Environment Canterbury
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Kaunihera Taiao ki Waitaha

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December 14th 2011

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Executive Summary

- Commissioning of this research was part of a larger study on the contamination of urban waterways through residential activities as initiated under Environment Canterbury's Improving Urban Waterway Health programme.

- A literature review into current activities affecting urban waterways (prepared by Sean Waters in stage 1 of this research) identified car washing as a potential significant contributor to urban waterway contamination. This concern was preceded by Environment Canterbury's query as to whether unmitigated car washing by Christchurch residents was substantially impairing the health of urban waterways. The stage 1 review also identified a lack of knowledge on the contaminants produced through washing vehicles in Christchurch in addition to a scarcity of data on the frequency of residential car washing in Canterbury.

- This stage 2 research examined the effects of car washing on water quality. Specifically, total suspended solids (TSS), key metals (both total and dissolved), nutrients (nitrate and reactive phosphates) and polycyclic aromatic hydrocarbon (PAH) concentrations were measured in untreated car wash water subjected to different conditions (vehicle age, interval between washes and, type of washing fluid employed).Two vehicles (fifteen and five years old, both compact hatchbacks) were used in the study. Each vehicle was washed a total of six times at three different wash intervals, with distance travelled by each vehicle between washes recorded by the car's odometer. All car wash water (untreated and treated through each of the simple mitigation systems) was compared to the 90% ANZECC water quality guidelines (ANZECC, 2005) for metals (Zn, Cu and Pb) and to the NRRP WQL1 guidelines (Environment Canterbury, 2011) for suspended solids (TSS) and nutrients (reactive phosphate and nitrate) to assess for potential ecotoxicity. A number of simple mitigation systems were established to reduce contaminant levels from the wash water. The systems trialled included; washing vehicles on grass, passing wash water through a compost sock or through a hay bale. In principle, an effective mitigation system could easily be employed by residents during car washing activities. The wash water effluent from each mitigation treatment was also measured for the same parameters as the untreated wash water.

- There were no consistent differences in contaminant levels when washing frequency, detergent type or age of vehicle, were compared. In untreated wash water, total concentrations of copper (Cu), lead (Pb) and zinc (Zn) exceeded the NRRP water quality standards/ANZECC 90% guidelines by 100, 20 and 8 times, respectively, highlighting the especially high levels of these metals in runoff from car washing activities. All three mitigation strategies were effective (55-85% range) at reducing total metals in car wash runoff, especially Pb, where concentrations dropped to approximately the NRRP water quality standard/ANZECC 90% guidelines and Zn, which exceeded these by only a maximum of 3%. TSS levels were substantially reduced by employing any of the simple mitigation systems by up to 90% (compost sock), 86% (hay bales) and 69% (grass) and consistently removed greater than 75% of TSS from solution to levels below the NRRP guideline of 100 mg/L. Reactive phosphate levels were typically between 4.6 and 7.2 mg/L, which exceeds the NRRP water quality (as DRP) standard of 0.016 mg/L by 288-450 times. Phosphate was not effectively removed from the wash water by any of the mitigation treatments. Nitrate levels in untreated wash water ranged from 0.6 to 3.1 mg/L and although were of less concern than the elevated DRP concentrations, mean

concentrations typically exceeded the NRRP (2011) guideline DIN value of 1.5 mg/L but were further reduced by up to 53% through employing a mitigation treatment barrier. PAHs were below detection limits in all samples.

- Mean dissolved metal concentrations in untreated wash water for Cu and Zn exceeded the NRRP water quality standards/ANZECC 90% guidelines by a factor of 12.6 and 3.0, respectively, concurring with local carpark stormwater quality in Christchurch (Wicke *et al*. 2011). This is concerning as it is well reported how the ecotoxicity, hence bioavailability, of metals is enhanced through dissolved speciation. Dissolved Pb was below the NRRP/90% ANZECC threshold level. Despite total metal concentrations being substantially reduced (55-85%) following each treatment system, the fractions of dissolved Cu (and to some extent Pb) increased following all three mitigation strategies, although Pb remained below the 90% species protection levels defined in the NRRP/ANZECC. However, dissolved Zn concentrations actually decreased in two of the treatment systems but still remained above (1.5 - 3 times) the NRRP/90% ANZECC guidelines. The increase in dissolved metal fractions can most likely be attributed to a lower pH effect where particulate metal fractions tend towards solution under acidic conditions (rainfall pH in this catchment was measured between 5.8-6.8 standard units).

- It might be anticipated that contaminants steadily accumulate on vehicles so that the longer wash intervals would release greater contaminant concentrations upon washing, but this was not observed. Higher rates of *contaminant deposition per km travelled* were found in the shortest wash interval (two days) than after 10 or >30 day wash intervals. The rate of deposition of contaminants on vehicles likely peaked within a few days after which, either little new deposition occurs or there is a cyclical sloughing off and renewal of fresh contaminant deposition resulting in the observed values. Results indicated that contaminant accumulation saturation reaches maxima in only a few days. Factors including wind, driving conditions and precipitation most likely contributed to these complex contaminant dynamics.

- Washing cars on grass, possibly the easiest behaviour change to influence, has the potential to decrease metal loads entering the city's waterways *monthly* by 17.3 kg (83%), 8.1 kg (66%) and 2.7 kg (87%) for Zn, Cu and Pb, respectively. For residents who do not have access to a grassed area on which to mitigate their car washing activities, a compost strategy would reduce metal loads *monthly* by 15.1 kg (73%), 6.8 kg (56%) and 2.6 kg (84%) for Zn, Cu and Pb, respectively. Alternatively, they could employ a hay bale to reduce metal loads *monthly* by 15.5 kg (70%), 6.5 kg (54%) and 2.7 kg (87%) for Zn, Cu and Pb, respectively. These estimations were based on the following assumptions: each light vehicle washed 1/month, 300 L of water used per wash, 250,000 light vehicles in Christchurch and that 90% of Christchurch residences have catchments draining into either the Avon/Ōtākaro or Heathcote/Ōpāwaho rivers. The grass estimation was somewhat conservative in that it assumed that washing cars on grass still results in some underdrain (i.e. partially treated) water feeding to the nearby waterway (as the grass experiments contained an underdrain). However, a more realistic scenario is that all car wash runoff onto grass would infiltrate to subsoil sequestering all metals.

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1. Introduction

Local (Christchurch) urban stormwater runoff has received increasing attention in recent years, advanced by research identifying heavy metal concentrations (especially zinc (Zn) and copper (Cu)) consistently above the most lenient (80%) levels of protection of aquatic species defined in the ANZECC guidelines (Wicke *et al*. 2009; Wicke *et al*. 2010, O'Sullivan et al., 2011). The Environment Canterbury-led Improving Urban Waterway Health (IUWH) programme is charged with improving the health of Christchurch's waterways. Environment Canterbury believes that recovery of water quality in the city's urban waterways can be assisted by decreasing the concentrations of diffuse, non-point source metal contaminants, such as those found in stormwater, including car wash runoff. One objective of the IUWH programme is to educate the general population about the effects of residential activities (e.g. car washing, disposal of paint and littering) on stormwater and waterways, and bring about a change in behaviour that can mitigate residential waterway pollution. Local and regional authorities have encouraged residents to modify their car washing behaviour to minimise the impact on the environment (e.g.: City of Federal Way www.cityoffederalway.com, in Wellington http://www.gw.govt.nz/car-washing, Auckland http://www.arc.govt.nz and Christchurch, http://ECan.govt.nz/publications/General/save-our-stream-okeover-stream-brochure). However, it is not clear what the impact of these initial campaigns has been to-date.

The "Getting the Stormwater Message Across" Stage 1 report (Waters, 2011) presented an analysis of previous research on anthropomorphic urban waterway contamination. The report suggested that car washing, roof cleaning and inappropriate disposal of engine lubricants can result in contaminant concentrations which exceed ecotoxicity levels and/or environmental guidelines for the protection of aquatic life in Christchurch's lowland rivers.

The most common contaminants in car wash water include: metals, polycyclic aromatic hydrocarbons (PAHs), and detergents/surfactants. The predominant metal contaminants in diffuse urban runoff are copper (Cu), lead (Pb) and zinc (Zn) (Ermens, 2007, Zanders, 2005), and these also constitute the dominant metal contaminants reported in car wash water (Engberg, 1995, 2000; Moores, 2010). Zn is derived mainly from vehicle tyres and Cu from brake pads (Armstrong, 1994; Barrios, 2000; Moores, 2010). PAHs in car wash water result from (incomplete combusted) exhaust emissions being deposited on car exteriors, while detergents and surfactants are ingredients in car washing products. Unfortunately, there are no guidelines (NRRP, ANZECC or other) available to set regulatory values for surfactant levels. This is confounded by the proprietary nature of the products in which many ingredients are unnamed or assigned generic names without provision of their chemical details.

