An Innovative Method for Spatial Quantification of Contaminant Buildup and Wash-off from Impermeable Urban Surfaces

D. Wicke*, T. Cochrane*, A. O'Sullivan*

* University of Canterbury, Department of Civil and Natural Resources Engineering, Private Bag 4800, Christchurch, New Zealand, Tel: ++ 64-3-364 2378
(Emails: *daniel.wicke@canterbury.ac.nz; tom.cochrane@canterbury.ac.nz; aisling.osullivan@canterbury.ac.nz)*

Abstract
A method was developed that employs thin boards (0.56 m^2) comprising different paving materials (2 asphalt types and concrete) typically used in urban environments. Boards can be placed at various locations of interest within an urban catchment to investigate accumulation of contaminants over specified periods of time. Boards are then placed under a rainfall simulator in order to generate runoff under controlled conditions. We successfully applied this method to investigate contaminant build-up at a University carpark, showing accumulation mainly occurred within the first 6 days. Resulting wash-off curves were used to determine coefficients for build-up and wash-off functions (maximum build-up, half-saturation time and wash-off coefficient) that can be applied to model the fate of contaminants in stormwater models (e.g. SWMM). Results also showed that concentrations of total suspended solids (TSS) are linearly correlated with total metal concentrations.

Keywords: contaminant build-up, urban catchment model, heavy metals, stormwater runoff

INTRODUCTION

Urban waterways can improve the aesthetics of cities and provide recreational functions, as well as the practical purpose of draining excess stormwater runoff from impervious surfaces. Unfortunately, pollutants accumulating on impervious surfaces in form of sediment, particulate and soluble heavy metals (and other contaminants) are efficiently transported to waterways during storm events, causing adverse environmental impacts in those receiving ecosystems.

Stormwater contaminants of greatest concern are usually heavy metals (particularly zinc, copper and lead) in particulate and dissolved forms (e.g. Gobel et al. 2007, Brown and Peake 2006). These principal metals originate from dust in vehicle tyres and brake linings, which accumulate on paved surfaces and become washed off during rainfall events into nearby waterways (Davis et al. 2001, Zanders 2005). Copper (Cu) and zinc (Zn) in stormwater also originate from roofing materials (Karlen et al. 2001, 2002). In a recent study by Wicke et al. (2009), Zn and Cu concentrations measured in runoff from a University of Canterbury carpark since 2006 were shown to be consistently higher than recommended guidelines for the protection of aquatic species (ANZECC 2000). Furthermore, their concentrations in the "first flush" exceeded these guidelines 5-10 fold, jeopardizing urban waterways health.

Although direct sampling of runoff during a given storm event effectively quantifies contaminant contributions from a specific area, it is expensive and time-consuming. Additionally, inherent variability in natural rainfall events makes it difficult to construct contaminant build-up and wash-off functions from natural storm events for modelling purposes. We therefore developed a unique experimental method for capturing contaminants on different impervious surfaces in order to: (i) accurately quantify contaminant sources; (ii) determine contaminant build-up and spatial variability within the catchment and; (iii) obtain large cost-effective data sets to develop build-up and wash-off functions for validating appropriate stormwater contaminant models.

METHODOLOGY

The experimental design employs constructed asphalt and concrete boards (75 cm L x 75 cm W x 3 cm total height) to capture contaminants accumulating over time in an urban catchment (e.g.

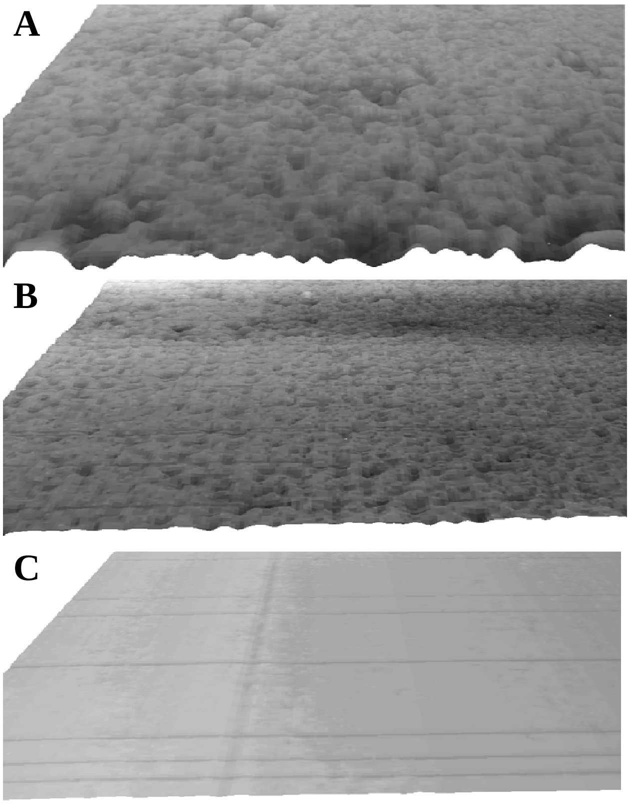

Figure 1: Three-dimensional images of different board types as derived from surface laser scanner. A – coarse asphalt, B – fine asphalt, C – concrete.
Heights are represented by differences in grey levels with dark tones showing lower elevations.

