Evaluation of media for the adsorption of stormwater pollutants

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ABSTRACT
This paper presents the findings of a two-stage investigation into the adsorption of stormwater pollutants by selected filter media, and consequently the performance of preferred media combinations. Eight media were selected for analysis; anthracite, lignite, granular activated carbon, clean river sand, vermiculite, perlite, zeolite and garden compost.

Untreated stormwater was collected at the onset of significant rainfall events as runoff from a modern, impervious, multi-storey car park. Four stormwater solutions were prepared, both filtered (passing a 0.45 μm filter) and unfiltered, and of high and low pollutant loads. Comparisons of efficacy were drawn from results of adsorption tests using a batch equilibrium method. Key pollutants examined included: total nitrogen, total phosphorous, total suspended solids, and heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn). Of the media tested, those with the greatest adsorptive capacities were: granular activated carbon, anthracite, vermiculite, and zeolite, in decreasing order of effectiveness.

The second stage of this investigation was conducted on eleven combinations of the four media outlined above. A similar methodology as per the first stage was used. The most complete pollutant removal combination was found to be equal proportions of granular activated carbon with zeolite. This combination removed 85% of heavy metals tested, and up to 62% of total nitrogen.

KEYWORDS
Adsorption, granular media, batch equilibrium method, CSO and stormwater treatment, priority pollutants

INTRODUCTION
This study evaluated the removal efficiency of both heavy metals and nutrients from natural stormwater. Coarse, granular media were identified in well-controlled batch tests for potential use in stormwater secondary treatment systems. The coexistence of the eight most important heavy metals, initial pH, and the presence of nutrients in natural stormwater were considered.

Stormwater is growing in recognition within Australia as a potential urban water source. Treatment technologies used in stormwater harvesting systems usually rely on technologies developed for pollution control in stormwater discharges (Mitchell *et al.*, 2007) such as stormwater ponds, wetlands, swales, and bioretention basins. These technologies require significant space and are not always able to deliver a consistently high standard effluent discharge. A novel technology for stormwater harvesting that could be retrofitted in a confined urban environment, should be reliable, and most importantly be sustainable is currently under development at Monash. It consists of a collection/treatment unit, with porous Permapave blocks on top and filter media underneath, and a PET storage tank at the side, as illustrated in Figure 1 below. This paper reports on the first stage of development of the technology, that focuses on filter media development.

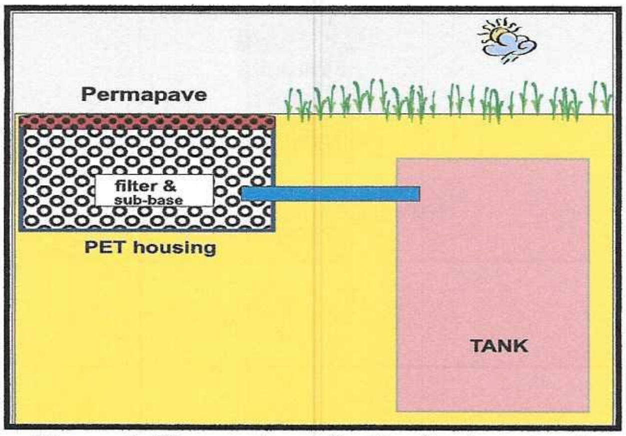


Figure 1. Stormwater collection/treatment unit

Major sources of heavy metals in stormwater runoff include building materials (e.g. Cu from roofs and Zn from galvanized steel), and traffic related sources such as brake linings (Cu, Ni, Cr, Zn, Pb), tire wear (Zn), and auto catalysts (Pt, Pb, Rh) (Genç-Fuhrman *et al.*, 2007). Due to short-term (e.g. acute toxicity) and long-term adverse effects of heavy metals in aquatic environments (e.g. carcinogenicity and damage to reproductive systems), treatment of stormwater runoff containing heavy metals is receiving increased attention (Butler and Davies, 2004).

