Science of the Total Environment 755 (2021) 142470

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

The influence of urban surface type and characteristics on runoff water quality

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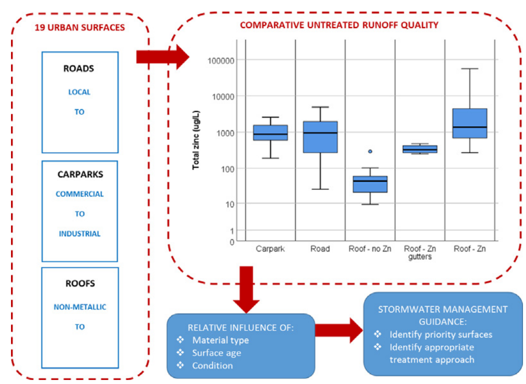
HIGHLIGHTS

- Untreated runoff compared from 19 urban surfaces under the same climatic conditions.
- Dataset compares TSS, zinc and copper across road, carpark and roof runoff.
- Surface type drives runoff quality regardless of local differences in land use.
- New, uncoated metal roofs leach more zinc than old, coated roofs.
- Coated roofs leach zinc levels comparable to roads, but primarily in dissolved form.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 4 June 2020
Received in revised form 22 August 2020
Accepted 16 September 2020
Available online 24 September 2020

Editor: Ashantha Goonetilleke

Keywords:
Impermeable surfaces
Total suspended solids
Zinc
Copper
Particulate metals
Dissolved metals

ABSTRACT

Untreated runoff was collected over multiple rain events from 19 impermeable urban surfaces, including nine roofs, six roads and four carparks, to quantify the differences in water quality due to surface type, age, condition and location. All 19 sites were exposed to the same climatic conditions. Samples were analysed for key urban pollutants of concern, namely total suspended solids and total and dissolved copper and zinc. Results showed uncoated zinc-based roofs produced zinc concentrations (up to 55 mg/L) several orders of magnitude higher than receiving environment water quality guidelines in New Zealand, of which the vast majority was in dissolved form. Even non-metallic roofs with zinc-based guttering produced zinc concentrations over ten times higher than the same roof material without zinc-based guttering. Older zinc-based roofs had approximately five times higher zinc concentrations, demonstrating a substantial age effect on the untreated runoff quality. Similarly, copper roofs produced more than an order of magnitude higher copper concentrations (up to 7.8 mg/L) above the next highest copper-producing surfaces: higher trafficked roads and carparks. Regardless of traffic volume or function, all roads and carparks produced high TSS concentrations. Dissolved metal concentrations were high across the dataset confirming that metal partitioning is an important consideration for effective pollutant control as different removal processes need to be used for dissolved versus particulate metals. This dataset provides an important benchmark of untreated runoff quality across different impermeable surface types within the same geographical area and clearly shows the influence of surface characteristics on water quality runoff regardless of the local differences in land use. These findings provide valuable guidance to stormwater managers in identifying priority surfaces and selection of appropriate treatment strategies for effective stormwater management for total suspended solids, zinc and copper.

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https://doi.org/10.1016/j.scitotenv.2020.142470
0048-9697/

1. Introduction

The contribution of pollutants such as sediment and heavy metals to urban waterways from untreated impermeable surface runoff is a significant global issue, due to the potential ecological and public health implications (Ancion et al., 2010; Gaffield et al., 2003). Sediment is considered a key stressor in the urban aquatic environment (Marshall et al., 2010), with its combination of suspended effects (e.g. fish gill clogging, reduced clarity and light penetration for aquatic plant photosynthesis) and deposited effects (e.g. waterway bed smothering, loss of benthic habitat). Heavy metals cause both acute and chronic toxic effects on aquatic species, and also pose a public health risk from the bioaccumulation of metals in fish and shellfish gathered for human consumption (Birch and Apostolatos, 2013). Better runoff quality management is needed to address these issues, but this requires a good understanding of what, where and how pollutants are being contributed from the runoff to the urban waterways. The typical urban catchment is a diverse array of impermeable surface types, and a clear understanding of the relative pollutant contributions from each surface type within a catchment is needed to enable prioritisation and selection of appropriate management approaches.

Impermeable surface material, age and condition are known to be key drivers of urban runoff quality (Göbel et al., 2007; Wicke et al., 2014). Condition can be described for different urban surface types as follows: for roofs, it refers to the level of maintenance and presence of a coating system over the base roof material; for roads, it refers to the traffic intensity; and for carparks, it encapsulates the traffic type (e.g. private cars or heavy vehicles). Likewise, rainfall characteristics are also key drivers of pollutant build-up and wash-off processes from urban impermeable surfaces (Liu et al., 2013). Previous studies have assessed untreated runoff quality from roofs, roads or carpark surfaces, but generally focused on only a few sites within the same catchment (Auckland Regional Council, 2010; Charters et al., 2016; Shajib et al., 2019), or only one type of surface (e.g. road runoff: Hilliges et al. (2017), Kayhanian et al. (2012); roof runoff: Davis et al. (2001), Farreny et al. (2011), Pennington and Webster-Brown (2008)). Nevertheless, due to the variation in rainfall characteristics in different climatic areas, comparisons of surfaces' runoff quality may not be valid, so it can be difficult to develop an accurate understanding of pollutant loads within a catchment from the diversity of urban surface types. Datasets of a wide range of common impermeable surface types within a single climatic location can help provide more accuracy of the relative water quality signatures from different surfaces as a function of their material, age and condition.