carparks, roads or paths). The boards were filled with three different materials to replicate different surface roughness and characteristics: concrete, smooth asphalt (3 mm max. aggregate size) and coarse asphalt (14 mm max. aggregate size). Concrete mixture was prepared with the following specifications (per board): 4.2 kg cement, 2.7 L tap water, 15 kg 5 mm gravel, 13.5 kg sand, 50 g shogun (plastic) fibres, 15 g sika (polymer) megafibres, and 13 mL water reducer. Asphalt was supplied by Fulton Hogan Construction from an actual road construction site. These boards were filled on site with hot asphalt and levelled using a standard plate compactor.

Boards were assessed for differences in surface roughness using a surface laser scanner as described in Darboux et al. (2003). Resulting elevation matrices were analysed in ArcGIS 9.3 (ESRI, USA) to generate three-dimensional images to visualize the surface topography as shown in Figure 1.

After boards were emplaced at the field sites and exposed for the designated time period, they were then placed under a rainfall simulator to quantify contaminant wash-off rates and determine contaminant accumulation amounts. A two-nozzle (Veerjet 80100) Norton type rainfall simulator (Herngren et al. 2005) was used to wash contaminants off the boards by applying a representative local rainfall intensity of 22 mm/hr. Rainfall droplet size distribution and velocity of the artificial rain generated by the rainfall were measured once using a Parsivel laser scanner (Ott, Germany). Comparison of droplet size distributions generated by the rainfall simulator with average size distribution from a natural rain event (45 minutes with a peak intensity of 20 mm/h) showed comparable size distributions with droplet size peaking at 0.5 mm (Figure 2).

Tap water was used for the experiment and pre-filtered through a 10 µm cartridge filter to remove potential particles. It was then adjusted to a pH of 6 (average pH of local rainwater) using concentrated nitric acid prior to application, concurrently depleting the buffer capacity of the tap water. The pH was monitored throughout the experiment to maintain it constant (with adjustments if required).

Runoff samples from the boards were collected at 0, 5, 10, 20, 40 and 60 minutes following accredited sampling regimes (ANZECC, 2000). Samples were instantaneously measured for pH, conductivity and turbidity using portable meters and coupled probes. Total suspended solids (TSS) and colour were measured within 24 hours following APHA method 2540D while key metals (Zn, Cu and Pb) were analysed by ICP-MS following APHA Method 3125B after HNO_3 digestion (APHA, 2005).

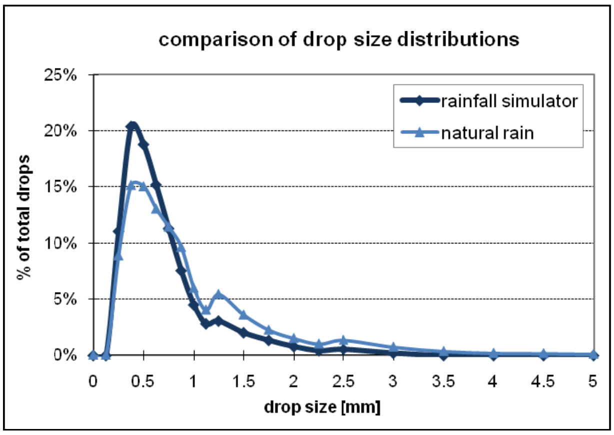

Figure 2: Average drop size distributions of a 45 minute natural storm event (peak intensity: 20 mm/h) compared to rain generated by the rainfall simulator at 22 mm/h.

Contaminant Build-up Experiment

Build-up of TSS, zinc, copper and lead over time and their respective wash-off were investigated by placing 5 boards of each of the three materials at one of the main carparks of the University of Canterbury, New Zealand, for 2 weeks (Figure 3). The 15 boards were placed on two adjacent parking spaces, and cars were prevented from parking or driving over the boards. In previous experiments, wind was shown to be the main factor in spreading contaminants across the car park. It was therefore assumed that any deposition of contaminants on the boards would occur from wind. A temporary roof was constructed comprising of a steel frame and plastic cover (average height 1m) to prevent unintended wash-off from rain events, however no rain occurred during the time of the experiment. To determine the contaminant build-up over time, one pair of boards (coarse asphalt and concrete) were collected after 2, 4, 6, 9, and 13 days. The five smooth asphalt boards (replicates) were all collected after 13 days. Each board was washed-off under the rainfall simulator after it was collected. Wash-off samples over time were measured for TSS, zinc, copper and lead.