To improve the quality of urban runoff before discharging, some method of treatment is required. A number of structural devices are already commercially available, typically utilising physical separation processes in the removal of suspended solids. Examples such as retention ponds, filtration trenches and bio-filtration ponds are used with demonstrated effectiveness. Several studies have documented the effectiveness of these most common management practices (Butler and Davies, 2004; Wong, 2006). Highly variable removal efficiencies have been reported depending on the pollutant in question, system type and design, as well as inflow conditions (Wong 2006).

The filtration of stormwater via sorption – where both colloidal and dissolved heavy metal fractions are removed – is one of the most promising technologies, provided that an effective filtration media is used. Although many studies of heavy metal removal from stormwater using a variety of sorbents exist, they typically only report removal percentages and do not document the experimental conditions thus making the results impossible to compare directly. Furthermore, the majority of previous work on heavy metal and nutrient removal using filtration/adsorption deals with the treatment of individual pollutants in isolation, and only a few studies are carried out under realistic experimental stormwater conditions (Genç-Fuhrman *et al.*, 2007; Tobiason *et al.*, 2007; Liu *et al.*, 2005). However, it is important to understand and quantify the removal of heavy metal pollutants where various species coexist (Genç-Fuhrman *et al.*, 2007; Jang *et al.*, 2005; Al-Asheh *et al.*, 2000). Finally, very little has been published on removal of pollutants using combination media (mixtures of several basic media).

The aim of this work was to study the adsorption of stormwater pollutants by selected filter media, and consequently the performance of preferred media combinations. Real stormwater was used in the study to assure the results robustness.

METHOD

This study is being conducted in two distinct stages. The first stage aims to investigate the adsorptive capacities of individual media. Results of the first stage were used to narrow the media selected for the second stage, that of the performance of preferred media combinations.

Adsorptive media

Eight adsorptive media were selected for analysis, as identified in recent literature; anthracite (black coal), lignite (brown coal), granular activated carbon (GAC) (Genç-Fuhrman *et al.*, 2007), clean river sand (acid washed) (Sansalone, 1999), vermiculite (Covelo *et al.*, 2007), perlite, zeolite (Genç-Fuhrman *et al.*, 2007) and garden compost (Jang *et al.*, 2007). Media samples were sourced from local commercial suppliers.

Stormwater solutions

Untreated stormwater runoff was used in these studies. Two stormwater samples for stage one, and one sample for stage two were collected from a modern, multi-storey, impervious car park that usually discharges stormwater with high metal concentrations.

The two solutions collected in the first stage were; high strength (representing pollutant loads during a first-flush event (Stenstrom *et al.*, 2001)) and low strength. In total four solutions were prepared, both filtered (passing a 0.45 μm filter) and unfiltered (to distinguish pollutants associated with particulates (Morquecho *et al.*, 2005)), of the high and low strength solutions. Only a single unfiltered solution was used in the second stage, to simulate long-term pollutant loads. The concentration of pollutants in the solutions used is given in Table 1 below.

Table 1. Stormwater pollutant concentrations.

Pollutants	First stage				Second stage	Method detection limit
	Low strength		High strength		Standard strength	
	Filtered (mg/L)	Unfiltered (mg/L)	Filtered (mg/L)	Unfiltered (mg/L)	Unfiltered (mg/L)	(mg/L)
TSS	0	27.5	0	233.7	62.7	0.1
TN	2.40	3.00	4.80	4.88	1.72	0.01
TP	0.09	0.10	1.47	1.60	0.01	0.01
Cd	0.0013	0.0022	0.0048	0.0057	0.0002	0.0001
Cr	0.0008	0.0012	0.0010	0.0015	0.0008	0.0003
Cu	0.032	0.036	0.469	0.334	0.018	0.0005
Fe	0.010	0.013	0.015	0.021	0.008	0.0002
Mn	0.0048	0.0094	0.0066	0.0113	0.0003	0.0002
Ni	0.0031	0.0023	0.0048	0.0048	0.0035	0.0005
Pb	0.170	0.168	0.653	0.727	0.007	0.003
Zn	0.760	0.998	1.47	1.60	0.01	0.0006

First stage batch experiments

Sorption experiments were carried out using stormwater samples in 50 mL centrifuge tubes at room temperature and pressure. Three replicates of each sample (including controls) were prepared. The pH of solutions was then checked and adjusted to 6.5 ± 0.1 pH using 0.01M solutions of HCl and NaOH. 1.00 ± 0.01 g of each sorbent was added to the 50 ± 1 mL of stormwater, to yield a ratio of 20 ± 0.6 g/L sorbent to stormwater solution.