As treatment technologies are designed to remove pollutants based on specific processes, it is important to characterise the pollutant form to ensure an appropriate treatment solution is selected. This can be especially important for pollutants such as heavy metals, which exist in both dissolved (i.e. < 0.45 μm) and particulate forms. Relative partitioning of metals in runoff has been found to vary across different urban surfaces. For example, precipitation processes, and to a lesser degree, sorption processes (whereby dissolved metals are transformed to particulate form) drive metals partitioning in road runoff (Djukić et al., 2016; Shajib et al., 2019), leading to lower percentage of dissolved metals than in roof runoff, where the majority of metals are in dissolved form (Charters et al., 2017; Hedberg et al., 2014). However, the majority of untreated runoff quality studies do not report on relative partitioning (i.e. they provide total metals concentrations only). Therefore having comparative partitioning data from a wide range of urban surfaces is valuable to guide the selection of appropriate treatment approaches.

This paper addresses the need for surface-specific runoff quality data within a single climatic location to better understand the different runoff quality signatures produced from various impermeable surfaces. The study encompasses untreated runoff quality from 19 surfaces during three sampling programmes in different catchments within Christchurch, New Zealand, and assesses the relative influence of impermeable surface type, age, condition and location. This information supports the prioritisation of managing polluting surfaces and in the selection of effective treatment systems to manage runoff from those common urban surfaces.

2. Methodology

2.1. Sampling collection and analysis

Untreated runoff samples were collected from 19 different impermeable surfaces across three catchments within Christchurch, New Zealand (Fig. 1) for sediment and heavy metal analysis. This included nine roofs, six roads and four carparks (Supplementary Information: Section A). The number of events sampled for each surface type ranged from 4 to 14 with an average of 7 events.

2.1.1. Okeover (OKE) sampling programme, 2013–2015

Four different surfaces were sampled over 25 rain events in the Okeover catchment, between December 2013 and March 2015. The selected surfaces were a concrete tile roof (a common residential roofing material), an uncoated copper roof (used primarily as an architectural material), a painted galvanized roof (a common industrial, commercial and residential roofing material) and a coarse asphalt road (most common road surface in Christchurch city). Further details of the sampled surfaces' characteristics are found in Charters et al. (2016).

Time-series samples were collected throughout the 25 rain events using a combination of grab sampling and automatic sampling (ISCO 6712C Compact Portable Automatic Sampler). Automatic sampling was used for the three roof surfaces, while grab sampling was used for the road surface. These samples were typically taken at 0, 15, 30, 60, 120 and 180 min from start of runoff (note for some events a sampling issue may have meant not all samples were taken). This intra-event sampling provided a clear indication of the transition period from initial high concentrations to consistently lower concentrations in the later stages of the rain event. First flush (FF) data was taken from the first sample from each rain event and second stage (SS) data was taken as the average of all samples after the transition period.

Samples were analysed for TSS (Method 2540D, American Public Health Association (2005)), total copper (TCu) and total zinc (TZn) (Methods 3030E, 3030B and 3125B, American Public Health Association (2005)), and dissolved copper (DCu) and dissolved zinc (DZn) concentrations (Methods 3030B and 3125B, American Public Health Association (2005)). All collected samples were held at 4 °C until analysis. For the Okeover programme, where analysis was undertaken at the University of Canterbury's Environmental Engineering Laboratory, metals filtration (for dissolved) and preservation with nitric acid at pH <2 was undertaken within 6 h of sample collection. Metals analysis using ICP-MS was then done within 6 months of preservation. TSS analysis was undertaken within 24 h of sample collection. Duplicates were taken for at least 10% of samples for each rain event and surface. Method blanks were also analysed for each rain event and analyte.

2.1.2. Addington (ADD) sampling programme, 2015

Seven surfaces were sampled over nine rain events in the Addington catchment, between September and December 2015. These surfaces were selected to expand the dataset of untreated runoff quality previously sampled in the Okeover catchment. Accordingly, the Addington surfaces comprised three carpark sumps: commercial (with low heavy traffic), a standard industrial carpark (heavy vehicles driving over the surface) and an industrial manoeuvring carpark (heavy vehicles braking and turning across the surface); two roofs: both uncoated galvanized roofs, but one old and in poor visual condition and the other <1 year old; and two road sumps: one 'major arterial' road with 40,700 annual average daily traffic (AADT) and significant heavy vehicle traffic, and the other a 'minor arterial' road with 19,200 AADT and limited heavy