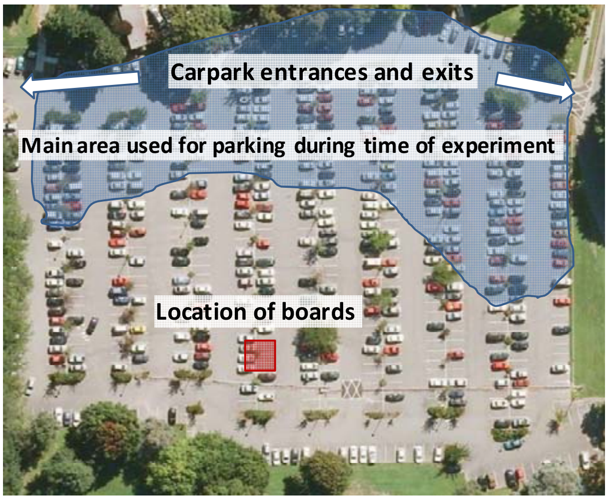

Figure 3: Location of boards in carpark .

Modelling of Contaminant Build-up and Wash-off functions

For modelling stormwater runoff from urban catchments, a variety of programmes can be used such as the stormwater management model (SWMM 5.0) developed by the US Environmental Protection Agency (EPA). In such models, the behaviour of contaminants is often incorporated using relationships for accumulation of a particular contaminant on a surface over time (build-up function) as well as dislodgement characteristics of the respective contaminant during a storm event (wash-off function). To apply these functions in a modelling scenario, the respective coefficients (depending on surface and contaminant) must be provided. We determined the required coefficients using data obtained from the experiment described above.

Two functions included in SWMM were selected to model contaminant build-up and wash-off. To model contaminant build-up, a saturation function (equation 1) was chosen:

$$B = \frac{B_{\max} \cdot t}{A + t} \tag{1}$$

B - Build-up [mg/m^2], B_{max} - maximum build-up [mg/m^2], A – half saturation time [d], t – number of antecedent dry days.

A first order decay relationship was employed to represent wash-off characteristics (equation 2):

$$W = C_1 \cdot q \cdot B \tag{2}$$

W - wash-off load [mg/h], q - runoff rate [mm/h], B - remaining amount of pollutant [mg], C_1 - wash-off coefficient.

The parameters A, B_{max}, and C_1 were determined by minimizing the sum of the squared differences between modelled and experimental results using EXCEL solver.

RESULTS AND DISCUSSION

General water quality parameters

Key water quality parameters measured in runoff from smooth asphalt and concrete boards are exemplarily shown in Figure 4.

The pH essentially influences metal speciation (i.e. dissolved or particulate fraction) with a pH of ≤6 affording greater potential for particulate metal fractions to dissolve, and thus become more bioavailable (Cambell and Tessier, 1991; Pitt, 1995). The pH in runoff samples showed a distinct difference between both surface types. The pH in runoff from concrete during the first few minutes was much higher at 7.7 compared to asphalt at 4.2, considering that the simulated rainfall had a constant pH of 6 (Figure 4a). The pH in runoff from concrete rose to 9 after 40 minutes, an increase which we think originates from hydroxide residues that are produced during the cement binding process. It is remarkable, however, that this effect is still observed 9 months after production of the boards and several wash-offs. The lower asphalt runoff pH of 4.2 rose to 6 after 60 minutes of runoff time, equal to the feed water pH. Further analysis is warranted to study the impact of the material and depositions on pH and the impact of pH on contaminant speciation. However, the extremely low pH in runoff from asphalt during the first 10-20 minutes is supposed to play an important role in metal mobilization processes.

Colour is indicative of dissolved organic carbon (DOC) concentrations (especially humic acids and humin). Since vegetation is almost exclusively organic and predominantly carbonaceous, a relationship between colour and decomposed soluble vegetative material can be inferred. Higher

