Characterising urban zinc generation to identify surface pollutant hotspots in a low intensity rainfall climate

F. J. Charters, T. A. Cochrane and A. D. O’Sullivan

ABSTRACT

Characterising stormwater runoff quality provides useful insights into the dynamics of pollutant generation and wash off rates. These can be used to prioritise stormwater management strategies. This study examined the effects of a low intensity rainfall climate on zinc contributions from different impermeable urban surface types. First flush (FF) and steady state samples were collected from seven different surfaces for characterisation, and the data were also used to calibrate an event-based pollutant load model to predict individual ‘hotspot’ surfaces across the catchment. Unpainted galvanised roofs generated very high concentrations of zinc, primarily in the more biologically available dissolved form. An older, unpainted galvanised roof had FF concentrations averaging 32,338 \( \mu g/L \), while the new unpainted roof averaged 4,782 \( \mu g/L \). Roads and carparks also had elevated zinc, but FF concentrations averaged only 822–1,584 \( \mu g/L \). Modelling and mapping expected zinc loads from individual impermeable surfaces across the catchment identified specific commercial roof surfaces to be targeted for zinc management. The results validate a policy strategy to replace old galvanised roof materials and avoid unpainted galvanised roofing in future urban development for better urban water quality outcomes. In the interim, readily-implemented treatment options are required to help mitigate chronic zinc impacts on receiving waterways.

Key words | dissolved zinc, impermeable urban surfaces, modelling, runoff quality, stormwater

INTRODUCTION

When it rains, water flows over impermeable surfaces collecting visible (e.g. particulate) and less visible (e.g. dissolved) pollutants. In urban areas, this stormwater drains into local streams and rivers through networks of open channels and underground pipes. Stormwater is not typically treated in older catchments (watersheds) and discharges directly into urban waterways, causing adverse effects on in-stream and downstream ecosystems. Stormwater is the largest single polluter of urban waterways and negatively impacts their aquatic organisms (Walsh et al. 2005), and can potentially affect public health. The quality of stormwater reaching the waterways can be improved through pollutant source reduction and treatment measures; however, it is critical to understand the untreated stormwater quality to be able to develop appropriate and effective management measures.

Stormwater quality is influenced not only by environmental factors, including rainfall characteristics such as intensity and length of antecedent dry period (road runoff: Barrett et al. 1998; Kayhanian et al. 2003; Crabbtree et al. 2006; roof runoff: Yaziz et al. 1989), but also by surface characteristics such as material type, age and condition (Odnevall Wallinder & Leygraf 1997; Wicke et al. 2014). Zinc pollution can originate from roads (abrasion of tyre rubber (Huber et al. 2010)) and from metal roofs (e.g. galvanised) through dissolution and degradation (Karlen et al. 2002; Charters et al. 2016). Few studies have reported untreated runoff quality in low intensity rainfall climates (typically <5 mm/hr) (Taebi & Droste 2004; Han et al. 2006; Charters et al. 2016) and it is uncertain how pollutant generation and wash off rates of different surfaces are affected by low intensity rainfall dynamics (e.g. less entrainment energy, increased surface contact time) compared with the more widely reported dynamics in high intensity catchments (e.g. Bannerman et al. 1996; Herngren et al. 2005).

Therefore, this research characterised untreated runoff quality from various impermeable surface types in a mixed land use catchment to highlight the significantly large zinc...
contribution from specific, yet commonly employed, surface types. The relationships derived between rainfall characteristics and runoff quality were then used to calibrate an event load pollutant model, Modelled Estimates of Discharges for Urban Stormwater Assessments (MEDUSA) (Charters et al. in review; Charters 2016a; Fraga et al. 2016). MEDUSA uses rainfall characteristics (pH, intensity, length of antecedent dry period and duration) and surface characteristics (material type, surface area and usage frequency (for roads and carparks)) to predict the amount of total suspended solids (TSS), zinc and copper being generated from individual surfaces in a single rain event. This model was applied to a low intensity rainfall catchment in Christchurch, New Zealand, to identify the spatial distribution of elevated zinc loads and thus identify zinc hotspots to be prioritised for improved stormwater management. The study’s findings have significant implications for both pollutant load modelling approaches and selection of targeted treatment methods for urban stormwater.