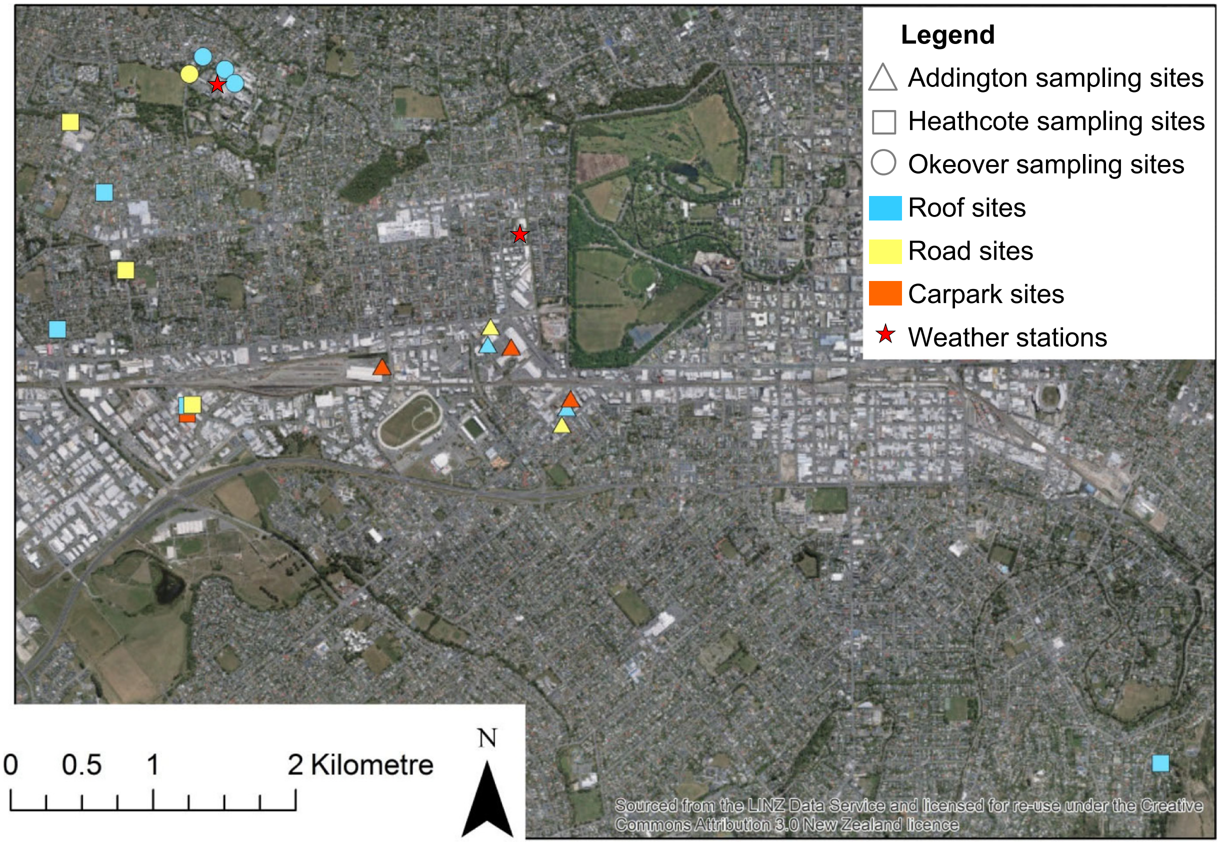

Fig. 1. Sampling site locations for the three sampling programmes.

vehicle traffic. Further details of the sampled surfaces' characteristics are found in Charters et al. (2017).

First flush (FF; defined for this programme as the first 1 L of runoff) was collected at each site using Thermo Scientific™ Nalgene™ Stormwater Sampler bottles. For carpark and road sites, they were deployed by suspending the bottles from the sump grate, in the corner of the sump where the initial runoff would flow in. For the roofs, the bottles were fitted within a Thermo Scientific™ Nalgene™ Stormwater Mounting Kit and fixed inline under the downpipe. Second stage (SS) samples (defined as a representative sample taken at least 1 h after first flush) were also taken at each site using grab sampling with 1 L HDPE bottles. The 1 h time delay before a second stage sample was taken was based on intensive intra-event untreated runoff sampling in the Okeover catchment, which identified that consistently lower concentrations were found compared to the start of the rain event, i.e. FF, after approximately 45 min of rainfall, for three roofs and one road surface (Charters et al., 2016). As runoff concentrations are dynamic throughout a rainfall event, second stage is intentionally not defined as 'steady state' for these reasons, but it considered representative of the relative magnitude of concentration found in the later stage of each rain event. Samples were held at 4 °C and delivered to an accredited lab within 24 h of collection and analysed for TSS, TCu, TZn, DCu and DZn (following standard APHA Methods as per the Okeover programme).

2.1.3. Heathcote (HCT) sampling programme, 2016

Eight surfaces were sampled over nine rain events in the Heathcote catchment, between July and November 2016. The aim was to capture comparative runoff quality from a mix of different surface types, as well as from some of the same surface types that had been sampled in the Okeover and Addington programmes. The selected surfaces were: one carpark sump (commercial); four roofs: a concrete roof (with galvanized guttering), a painted galvanized roof, and two coated zinc-based (Colorsteel®) roofs, one 22 years old, the other <1 year old; and three road sumps: one 'minor arterial' road with 14,300 AADT, one 'collector road with 6,600 AADT (limited heavy vehicles), and one 'local' road with 4200 AADT (limited heavy vehicles).

The same sampling method using first flush samplers and second stage grab sampling was followed as for the Addington programme. Likewise, samples were held at 4 °C and delivered to an accredited lab within 24 h of collection. They were analysed for TSS, TCu, TZn, DCu and DZn (following standard APHA Methods as per the previous Okeover and Addington programmes).

2.1.4. Comparative surface types across the three sampling programmes

Within the 19 sites, three replicate surface types were sampled: a painted galvanized roof and a collector road in both the Okeover and Heathcote programmes, and a commercial carpark in both the Addington and Heathcote programmes. This provided consistency of runoff quality from individual surfaces of the same surface type (and condition) in different geographical locations within the same climatic conditions in Christchurch. The sampling also enabled comparative pairs of new and old roof surfaces for two roof types: Colorsteel® and uncoated galvanized roofs.