2. Objectives

Environment Canterbury wishes to provide messages appropriate for Christchurch residents that were based on local scientific data. Local residents have been asking the council how badly the waterways would be affected if car wash water in the stormwater was conveyed untreated to the stream. The focus of this study was to quantify contaminants from car washing on water quality and to assess the potential of several simple and easily implemented mitigation strategies to reduce those contaminant levels. The contaminant levels were compared to the relevant guidelines based on receiving water standards for discharges in the Canterbury Natural Resources Regional Plan (ENVIRONMENT CANTERBURY, 2011) and the Auckland Regional Council TP10 (Technical Publication 10; ARC 2003) stormwater design criteria for water quality treatment (i.e. 75% TSS removal). Data arising from this research can be used to derive relevant messages for Christchurch residents as a means of affecting behavioural change about car washing practices.

Specific objectives from this Stage 2 of the research efforts included;

1. Wash cars and compare contaminant levels resulting from:
    a) Old (1997) vs. new (2007) vehicles
    b) Different interval period between washes (2, 10, ≥30 days)
    c) Distances travelled (kilometres between washes)
    d) Soap and water vs. commercial car cleaner employed (Sunlight Dishwashing Liquid vs. Armor All® Wash & Wax)
2. Capture wash water and analyse by accredited methods for key contaminants identified in Stage 1. Key contaminants include: Total suspended solids (TSS), Nitrate (NO_3^-), Phosphate (PO_4^{3-}), PAHs and the metals Cu, Pb and Zn in both total and dissolved forms.
3. Assess three simple mitigation strategies (treatment systems) for their ability to remove key contaminants from car wash water. Mitigation strategies included:
    a) Hay bales
    b) Compost filled sock
    c) Grass lawn

3. Methodology

3.1 Overview

3.1.1 Experimental set up

Two vehicles (Figure 3.1.1.) were used in the study designated: New (5 y/o) and Old (15 y/o). Each vehicle had a total of 6 washes (Table 3.1.1.) generating untreated wash water, which was then used in three simple mitigation strategy experiments. Both vehicles were approximately the same size (compact hatchbacks). The distance (Km) travelled between washes was monitored for each vehicle using the onboard odometer. Vehicles were washed with either soap and water or with a commercially available car washing detergent. Three time periods between car washes (2 days, 10 days, and 30+ days) were included to quantify potential differences in contaminant concentrations. Actual antecedent dry periods were not possible to control. As both vehicles were in private use during the wash intervals, it was impossible to expose them to the same precise environmental conditions (e.g. location during rain event, parked vs. moving, wind speed etc). As such, the vehicles were washed irrespective of whether there had been any precipitation between washes. This was justified by the fact that behavioural change about car washing practice could be influenced, but antecedent interval could not be controlled.

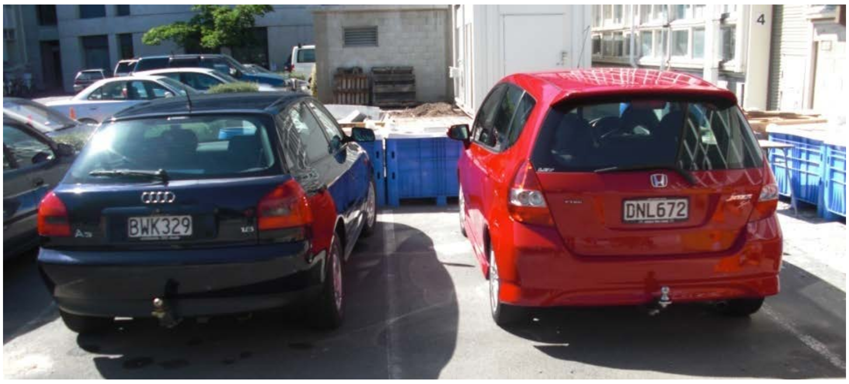


Figure 3.1.1. The two vehicles used in the study after cleaning. The left hand vehicle is the older model (1997) while vehicle on the right is the newer one (2007).

Table 3.1.1. Total number of washes performed on each vehicle. W designates the car was washed, X= mitigation treatments downstream of untreated wash water collection.

Wash Detergent»	Specialised Car Cleaner			Soap and Water		
Days»	2	10	30+	2	10	30+
No Treatment	W	W	W	W	W	W
Hay Bales	X	X	X	X	X	X
Compost Sock	X	X	X	X	X	X
Grass	X	X	X	X	X	X

3.1.2 Analytical measurements

Wash water quality was analyzed following Australian and New Zealand Environment and Conservation Council (ANZECC. 2000) accredited methods (APHA, 2005) for key stormwater parameters. Contaminants measured from each washing event included phosphates (PO_4^{3-}), nitrates (NO_3^-), polycyclic aromatic hydrocarbons (PAH), zinc (Zn), copper (Cu), lead (Pb) (Zn, Cu and Pb in both dissolved and total form) and total suspended solids (TSS).

3.2 Car washing Process

Prior to each car washing experiment, a concrete pad designated for the experiments was power-washed and lined with polythene sheeting to reduce potential contaminant adsorption to concrete from runoff. All seams of the plastic sheeting were sealed with glue to ensure no water was lost through seams. Polythene sheeting was raised around the perimeter using metal barricades to ensure all wash water was captured. A drain was fitted immediately down-gradient of the concrete pad with a plug and bucket (approximately 20 litres) to collect wash water, which was pumped to a 350-litre storage (Figure 3.2.1A) container for sampling and subsequent application to the mitigation systems (Figure 3.2.1 B, C, D).

The two vehicles were washed by hand on the same day and in all cases by the same person. All car washes were performed on plastic sheeting to allow collection of all wash water so that total volume and concentrations for each contaminant could be calculated. Wash water draining from the cars was then applied to three different simple treatment systems (hay bales (Figure 3.2.1B), compost sock (Figure 3.2.1C), and grass filter (Figure 3.2.1D) to quantify contaminant removal. Purged pumps were employed to convey the wash water from the collection site to the different treatment systems. Wash water draining from each treatment was manually sampled following the ANZECC guidelines. In compliance with these guidelines, at least 10% of samples were duplicated for Quality Assurance/Quality Control purposes.

A.


B.


C.

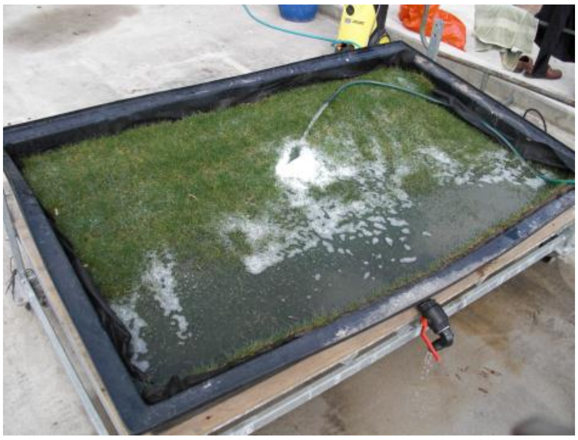

D.


Figure 3.2.1. Car wash water treatment options including: A) untreated wash water, B) hay bale, C) compost treatment sock, and D) grass filter strip

3.3 Chemical analysis

3.3.1 Metals

Total metal samples were preserved with concentrated (69%) nitric acid (Fisher, trace analysis grade) to reduce the pH to less than 2.0 (APHA 2005). Dissolved metal samples were pre-filtered through disposable LabServ 0.45-µm filters before HNO_3 acidification. All metals (Zn, Cu and Pb) were analysed by inductively coupled plasma mass spectroscopy (ICP-MS) (Agilent) following Method 3125B (APHA 2005). Total metal samples for digestion were mixed on a magnetic stir plate, before 25 ml of sample was transferred to a 50-mL polypropylene tube. After the addition of 5 ml concentrated HNO_3, tubes were placed in a heating block, and samples were boiled for 1 hour. Cooled samples were then filtered through an encapsulated 0.45-µm PVDF filter (47 mm, LabServ) directly into the analysis tube and analysed via ICP-MS. Quality assurance protocols, including blanks, duplicates (10% of samples), spiked samples (5% of samples) and instrument calibration were conducted throughout each batch analysis.

3.3.2 Total Suspended Solids

Total suspended solids (TSS) samples were collected in separate 1,000-mL HDPE containers and were measured within 24 hours following Method 2540D (APHA 2005). Glass fibre composite filter paper was oven dried at 105°C using a Contherm Thermotec 2000 oven and weighed (mass filter paper) on a Sartorius GC1603P analytical balance. The water sample was filtered through the glass fibre filter, dried at 105°C for 1-2 hours, and weighed (mass sample + filter paper). A blank sample was also performed using deionised water instead of the sample (wt. blank). Suspended solids concentration (mg/L) was calculated according to Equation 1.

$$TSS = \frac{[(\text{wt sample + filter paper}) - (\text{wt filter paper}) - (\text{wt blank})] * 1{,}000{,}000}{\text{Sample Volume}}$$

Eqn. 1.

