PERFORMANCE COMPARISON OF CRUSHED MUSSEL SHELLS AND SAND AS FILTRATION MEDIA

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ABSTRACT (200 WORDS MAXIMUM)

Removing contaminants from stormwater sustainably is challenging, particularly at industrial sites. The issue is currently addressed by filtration or infiltration devices. The goal of this field study was to compare the effectiveness of contaminant removal utilizing two different filter media. Half Moon Bay Marina's hardstand area was selected as a trial site.

A dual-chamber splitter filter was built in which one chamber utilized crushed mussel shells and the other the sand medium currently recommended in TP10. The filter collected stormwater runoff from the marina hardstand area which entered a settling forebay before being evenly distributed over the sand and mussel shell filter areas. A range of parameters were monitored which included inflow, outflow, total suspended solids, dissolved copper, dissolved zinc, total copper, total zinc and site rainfall for a period of 14 months. Parameter data was analyzed to evaluate the effectiveness of each medium.

The paper discusses field experiment set-up and instrumentation plan; media characteristics and specifications; hydrological characteristics of the site; and performance of the two media.

KEYWORDS

Crushed Mussel Shells, Sand, Heavy Metal, Filtration, Sand Filter, Event Mean Concentration, Removal Efficiency

PRESENTER PROFILE

Nick Vigar has a background in chemistry and a particular interest in water quality aspects of stormwater management. He is a Stormwater Technical Specialist with Auckland Council's Stormwater Technical Services team.

1 INTRODUCTION

The green-lipped mussel (*Perna canaliculus*) is the basis of a significant aquaculture industry in New Zealand, with *ca.* 100 000 tons harvested annually (Food and Agriculture Organization of the United Nations, 2012). A significant quantity of mussel shell is produced as a byproduct of the industry, making it a comparatively cheap and sustainable resource with widespread availability.

Mollusc and crustacean shell, generally, has been found to have significant capacity to remove dissolved heavy metals from the water column. Various mechanisms for this removal have been postulated, including:

- Adsorption to the chitin polysaccharide component of the shell (Kim & Park, 2001).
- Ion-exchange with calcium ion from the sparingly soluble calcium carbonate component of the shell (Tudor, Gryte, & Harris, 2006).
- Non-specific adsorption associated with the high surface area of the shell (Tudor, 1999).

Laboratory investigations into the metal sorption capacity of *P. canaliculus* showed promising results for zinc and copper removal from synthetic stormwater (Auckland Regional Council, 2012). On the basis of these results, a field trial was undertaken to measure the relative effectiveness of crushed mussel shell and sand at removing the contaminants of concern from marina hardstand runoff. The contaminants of concern were considered to be copper from antifoulant paint removal and zinc from galvanized surfaces and sacrificial zinc anodes, in particular.

2 EXPERIMENTAL PROCEDURE

2.1 TREATMENT DESIGN AND OPERATION

2.1.1 SITE LAYOUT

The site for this field trial was at Half Moon Bay Marina, on Auckland's Tamaki Estuary. The marina provides berths for predominantly recreational water craft, as well as facilities for boat maintenance. Runoff was collected from a portion of the hardstand area which is set aside for the cleaning of boat hulls and the removal of antifoulant coatings. The latter are removed by a combination of high pressure water blasting and sanding. Where possible, vacuum sanding is encouraged and the marina requires that boat owners remove obvious debris by sweeping and vacuuming to minimize the load delivered to the stormwater system.

Runoff from the catchment area drained to a single catchpit, which was fitted with a proprietary catchpit filter with a 400 micron mesh. The material retained by the catchpit filter was not quantified. In this regard, the total influent load recorded during this study should be regarded as conservative.

After pre-treatment at the catchpit, runoff flowed to a 1200 mm diameter manhole that functioned as a pump chamber. A submersible pump, configured with a float switch, pumped the runoff to the filtration unit, which was situated above ground at one end of the hardstand area.

2.1.2 FILTRATION UNIT DESIGN

The filtration unit was configured as two treatment units in parallel. Inflow was split by a flow splitter box with adjustable weirs. Following the flow splitter unit, runoff passed through a forebay before passing into the filter bay for treatment. Each filter bay contained a perforated under drain surrounded by a 100 mm thick layer of scoria drainage aggregate. A layer of non-woven geotextile was placed over the drainage aggregate to prevent media migration. A 400 mm thick layer of each filtration media was placed above the drainage layer. Design and sizing of the device was in general accordance with Auckland Regional Council technical publications 'TP10' (Auckland Regional Council, 2003) and 'TP108' (Auckland Regional Council, 1999), respectively.

Each treatment unit was configured with its own bypass, in an on-line arrangement. The elevation of the bypass invert was *ca.* 150 mm above the elevation of the flow splitter weirs. The implication of this configuration was that, although the splitter weir divided the flow approximately evenly, when the water level in the one filter chamber was above these weirs, flow could proceed preferentially to the other chamber, if its water level was lower. For this reason the filter bed with the more rapidly draining media tended to receive more flow and thus, more contaminant load. For this reason the relative capacities of each media for sediment and ion exchange could not be readily established.

2.1.3 FILTRATION UNIT OPERATION

The treatment unit was charged with fresh filter media in early September 2010. Each unit was operated until November 2011. The media were rejuvenated to counteract clogging by raking the surface in early August 2011.

