 mg/l as CaCO₃, and DOC ranged from 0.3 to 0.5 mg/l. Daphnid survival was 100% in all eleven of the influent controls. In the effluent controls, daphnid survival was 95 to 100% for all media except for the sponge, which exhibited zero survival. These results revealed that the sponge apparently generated considerable toxicity, hinted at by the considerable foam, odor and yellow color in the effluent.

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Table 3 Media testing results

Γ	note	<u> </u> -	_	-		Γ	Γ	 -		Τ	Γ			_	-	-						Γ		7	-	-	-	F							2
H		3%	93%	75%	77%	63%	77%	20%	47%	53%	55%	42%	22%	%96	93%	%06	%02	%89	%02	28%	29%	52%	17%	62%	%66	%86	%/6	71%	%69	%99	25%	43%	27%	.5%	4.%
Zinc removal	%	72 8	0.081 9	0.027 7	0.235 7		0.150 7	0.011 5	0.055 4	0.056 5	0.056 5	0.062 4	0.023 2	0.472 9	0.127 9	0.129	0.216 7	0.178	0.250 7	0.153 5	0.231 5	0.200	0.039	0.172 6	4.346 9	1.364 9	0.661 9	0.765 7	0.437 6	0.691	0.807 5	0.428 4	0.188 2	0.300 22%	0.229 24%
	mg/	3	1		_				Ц.		<u> </u>				1		L			L				L						1	L	<u> </u>			0.7
	%	88%	7 84%	%62 1	2 75%	3 72%	4 68%	4 62%		7 51%	3 46%	2 45%	3 31%	%96 I	1 95%	5 94%	3 74%	2 72%	7 64%	2 60%	3 59%	20%	3 17%	7 -2%	86 7	1 98%	4 98%	3 69%	%99 9	%85 /	%95 9	5 51%	2 46%	0 21%	%9- 0
	mg/l	0.219	0.097	0.054	0.242	0.149	0.134	0.024	0.081	0.067	0.049	0.072	0.068	0.481	0.231	0.255	0.279	0.272	0.237	0.165	0.248	0.206	0.063	-0.007	4.382	1.591	0.944	0.793	0.555	0.817	0.936	0.65	0.432		-0.110
effluent (mgll)	200	16	5.2	3.24	1.94	3.02	5.47	4.96	2.5	2.95	2.7	25.8	0.355	7.22	3.74	2.67	2.74	2.63	2.4	2.49	1.83	25.4	0.362	2.9	4.35	5.83	2.85	1.94	2.63	1.73	23.3	2.21	1.9	0.387	2.63
	Hard DOC	20.9	77	14.6	88.5	87.8	77.2	17.3	94.8	96.2	90.5	48.5	92.6	17.7	15	14	95.2	9.98	85.8	87.9	91.3	49.8	92	75.4	17.9	18.9	12.3	96.7	87.6	97.8	52.6	88.5	88.1	95.2	11
		85%	33%	64%	85%	85%	73%	73%	<u> </u>	78%	81%	%/6	54%	85%	%69	88%	%96	80%	%08	03%		%76	61%	27%	71%	%06	81%	85%	71%	89%	%06	%06		_	39%
	TRZN Diss Zn %diss	0.023	900.0	0.00	0.07	0.050	0.046	0.011	0.061	0.050	0.046	0.085	0.082	0.018	0.009	0.015	0.092	0.084	0.105			0.187	0.189	0.106	0.034	0.026	0.017	0.305	0.200	0.539	0.673	0.56	0.510	1.060	0.716
	Diss	L	Ш	L				L					Ц						L								Ц								
eff	TRZN	0.027	0.018	0.014	0.082	0.059	0.063	0.015		0.064	0.057	0.088	0.151			0.017	960'0	0.105	0.131	0.110	0.170		0.308	0.396		0.029	0.021	0.357	0.282	0.603	0.744	0.62	0.513		1.820
	Ŧ	3.4	3.4	3.4	7.4	7.4	7.7	3.5	7.9	7.2	7.7	6.9	7.4	3.6	3.5	3.5	7.3	7.4	7.1	7.7	7.6	6.9	7.4	7.5	3.5	3.6	3.5		7.3	7.1	7	7.5	7.6	7.3	7.5
	% survival	100	100	100	70	100	100	100	100	100	100	0	90	100	100	100	100	85	15	95	25	0	0	35	100	100	100	0	0	0	0	0	5	0	0
r	DOC	0.125	0.357	0.125	0.125	0.125	0.522	0.125	0.292	0.125	0.125	0.341	0.125	0.125	0.357	0.125	0.125	0.125	0.292	0.125	0.125	0.341	0.125	0.522	0.125	0.125	0.357	0.125	0.125	0.292	0.341	0.125	0.125	0.125	0.522
	Hard [78.3 (94.4 (93.6	89.7 (82.8 (74.3	93.6	89.7 (96.9 (89.7 (76.8 (95.2 (78.3 (94.4	93.6							95.2 (74.3 (78.3	94.4		82.8	89.7 (76.8	89.7 (89.7	95.2	74.3 (
(llbi	%diss H	. %62	3 %9/		94%	65%	_		3 %62	81% 8					26%			_	_						_		_	_	3 %9 /	87% 8		3 %82			55%
influent (mgll		0.195	87	1	0.305	0.136		0.022	0.116	0.106	0.102				0.136															.230		0.988			0.945
1	Diss Zn		0.087																																
	TRZN	0.246	0.115	0.068	0.324	0.208	0.197	0.039	0.147	0.131	0.106	0.160	0.219	0.503	0.244	0.272	0.375	0.377	0.368	0.275	0.418	0.409	0.371	0.389	4.430	1.620	0.965	1.150	0.837	1.420	1.680	1.270	0.945	1.530	1.710
!	핌	7.2	7.7	7.1	7.7	7.8	7.8	7	7.1	7.4	7.8	7.8	₹.	7.4	7.5	7	6.7	7.4	7	7.7	7.5	7.4	7.5	8.	7.2		7.2	7.3	7.	7.	7.5	7.4	7.5	77	7.5
test	range	woj	ΝO	MO	ΝO	ΜO	wo	No.	wo	νo	ΜO	ΜO	M O	Βig	mid	Βig	멅	ള	Бiğ	Đ.E	ΒiΕ	Βġ	Β̈́Ε	BE	Fig.	high	Į.	Ę.	high	high	high	high	퉏	년 당	high
	Ε	SBH	SBH	SBH	CSF	XFCSF	CSF	SBH	CSF@7.5	XFCSF	CSF	sponge	ζb	SBH	SBH	SBH	XFCSF	XFCSF	CSF@7.5	iS.	SSF	sponge	ZP	SS.	SBH	SBH	SBH	XFCSF	-	CSF@7.5	0	SF	SS	┪	CSF
	date	12-Jul	7-Jun	15-Jun	3-Мау	17-May	13-Apr			30-May	25-Apr	18-Apr	23-May	12-Jul	7-Jun	15-Jun	30-May	17-May	20-Jun	25-Apr	3-Мау	18-Apr	23-May	13-Apr	12-Jul	12-Jul	7-Jun	30-Мау			18-Apr	3-Мау	25-Apr	23-May	13-Apr
	rep	4	-	၉	က	-	-	2	-	7	7	-	-	6	-	2	7	-	-	7	၈	-	-	-	6	7	-	7	-	-	-	<u>س</u>	7	-	-