2.2. Sampled event rainfall characteristics

Rainfall characteristics such as intensity and the length of the antecedent dry period are known to drive the build-up and wash-off of pollutants from impermeable surfaces (Kayhanian et al., 2003; Liu et al., 2013). Accordingly, each sampled event was described by its average rainfall intensity, rainfall pH, event duration, length of antecedent dry period and total rainfall depth (Supplementary Information: Section C). Rainfall was collected and measured for pH during every sampled event. For the Okeover data, rainfall data was sourced from a Campbell® weather station data at the University of Canterbury within

Table 1
Summary statistics for sampled event characteristics.

Catchment	Rainfall pH	Average intensity (mm/h)	Peak intensity (mm/h)[a]	Antecedent dry period (days)	Duration (hrs)	Depth (mm)	Depth of previous event (mm)
Median (and range) for each sampling programme							
Okeover (OKE)	5.96 (5.10–7.86)	1.39 (0.2–4.61)	4.32 (0.2–19.56)	3.75 (0.2–13.5)	3.5 (0.1–31.4)	2.2 (0.2–144.2)	1.2 (0.2–144.2)
Addington (ADD)	6.52 (5.67–6.98)	0.86 (0.2–3.87)	4.2 (0.84–31.56)	3.95 (1.1–6.15)	4.6 (0.7–19)	4.79 (0.3–16.3)	0.6 (0.3–2.2)
Heathcote (HCT)	6.57 (6.02–6.79)	0.49 (0.16–1.76)	2.48 (1.44–14.04)	2.22 (0.71–9.66)	8.8 (4–24.8)	7.0 (1.4–37.8)	0.9 (0.2–3.3)
Median (and range) for combined programmes							
All events	6.26 (5.10–7.86)	0.86 (0.2–4.61)	3.22 (0.2–31.56)	3.6 (0.2–13.5)	4.15 (0.1–31.4)	3.05 (0.2–144.2)	1.15 (0.2–144.2)

[a] Peak intensity based on 5 min data intervals (Okeover) or 15 min data intervals (Addington, Heathcote), depending on weather station used.

the Okeover catchment. For the Addington and Heathcote programmes, rainfall data was sourced from the National Institute of Water and Atmosphere's (NIWA) Kyle St Weather Station, 2.5 km north of the Addington catchment boundary (Fig. 1). Rainfall data was compared between the University of Canterbury station and the NIWA station (2.2. km apart) for the same Okeover sampling programme rain events. As little difference was found in rainfall depth and start and end of rain timing, it was considered appropriate to use the NIWA station data for the Heathcote and Addington sites. For both weather stations, adjacent rain events were considered separate events once there was no rainfall for at least 6 h. A minimum event depth of 0.2 mm was used, as the climate of Christchurch is of low rainfall intensity and runoff was observed from events of only 0.2 mm (particularly from smooth metal roofs).

Overall, a wide range of event characteristics was captured for each of the sampling programmes (Table 1). The sampled events for the Heathcote programme had lower intensities and antecedent dry days but greater duration and depth, compared to Addington and Okeover programmes. However, both the Addington and Heathcote programmes were of limited duration (4–5 months each). Therefore, the rainfall characteristics will differ between programmes as they reflect specific climate conditions over the period of sampling rather than a typical average across multiple seasons (compared to the Okeover's 16-month-long programme).

3. Results

3.1. Runoff quality variation by material type

3.1.1. Zinc

Uncoated galvanized roofs produced higher zinc concentrations than any other sampled surface (Fig. 2) (see also Supplementary Information: Section D for summary of all results). The uncoated galvanized roof sampled in the Addington catchment produced TZn concentrations up to 55 mg/L, where the regional receiving environment water quality limit for zinc is 15 μg/L (Environment Canterbury, 2019) (i.e. the untreated runoff contained TZn levels over 1000 times greater than the guidelines). First flush (FF) concentrations were substantially higher