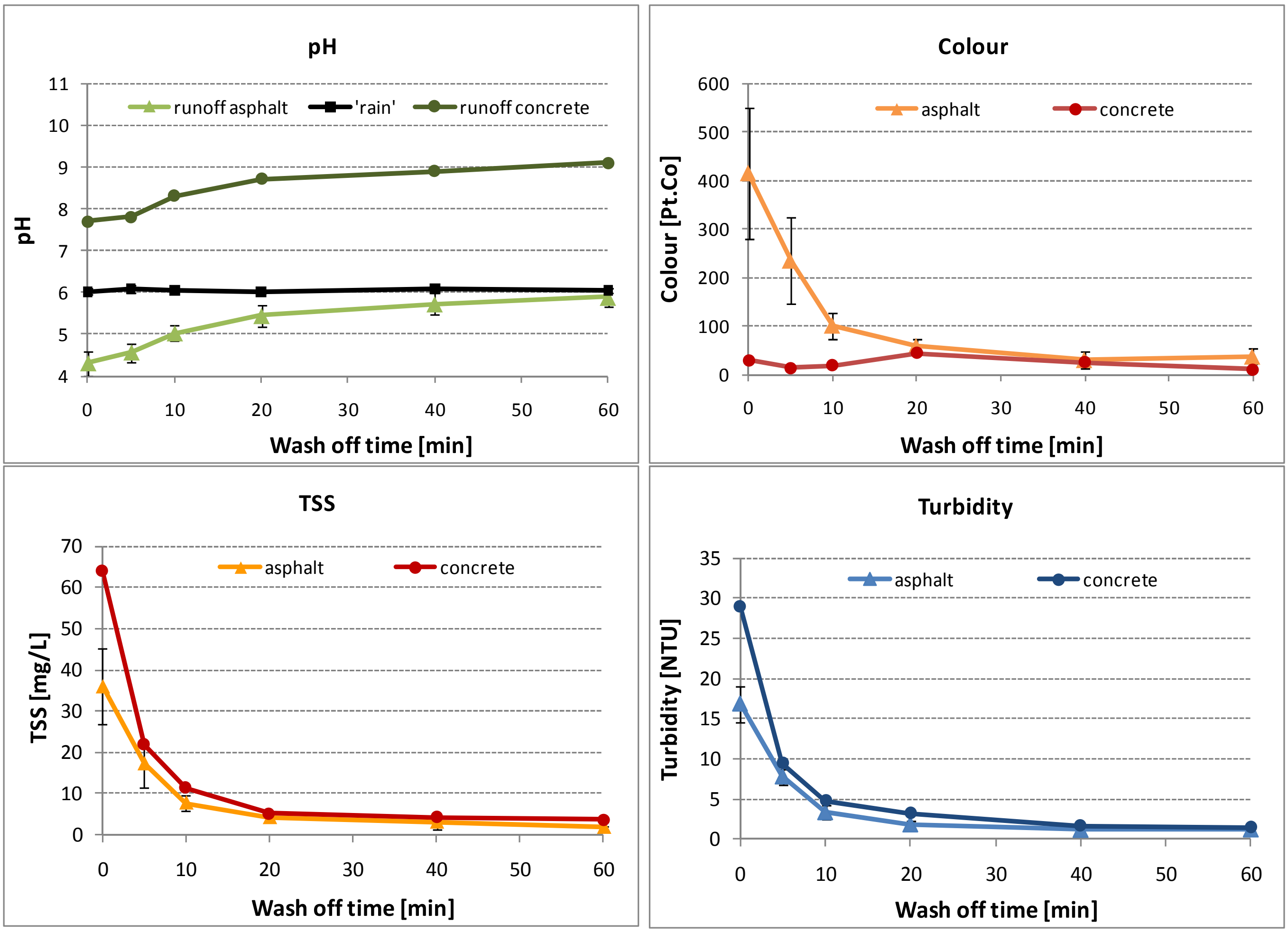

Figure 4: pH, colour, turbidity and TSS concentrations in runoff from smooth (2mm aggregate) asphalt (average, n=5) and concrete boards (n=1) after being exposed for 13 days at a carpark.

initial colour concentrations (averaging 400 Pt.Co) in runoff from asphalt boards (both roughness types) compared to concrete boards (at <50 Pt.Co; effectively colourless) could be due to vegetative material that became trapped in the microcavities of the asphalt surface structure (e.g. seeds from trees), which were actually visible before wash-off applications (Fig. 4b). The sharp exponential decline in colour concentration reflects the initial wash-off pattern seen for other water quality parameters (Figure 4).

Turbidity (instantaneous measurement) can be correlated to total suspended solid (TSS) concentrations (laboratory measured), which can be a useful surrogate parameter of suspended solids in stormwater applications (Thomson et al., 1997). The turbidity and TSS relationship derived during this study is approximately TSS [mg/L] = 2 · Turbidity [NTU] (Figure 4). Higher concentrations of suspended particles washed off from concrete surfaces, especially at the beginning of the experiment, were observed from exponential declining concentrations of both TSS (Figure 4a) and turbidity (Figure 4b). Differences in surface roughness between the paving materials is considered to influence particle removal from the surfaces, as particles deposited on the smooth concrete surface can be more easily dislodged compared to asphalt (Figure 1).

Heavy Metals and TSS

Results for TSS (Figure 4a) and heavy metal (Figure 4b-d) concentrations in runoff samples from boards exposed for 2, 4, 6, 9, or 13 days are exemplarily shown for the coarse asphalt surface. Concentrations for all contaminants quickly dropped during the first 20 minutes of the wash-off constituting the "first flush" phenomenon (Lee et al. 2002, Sansalone and Buchberger 1997). Maximum TSS concentrations were 64 mg/L in runoff from concrete boards and 37 mg/L in asphalt runoff (Figure 4a; Table 1). Maximum heavy metal concentrations from all surface