3.3.3 Polycyclic aromatic hydrocarbons

PAHs were analysed by RJ Hill Laboratories, an International Accreditation New Zealand (IANZ) laboratory using liquid extraction, with GC-MS SIM analysis (APHA, 2005).

3.3.4. Nitrate and Reactive Phosphorus

Nitrate and reactive phosphate were analysed on a Hach DR2000 or Hach Odyssey spectrophotometer using standard reagents. Nitrate-nitrogen (NO_3-N) was analysed in accordance with Hach (2003), based on the cadmium reduction method. Reactive phosphorus (i.e. DRP) was analysed on Hach spectrophotometer using Molybdovanadate reagent in accordance with Hach (2003). Some samples were analysed for nitrate and phosphate by Hill Laboratories, an International Accreditation New Zealand (IANZ) laboratory. Nitrate was calculated by:

$$NO_3^- = (\text{Nitrate-N} + \text{Nitrite-N}) - NO_2^-$$

Eqn. 2.

Total oxidised nitrogen (Nitrate-N + Nitrite-N) was measured following Method 4500-NO3- I (APHA 2005). Nitrite (NO_2^-) was also measured following Method 4500-NO3- I (APHA 2005).

3.4 Data analysis

3.4.1 Comparisons

Contaminant levels (Table 3.4.1) were compared to relevant guidelines. The NRRP standards (Environment Canterbury, 2011) for metals were derived from the toxicant trigger values in the ANZECC (2000) water quality guidelines, with the 90% protection level used for urban streams.

Table 3.4.1. Contaminant level guidelines

Contaminant	Concentration	Source
DIN*	1.5 mg/L	NRRP Schedule WQL1
DRP	0.016 mg/L	NRRP Schedule WQL1
TSS	100 mg/L	NRRP Rule WQL48
TSS	75% removal	ARC (2003)
Copper	18 µg/L	NRRP / ANZECC
Lead	5.6 µg/L	NRRP / ANZECC
Zinc	15 µg/L	NRRP / ANZECC

* nitrate-N constitutes the majority of DIN in lowland spring-fed waterways in Canterbury

To assess whether there were differences in the factors being tested, data for all of the key contaminants (TSS, NO_3^-, PO_4^{3-}, Cu_{total}, $Cu_{dissolved}$, Pb_{total}, $Pb_{dissolved}$, Zn_{total}, $Zn_{dissolved}$) from each wash were averaged and standard deviations determined. Analysis of Variance (ANOVA) statistical analyses were initially performed but since the data (even log-transformed) were not normally distributed, these statistical analyses were deemed invalid and so are not presented.

Comparisons were made between the following experimental conditions:

- Old (1997) vs. new (2007) vehicle
- Interval period between washes (2, 10, ≥30 days)
- Distances travelled (kilometres between washes)
- Soap and water vs. commercial car cleaner (Sunlight Dishwashing Liquid vs. Armor All® Wash & Wax)
- Mitigation strategies.
    - Hay bales
    - Compost sock
    - Grass lawn

4 Results and Discussion

4.1 Contaminant Levels in Untreated Wash Water

Many environmental factors may affect the rate of contaminant deposition on vehicles including: overnight parking in a garage or covered area, distance travelled, road surface travelled on, time of primary use (i.e. rush hour vs. weekend), parking under trees or nesting areas, temperature and rainfall. The complexity of these myriad of variables could not be measured in the scope of this research, or in most cases, likely to be of any meaningful use in influencing people's behaviour about car washing practice. However, the effects of four quantifiable factors were assessed within this study, which may have influenced the concentration of contaminants in untreated wash water. These varying experimental conditions are summarised in Table 4.1.1. Distance travelled by each vehicle before the experiments commenced were not recorded although most cars did not undergo regular car washing, if any, prior to the experiments.

Table 4.1.1. Vehicle wash schedule and associated kilometres travelled. NA= not applicable. Spec = specialised

Date	Interval	Detergent	New car / km	Old car / km
19-Sep-11	30	Spec	NA	NA
22-Sep-11	2	Spec	50	160
25-Sep-11	2	Soap	92	79
26-Oct-11	30	Soap	1033	649
6-Nov-11	10	Soap	328	185
17-Nov-11	10	Spec	258	157

To determine if any one of these factors was dominant over the other, the data for all key metal contaminants were combined (units remaining constant) and then averaged for each wash event. While there were differences between mean values for all conditions, there were no trends that could be attributed to any one of the factors tested (Figure 4.1.1). Specifically, there were no cases where the concentration of contaminants was consistently higher (or lower) for the same variable. Additional analysis of three randomly chosen target contaminants analysed individually produced similar results (Appendix 1).

It is surprising that there were no consistent differences in the two detergents used to clean the vehicles. Specialised car washing products contain surfactants (often proprietary) that are employed to aid in the "lifting" of dirt from vehicles in addition to chemicals that produce an aesthetically pleasing finish. In this study, there appeared to be little benefit to using specialised products over soap and water for dislodging contaminants.

Given the number of variables that can affect contaminant deposition on vehicles, it is also surprising that there were no consistent differences between the two vehicles. It might be expected that very old vehicles with significant rust might alter these results but these conditions did not apply to the vehicles in this study.

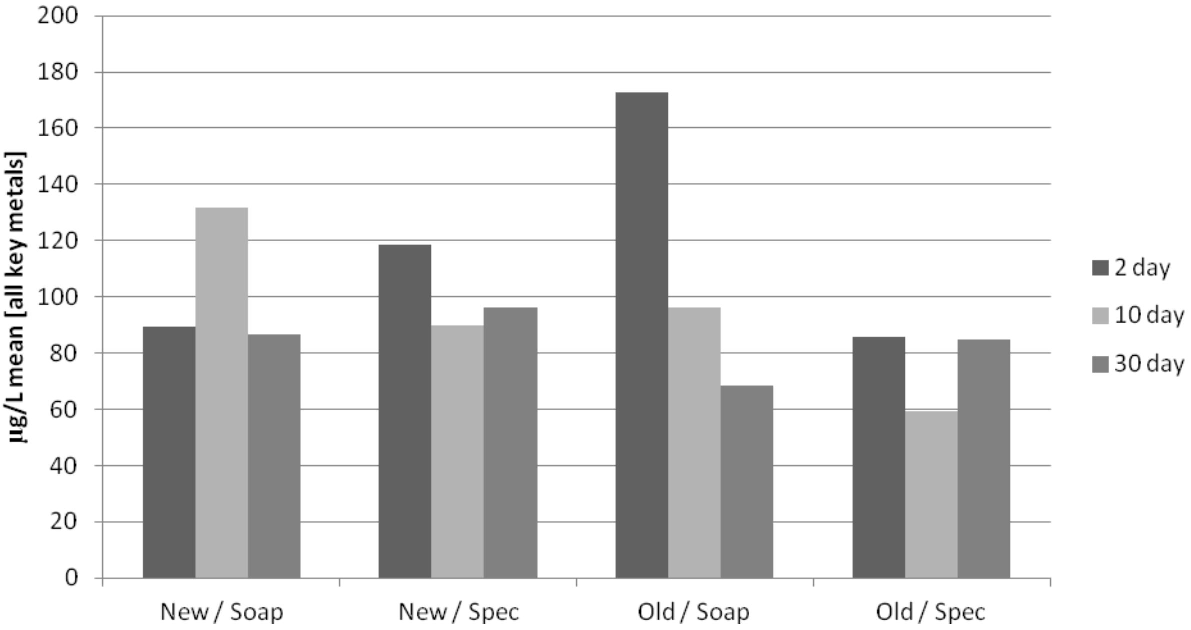


Figure 4.1.1. Comparison of Wash interval (2, 10 or 30-day), Detergent (soap or specialised) and Vehicle Age (new or old) in untreated wash water. Concentrations of each metal (Cu, Pb, Zn, both total and dissolved) were averaged (to provide a summary mean). Due to the range of concentrations between the different metals (765 down to to 0 µg/L) standard deviations are not shown (see Appendix 1 for individual contaminant plots with standard deviations), n=12

It is somewhat surprising that wash interval did not show an increase in contaminants over time. When the mean values (all metals) were divided by the respective car's distance travelled between washes to provide rates of µg/l/km (Figure 4.1.2), it is apparent that the build-up of contaminants on a vehicle occurs at a much higher rate in the first few days per km travelled following a wash, with a decreasing accumulation rate as time progresses. This is apparent from the substantially higher contaminant accumulation rate (µg/L/km) at 2-day compared with greater wash interval periods (mean 2, 10 and > 30 day interval rates were 1.5, 0.4 and 0.1 µg/L/km, respectively). These results indicate that contaminant accumulation reaches maxima in only a few days, after which, either little new deposition occurs or there is a cyclical sloughing off and renewal of fresh contaminant deposition. This is consistent with data obtained by Wicke et al. (2011) who show that contaminant build up on carpark surfaces also reaches a saturation point by 6-9 days, beyond which there is little increase in contaminants.