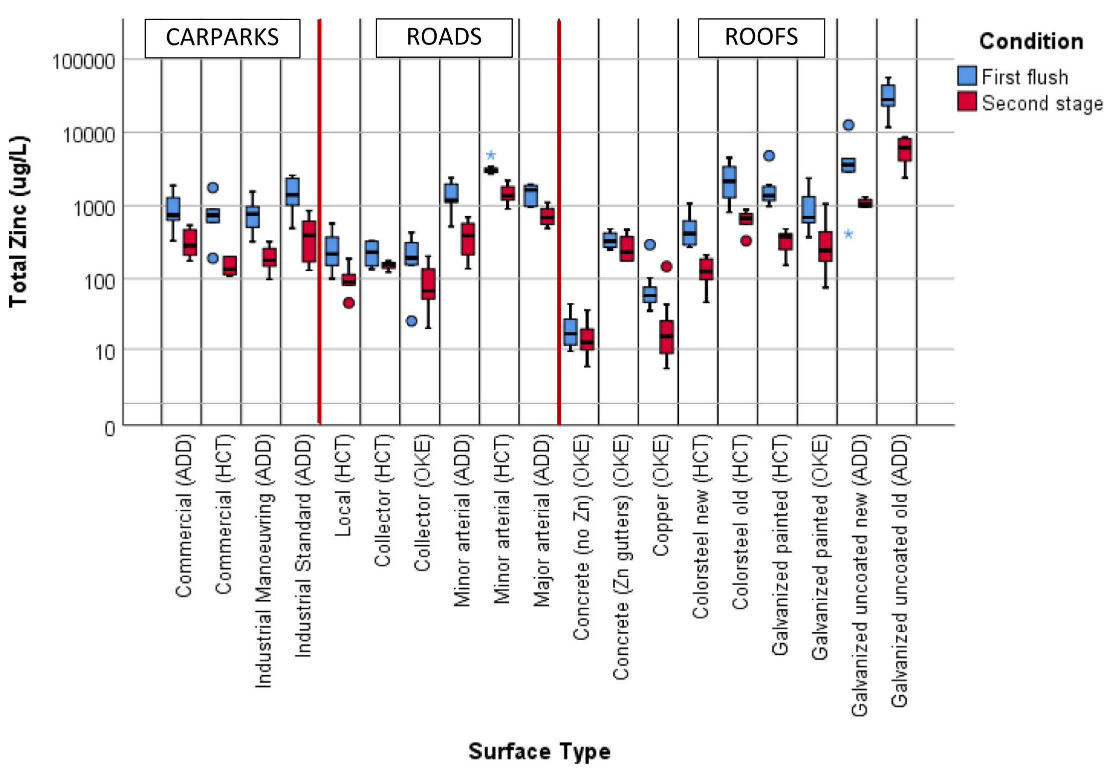

Fig. 2. Average total zinc concentrations at each sample site (○ denotes outlier ±1.5 x inter quartile range (IQR), * denotes outliers ±3 x IQR). Catchments are Addington (ADD), Heathcote (HCT) and Okeover (OKE).

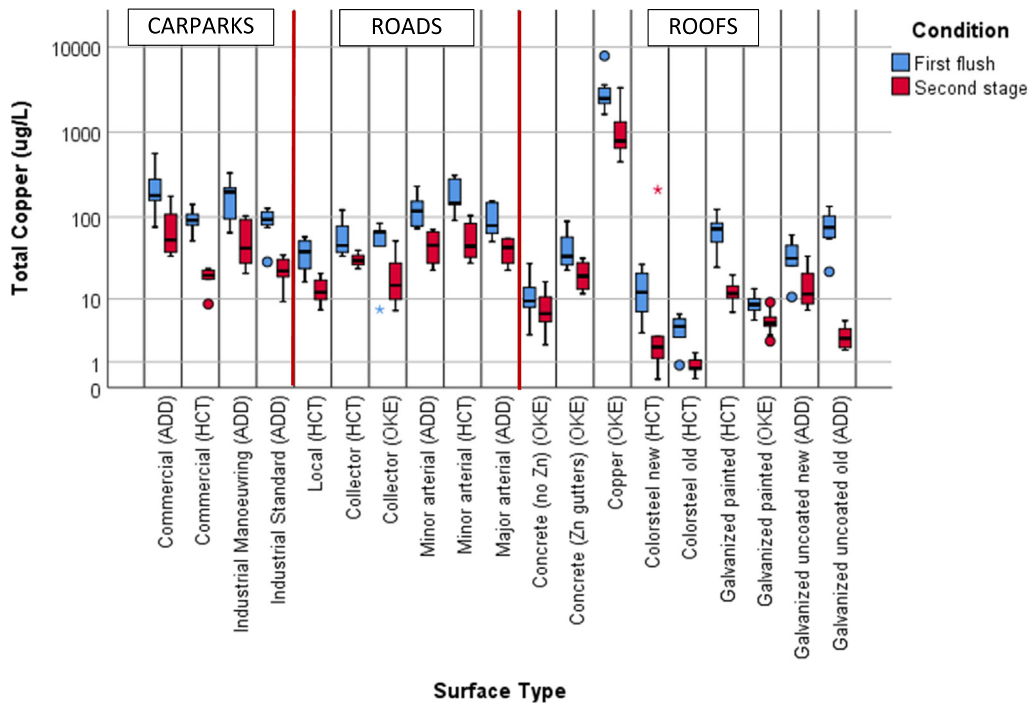

Fig. 3. Average total copper concentrations at each sample site (○ denotes outlier ±1.5 x inter quartile range (IQR), * denotes outliers ±3 x IQR). Catchments are Addington (ADD), Heathcote (HCT) and Okeover (OKE).

than second stage (SS) concentrations for all surfaces, except the two concrete roofs.

An assessment of zinc concentrations across roof material types shows substantial differences if the material is uncoated or coated, or new or old. The 22-year-old Colorsteel® 'old' roof had higher zinc concentrations than the new <1 year-old Colorsteel® roof (FF range of 810–4500 μg/L compared to 270–1070 μg/L). Likewise, the older (>25 years) uncoated galvanized roof (which was in poor weathered condition) had substantially higher zinc concentrations than the new uncoated galvanized roof (FF range of 11,700–56,000 μg/L compared to 410–12,600 μg/L). Nevertheless, the new galvanized roof still had zinc concentrations greater than those from painted (but not new) galvanized roofs (FF range of 410–12,600 μg/L compared to ranges of 980–4800 μg/L and 372–2369 μg/L for the Heathcote and Okeover painted galvanized roofs, respectively), demonstrating the effectiveness of providing a coating on galvanized zinc. Similarly, the older Colorsteel® roof produced higher zinc concentrations than the painted galvanized roofs whose paint coating looked to have more recent maintenance that the old Colorsteel® roof (Fig. 2). This all reinforces that roof condition (i.e. whether it is coated or has been well-maintained) and age are key influences on metals concentrations.