¹ pH adjusted: survival was zero in the unadjusted sample.
² particulate Zn fraction increased due to turbidity in effluent. Dissolved Zn removal results plotted in figures 2 and 3.
³ influent hardness and DOC values from influent controls

CONCLUSIONS

All of the media tested showed some degree of dissolved metals removal, though it was most pronounced for the organic media. The SBH media performed exceptionally well, removing 80 to 90% of the zinc, with up to 99% removal for the highest (4.4 mg/l) zinc influent. Compared to the other media, the SBH effluent zinc concentrations were consistently low (20-40 µg/l) over all ranges tested. Despite achieving these low zinc concentrations, the SBH media needs pH buffering to prevent pH-induced toxicity. In this case, the CSF® media is a suitable pH buffer, and will provide metals removal as well. The CSF® media performed well over the low and mid concentrations tested. Enhancements of the basic CSF® media (lower flow rates and extra fine) achieved modestly improved results. Because media suited for one application (e.g. industrial wastewater) may not always be suitable for others, they should first be screened for inherent toxicity before consideration as a stormwater BMP.

The organic-based media (CSF®, sponge, SBH) added considerable DOC, while the mineral-based medium (zeolite/perlite) did not. Adding DOC would be favorable because of its potential to reduce potential bioavailability by binding dissolved metals and other constituents of concern. Compared to the organic media, the mineral based medium did not provide enough dissolved zinc removal to warrant further testing. The highly dissolved zinc fractions tested may under represent the particulate metal removal capabilities for the zeolite/perlite mixture, and certainly do not reflect on zeolite's well-known nutrient removal ability. Finally, though these are laboratory data, the results suggest that the metric typically used to rate BMP performance, i.e. percent metals removal (based on influent/effluent concentrations) may not be sufficient to judge performance relative to the toxicity endpoints that are the basis for water quality standards for metals.

ACKNOWLEDGEMENTS

The Port appreciates the cooperation of Bryan Wigginton of Stormwater Management Inc (Portland, OR) who supplied the CSF®, zeolite/perlite, and sponge media and Stormfilter test chambers at no cost. The Port is grateful for the assistance of Lynda Wartelle of the USDA Agricultural Research Service, Southern Regional Research Center (New Orleans, LA) who supplied the soybean hull media and continues to assist the Port's work.

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