2.2 FILTER MEDIA

Two different media were employed in each side of the parallel treatment unit. One side contained crushed mussel shell media and the other contained sand.

Crushed mussel shell media was processed by a glass crushing facility[1] to the appropriate grade. Particle size analysis showed that *ca.* 3% of the media was finer than 63 microns, *ca.* 45% of the media was in the range of 63 to 2000 microns, and *ca.* 51% of the media was larger than 2000 microns.

Sand media consisted of a locally sourced grade[2], typically used to satisfy the requirements of TP10, with respect to particle size distribution (Auckland Regional Council, 2003).

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[1] Silaca Glass Crushers, Otaki.

[2] Puni AP3 Grade, Winston Aggregates.

2.3 DATA AND SAMPLE COLLECTION

Flow into the filtration unit was measured by a turbine meter, which gave an output pulse for every 10 L of volume passed. Outflow from each filter bed was measured as instantaneous flow rate, based on stage data through a 60° v-notch weir. Stage data was measured by pressure transducers in each weir. All data was logged by programmable data loggers (IQuest DS4483) and uploaded to Auckland Council's live database by GSM cell phone modems.

Sampling of inflow and outflow was controlled by the programmable loggers, using a time based protocol. Samples were collected by peristaltic auto-samplers (ISCO 3700), programmed to flush the sample lines prior to each sample collected.

2.4 WATER QUALITY ANALYSIS

Water samples were collected by Auckland Council's Research, Investigation and Monitoring Unit (RIMU) directly following an event. Samples were processed by Watercare Laboratories for total suspended solids (TSS); and total and dissolved copper and zinc. The latter were analyzed by inductively coupled plasma mass spectrometry (ICP-MS).

For each event, event mean concentrations (EMCs) were calculated mathematically, based on flow data.

2.5 DATA QUALITY REQUIREMENTS

In order for a storm event to be deemed qualifying the following requirements needed to be met, for both inflow and outflow:

- Complete sampling during the first flush.
- Sampled volume represents at least 60% of the total recorded volume.
- Good agreement of inflow and outflow volumes.
- Minimal bypass flow

No duplicate field samples were processed as part of the experimental protocol. Watercare Laboratories performed laboratory duplicate analysis and other compliance procedures in accordance with its accreditation to NZS/ISO/IEC 17025.

3 RESULTS

19 storm events were sampled over the course of 14 months. Of these, 12 were considered to be qualifying on the basis of the data quality requirements. The rainfall depth and duration; together with runoff volumes for all qualifying events are summarized in Table 1.

A summary of EMCs, for all analytical parameters, for all qualifying events is provided in Table 2. This table also includes an aggregate load reduction for each analyte, calculated over all qualifying events.

Analysis of inflow and outflow data showed that outflow was routinely under-represented with respect to inflow. Typically, the outflow volumes were between 75% and 95% of the inflow volumes. This observation was ascribed to the very low flows towards the end of the drain down of each filter bed, which were beyond the resolution of the monitoring setup to record. In order that the outflow loads were not under-represented, the latter were calculated by multiplying the calculated effluent EMCs by the *influent* volumes, rather than the measured effluent volumes.

As mentioned above, the configuration of the parallel filtration chambers meant that the more rapid filtration media received more flow than the slower media. The initial flow rate of the crushed mussel shell media was approximately double that of the sand media. Accordingly, this received approximately double the volume of runoff over the course of the field trial than did the sand media. It is difficult to determine what proportion of the contaminant load was experienced by each filter, given that a distinct first-flush phenomenon was observed, and the initial inflow was relatively well split between the two filter chambers (*i.e.* prior to the water level in the filters rising above the flow-splitting weirs). In light of the above, it is difficult to draw conclusions on the longevity of each of the media.

Table 1: Summary of qualifying storm events

Event number	Date	Duration (h)	Rainfall Depth (mm)	Volume Runoff (L)	Comment
1	06.09.2010	17	14	10 200	
2	01.10.2010	8	11	7 140	
3	04.11.2010	9	6	6 020	
4	28.01.2011	24	117	92 240	
5	05.04.2011	14	11	6 200	
6	16.04.2011	8	13	18 670	
7	03.06.2011	20	12	23 260	
8	06.07.2011	20	7	12 330	
9	27.09.2011	3	0	1 060	Washdown event. No rainfall
10	02.10.2011	8	3	5 920	Initial part of larger 31 hour event. Full drain down of filters before second part of storm.
11	10.10.2011	7	24	34 960	
12	01.11.2011	22	5	21 010	Apparent discrepancy between rainfall depth and runoff volume.