Comparison of the lowest-zinc-producing galvanized roof (i.e. the new Colorsteel® roof) with the inert concrete roof, revealed that the Colorsteel® roof still leached 20–30 times more zinc than an inert roof exposed only to atmospheric deposition of zinc (FF range of 270–1070 μg/L compared to 9–44 μg/L). Where some uncoated zinc guttering was present on an inert concrete roof, the zinc concentrations were over 10 times higher than the roof with no zinc materials (250–480 μg/L compared to 9–44 μg/L) and in a similar range to the painted galvanized roofs. These data highlight the effect of having even a proportion of the roof system in a zinc-based material (i.e. the main roof material was inert).

3.1.2. Copper

The copper roof produced the highest copper concentrations (regardless of whether FF or SS conditions) of all sampled surfaces (Fig. 3) and these were over an order of magnitude higher than the concentrations from next highest copper-contributing surfaces: carparks (both industrial and commercial) and higher trafficked roads. There was a clear distinction in copper concentrations based on traffic intensity, with higher concentrations seen from higher-trafficked roads (major and minor arterial) in comparison to the lower trafficked roads (collector and local roads). Again, FF concentrations were substantially higher than SS concentrations for all surfaces. These comparative results indicate that dissolution processes produce more copper (per volume) (e.g. from roof runoff) that particle entrainment or wash off processes (e.g. from road runoff).

3.1.3. Total suspended solids

Roads and carpark surfaces, regardless of traffic intensity or vehicle type, all produced higher TSS loads than the roof surfaces, with the sole exceptions of the two 'old' roofs: the galvanized uncoated roof (>25 years old) and the copper roof (approximately 40 years old) (Fig. 4). These two roofs showed high FF TSS concentrations but much lower SS concentrations. Carparks showed a greater variability in TSS concentration than road surfaces.

There was a distinct difference between FF and SS concentrations at every sampled site: FF was substantially higher than SS concentrations and also tended to show greater variability than SS. The surfaces with the largest difference between average FF and average SS TSS concentrations were the old uncoated galvanized roof (SS average 0.7% of FF average), the copper roof (SS average 3% of FF average), the commercial carpark in Addington (SS average 11% of FF average), and the industrial manoeuvring carpark and new Colorsteel® roof (both with SS average 15% of FF average). All surfaces had a SS average of less than 45% of the FF average, with the sole exception of the concrete roof with zinc guttering (SS average 51% of FF average).

Industrial carparks produced more TSS than commercial carparks. Higher trafficked roads typically produced proportionally higher TSS than lower trafficked roads. The higher FF results indicate substantial contributions of TSS from dry weather deposition and build up (either via direct deposition on the surfaces or via atmospheric deposition).

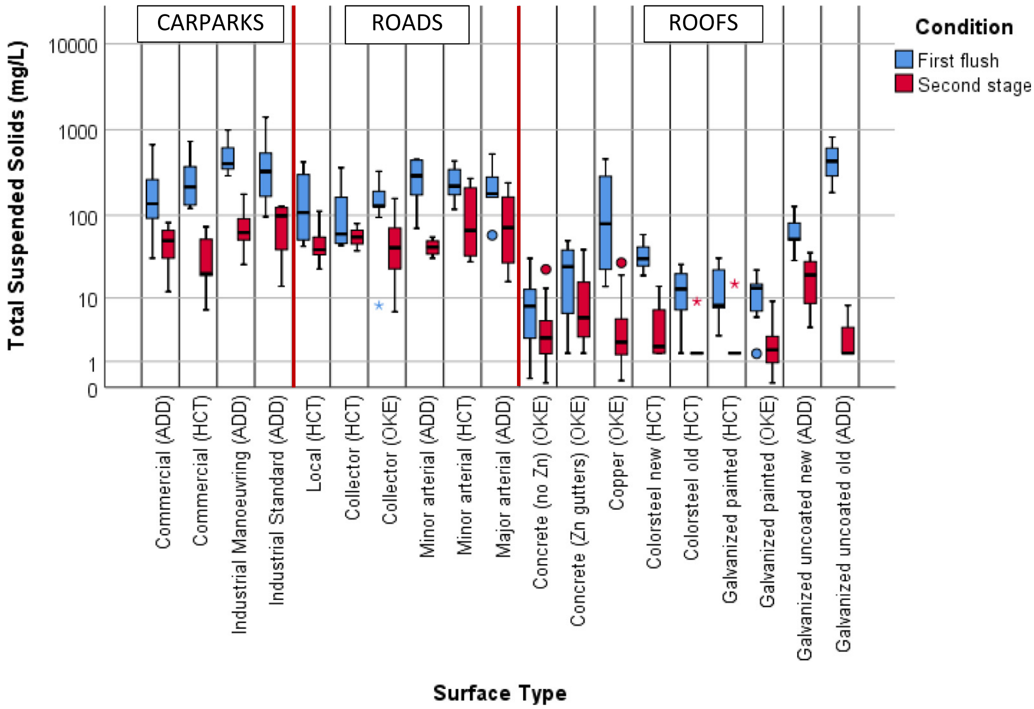

Fig. 4. Average TSS concentrations at each sample site (○ denotes outlier ±1.5 x inter quartile range (IQR), * denotes outliers ±3 x IQR). Catchments are Addington (ADD), Heathcote (HCT) and Okeover (OKE).

3.2. Runoff quality variation for the same surface type in different locations (spatial effects)

The TZn and TSS concentrations for the two painted galvanized roofs were of similar scale for both FF and SS (Table 2). However, a substantial difference in copper concentration was seen between the roofs, despite them being the same material type (and condition).