MATERIAL AND METHODS

Untreated runoff was sampled within an urban (Addington) catchment, in western Christchurch, New Zealand, which comprises 246 ha of mixed industrial, commercial, and residential activities (Figure 1). Runoff (largely untreated) generated in the catchment is collected via piped stormwater networks and discharged at multiple points into a stream named the Addington Brook. The stream rises fast during rain events, responding rapidly to the catchment runoff, and has elevated heavy metals, particularly during stormflow conditions (Stevenson & Margetts 2015). First flush (FF) and steady state (SS) grab samples of untreated runoff were collected during nine storm events between mid-September (spring) and mid-December (summer) 2015. Seven different impermeable surface types in the catchment were sampled: a weathered unpainted galvanised roof (industrial site), a new unpainted galvanised roof (commercial site), three carparks (two on industrial sites with heavy vehicle traffic (i.e. trucks), one on a commercial site) and two roadside sumps (one with 40,700 annual average daily traffic (AADT) and significant heavy vehicle traffic; one with 19,200 AADT and limited heavy vehicle traffic) (Figure 1). All water samples were analysed by an accredited laboratory for total and dissolved zinc (APHA Method 3125B). Rainfall characteristics were recorded for each sampled event and included rainfall pH, rainfall intensity (average and peak 5-minute), length of antecedent dry period, duration and total depth. Meteorological data were taken from the nearest National Institute of Water and Atmosphere’s (NIWA) Weather Station (Kyle Street), located 500 m north of the Addington catchment boundary.

Zinc loads per storm event were derived from water quality FF and SS concentrations and represented as a per area basis. The transition between FF to SS occurred as an approximate linear decay over an assumed time of 45 minutes, which was based on the observed transition time from extensive intra-event sampling in the Okeover catchment 2 km away (Charters 2016a). Loads derived from the observed concentrations (hereafter, the observed loads) were then compared against MEDUSA model predicted loads to assess the model predictive performance.

The MEDUSA model assumes that the rate at which the material is washed from a surface is proportional to the amount of material built up on the surface at the start of a rain event and that the rate can be described by an exponential equation (Sartor et al. 1974; Barrett et al. 1998; Egodawattha et al. 2007). A sensitivity analysis has previously been applied to the model framework to identify the critical parameters that influence pollutant build-up and wash-off processes (Fraga et al. 2016). Such sensitivity analyses help to prioritise monitoring for local calibration data. For zinc predictions, the model was found to be most sensitive to initial zinc concentrations. Therefore, care was taken in this sampling programme to characterise the FF concentrations to inform the model calibration.

Model predictive performance was measured using the Nash-Sutcliffe Model Efficiency (NSE) statistic. The NSE was developed for assessing hydrological models (Nash & Sutcliffe 1970), but has also been employed for modelling sediment and nutrient loadings (Moriasi et al. 2007). It describes the predictive accuracy of the model in comparison to the observed data. The NSE is defined as:

\[ E = 1 - \frac{\sum_{j=1}^{J} (x_o^j - x_m^j)^2}{\sum_{j=1}^{J} (x_o^j - \bar{x_o})^2} \]  

where \( \bar{x_o} \) is the mean of the observed pollutant loads, \( x_m^j \) is the modelled load and \( x_o^j \) is the observed load for rain event \( j \). An efficiency, \( E \), of 1 indicates a perfect fit between the modelled and observed loads, an efficiency of \( 0 < E < 1 \) indicates the model is a better predictor than the observed mean, \( E = 0 \) indicates the model is only as accurate as the observed mean, while \( E < 0 \) indicates the observed mean is a better predictor than the model. Modelled and observed loads were log-transformed before the NSE was applied to reduce the influence of any peak events which could increase the sensitivity.
of NSE to systematic over- or under- prediction (Krause et al. 2005).

RESULTS AND DISCUSSION

Sampled event characteristics

The sampling period from mid-September to mid-December 2015 was unusually dry, with monthly rainfalls in October and November at 23% and 63%, respectively, of their average monthly rainfall (NIWA 2015a, 2015b), although September and December had more typical rainfall (NIWA 2015c). Nevertheless, nine events were sampled (Table 1). Due to sampling logistics, not all surfaces could be sampled for every event; however, all seven sites were sampled during Events 5, 7, 8 and 9. All sampled events were within the 50% annual exceedance probability for a rainfall event in the catchment, as predicted by the High Intensity Rainfall Design System Version 3 (HIRDS,V3) (NIWA 2011).

Untreated runoff quality

The two galvanised roofs produced substantially more zinc than any of the other surfaces (Table 2), with FF concentrations from the old galvanised roof producing up to two orders of magnitude or higher zinc concentrations that exceed values reported elsewhere in literature (Good 1993; Göbel et al. 2007; Schriewer et al. 2008) (Figure 2). This suggests that the contribution of zinc to urban runoff from such roof surfaces may have been previously underestimated. SS zinc concentrations from the two sampled roofs were also elevated, although typically they were an order of magnitude lower than the FF concentrations. The sampled road runoff was of similar quality to what has been reported elsewhere both internationally and within New Zealand. This implies that successful strategies for treating road runoff applied elsewhere are directly relevant to the Addington catchment. Zinc concentrations in carpark runoff are not clearly reported in literature. This study’s results found that zinc concentrations from a standard...
industrial carpark surface are within the range from the more commonly studied road surfaces. However, both the commercial carpark and the industrial carpark with slow-moving manoeuvring heavy vehicles were found to have lower zinc concentrations, albeit still within the range of road runoff concentrations reported in literature.