Given the number of complex factors that can influence contaminant deposition, determination of the primary factors influencing environmental deposition of contaminants on vehicle surfaces would require additional studies including: experimental deposition of known concentrations of contaminants onto a vehicle, overnight storage of vehicles in the same locations and the use of multiple vehicles with similar usages.

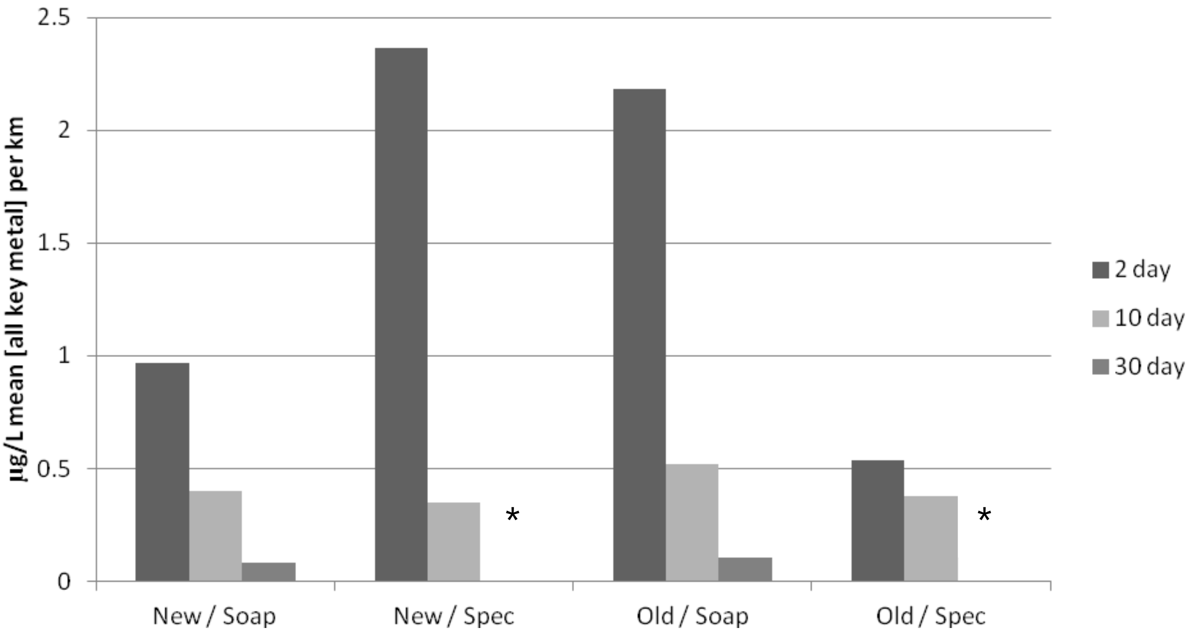


Figure 4.1.2. Comparison of all metal accumulation rates as function of distance travelled in untreated wash water. The concentrations of each metal (Cu, Pb, Zn, both total and dissolved) were averaged (mean of their sum) and divided by the distance travelled by the respective car prior to each wash. * = not applicable. 2, 10 and 30 day represent the wash intervals. New and Old represent vehicle age. Spec and Soap the detergent used; specialised car wash or soap and water. See Appendix 1 for individual contaminant plots, n=12

4.2. Mitigation Treatments

4.2.1 Total Suspended Solids (TSS)

Auckland stormwater design criteria (ARC 2003), which are widely applied throughout New Zealand, are based on the premise that metals are removed with concurrent removal of 75% TSS (Smythe et al. 2007). In 2011, Canterbury adopted the NRRP water quality standards which specify that TSS should be at concentrations less than 100 mg/L (Environment Canterbury, 2011). Figure 4.2.1 shows that all three mitigation treatments were effective at removing TSS from vehicle wash water. Hay bales (86%) and compost socks (90%) were more effective than grass (69%) and consistently removed greater than 75% of TSS from solution, all to below 100 mg/L NRRP standards (Figure 4.2.1). The reason for the slightly lower removal values for the grass system may have resulted from the very conservative design of this particular mitigation system, which included an underdrain to collect the treated wash water. However, in practice where a vehicle is washed on the lawn and no underdrain exists, the washoff would likely infiltrate through the lawn, resulting in no diffuse runoff into stormwater drains. Therefore, all TSS and metal contaminants should theoretically accumulate on the lawn surface.

The importance of preventing TSS from entering waterways is multifaceted. Many metals are known to adsorb to TSS and are consequently removed from the solution with TSS (Smythe et al. 2007). In addition, microorganisms adsorbed to TSS use oxygen from the water thus creating an increased biochemical oxygen demand and therefore a stressful environment for aquatic life. TSS can also: occupy egg laying sites for fish and macroinvertebrates reducing the available habitat, increase the waterway turbidity preventing predator species from seeing prey, and TSS can clog gills of fish and invertebrates creating respiratory difficulties (Harding, 2005).

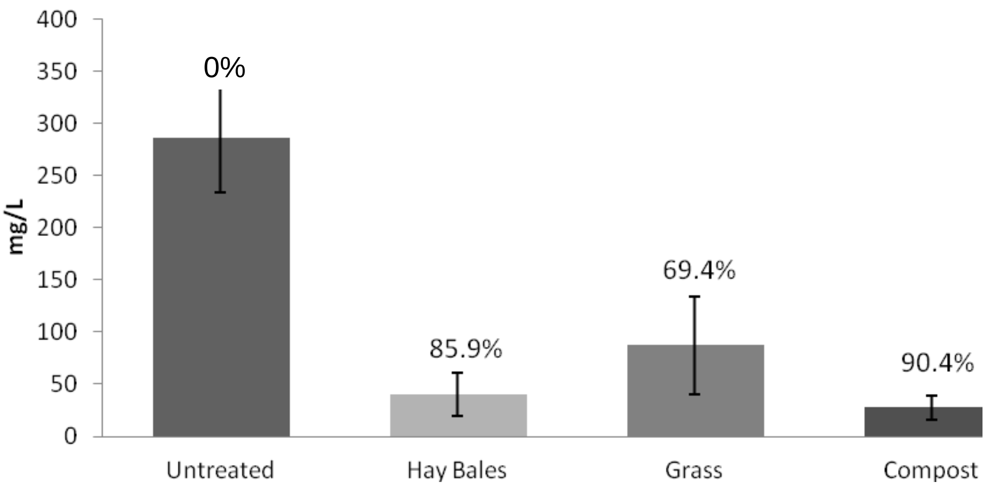


Figure 4.2.1. Concentrations of TSS (mg/L ± S.D.) from untreated and treated car wash water. Values are an average of Vehicle age, Wash Interval and Detergent used. n=12. Percentages above mitigation treatments show the average percent removal of TSS

4.2.2 Polycyclic aromatic hydrocarbons (PAHs)

As identified in the Stage 1 report, numerous international studies have shown petroleum based compounds (e.g.: Margesin, 1998; ICA, 2002 Smith, 2009; Bhatti et al, 2010; Sablayrolles et al, 2010) and PAHs (Sablayrolles et al, 2010) to be present in car wash water. Due to the typically eco-toxic nature of these compounds (Ahrens and Depree, 2005), PAHs were included in the array of car wash water tests in this study. Interestingly, no PAHs were detected above the limits of detection in all experiments (detection limits of PAHs are presented in Table 4.2.1). This is consistent with locally obtained data (Taffs and O'Sullivan, 2007) in which PAHs have failed to be detected in Christchurch stormwater, which may be due to their rapid volatilisation nature and ability to adhere to sediments.

Table 4.2.1. PAHs tested and detection limits thereof

Polycyclic Aromatic Hydrocarbons	Detection limit (g/m3)
Acenaphthene	0.00010
Acenaphthylene	0.00010
Anthracene	0.00010
Benzo[a]anthracene	0.00010
Benzo[a]pyrene	0.00010
Benzo[b]fluoranthene + Benzo[j]fluoranthene	0.00010
Benzo[g,h,i]perylene	0.00010
Benzo[k]fluoranthene	0.00010
Chrysene	0.00010
Dibenzo[a,h]anthracene	0.00010
Fluoranthene	0.00010
Fluorene	0.00020
Indeno(1,2,3-c,d)pyrene	0.00010
Naphthalene	0.00050
Phenanthrene	0.00040
Pyrene	0.00020

4.2.3. Nutrients

The NRRP (2011) water quality standards are the main thresholds adopted in Christchurch for estimating likely ecotoxicity from discharges into surface water bodies. The WQL1 schedule values from lowland spring-fed waterways are used for urban streams in Christchurch.