Table 2: Summary of water quality results

Analyte	n	Influent			Effluent -- Mussel Shell				Effluent -- Sand			
		Minimum (mg/L)	Median (mg/L)	Maximum (mg/L)	Minimum (mg/L)	Median (mg/L)	Maximum (mg/L)	*Aggregate Load Reduction*	Minimum (mg/L)	Median (mg/L)	Maximum (mg/L)	*Aggregate Load Reduction*
TSS (mg/L)	12	11.3	50.4	90.6	1.2	4.7	9.4	*91%*	1.2	7.4	48.5	*74%*
Dissolved Cu (mg/L)	12	0.299	0.511	1.187	0.070	0.168	0.450	*73%*	0.064	0.243	0.639	*59%*
Particulate Cu (mg/L)	12	0.493	5.471	18.586	0.023	0.251	0.624	*97%*	0.024	0.398	6.755	*84%*
Total Cu (mg/L)	12	1.281	6.237	18.885	0.093	0.409	1.074	*95%*	0.088	0.684	7.384	*82%*
Dissolved Zn (mg/L)	12	1.390	2.644	5.988	0.209	0.772	2.267	*70%*	1.209	2.199	7.650	*7%*
Particulate Zn (mg/L)	12	0.395	4.720	13.798	0.026	0.527	1.120	*91%*	0.080	0.858	9.783	*64%*
Total Zn (mg/L)	12	2.780	8.917	16.410	0.235	1.335	3.387	*82%*	1.386	3.171	13.460	*42%*

4 DISCUSSION

4.1 INFLUENT WATER QUALITY

4.1.1 SUSPENDED SOLIDS

EMCs of TSS during this period of monitoring were in the range of 11 to 91 mg/L, and the median EMC was 50 mg/L. In this regard the suspended solids load is comparable to that recorded from moderate and heavily trafficked roads. For comparison, a comprehensive study of the water quality of runoff from four Auckland roads, with between 14 000 and 51 000 vehicles per day, found that median EMCs for TSS were in the range of 9 to 101 mg/L, and were typically *ca.* 75 mg/L (Moores, Pattinson, & Hyde, 2009).

It should be pointed out that the TSS EMCs recorded in this study do not represent the total solids load from the marina hardstand, due to pre-treatment of the runoff with a catchpit insert with 400 micron mesh.

4.1.2 COPPER

In contrast to the TSS load, the load of copper from marina hardstand runoff is exceedingly high. Over all recorded events the EMCs for total copper were between 1.3 and 18.9 mg/L, and the median EMC for total copper was 6.2 mg/L. This concentration is *ca.* 300 times the median EMCs recorded for highly trafficked Auckland roads (Moores, Pattinson, & Hyde, 2009).

Aside from the much heavier load of total copper, the marina hardstand runoff has a significantly lower proportion of dissolved copper than might be expected from road runoff. Figure 1 displays the influent EMCs for total copper (entire columns), broken down into dissolved and particulate fractions (blue and red columns, respectively). Over all events the median EMC for dissolved copper is only 8% of the median EMC for total copper. This contrasts starkly with the case of road runoff, where dissolved copper was typically found to be in the range of 26 to 82% of total copper (Moores, Pattinson, & Hyde, 2009). The lower relative proportion of dissolved copper from marina hardstand is possibly indicative of the fact that antifoulant paints are engineered to release copper over a sustained time frame, whereas copper from brake pad residue is predominantly elemental (metallic); making it more prone to oxidation and dissolution processes. It may also be the case that much of the load of antifoulant paint consists of flakes rather than dust. The lower surface area to volume ratio of flakes might reduce the degree of dissolved copper leaching.

It should be pointed out that, despite the fact that proportion of dissolved *vs.* total copper is relatively low compared to road runoff, the actual concentration of dissolved copper is exceedingly large. The median EMC for dissolved copper during this study (0.51 mg/L) is *ca.* 400 times the ANZECC trigger value for marine water at the 95% protection level, which is 0.0013 mg/L (ANZECC, 2000).

4.1.3 ZINC

As for copper, the load of total zinc from the untreated marina hardstand is also significantly higher than might be expected from a heavily trafficked road. Over all recorded events the minimum and maximum EMCs for total zinc were 2.8 and 16.4 mg/L, and the median EMC was 8.9 mg/L. This concentration is *ca.* 100 times the median EMCs recorded for highly trafficked Auckland roads (Moores, Pattinson, & Hyde, 2009).

With respect to dissolved zinc, the minimum and maximum EMCs were 1.4 and 6.0 mg/L, and the median EMC was 2.6 mg/L. This represents *ca.* 30% of the total zinc EMC, which is comparable to proportion of dissolved *vs.* total zinc found in road runoff, which has been reported to be in the range of 14 to 69%, but is typically *ca.* 20% (Moores, Pattinson, & Hyde, 2009).

Again, it should be pointed out that the actual concentration of dissolved zinc is exceedingly large. The median EMC for dissolved zinc (2.64 mg/L) is *ca.* 100 times the ANZECC trigger value for marine water at the 95% protection level, which is 0.015 mg/L (ANZECC, 2000).

Figure 1: Particulate and dissolved components of influent total copper EMCs.