The two collector roads had comparable TSS, TZn and TCu FF concentrations. The difference between the two commercial carpark sites were more pronounced, with a good similarity for TSS and FF TZn concentrations, but a substantial difference in TCu concentrations.

3.3. Runoff quality variation for the same surface type of different condition (age effects)

There were two pairs of roofs of the same material type but of different age (i.e. new and old) (Table 2). Nearly five times more zinc (both total and dissolved) was found in the runoff from the older 22-year-old Colorsteel® roof compared to the <1-year-old new Colorsteel® roof in the Heathcote catchment (Table 2). Five to six times more zinc (both total and dissolved) was found in the runoff from the >25-year-old uncoated galvanized roof than the <1-year-old uncoated galvanized roof runoff in the Addington catchment. For TSS and copper

Table 2
Comparative average pollutant concentrations for paired surfaces types of different location or age, grouped by first flush (FF) and second stage (SS) samples.

Surface type	Program		Condition	TZn (ug/L)	DZn (ug/L)	TCu (ug/L)	DCu (ug/L)	TSS (mg/L)
Paired surfaces – different locations								
Roof – painted galvanized	Heathcote		FF	1879	1827	70	46	15
			SS	342	337	13	7	4
	Okeover		FF	1005	993	9	4	12
			SS	335	332	5	2	2
Road – collector	Heathcote		FF	237	134	62	42	132
			SS	152	91	31	20	58
	Okeover		FF	222	60	54	17	155
			SS	86	46	20	5	49
Carpark – commercial	Heathcote		FF	977	463	248	60	229
			SS	328	149	77	19	49
	Addington		FF	822	348	94	42	305
			SS	151	96	19	11	34
Paired surfaces – different ages								
Roof – Colorsteel®	Heathcote	New	FF	520	480	14	5	34
			SS	133	98	43	1	5
		Old	FF	2415	2330	4	2	13
			SS	644	640	1	0.5	3
Roof– Uncoated galvanized	Addington	New	FF	4782	4442	35	12	68
			SS	1085	1018	16	5	20
		Old	FF	32,338	28,250	78	7	458
			SS	5920	5900	3	1	3

concentrations (likely contributed by atmospheric deposition), there was no relationship between roof age and pollutant concentrations for either the Colorsteel® or uncoated galvanized roofs.

Both pairs of roofs are in the same catchment, so any spatial effects such as rainfall are minimised in the comparison. An analysis of the events' rainfall characteristics for each paired surface confirmed that ADD, average event intensity and duration were all very similar between the new and old roof pairs (Supplementary Information Table D1).

3.4. Inter-event variation in runoff quality

Many surfaces had substantial variation in FF or SS concentrations across the sampled rain events (ranges shown in Fig. 2 to Fig. 4), confirming rainfall characteristics are also driving the pollutant generation (e.g. length of antecedent dry period for UV and wind weathering) and mobilization (e.g. entrainment of particles, contact time for dissolution) processes, along with surface material type and condition. The surfaces with the greatest inter-event variation in pollutant concentration generally correlated to the surface with the highest concentration for any given water quality parameter. For instance, the most substantial variation in TZn across multiple sampled rain events was seen in the old uncoated galvanized roof. TCu concentration varied substantially only for the copper roof, although some moderate variation was seen in the minor arterial roads, industrial manoeuvring carpark and one commercial carpark. Conversely, TSS from carparks and roads had much greater variation than any roof surface, with the exception of the two old roofs (uncoated galvanized and copper).

3.5. Metals partitioning

Understanding the relative proportion of metals partitioned into particulate or dissolved forms is important to ensure an appropriate treatment solution is selected, as the partitioning forms respond differently to pollutant removal processes (Hilliges et al., 2017). Zinc partitioning was strongly biased towards dissolved forms for the zinc-based roofs (all Zn concentrations were >80% dissolved, Fig. 5), as could be expected due to dissolution processes being the main zinc generation process on those surfaces (Förster, 1999; Sage et al., 2016). A proportion of metals are assumed to be removed by proxy through sediment removal processes, due to the affinity of metal to particles (Kayhanian et al., 2012; Maniquiz-Redillas and Kim, 2016). However, because this data shows that zinc is preferentially in the dissolved rather than particulate form, minimal amounts of zinc are removed with

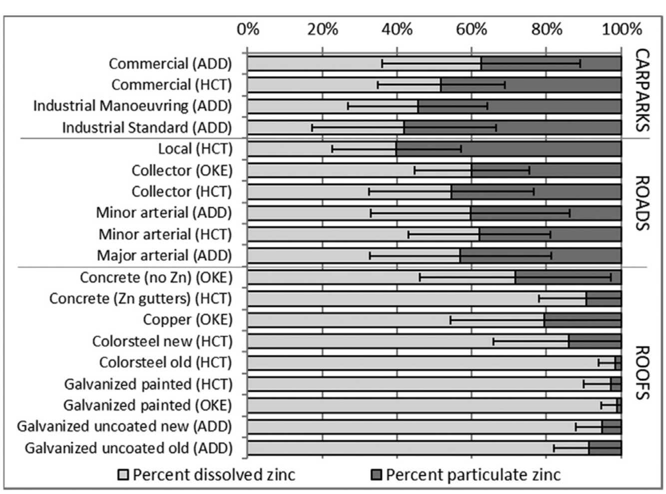

Fig. 5. Average dissolved and particulate percentage of zinc for each site. Error bars show ±1 standard deviation for percentage dissolved zinc. Catchments are Addington (ADD), Heathcote (HCT) and Okeover (OKE).