Almost all the zinc from the galvanised roofs was in dissolved form (Figure 3), enhancing its bioavailability within receiving water ecosystems. These data confirm that the key mechanism for heavy metal generation from roofs is direct dissolution of the roof material, enhanced and sustained by the exposure and breakdown of the galvanising layer through weathering. Since dissolved zinc is more challenging to remove from stormwater, source control is the optimum solution for preventing elevated zinc levels reaching urban waterways. Replacement of weathered roofing materials would therefore be an effective measure for reducing the amount of zinc entering urban waterways.

**Model calibration and predictive performance**

The calibrated MEDUSA model generally showed a good fit to the measured (observed) data across a wide range of zinc loads (Figure 4). The model produced high (≥0.85) NSE values for total zinc (TZn), with the exceptions of the

#### Table 1 | Rainfall event characteristics for each sampled event (September to December 2015)

<table>
<thead>
<tr>
<th>Event no.</th>
<th>Start date</th>
<th>Rainfall pH (S.U.)</th>
<th>Average intensity (mm/hr)</th>
<th>Peak 5-min intensity (mm/hr)</th>
<th>ADP (days)</th>
<th>Duration (hrs)</th>
<th>Depth (mm)</th>
<th>Depth of preceding event (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10 Sep</td>
<td>6.98</td>
<td>1.82</td>
<td>9.36</td>
<td>4.49</td>
<td>4.6</td>
<td>8.34</td>
<td>0.32</td>
</tr>
<tr>
<td>2</td>
<td>18 Sep</td>
<td>6.20</td>
<td>0.86</td>
<td>2.16</td>
<td>1.50</td>
<td>0.8</td>
<td>0.72</td>
<td>0.50</td>
</tr>
<tr>
<td>3</td>
<td>22 Sep</td>
<td>6.46</td>
<td>0.86</td>
<td>5.28</td>
<td>1.10</td>
<td>19.0</td>
<td>16.26</td>
<td>0.50</td>
</tr>
<tr>
<td>4</td>
<td>22 Oct</td>
<td>6.52</td>
<td>0.45</td>
<td>0.84</td>
<td>3.95</td>
<td>0.7</td>
<td>0.30</td>
<td>1.10</td>
</tr>
<tr>
<td>5</td>
<td>28 Oct</td>
<td>6.67</td>
<td>0.97</td>
<td>4.20</td>
<td>6.15</td>
<td>4.9</td>
<td>4.79</td>
<td>0.30</td>
</tr>
<tr>
<td>6</td>
<td>3 Nov</td>
<td>6.71</td>
<td>0.35</td>
<td>5.78</td>
<td>5.78</td>
<td>0.9</td>
<td>0.32</td>
<td>2.01</td>
</tr>
<tr>
<td>7</td>
<td>11 Nov</td>
<td>6.82</td>
<td>0.51</td>
<td>5.64</td>
<td>3.19</td>
<td>18.5</td>
<td>9.40</td>
<td>0.60</td>
</tr>
<tr>
<td>8</td>
<td>6 Dec</td>
<td>5.67</td>
<td>0.20</td>
<td>0.96</td>
<td>2.16</td>
<td>6.4</td>
<td>1.26</td>
<td>1.40</td>
</tr>
<tr>
<td>9</td>
<td>13 Dec</td>
<td>5.69</td>
<td>3.87</td>
<td>31.56</td>
<td>5.65</td>
<td>3.3</td>
<td>12.90</td>
<td>2.20</td>
</tr>
<tr>
<td><strong>Median</strong></td>
<td></td>
<td><strong>6.52</strong></td>
<td><strong>0.86</strong></td>
<td><strong>4.20</strong></td>
<td><strong>3.95</strong></td>
<td><strong>4.6</strong></td>
<td><strong>4.79</strong></td>
<td><strong>0.60</strong></td>
</tr>
<tr>
<td><strong>Minimum</strong></td>
<td></td>
<td><strong>5.67</strong></td>
<td><strong>0.20</strong></td>
<td><strong>0.84</strong></td>
<td><strong>1.10</strong></td>
<td><strong>0.7</strong></td>
<td><strong>0.30</strong></td>
<td><strong>0.30</strong></td>
</tr>
<tr>
<td><strong>Maximum</strong></td>
<td></td>
<td><strong>6.98</strong></td>
<td><strong>3.87</strong></td>
<td><strong>31.56</strong></td>
<td><strong>6.15</strong></td>
<td><strong>19.0</strong></td>
<td><strong>16.26</strong></td>
<td><strong>2.20</strong></td>
</tr>
</tbody>
</table>

ADP, antecedent dry period.