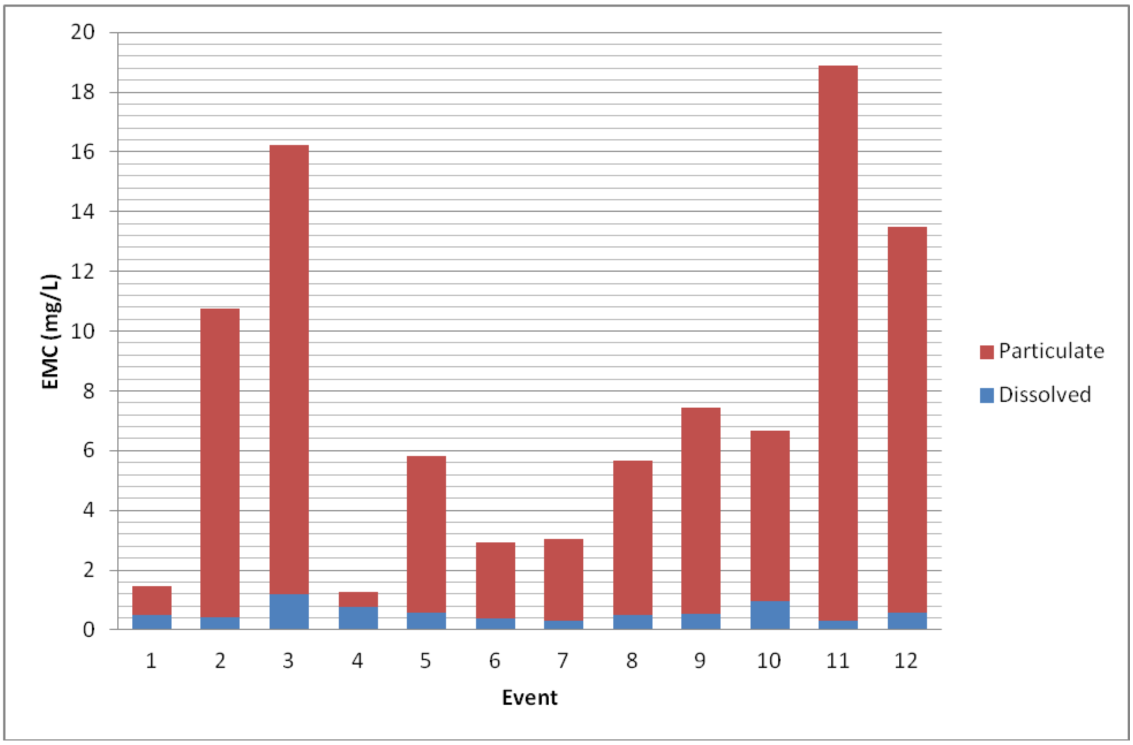
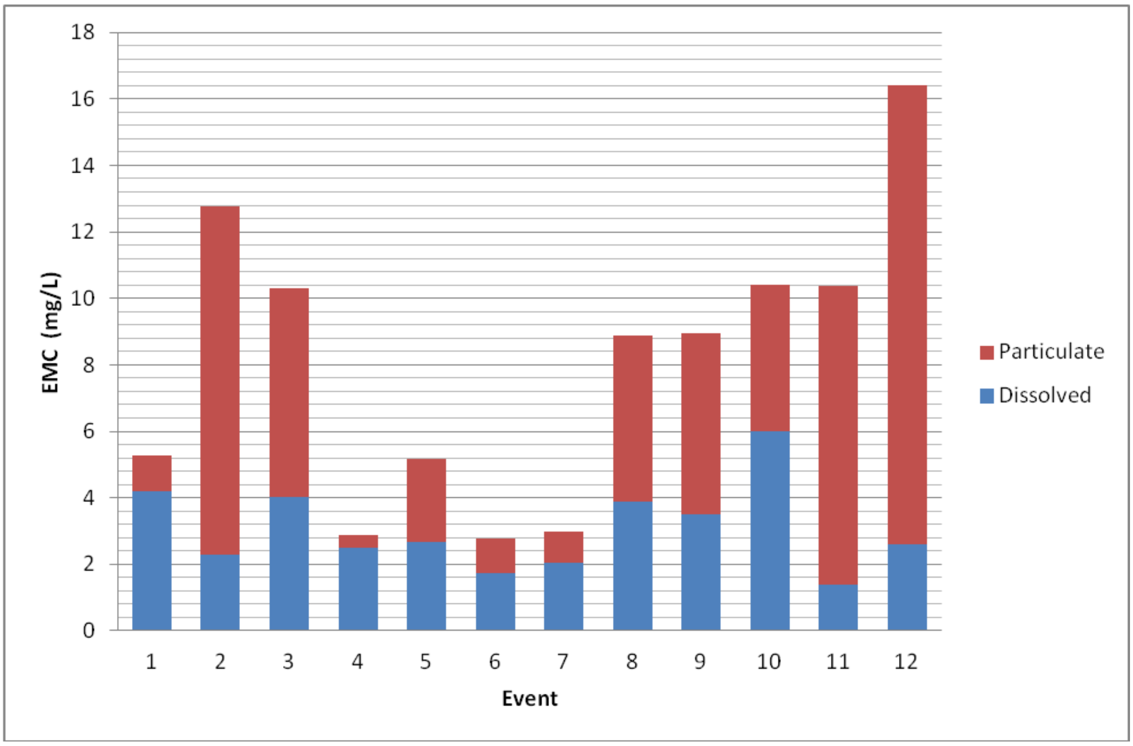


Figure 2: Particulate and dissolved components of influent total zinc EMCs.