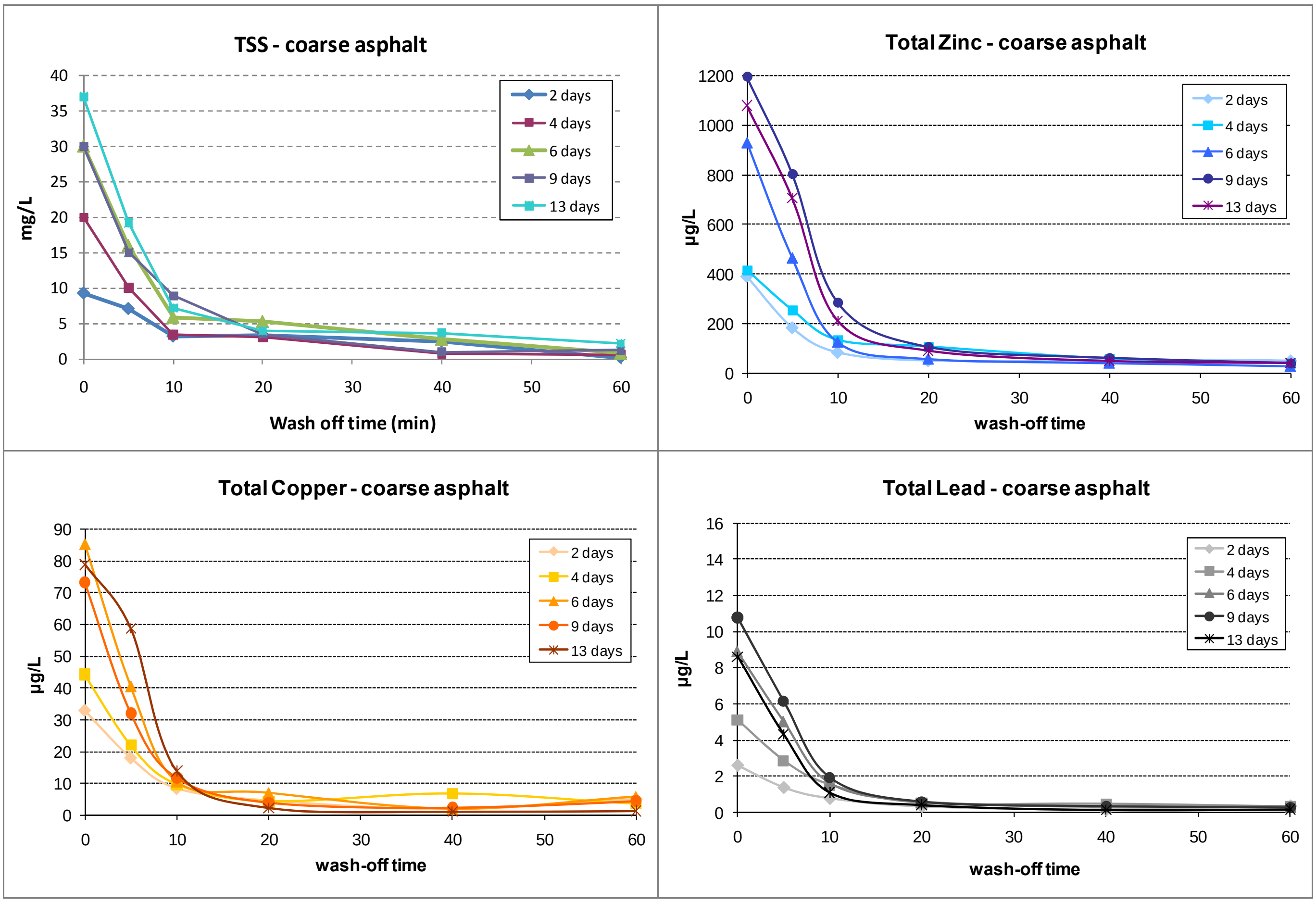

Figure 5: TSS, Zn, Cu and Pb concentrations in runoff from coarse (14 mm aggregate) asphalt boards using a rainfall simulator at a rain intensity of 22 mm/h after exposure at a carpark for 2 – 13 days.

types at t=0 were 1194 µg/L for total zinc, 85.3 µg/L for total copper (both coarse and asphalt) and 15.4 µg/L for total lead (concrete), showing that contaminant concentrations from carpark runoff exceeded relevant guideline values (ANZECC 2000) several-fold (80-fold for first flush zinc concentrations). Although these initial high concentrations quickly drop, their exceedance magnitudes inevitably impose adverse effects on the receiving ecosystems (O'Halloran and Harding, 2008; Beasley and Kneale, 2002). Furthermore, particulate contaminants deposited in stream beds of receiving waterways can act as a long term source of heavy metals.

Contaminant yields (mg/m^2) were calculated using runoff concentrations from boards (shown for 2, 6 and 13 days exposure in Table 1). By 13 antecedent dry days, 76-144 mg/m^2 TSS, 0.8-3.5 mg/m^2 total Zn, 0.1-0.2 mg/m^2 total Cu and 0.02-0.04 mg/m^2 total Pb accumulated on the different surfaces (Table 1). Contaminant build-up occurred until day 6, after which contaminant yields remained relatively constant for copper and lead or increased only slightly for TSS and zinc.

Table 1: Contaminant yields over time, shown for 2, 6 and 13 antecedent dry days [mg/m^2].