Reactive phosphate levels ranged from below detection limits of 0.004 mg/L to 7.2 mg/L and were highly variable (Figure 4.2.2, Table 4.2.2). There was no consistent quantifiable reduction of reactive PO_4^{3-} by the mitigation strategies and all mean values were 288-450 times in exceedence of the NRRP (2011) guideline DRP value of 0.016 mg/L. Phosphate in the wash water was almost certainly derived from the detergents, neither of which was specified on the product labels as phosphate-free. A future study could employ a variety of known phosphate-reduced solutions to assess the concentration in car wash runoff.

Nitrate concentrations measured in the vehicle wash water ranged from 0.6 to 3.1 mg/L and although were of less concern than the elevated DRP concentrations, mean concentrations typically exceeded the NRRP (2011) guideline DIN value of 1.5 mg/L (Figure 4.2.2, Table 4.2.2). Mitigation strategies were effective at removing up to 53% nitrate from the untreated wash water, with grass the most effective and hay bales the least. Nitrates can be an issue in Christchurch because of horticultural activities in the urban area, stormwater runoff from industrial areas and use of fertiliser around the home garden. However, in an urban catchment in New Zealand, nutrients are typically considered to be less of a problem than rural agricultural areas where nitrate and phosphate are present in excess due to incomplete uptake of nutrients from fertiliser applications and discharge from animal effluent.

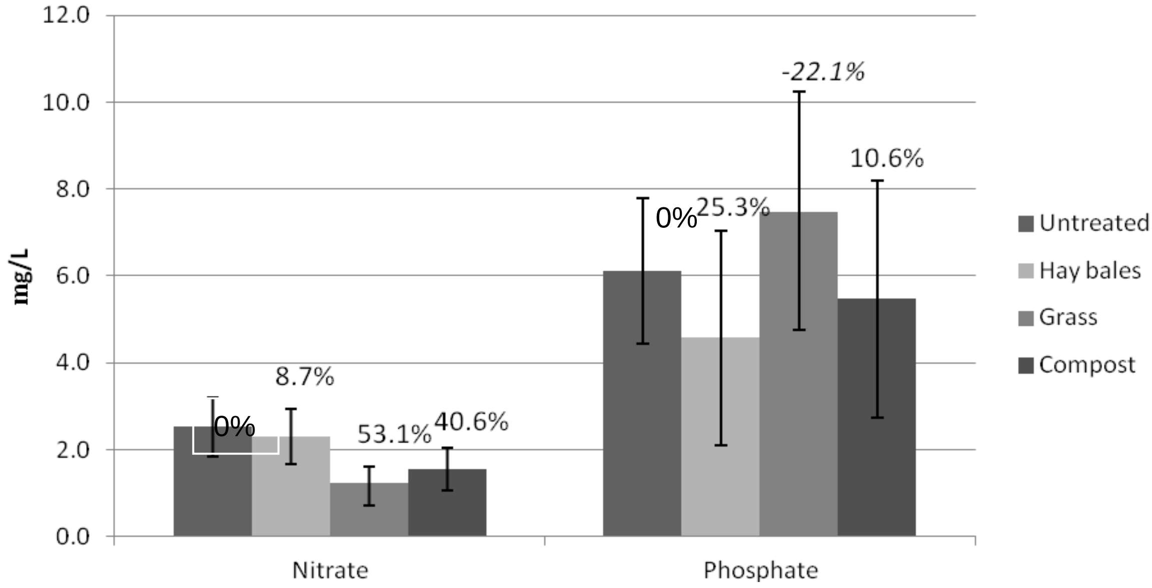


Figure 4.2.2. Concentrations of total NO_3^- and reactive PO_4^{3-} in untreated and treated car wash water. Values are an average of Vehicle age, Wash Interval and Detergent used. n=12. Numbers above mitigation treatments show the percent removal of NO_3^- and reactive PO_4^{3-} from the untreated sample

4.2.4 Metals

Mean metal (Zn, Pb and Cu) concentrations in untreated wash water are reported in Table 4.2.2. Mean total metal concentrations in untreated wash water (Cu= 180.8 µg/L, Zn=308.5 µg/L and Pb=46.4 µg/L) greatly exceeded the recommended NRRP/90% ANZECC guidelines by a factor of 100.4 (Cu), 20.5 (Zn) and 8.2 (Pb) (Table 4.2.2). Comparing total metal concentrations will often overestimate the bioavailable fraction (Landner and Reuther 2004) and thus ANZECC (2000) stipulates to compare the dissolved fraction if total metal concentrations exceed the stipulated trigger values. Mean *dissolved* metal concentrations for Cu and Zn exceeded the 90% trigger values by a factor of 12.6 and 3.0, respectively (Table 4.2.2): however dissolved Pb was below the threshold level.

Table 4.2.2 also reports the mean total metal (and sediment and nutrient) concentrations for the mitigation strategies tested in this study. Despite substantial removal of total metals, the levels of Cu and Zn exceeded the 90% species protection levels set by NRRP/ANZECC by factors ranging from 34.1-46.9 µg/L and 3.5-6.3 µg/L, respectively. Dissolved Cu and Pb increased following all of the mitigation strategies as did dissolved Zn with hay bale mitigation. Consequently, dissolved Cu and Zn still exceeded 90% species protection levels set by NRRP/ANZECC even following the mitigation strategies.

It is assumed that particulate metals, particulate nutrients, and oil, grease and bacteria attached to sediments are concurrently removed with TSS in stormwater treatment (Smythe et al. 2007). However, dissolved metal concentrations are not necessarily removed with TSS and can impact downstream ecosystems. Dissolved metals are more bioavailable and thus more concerning than some of the particulate fractions, which are typically less toxic

(Engstrom 2004). The partitioning between the particulate-bound and dissolved metal forms shifts towards the dissolved species below approximately pH 7 as particulate-bound trace metals are released from particles as free ions (Dempsey et al. 1993, Engstrom 2004). In this experiment, the pH of untreated and treated water was not tested, however the pH of local stormwater water was measured at pH 6.0-7.3 (O'Sullivan et al., 2011, Wicke et al., 2011) suggesting that the formation of dissolved metals is favoured within this slightly acidic pH range.

Since particulate fractions are removed more efficiently in (bio)filtration systems such as these simple mitigation systems, greater dissolved fractions can result in poorer overall treatment performance (Fletcher et al. 2004). One method to counteract this which has been trailed for Christchurch stormwater systems is the inclusion of a pH-buffering substrate such as mussel shells. These shells provide the alkalinity required to affect an increase in pH, which helps to shift the dissolved metal forms into the particulate form so that they can be removed easier from stormwater (Good et al, 2012).

New Zealand Ministry of Health Drinking Water Standards (NZMOH 2005) are also given (Table 4.2.2). If vehicle wash water infiltrates to groundwater (i.e. through grass mitigation) and is in the vicinity of a drinking water supply well the discharge may be subjected to drinking water standards instead of the surface water NRRP/ANZECC guidelines so would need to comply to these less stringent concentration thresholds.

Table 4.2.2. Vehicle wash off concentrations of metals (total and dissolved) and nutrients, from Untreated and Mitigated treatments compared with the NRRP (Table 3.4.1) and drinking water, NZDWS (2005) standards. Values represent mean ± standard deviation (µg/L). (n = 12). Metal data is also presented in graphical form in Appendix C

Contaminant		Untreated			Hay Bales			Grass			Compost worm			Guidelines	Guideline Exceedance Factor				New Zealand Drinking-Water Standards (2005) (µg/L)
		Mean			Mean			Mean			Mean				Untreated	Hay	Grass	Compost	
Copper µg/L	-Total	180.8	±	84.1	84.5	±	63.1	61.3	±	33.4	79.7	±	56.8	1.8 µg/L	100.4	46.9	34.1	44.3	2000
	-Dissolved	22.7	±	11.8	52.3	±	34.9	32.6	±	13.4	31.1	±	19.7	-	12.6	29.1	18.1	17.3	
Zinc µg/L	-Total	308.5	±	155.7	93.8	±	22.4	52.0	±	16.7	84.9	±	15.4	15 µg/L	20.5	6.3	3.5	5.7	1500*
	-Dissolved	45.2	±	23.5	45.7	±	19.3	22.1	±	9.2	29.3	±	15.8	-	3.01	3.0	1.5	2.0	
Lead µg/L	-Total	46.4	±	38.6	5.9	±	3.7	5.7	±	3.2	6.7	±	2.0	5.6 µg/L	8.2	1.1	1.0	1.2	10
	-Dissolved	0.2	±	0.2	0.4	±	0.5	0.4	±	0.2	0.3	±	0.2	-	0.0	0.1	0.1	0.1	
TSS mg/L	-	285.9	±	52.4	40.2	±	21.3	87.4	±	77.2	27.6	±	11.9	100 mg/L	2.9	0.4	0.9	0.3	
PO_4^{3-} mg/L	-	6.1	±	1.7	4.6	±	2.5	7.5	±	2.8	5.5	±	2.7	0.016 mg/L	382.2	285.5	466.5	341.5	
NO_3^- mg/L	-	2.5	±	0.7	2.3	±	0.6	1.2	±	0.4	1.6	±	0.5	1.5 mg/L	1.7	1.5	0.8	1.0	

* The New Zealand Drinking-water Standards (2005) do not provide a standard for Zinc but give a 1,500 µg/L guidance value.