4.2 TREATMENT PERFORMANCE

4.2.1 SUSPENDED SOLIDS

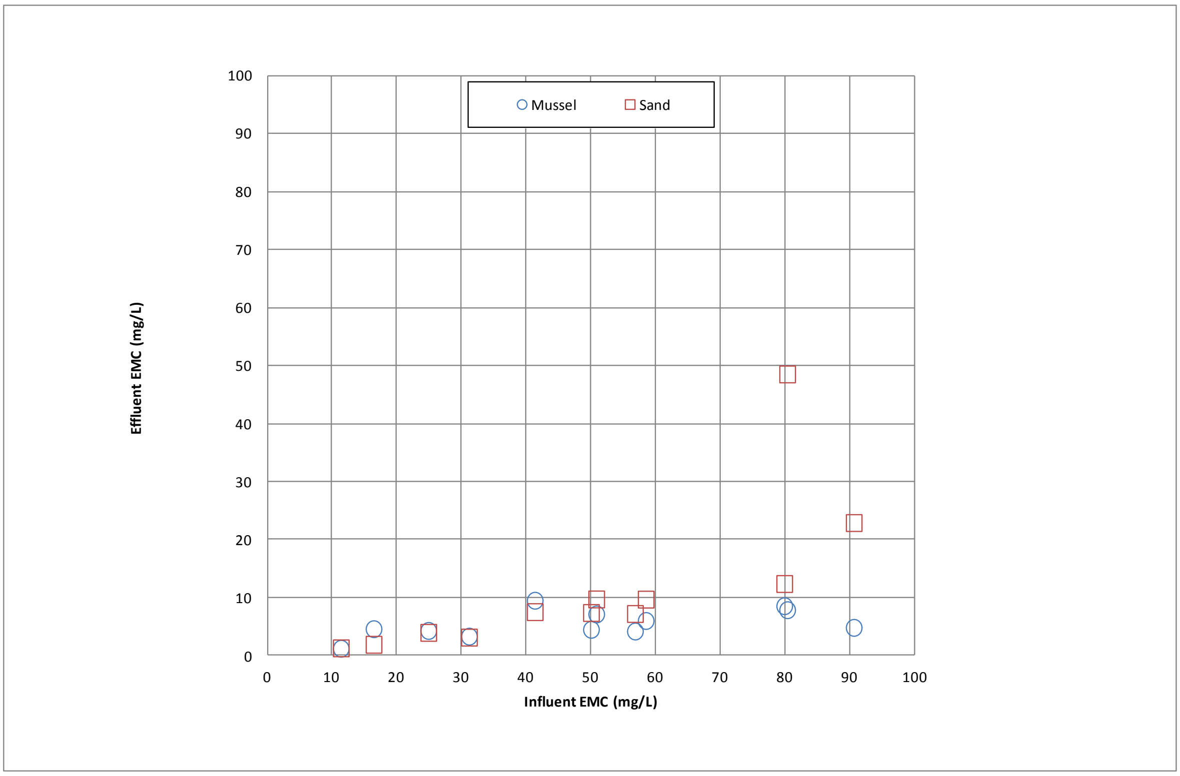
Figure 3 is a scatter plot of the effluent TSS EMC (y-axis), as a function of the influent EMC (x-axis), for each filter medium, for each qualifying event. The influent EMCs are well distributed between 11 and 91 mg/L, with a median influent EMC of 50 mg/L (Table 2).

Inspection of the scatter plot shows that the effluent from the mussel shell medium was below 10 mg/L for all monitored events.

Effluent EMCs of TSS from the sand filter were similar to the mussel shell media for lower influent concentrations. However, it is notable that the effluent EMCs were significantly higher than the mussel shell media where the influent EMC was high.

Across all events, the aggregate load reduction for TSS was 91% and 74% for the mussel shell media and sand media, respectively.

Figure 3: Total Suspended Solids



4.2.2 COPPER

Figure 4 is a scatter plot of dissolved copper EMCs, for all events. Influent EMCs are distributed between 0.3 and 1.2 mg/L. The median influent EMC for dissolved copper was 0.51 mg/L (Table 2).

Inspection of Figure 4 shows that for each event the mussel shell media showed a net removal of dissolved copper. On an event by event basis, discrete removal efficiencies ranged from 22% to 86%. The aggregate load reduction of dissolved copper across all events was 91% (Table 2).

Sand media was not as effective as the mussel shell media for dissolved copper removal. Figure 4 indicates that in two events the effluent EMC was larger than the influent EMC (*i.e.* net addition of dissolved copper over the event). Over the remainder of the events the effluent EMC from the sand media was generally higher than the effluent EMC from the mussel shell media. On an event by event basis, discrete removal efficiencies ranged from -9% (*i.e.* 9% addition) to 87%. The aggregate load reduction of dissolved copper across all events was 59% (Table 2).

Figure 5 plots total copper EMCs over all events. As discussed above, the influent total copper EMCs are an order of magnitude larger than those for dissolved copper, indicating that most of the copper load is carried as particulate. Influent EMCs for total copper are distributed between 1.3 and 18.9 mg/L. The median EMC for total copper was 6.2 mg/L (Table 2).

In the case of mussel shell media, effluent EMCs were in the range of 0.09 to 1.07 mg/L. On an event by event basis, discrete removal efficiencies ranged from 88% to 98%. The aggregate load reduction of total copper across all events was 95% (Table 2).