	Concrete			Coarse Asphalt		
days	2	6	13	2	6	13
TSS	48	131	144	35	64	76
Total zinc	0.39	0.65	0.77	1.7	2.5	3.5
Total copper	0.12	0.19	0.20	0.07	0.13	0.13
Total lead	0.021	0.040	0.036	0.006	0.014	0.015

TSS-metal correlations

Simplicity of the water quality sampling and in-situ measurements associated with this experimental set-up helped develop correlations between key stormwater quality parameters. Since heavy metals in urban stormwater typically originate from particulate materials (e.g. copper and lead in brake linings; zinc in tyre wear and roofing), total heavy metal and TSS concentrations were correlated. Correlations for all three surface types were derived by plotting TSS and total metal concentrations of the same sample, showing a linear relationship (Figure 6). Correlation coefficients (R^2) were strong in all instances (mostly around 0.9 and always ≥0.75)

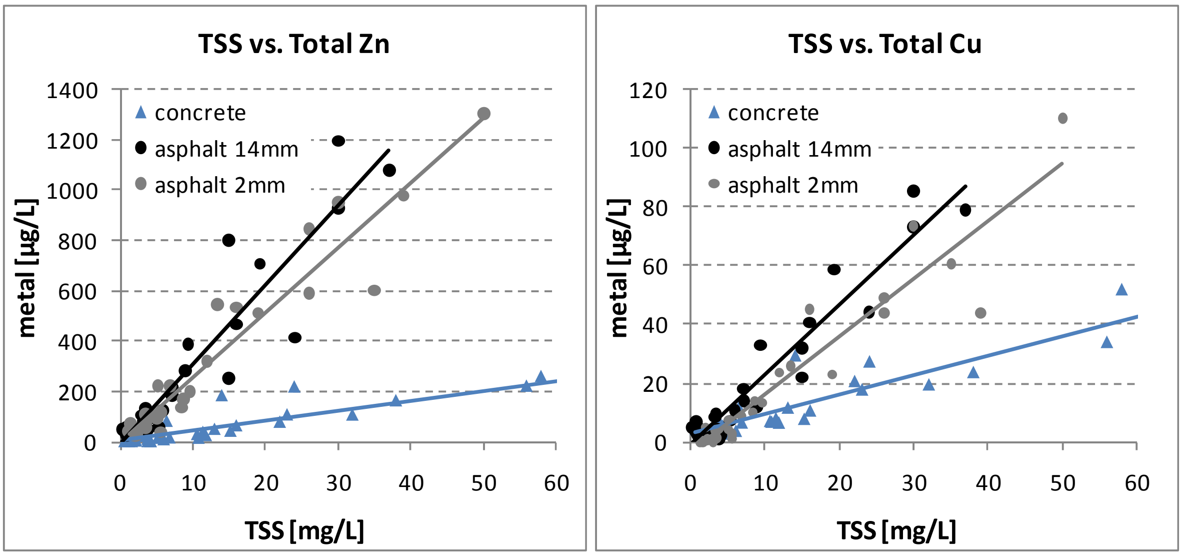

Figure 6: Correlations between TSS vs. zinc and copper concentrations in runoff from concrete and asphalt boards after exposure up to 13 days.

as shown in Table 2. Overall, steeper gradients were obtained for all three metals from both asphalt types compared to concrete runoff, with greatest difference for zinc. A possible explanation for this is that although metals appear to be attached more strongly in asphalt cavities compared with concrete, a lower pH from asphalt during wash-off (see Figure 4) effectively dissolves these metals so particulate fractions would be consequently lower. This effect would be even stronger for the coarse (14 mm) asphalt with its deeper cavities (see Figure 1) enhancing particle entrapment, resulting in steeper correlation gradients compared with smoother asphalt material (as seen in Figure 6).

Table 2: Coefficients (Slope and R^2) for the correlation of total heavy metal and TSS concentrations of the general form: metal [µg/L] = Slope · TSS [mg/L]

	Concrete		Smooth Asphalt		Coarse Asphalt	
	Slope	R^2	Slope	R^2	Slope	R^2
TSS vs. zinc	4.0	0.75	25.8	0.92	31.0	0.88
TSS vs. copper	0.74	0.81	1.83	0.89	2.32	0.93
TSS vs. lead	0.2	0.90	0.41	0.90	0.27	0.92

A distinct advantage of employing surrogate measurements in stormwater applications is the immediacy and cost-efficiency of obtaining large data sets, especially for modelling purposes. This can be achieved by continuously logging measurements such as turbidity, pH and conductivity, and colour as an indicator of total suspended solids, metal concentrations and potential DOC concentrations, respectively, once robust (albeit site-specific) relationships between these parameters have been established.

Build-up and Wash-off functions

Contaminant yields calculated in Table 1 were used to plot contaminant build-up over time. It was assumed that build-up can only occur for a certain period of time and will eventually reach a saturation maximum. The experiment described here was designed to verify this assumption and also to determine the time it takes to reach this saturation maximum.

Contaminant yields as a function of the number of antecedent dry days is shown in Figure 7a for total lead on an asphalt surface. Clearly, Pb yields increased steadily until day 6, after which time the contaminant build-up curve flattens and even tapers off so that yields from 13 days exposure are similar to that at 6 days. Similar patterns were observed for the other surface types and contaminants indicating that it took more than 6 days for contaminant saturation maximum to be reached.