Table 4.2.3. Mean percent removal and standard deviations of key contaminants. Where contaminants increased following mitigation strategies, the value is boldfaced

	Mitigation Treatment								
Analysis	Hay			Grass			Compost		
TSS	85.9	±	12.4	69.4	±	17.7	90.4	±	5.8
$Cu_{(total)}$	55.0	±	15.2	65.7	±	9.8	57.5	±	13.5
$Cu_{(dissolved)}$	**-147.3**	±	**103.2**	**-58.2**	±	**40.0**	**-41.7**	±	**49.1**
$Pb_{(total)}$	85.5	±	8.1	85.4	±	11.4	82.5	±	9.2
$Pb_{(dissolved)}$	**-81.1**	±	**131.4**	**-118.5**	±	**155.1**	**-50.5**	±	**84.8**
$Zn_{(total)}$	65.9	±	14.2	80.7	±	8.5	68.6	±	13.5
$Zn_{(dissolved)}$	**-7.3**	±	34.5	45.5	±	21.4	30.8	±	20.9
NO_3^-	8.4	±	9.1	53.1	±	13.7	40.6	±	15.7
PO_4^{3-}	16.1	±	38.9	-25.6	±	32.4	4.6	±	30.9

5. Conclusion/Summary

Residential activities have the potential to impact on waterway quality via direct toxicity (e.g. metals) and indirect effects such as habitat modification and dissolved oxygen reduction (e.g. from TSS and excess nutrients). The four behaviours (car washing, use of outdoor cleaners and moss treatment, littering of cigarette butts, and inappropriate disposal of hazardous DIY waste) researched in Stage 1 of this research all identified contaminants above which threshold concentrations can impact aquatic ecosystems. Of these behaviours, only cigarette butts are unlikely to have significant contribution to stormwater contaminant loads. The Stage 1 report targeted surfactants liberated into the environment by car washing as being a potentially major contaminant of urban waterways, and due to the lack of ecotoxicological data, considered surfactants to be a good choice for future research. However, there is insufficient data on the chemical composition of cleaning products, and existing concentrations or ecotoxicological impact of surfactants in Christchurch waterways and therefore it is not possible at present to assess the contribution of residential car washing to surfactant load or its ecotoxicological impact on local rivers or the Avon-Heathcote Estuary/Ihutai. In this Stage 2 study we adopted a conventional approach to waterway contamination by looking at the contaminants for which ecological effects-based guidelines are available (Environment Canterbury, 2011; ANZECC, 2000), and for which stormwater treatment systems are currently designed upon (ARC TP10, 2003). We also assessed three simple mitigation strategies that could be easily adopted by Christchurch residents to determine how "filtering" wash water would affect key contaminant concentrations.

This study examined the effects of car washing on water quality. Specifically, total suspended solids (TSS), key metals (both total and dissolved), nutrients (nitrate and reactive phosphate) and polycyclic aromatic hydrocarbon (PAH) concentrations were measured in untreated car wash water subjected to different conditions (vehicle age, interval between washes and type of washing fluid employed). No specific trends were found when comparing untreated wash water from different cars, wash intervals or the use of different detergents. High concentrations of TSS, nutrients, total and dissolved Cu and Zn and total Pb were found in untreated wash water. Total copper (Cu), lead (Pb) and zinc (Zn) in untreated wash water was in excess of 100, 20 and 8 times the NRRP standards, respectively while phosphates were excess by 288-450 times the NRRP standards (nitrate was close to the threshold value).

The three mitigation systems that were tested all filtered untreated wash water through an organic substrate (grass lawn, hay bale or compost sock) with the goal to remove 75% or greater of target contaminants. All three systems were successful in reducing concentrations of total Cu, Zn and Pb (55-85% range) from the car wash runoff. Pb levels in particular were reduced to below the 90% protection NRRP/ANZECC trigger values and Zn ,which exceeded ANZECC guidelines by 20.5 times in untreated wash water, was reduced to only an exceedance factor of 3.5 following filtering through grass. In addition, TSS levels were reduced by up to 90% of the untreated runoff. However, dissolved Cu and Pb concentrations actually increased following the treatment systems. Consequently, dissolved Cu and Zn still exceeded 90% species protection levels set by NRRP/ANZECC even following the mitigation strategies. This might have occurred because of the organic component in each treatment system, which would have affected a slight pH decrease from weak organic acids. At a lower pH, dissolved metals (which are more difficult to remove) typically prevail and so any mitigation system should probably consider this pH effect with the goal of supplementing the organic component with some alkalinity material to help enhance the pH to achieve higher total metal removal efficiencies. This might be most easily achieved using the compost sock strategy.

The Stage 1 report (Waters, 2011) determined that there are approximately 250,000 light vehicles in Christchurch and that 90% of Christchurch's population reside in either the Avon/Ōtākaro or Heathcote/Ōpāwaho river catchments, equating to 225,000 vehicles that when washed on impermeable surfaces (i.e. road, driveways) would drain wash water into these rivers and ultimately the Avon-Heathcote Estuary/Ihutai. Using the total metal concentrations obtained in this study, with the Stage 1 data, we estimated that 12.2 kg of Cu, 20.8 kg of zinc and 3.1 kg of Pb would directly enter the city's waterways monthly (Figure 5.1.1). This equates to nearly 150 kg of copper, 250 kg of zinc and 37 kg of lead per year (Table 5.1.1). In the event that all of the vehicles were washed on grass, these values would drop dramatically to 4.1, 3.5 and 0.4 kg per month of Cu, Zn and Pb, respectively. This estimation is somewhat conservative in that it assumes that washing cars on grass results in some underdrain (i.e. partially treated) water feeding to the nearby waterway (as the grass experiments contained an under drain). However, a more realistic scenario is that all car wash runoff would infiltrate to subsoil sequestering all metals, in which case the amounts of Zn, Cu and Pb entering waterways as a result of domestic car washing activities would be zero. If residents did not have access to a grassed area on which to mitigate their car washing activity, they could employ the compost sock which would reduce those monthly contaminant loads for Cu (5.4 kg/month), Zn (5.7 kg/month) and Pb (0.5 kg/month). Alternatively, the haybale mitigation approach would reduce the metal loads to Cu (5.7 kg/month), Zn (6.3 kg/month) and Pb (0.4 kg/month).

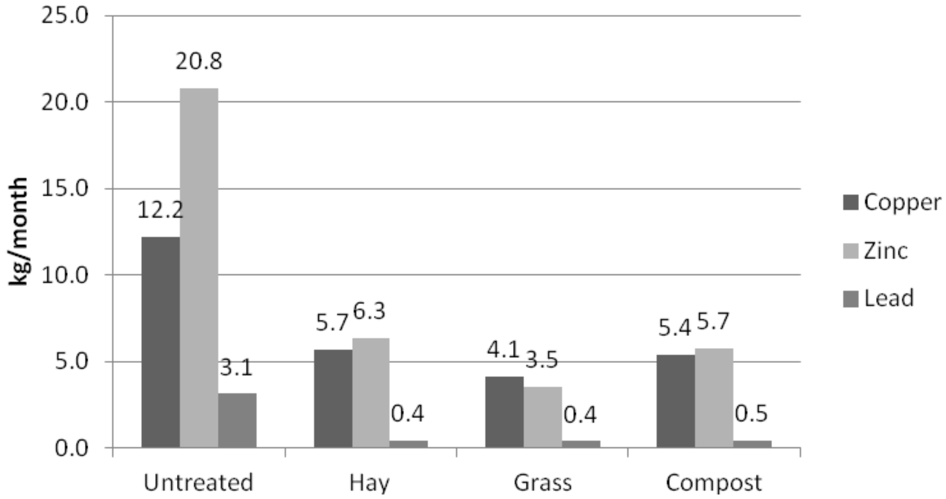


Figure 5.1.1. Hypothetical mass in kilograms of total metals derived from residential car washing entering Christchurch waterways every month. Values for metal concentrations were derived from Table 4.2.2. Assumptions include: each light vehicle washed 1/month, 300L of water used per wash