The performance of sand media was inferior to mussel shell media for total copper. Figure 5 shows that, on an event by event basis, the effluent EMC for total copper from the sand media was invariably higher than the effluent EMC from the mussel shell media. Effluent EMCs were in the range of 0.09 to 1.07 mg/L. Discrete removal efficiencies ranged from 45% to 95%. The aggregate load reduction of total copper across all events was 84% (Table 2), although this value may be significantly impacted by the one event with an unusually high effluent EMC. The reason for poor performance during this event is unknown.

Figure 4: Dissolved Copper

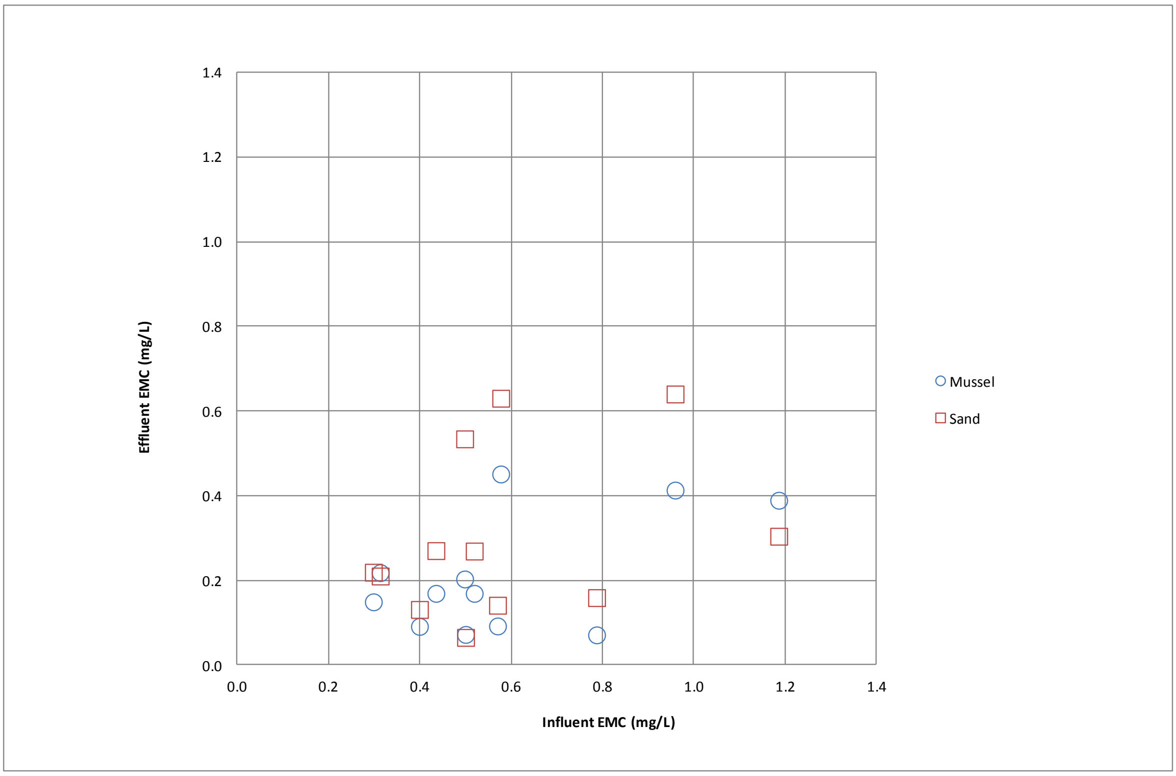
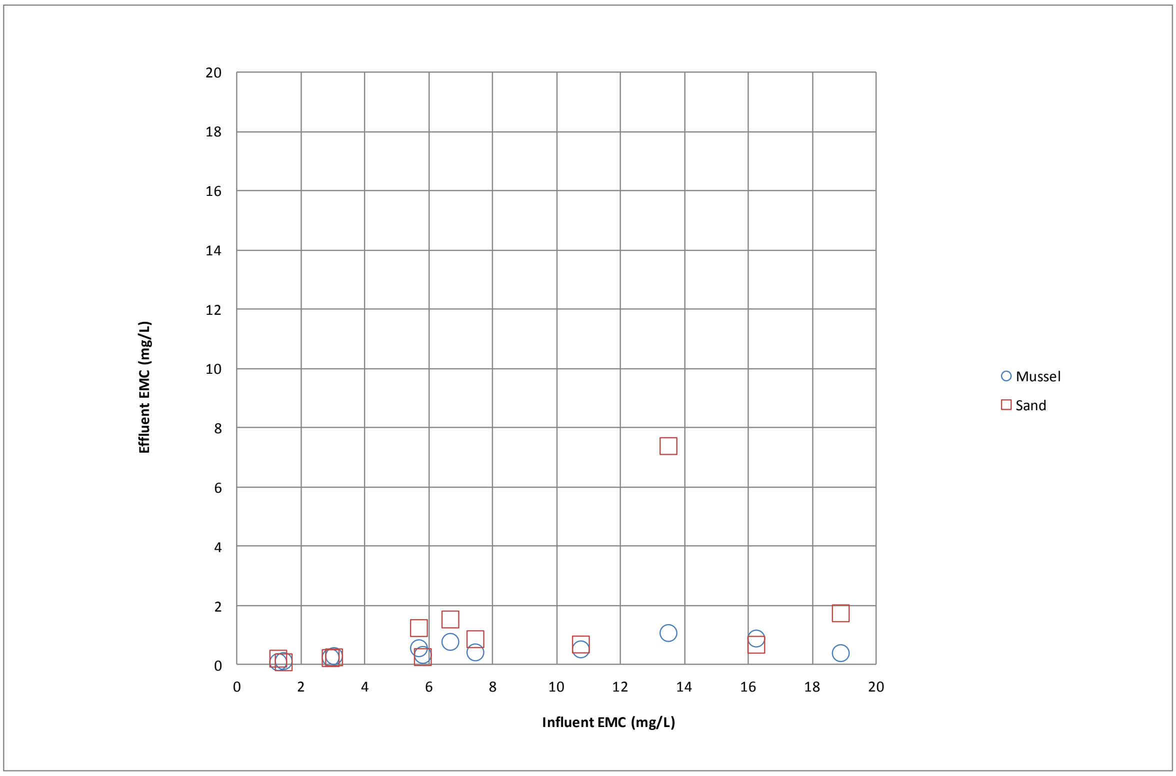