The mixtures were shaken vigorously, the pH re-measured and subsequently re-adjusted to 6.5 within a few minutes. Samples were agitated vigorously on a shaker table for 48 hours at room temperature. After this period, batches were centrifuged for 20 minutes at 4000 rpm. The separation of the supernatant and filter media concluded the test. Of the sampled supernatant, 20 mL was prepared for nutrients analysis (TN, TP). A further 20 mL of each supernatant was retained for heavy metals analysis. These solutions were acidified with two drops of HNO_3 to preserve the metal concentration in solution. All samples were capped tightly and stored at 4 °C until analysis. The tests were done in accordance with standard methods for the examination of water and wastewater (APHA, 1992; OECD, 2000).

The collected supernatants were sampled for analysis in a NATA accredited laboratory for the following pollutants; total nitrogen (TN), total phosphorous (TP), and total suspended solids (TSS) (APHA-AWWA-WPCF 1998). Heavy metals Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn were analysed using the latest ICP-OES machine. Method detection limits are presented in Table 1.

Second stage batch experiments

Recognising that individual pollutants were adsorbed in different quantities by different media, the aim of this second stage was to determine proportions for a combination granular media filter. The four best performing media from the first stage were combined in eleven different combinations of quantities, and trialled in batch tests. The combinations investigated are outlined in Table 2 below. Combinations such as A_2G_2 were not investigated, as the materials were considered to be very similar in performance.

The batch test methodology was identical to that described above, with the exception of the following variations. Five replicates of each combination (including controls), were prepared. Only one standard strength stormwater solution was prepared to represent long-term pollutant loads. The initial pH was (6.7 ± 0.1) and it was not controlled during the experiments. Samples were again analysed for nutrient and heavy metal adsorption.

Table 2. Granular media combinations investigated.

Code	GAC (g)	Anthracite (g)	Vermiculite (g)	Zeolite (g)
GAVZ	0.25	0.25	0.25	0.25
GAV_2	0.25	0.25	0.50	-
GAZ_2	0.25	0.25	-	0.50
G_2VZ	0.50	-	0.25	0.25
A_2VZ	-	0.50	0.25	0.25
A_2V_2	-	0.50	0.50	-
G_2Z_2	0.50	-	-	0.50
GAV	0.33	0.33	0.33	-
GAZ	0.33	0.33	-	0.33
GVZ	0.33	-	0.33	0.33
AVZ	-	0.33	0.33	0.33

RESULTS AND DISCUSSION

The results of the first and second stages are presented separately below.

First stage

Figures 2 through 5 present the results of the first stage of tests. Pollutant adsorption is presented for each stormwater solution. Please refer to Table 1 (which presents initial concentrations) to estimate the outflow concentrations from these results.

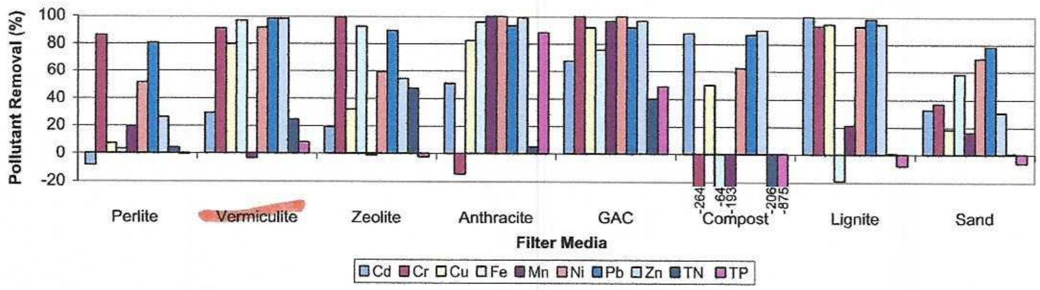


Figure 2. High strength, unfiltered stormwater.