#### Table 2 | FF and SS zinc concentrations from the seven sampled surfaces

<table>
<thead>
<tr>
<th>Sampled surface</th>
<th>Total zinc (μg/L)</th>
<th>Dissolved zinc (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FF</td>
<td>SS</td>
</tr>
<tr>
<td>Roof (Old unpainted galvanised)</td>
<td>32,338 (11,700–56,000)</td>
<td>5,920 (2,400–8,700)</td>
</tr>
<tr>
<td>Roof (New unpainted galvanised)</td>
<td>4,782 (410–12,600)</td>
<td>1,085 (940–1,120)</td>
</tr>
<tr>
<td>Road (Major arterial)</td>
<td>1,480 (950–1,950)</td>
<td>738 (490–1,080)</td>
</tr>
<tr>
<td>Road (Minor arterial)</td>
<td>1,393 (520–2,400)</td>
<td>407 (137–700)</td>
</tr>
<tr>
<td>Carpark (Commercial)</td>
<td>822 (190–1,760)</td>
<td>151 (108–200)</td>
</tr>
<tr>
<td>Carpark (Industrial Std.)a</td>
<td>1,584 (490–2,600)</td>
<td>425 (130–850)</td>
</tr>
<tr>
<td>Carpark (Industrial Mnv.)b</td>
<td>800 (320–1,550)</td>
<td>198 (98–320)</td>
</tr>
</tbody>
</table>

Concentrations are median values with ranges in parenthesis.

aIndustrial Standard (Std.) – private vehicle parking and heavy vehicles driving through carpark to adjacent yard.
bIndustrial Manoeuvring (Mnv.) – frequent heavy vehicles manoeuvring (stops, starts) within carpark.
industrial (mnv.) carpark (NSE of 0.69) and the minor arterial road (NSE of 0.28). The model also had high NSE values (≥0.74) for dissolved zinc from the roof and commercial carpark surfaces.

Application of calibrated model to the Addington catchment

The calibrated MEDUSA model was then applied to each road, roof and carpark surface (as delineated using GIS and shown in Figure 1) within the Addington catchment for 88 rainfall events of the year 2012 - a year when rainfall pH, intensity, ADD and duration data were readily available and represented typical climatic characteristics for the area. The model results summarised in Figure 5 show the relative contributions of zinc for each impermeable surface category within the catchment. Zinc derived from galvanised roofs (which constitute more than 90% of the roof area) is identified as a key surface that should be prioritised for stormwater management (Figure 5). Spatial
mapping of the model-predicted loads enables specific ‘hot-spot’ surfaces (even at the individual level) to be graphically represented and targeted for zinc load reductions (Figure 6). The data highlighted that four large commercial roof areas are predicted to contribute on average more than 295 g of zinc per storm event (12% of total zinc for roofs). Identification of individual impermeable (and other) surfaces provides an opportunity for engagement with individual property owners and education and development of appropriate pollution prevention programmes at tangible levels within a catchment to effect positive change for the wider catchment.

CONCLUSIONS

Zinc concentration yields from old unpainted galvanised roof surfaces under low intensity rainfall can be more than 20 times larger than from road surfaces for FF and more than eight times larger for SS conditions. Zinc yields from new unpainted galvanised roof were five to seven times lower than the old roofs, but were still significantly higher than roads or carpark yields. Treatment of zinc is challenging because zinc yields from carparks, roads, and roofs are over 35, 50, and 90% in dissolved format, respectively.
This research demonstrates that pollutant load modelling based on individual surfaces and specific rainfall events is very valuable for effectively predicting diffuse zinc (and potentially other key pollutants) in low intensity rainfall climates. The runoff quality characterisation and MEDUSA model application have produced clear evidence for where (and how) to target zinc hotspots for improved stormwater management in this catchment.

Developing interim near-source zinc removal options that can be readily implemented is a priority while longer term changes, such as roof material policies and roof replacements, will ultimately reduce the generation of such pollution in the future.

Application of this approach to other common urban runoff pollutants (e.g. copper, total suspended solids) is being concurrently undertaken and will help inform local and regional stormwater management directives in older urban catchments.

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