Figure 5: Total Copper



4.2.3 ZINC

Figure 6 indicates a clear difference between mussel shell and sand media, in terms of dissolved zinc removal.

For all events, mussel shell media showed a net removal of dissolved zinc. Effluent EMCs were in the range of 0.2 to 2.3 mg/L, which amounts to discrete removal efficiencies between 13 and 92%. The aggregate load reduction of dissolved zinc across all events was 70% (Table 2).

In contrast to the mussel shell media, the performance of sand for dissolved zinc was poor. Inspection of Figure 6 indicates that 7 of the 12 events exhibited dissolved zinc release. The poorest performance during a single event was a 109% addition, whilst the best performance during a single event was a 68% removal. The aggregate load reduction of dissolved zinc across all events was only 7% (Table 2), indicating near neutral performance.

With respect to total zinc, there is also a clear difference between the performance of the mussel shell media and the sand media. Figure 7 indicates that the effluent EMCs for total zinc are routinely higher from the sand media. At high influent concentrations this effect is particularly marked. The aggregate load reductions for total zinc were 82% and 42% for mussel shell and sand media, respectively.

Figure 6: Dissolved Zinc

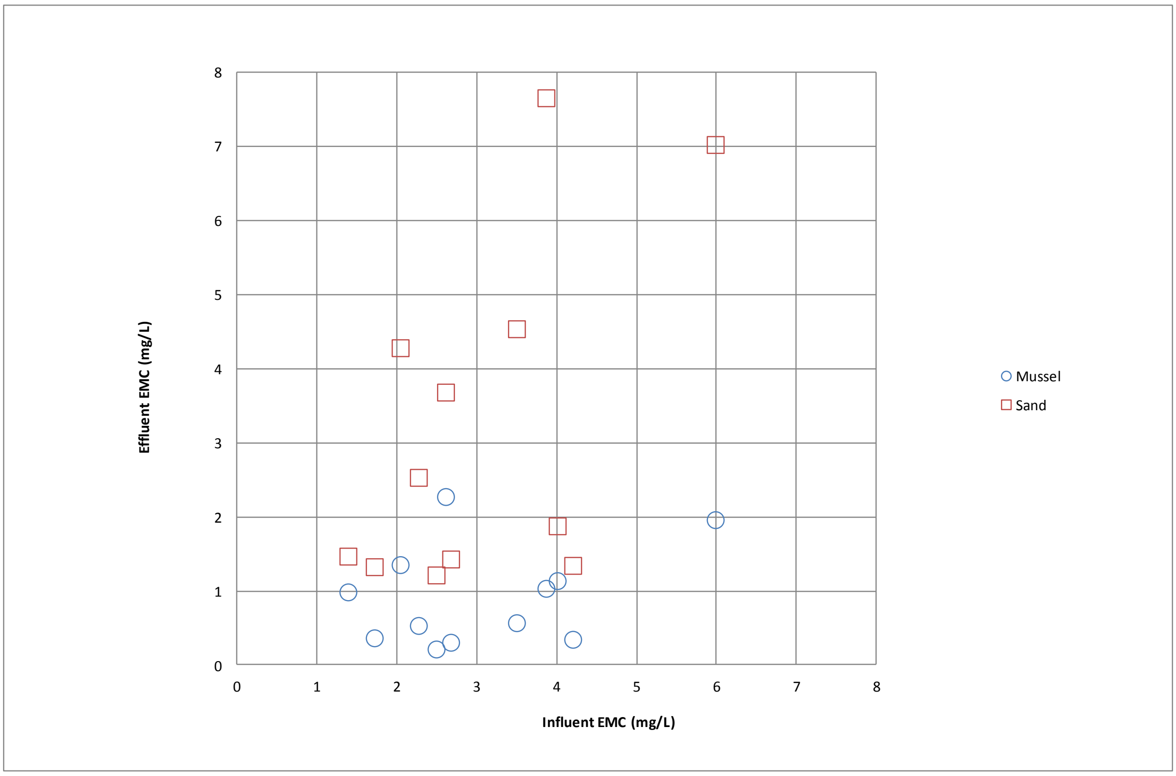
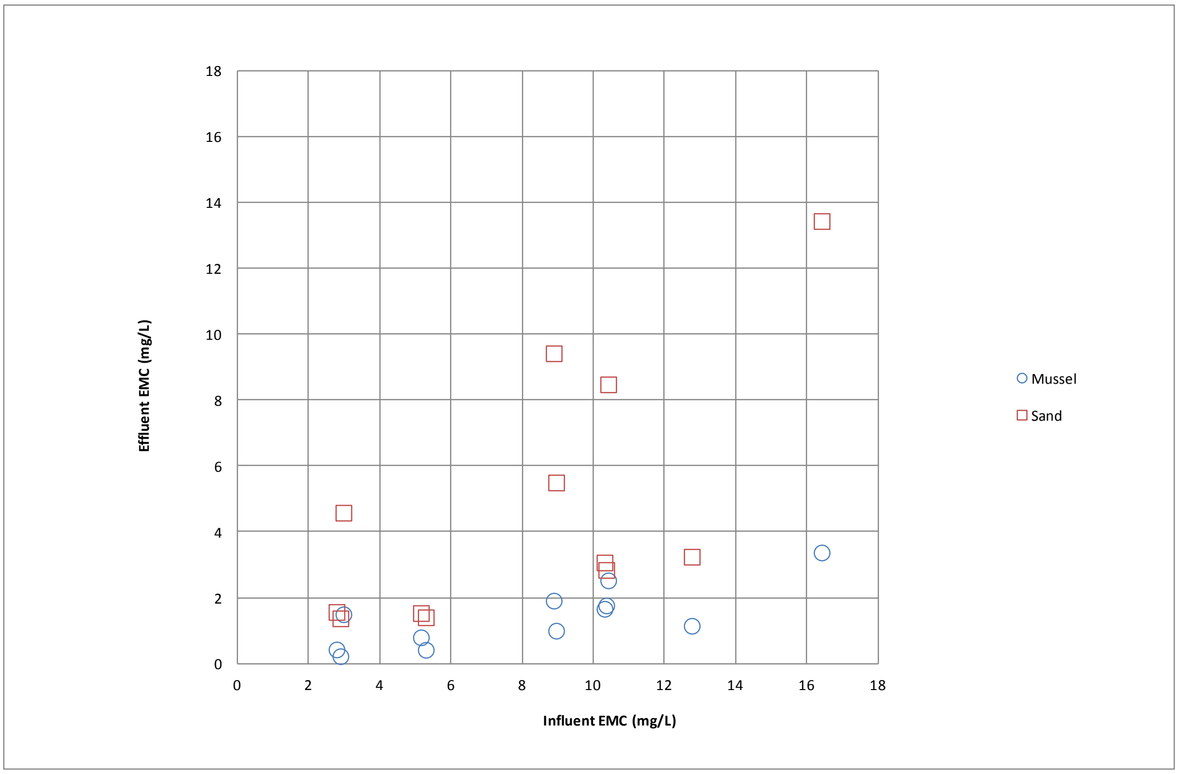


Figure 7: Total Zinc



5 CONCLUSIONS

A field trial was undertaken to test the relative performance of sand and crushed mussel shell media for treating the runoff from a marina hardstand area. The media were evaluated in a parallel experimental configuration. This allowed good comparison of the water quality from each medium, although the experimental design meant that the crushed mussel shell, which had a much higher initial flow rate, received a higher volume of runoff and thus a higher proportion of total contaminant load. For this reason, conclusions about the relative longevity of the media could not be drawn.