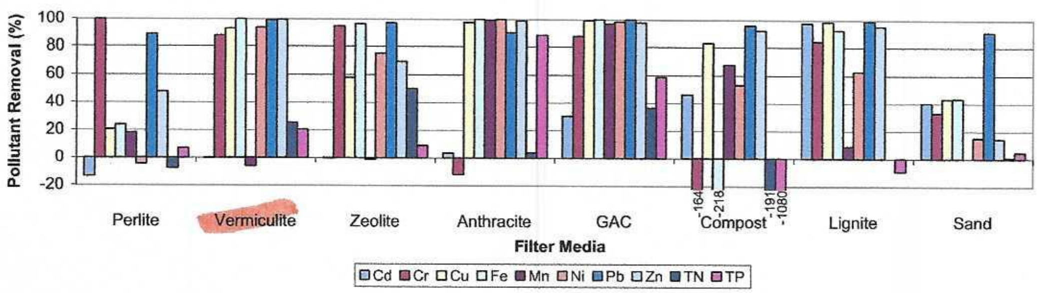


Figure 3. High strength, filtered stormwater.

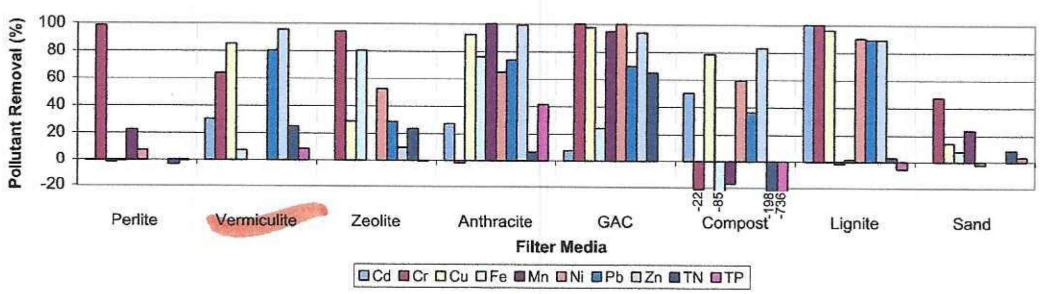


Figure 4. Low strength, unfiltered stormwater.

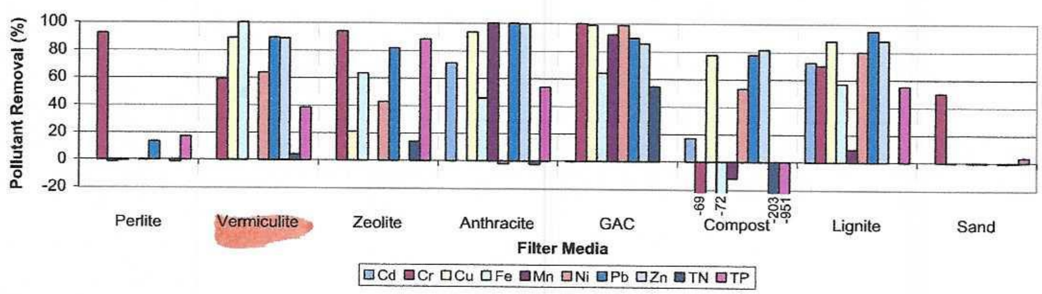


Figure 5. Low strength, filtered stormwater.

The leaching of pollutants by the tested media is reported as a negative adsorption – values of excessive (off-the-chart) leaching by compost are reported adjacent to the graph. This data was analysed in conjunction with Table 1, to present adsorptive capacities of the materials for each of the pollutants tested. These results are presented in Table 3 below.