Table 5.1.1. Hypothetical mass in kilograms of total metals derived from residential car washing entering Christchurch waterways. Values for metal concentrations were derived from Table 4.2.2. Assumptions include: each light vehicle washed 1/month, 300L of water used per wash

	Copper				Zinc				Lead			
	Untreated	Hay	Grass	Compost	Untreated	Hay	Grass	Compost	Untreated	Hay	Grass	Compost
Kg/month	12.2	5.7	4.1	5.4	20.8	6.3	3.5	5.7	3.1	0.4	0.4	0.5
Kg/year	146.4	68.4	49.2	64.6	249.6	76.0	42.1	68.8	37.2	4.8	4.8	5.4
Kg decrease/ month		6.5	8.1	6.8		14.5	17.3	15.1		2.7	2.7	2.7
Kg decrease/ year		78.0	96.8	81.9		173.9	207.8	181.1		32.8	33.0	32.2

6 Future studies recommend considering the following;

- Wheel washing only to determine level of contaminants coming from wheels only,
- Vehicle washing survey of residents to ascertain current behaviours,
- Eco friendly vs. traditional car washing solutions,
- Controlled ecotoxicity studies on effluent (biologists).
- Greater number of cars including, paired cars or wash one half with each detergent.
- Measure detergents/surfactants in waterways and car wash water once ecotoxicity criteria established for these and chemical compositions of washing fluids can be fully elucidated.

7 Potential marketing messages that could be developed from this data to affect behavioural car wash practices in Christchurch

- Wash a wheel, kill an eel. Let's make a wish, don't kill our fish!
- Washing cars on your (impermeable) driveway or on the road can add as much as 146 kg of copper into the City's rivers per year. That's enough copper to ..e.g. re-roof the cathedral x number of times, re-wire xxx number of houses etc...
- Washing cars on your (impermeable) driveway can add as much as 250 kg of zinc into the City's rivers per year. That's enough zinc to re-roof the xxx number of new houses etc...
- Don't be an ass, wash your car on the grass!

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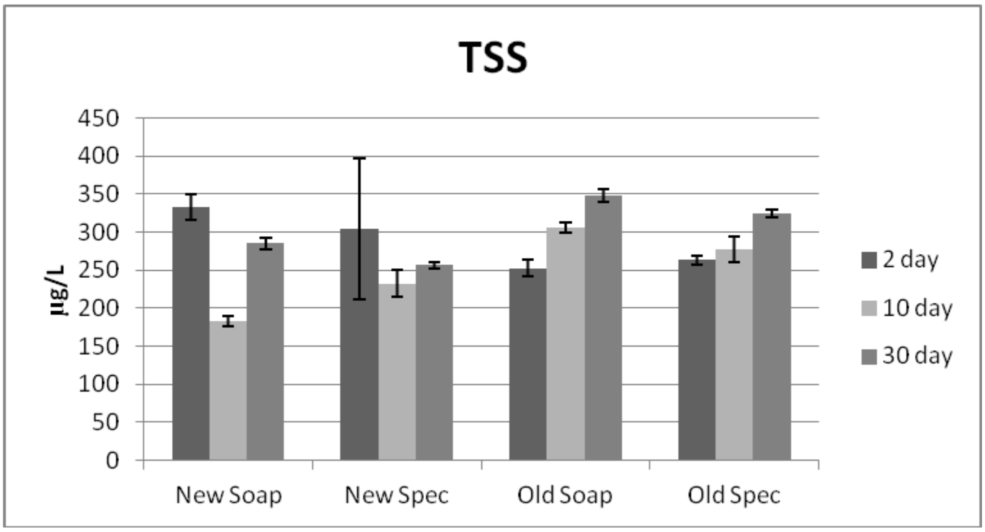
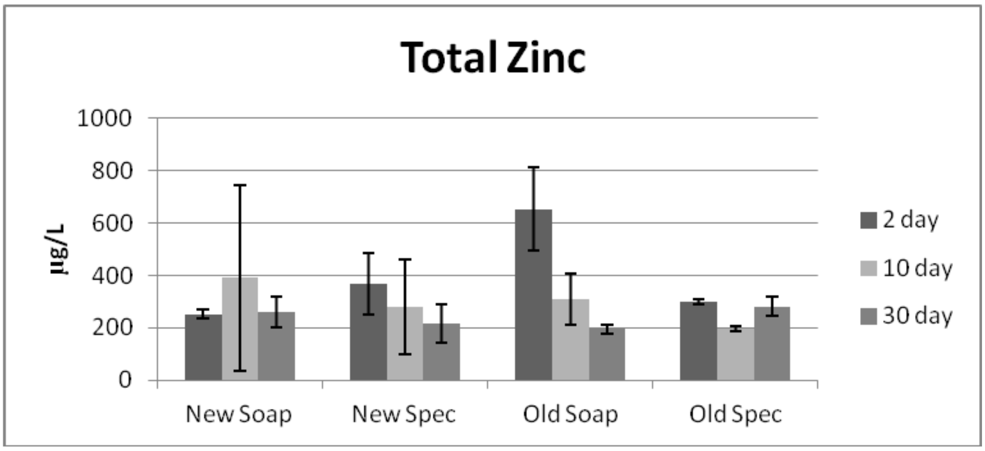
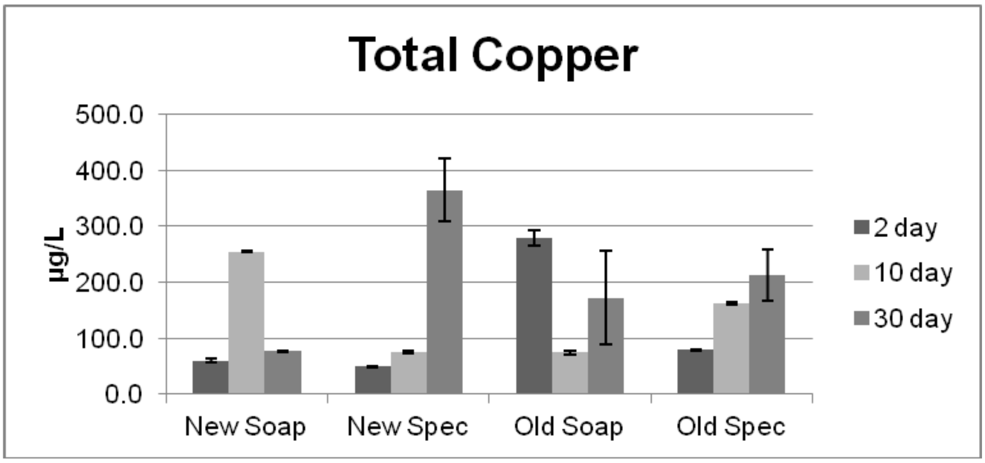
9. Appendices

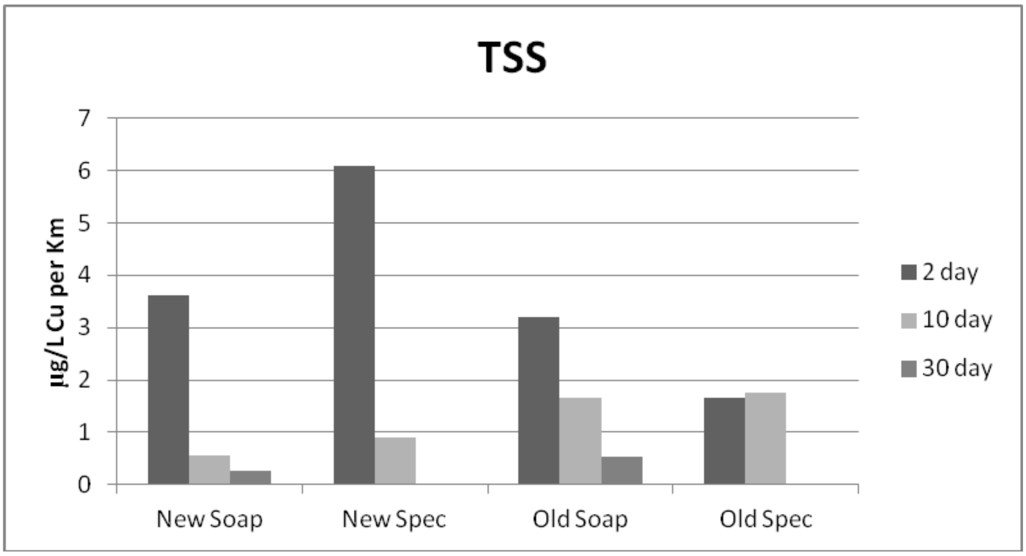
A. Comparisons for TSS and individual metals