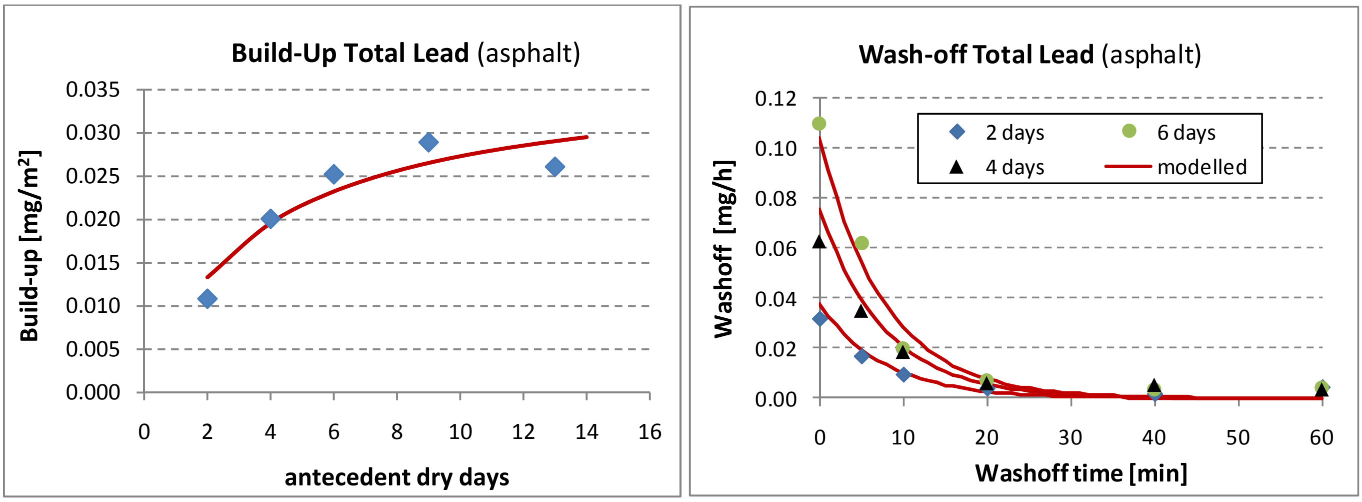

Figure 7: Experimental and modelling results of build-up (left: 7a) and wash-off (right: 7b) relationships of total lead deposited on coarse asphalt during 13 day exposure on a carpark.

Build-up characteristics were modelled applying equation 1 (described earlier) to derive coefficients for maximum build-up (B_{max}) and the half saturation time A (time it takes to reach half of the maximum concentration) as presented in Table 3Table 3. Maximum build-up amounts were up to 2 kg/ha TSS, 52 g/ha zinc, 2.5 g/ha copper and 0.4 g/ha lead for an antecedent dry period of > 2 weeks that would be washed off in a 20 mm storm event. It is likely that contaminant build-up depends on several other factors (beside surface type and structure) such as wind speed and directions and traffic volumes (e.g. Moores and Pattinson 2008).

Comparison of experimental and modelled wash-off rates are also shown for total lead in Figure 7b. Equation 2 was used to derive one wash-off coefficient per contaminant and surface that mathematically describes all 5 wash-off curves (day 2-13). Modelled curves well reproduced experimental values (Figure 7b) highlighting the validity of our model. Resulting coefficients are listed in Table 3. Differences of build-up and wash-off coefficients between concrete and coarse asphalt surfaces are likely to reflect the different wash-off dynamics due to distinct differences in materials surface roughness. The most significant differences observed between surface types were for maximum build-up of TSS and zinc, whereas wash-off coefficients varied only slightly between contaminants. Half saturation time (A) for all contaminants was between 2 and 5 days.

Table 3: Coefficients for build-up and wash-off functions for concrete and coarse asphalt surfaces

	Concrete			Asphalt		
	Build-up		Wash-off	Build-up		Wash-off
	B_{max} mg/m^2	A [d]	C_1	B_{max} mg/m^2	A [d]	C_1
TSS	353	5.4	0.24	165	3.9	0.27
Total zinc	1.0	5.4	0.32	5.2	4.8	0.32
Total copper	0.25	3.2	0.20	0.27	2.4	0.34
Total lead	0.04	1.7	0.29	0.04	3.6	0.33

Coefficients for both build-up and wash-off can be used in widely accepted models such as SWMM to better predict contaminant behaviour in urban stormwater. These relationships more accurately represent the fate of urban stormwater pollutants compared to employing event mean concentrations, which are often applied instead of wash-off functions.

CONCLUSIONS

The innovative method for spatial quantification of contaminant build-up and wash-off from impermeable urban surfaces described in this study was successfully applied to investigate accumulation potential of the three main heavy metals zinc, copper and lead as well as total suspended solids (TSS). Pollution build-up and wash-off coefficients were determined that can be used to model the accumulation and runoff of these contaminants in SWMM or similar stormwater programmes. Wash-off from constructed boards (filled with concrete and two different asphalt grades) using a rainfall simulator under controlled conditions enabled us to study water quality parameters in greater detail. For example, it was shown that asphalt and concrete produced runoff with very different pH values; asphalt runoff had a pH as low as 4.2, whereas runoff pH from concrete was up to 9, thus considerably affecting dissolved metal concentrations and bioavailability. Metal concentrations and yields also differed between both surface types, especially for zinc from asphalt material showing 2-5 times higher first flush concentrations.