Results for influent water quality indicate that the TSS loads experienced by the filters were comparable to those from typical urban stormwater. In contrast, the loads of copper and zinc in the runoff were at least two orders of magnitude higher than typical urban stormwater. Dissolved copper was found to be a lower proportion of the total copper load than is typically the case from heavily trafficked roads. In spite of this, the median influent EMC of dissolved copper was sufficiently large that it would require 400 fold dilution in order not to exceed ANZECC trigger values for moderately disturbed marine receiving bodies. The ratio of dissolved to total zinc was found to be comparable to road runoff, however the extreme load means that the median influent EMC of dissolved zinc would require 200 fold dilution in order not to exceed appropriate ANZECC trigger values.

Effluent water quality results indicate that the crushed mussel shell media was superior to sand for all water quality parameters analyzed. Crushed mussel shell was superior to sand for dissolved copper removal, although sand showed some capacity to remove this contaminant. Crushed mussel shell was superior to sand for total copper removal, however the implication of the relatively low dissolved fraction is that particulate copper removal plays the major role reducing total copper load, rather than the removal of dissolved copper. In contrast to the situation with dissolved copper, sand media showed little or no ability to remove dissolved zinc from the hardstand runoff. Crushed mussel shell, on the other hand, removed a significant proportion of the dissolved zinc load. In addition, the implication of the relatively high proportion of dissolved zinc in the total zinc load is that crushed mussel shell media is significantly better at lowering the total zinc load than sand media.

In spite of the crushed mussel shell media's relatively good removal efficiencies for both copper and zinc it must be recognized that the post-treatment loads remain significantly elevated, when compared with urban stormwater. Consideration should be given as to whether secondary treatment is appropriate.

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