Table 3. Adsorptive capacities of granular media – summary of experiment and literature

Media	Pollutant adsorptive capacity per unit mass media (µg/g)							
	Cd		Cr		Cu		Fe	Mn
	Exp	Lit	Exp	Lit	Exp	Lit	Exp	Exp
Perlite	0		>0.06		4.8		0.2	0.10
Vermiculite	0.08		0.04		17		>1	0
Zeolite	0.05	2[1]	>0.07	0[1]	13	100[1]	>1	0
Anthracite	0.1		0		>23		>1	>0.6
GAC	0.2	9[1]	>0.08	1[1]	>23	50[1]	0.8	>0.6
Compost	0.2		0		19	>100[2]	0	0
Lignite	>0.29		0.07		>23		0.7	0.02
Sand	0.095	0.2[1]	0.028	0[1]	10	8[1]	0.6	0.1

	Ni		Pb		Zn		TN		TP	
	Exp	Lit	Exp	Lit	Exp	Lit	Exp	Lit	Exp	Lit
Perlite	0		29		35		10		5	
Vermiculite	>0.22		>36		>78		60		15	
Zeolite	0.15	0.1[1]	33		51	150[1]	120	0[3]	7	
Anthracite	>0.24		34		>79		12		71	
GAC	>0.24	10[1]	33		>77	100[1]	98		42	
Compost	0.15		31	>39[2]	72	>890[2]	0	0[3]	0	0[3]
Lignite	0.22		>36		>76		5		2.4	
Sand	0.12	0.1[1]	30		24	2[1]	13		3.3	

> adsorptive capacity greater than or equal to experimental value

[1] Genç-Fuhrman *et al.*, 2007

[2] Davis *et al.*, 2001

[3] Trowsdale *et al.*, 2007

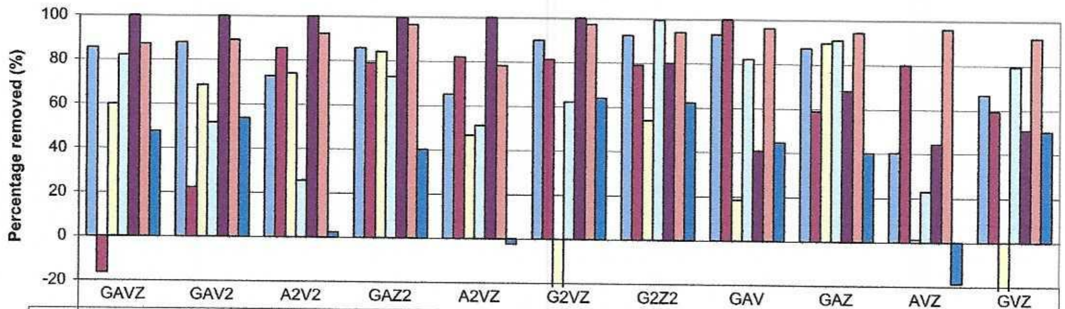
Media capacities (for which comparisons are available) compare favourably with numerical values given in relevant literature. Points of difference with literature include zeolite, which was found in this study to be the best adsorptive material for nitrogen, instead of leaching (Trowsdale *et al.*, 2007). Weak leaching of phosphorous was observed for zeolite, in agreement with similar literature (Trowsdale *et al.*, 2007, Clark *et al.*, 2005). Compost was found to have adsorptive capacity for most metals, but significantly leached nutrients (Trowsdale *et al.*, 2007). This could be attributed to the significant entrained nitrogen and phosphorous in the compost.

Of the media tested, those with the greatest adsorptive capacities were: granular activated carbon, anthracite, vermiculite, and zeolite, in decreasing order of overall effectiveness. It is worth noting that each material has a different adsorption capacity for individual pollutants, and that no single material addresses each pollutant equally.

The value of this and previous work (Clark *et al.*, 2005) is the use of **actual stormwater**, whereas similar studies consider only a synthetic matrix (Liu *et al.*, 2005, Trowsdale *et al.*, 2007).