This methodology has enabled urban contaminant build-up and wash-off functions to be developed that are required for modelling scenarios. Results of these models will help decision makers ascertain best structural and other management practices to reduce contaminant loading to urban waterways. Continued research is refining contaminant-surface relationships while also investigating the influence of surface type and runoff management practices on water quality entering urban waterways. Further studies will help refine our understanding of contaminant-surface relationships applicable in developing more accurate models for estimating (and hence mitigating) stormwater related contamination in receiving ecosystems.

Acknowledgements

The authors wish to thank the following people, who significantly contributed to the outcome of this study: Ingrid Cooper and William Jacobson for sampling and analysis, Joseph Good for digestion of samples as preparation for total metal analysis, Sally Gaw and Robert Stainthorpe for ICP-MS analysis, Christchurch City Council for funding a student, Fulton Hogan for supplying asphalt, and Tim Perigo for his help regarding construction of concrete boards.

References

ANZECC (2000). "Australian and New Zealand Guidelines for Fresh and Marine Water Quality.", Australian and New Zealand Environment and Conservation Council.

APHA (2005). "Standards Methods for the Examination of Water and Wastewater", American Public Health Association. 21st Edition, Washington DC.

Beasley, G. and Kneale, P. (2002). “Reviewing the impact of metals and PAHs on macroinvertebrates in urban watercourses.” Progress in Physical Geography 26(2): 236–270.

Brown, J. N. and Peake, B. M. (2006). "Sources of heavy metals and polycyclic aromatic hydrocarbons in urban stormwater runoff." Science of the Total Environment 359(1-3): 145-155.

Cambell, P. and Tessier, A. (1991). “Biological Availability of Metals in Sediments: Analytical Approaches”, in JP Vernet (ed.), Heavy Metals in the Environment, Elsevier, Amsterdam, pp. 161-174.

Darboux, F. and Huang, C. (2003). "An instantaneous-profile laser scanner to measure soil surface microtopography." Soil Science Society of America Journal 67(1): 92-99.

Davis, A. P., Shokouhian, M. and Ni, S. B. (2001). "Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources." Chemosphere 44(5): 997-1009.

Gobel, P., Dierkes, C. and Coldewey, W. C. (2007). "Storm water runoff concentration matrix for urban areas." Journal of Contaminant Hydrology 91(1-2): 26-42.

Herngren, L., Goonetilleke, A. and Ayoko, G. A. (2005). "Understanding heavy metal and suspended solids relationships in urban stormwater using simulated rainfall." Journal of Environmental Management 76(2): 149-158.

Karlen, C., Wallinder, I. O., Heijerick, D., Leygraf, C. and Janssen, C. R. (2001). "Runoff rates and ecotoxicity of zinc induced by atmospheric corrosion." Science of the Total Environment 277(1-3): 169-180.

Karlen, C., Wallinder, I. O., Heijerick, D. and Leygraf, C. (2002). "Runoff rates, chemical speciation and bioavailability of copper released from naturally patinated copper." Environmental Pollution 120(3): 691-700.

Lee, J. H., Bang, K. W., Ketchum, L. H., Choe, J. S. and Yu, M. J. (2002). "First flush analysis of urban storm runoff." Science of the Total Environment 293(1-3): 163-175.

Moores, J. and Pattinson, P. (2008). "Characterizing loads of copper and zinc in road runoff". Conference Proceedings of 5th South Pacific Stormwater Conference “Stormwater 08”, Rotorua, New Zealand.

O'Halloran, Cavagannah, Harding (2008). “The response of a New Zealand mayfly to toxicity from acid mine drainage.” Environmental Toxicology & Chemistry 27 *(*5): 1135-1140.

Pitt, R. E. (1995). “Biological Effects of Urban Runoff Discharges”, in EE Herricks (ed.), Stormwater Runoff and Receiving Systems. Impact, Monitoring, and Assessment, Lewis Publishers, Boca Raton, pp. 127-162.

Sansalone, J. J. and Buchberger, S. G. (1997). "Partitioning and first flush of metals in urban roadway storm water." Journal of Environmental Engineering-Asce 123(2): 134-143.

Thomson, N. R., McBean, E. A., Snodgrass, W. and Monstrenko, I. B. (1997). "Highway stormwater runoff quality: Development of surrogate parameter relationships." Water Air and Soil Pollution 94(3-4): 307-347.

Wicke, D., Cochrane, T and O’Sullivan, A. (2009). Developing a rainfall contaminant relationship model for Christchurch urban catchments, Proceedings of 6th South Pacific Stormwater Conference, April/May 2009, Auckland, New Zealand.

Zanders, J.M. (2005). "Road Sediment: Characterisation and implications for the performance of vegetated strips treating road runoff", Science of the Total Environment 339(1-3): 41-47.