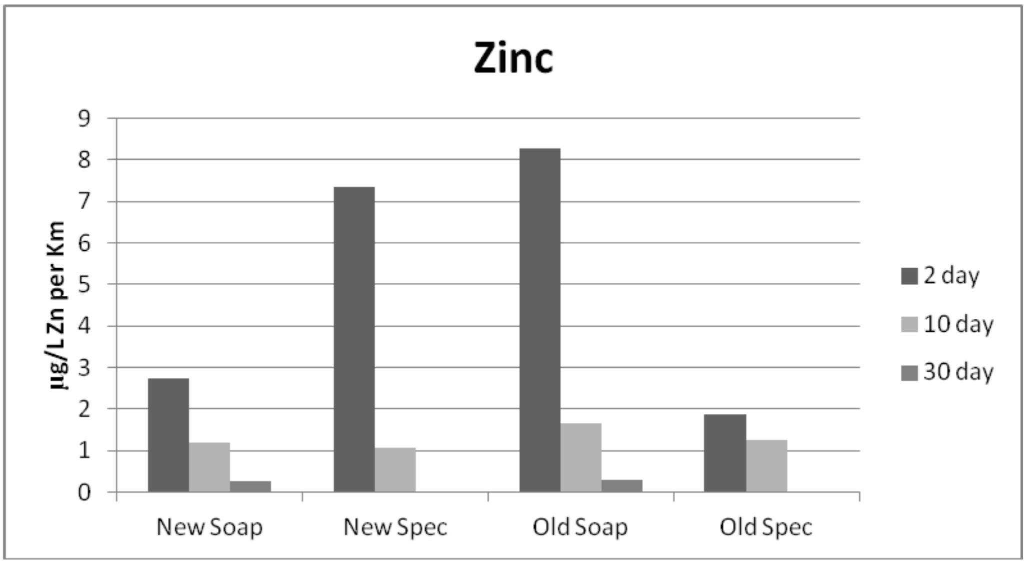


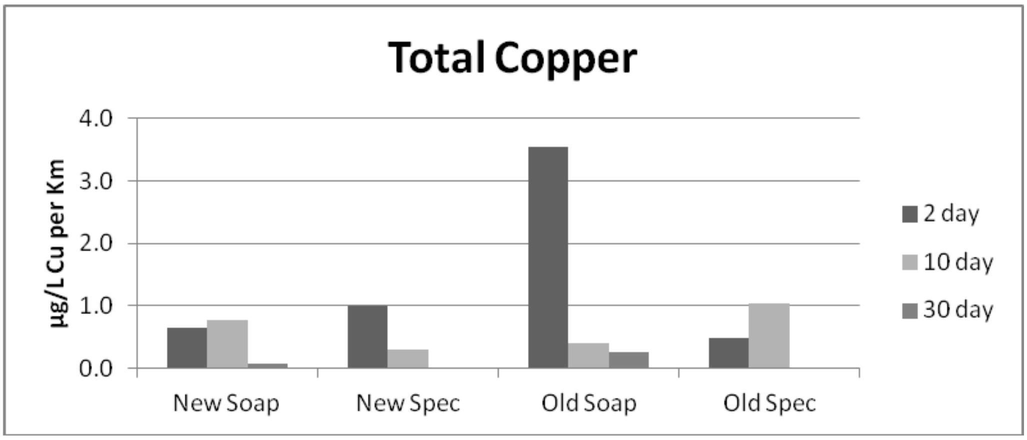




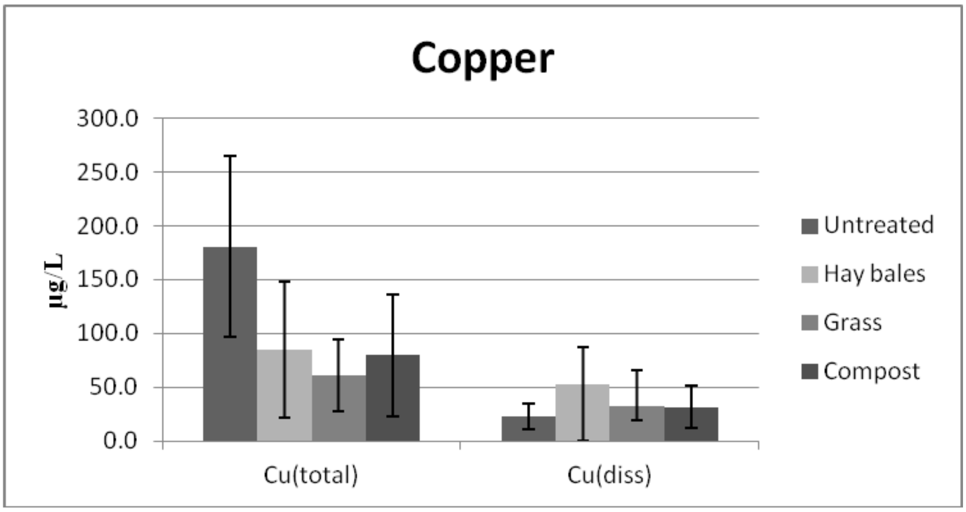
B. Rates of Contaminant deposition for three random individual contaminants.

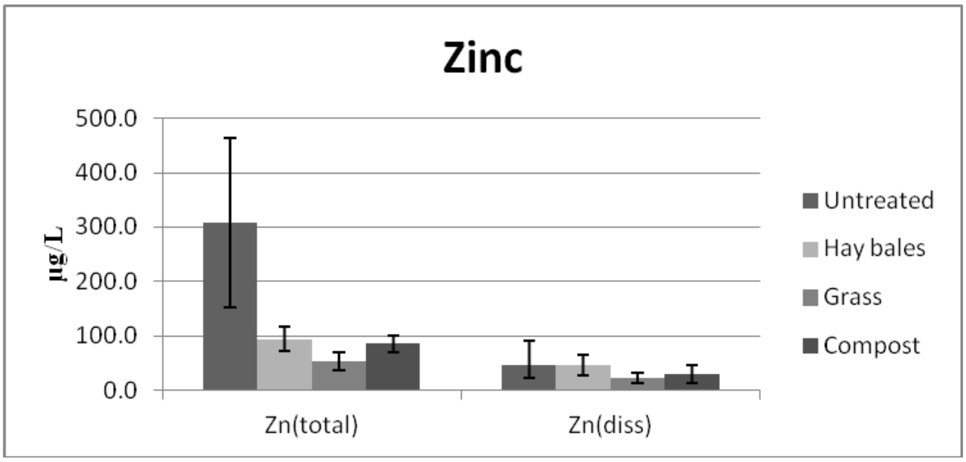


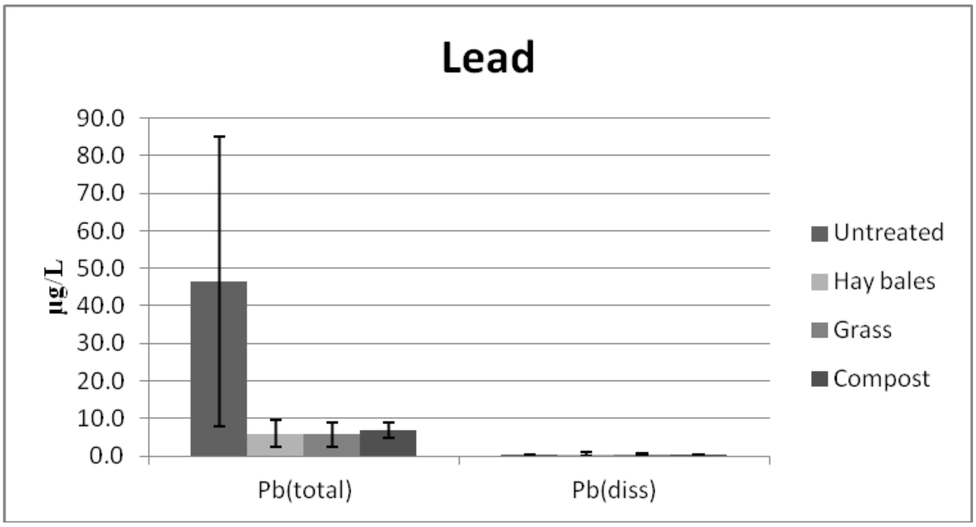




C. Concentrations of total and dissolved metals in untreated and treated car wash water. Values are an average of Vehicle age, Wash Interval and Detergent used. n=12.







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