Second Stage

Figure 6 presents the results of the second stage of the investigation.



	GAVZ	GAV2	A2V2	GAZ2	A2VZ	G2VZ	G2Z2	GAV	GAZ	AVZ	GVZ
Cu	86	88	73	86	65	90	93	93	87	40	67
Fe	-16	22	86	79	82	81	79	100	59	80	59
Mn	60	69	74	84	47	-39	54	19	90	1	-78
Ni	82	52	26	73	51	62	100	82	91	23	79
Pb	100	100	100	100	100	100	80	41	68	45	51
Zn	87	89	92	97	79	97	94	96	94	96	92
TN	48	54	2	40	-2	64	62	45	40	-19	50

Combination media

Cu Fe Mn Ni Pb Zn TN

Figure 6. Filter media combination results.

The adsorptive capacity of TP in this second stage was not determined, as the concentration in the stormwater used was below the detection limit (<0.01mg/L). Leaching of TN is observed in samples containing anthracite, and less (or zero) GAC than anthracite by mass. This leaching of TN by anthracite is observed also in Figure 5. The highest nitrogen removals were found in samples containing GAC, again in agreement with results of the first stage.

Of the combinations investigated, the most complete treatments (of both metals and nutrients) were observed in GAZ_2, G_2Z_2, and GAV_2. The cation exchange capacity (CEC) of these three combinations was externally assessed; the results of which are produced in Table 4 below.

Table 4. Cation exchange capacities of the best combination media.

Media	CEC (meq/100g)
G_2Z_2	45
GAV_2	24
GAZ_2	14

It was found that the combination of granular activated carbon and zeolite (G_2Z_2) in equal quantities by mass was the best investigated. The adsorptive capacity of this combination for both metals and nitrogen (TN) was high for the actual stormwater tested. As such, G_2Z_2 was assessed as the best all-purpose combination filter. In the first stage, other materials were found to be more effective than zeolite for most pollutants. However, the combination filter effectively covered the metals tested, and additionally provided nutrient removal.

The combinations GAZ_2 and GAV_2 were assessed as the next-best combinations – leading in either metals or nutrients removal, respectively. This illustrates that the optimisation of media combinations to suit site-specific stormwater conditions should be possible to improve effluent quality.

The results of this report will inform the final practical stage in this investigation – full-scale column tests of combinations G_2Z_2 and GAV_2 in conjunction with porous pavement surfaces, as presented in similar investigations (Dierkes *et al.*, 2002). The 1-dimensional columns will be filled with either a mixture or layers of adsorbent media, with a porous paver fitted above. Running for an extended period, this stage will assess the degradation of the performance in pollutant adsorption over several months, as well as specify an appropriate maintenance interval.

CONCLUSIONS

The results of the first stage indicate that granular activated carbon had the greatest adsorptive capacity of the materials tested. Anthracite, lignite, vermiculite and zeolite were the next most adsorptive, in decreasing order of effectiveness. These materials demonstrated good adsorptive capacity for TN and TP (20-60%), and heavy metals (20-100%). GAC demonstrates excellent metal removal percentages (69-100%), as do anthracite and lignite similarly (45-90%). Weak leaching of phosphorous was observed for zeolite. Other materials examined included perlite, sand and compost – in order of decreasing effectiveness. Compost leached significant concentrations of nutrients, and metals to a lesser degree. These leachates could be attributed to the high quantities of entrained nutrients. It was determined from these results of first stage that GAC, anthracite, vermiculite, and zeolite were the most adsorbent media (of those tested) for stormwater pollutants.

The second stage was conducted on combinations of the four most effective filter media identified in the first stage. The most complete pollutant removal combination was found to be equal proportions of granular activated carbon with zeolite. This combination removed 85% of heavy metals tested, and up to 62% of total nitrogen. The combinations GAZ_2 and GAV_2 were assessed as the next-best combinations – leading in either metals or nutrients removal, respectively.

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