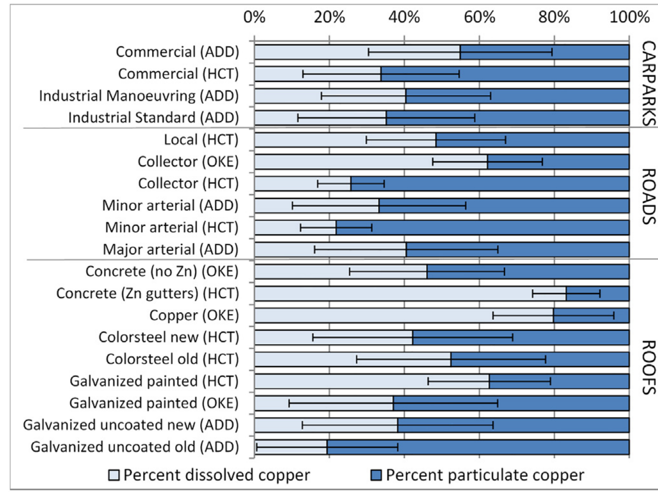

Fig. 6. Average dissolved and particulate percentage of copper for each site. Error bars show ±1 standard deviation for percentage dissolved copper. Catchments are Addington (ADD), Heathcote (HCT) and Okeover (OKE).

sediments. This is further confirmed by the highly variable relationship between TSS and dissolved zinc across the surface types. Even for the road and carpark surfaces, zinc was between 40 and 60% dissolved on average. Zinc partitioning between each paired surface type (commercial carpark, collector road and galvanized painted roof) was found to be very similar.

Copper partitioning varied widely between road, carpark and roof sites (Fig. 6), with a substantial spread also within the different roof categories (19–83%). Roads had a moderate range (21–62%), while carparks had the smallest range (34–55%) but only a small number of carpark sites were sampled in comparison to the other surfaces. Most surfaces have dissolved copper ranges between 40 and 60% (7 out of 19) or 30–70% (14 out of 19). These data highlight that careful consideration needs to be given in selecting treatment systems for managing copper as dissolved and particulate forms require different treatment processes for effective treatment. There was a substantial difference in the copper partitioning between each paired surface type (commercial carpark, collector road and galvanized painted roof).

4. Discussion

4.1. Influence of material type and condition on pollutant concentrations

Material type and its condition (age) were seen to be major drivers of untreated runoff quality from impermeable surfaces in urban catchments. Older (>20 years old), more weathered roof surfaces had five to six times higher Zn concentrations than new roofs (with higher FF TSS as further evidence of weathering). However, painted galvanized roofs had FF Zn concentrations three to five times lower than the new uncoated galvanized roof; even though the uncoated roof was brand new, the lack of coating meant it leached more Zn than the older painted galvanized roofs. This reinforces the importance of adequate maintenance (such as a regular painting programme) for metallic roofs or selecting pre-coated materials to minimise the amount of metal pollutants generated in roof runoff. This applies not only to the main roof material, but also to associated gutters and downpipes, as high Zn concentrations were observed where uncoated zinc-based guttering was present on the concrete (non-metallic) roofs. Even a small amount of exposed galvanizing leached Zn concentrations equivalent to that of a full roof of coated zinc-based material. Furthermore, the new Colorsteel® roof (factory coated) still produced Zn concentrations 25 times higher than the inert concrete roof (that also had inert guttering).

While the focus for zinc-based roofs was to quantify the magnitude of zinc concentrations, the comparative concentrations of TSS and copper for the paired new and old roof surfaces (Colorsteel® and uncoated galvanized; Table 2) indicate an influence of factors beyond rainfall characteristics and surface material type driving the generation and subsequent mobilization of these pollutants. As the sampled zinc-based roof surfaces do not contain any copper, the elevated copper concentrations measured were attributed to atmospheric deposition, which can account for 10–100% of stormwater export loads (Müller et al., 2019). While some studies have found an increase in atmospherically deposited copper where traffic congestion is present (Davis and Birch, 2011; Gunawardena et al., 2013), a local Christchurch, New Zealand, study found relatively homogeneous copper loadings from atmospheric deposition across three sites of varying traffic characteristics (Murphy et al., 2014).

For pollutants in road and carpark runoff, traffic conditions such as the presence of heavy vehicles (with larger brake pads as a source of copper and increased tyre wear as a source of zinc (Huber et al., 2016, Hwang et al., 2016)), braking and manoeuvring associated with intersections and traffic volume are also important factors (Brezonik and Stadelmann, 2002; Gunawardena et al., 2015). Accordingly, higher trafficked roads and all the carparks (i.e. frequent vehicle manoeuvring) produced zinc concentrations comparable with the painted galvanized and old Colorsteel® roofs, while the lower trafficked roads produced zinc levels comparable with the new Colorsteel® and zinc-guttered concrete roof. There was a step change in TSS and copper concentrations from lower trafficked roads (collector and local roads to arterial roads (major and minor)). TSS and copper generally increased at the carpark sites from commercial sites to industrial sites with heavy vehicle manoeuvring. However, there was a more pronounced difference in copper concentrations between the two commercial carpark sites (Table 2). This is considered to be likely due to increased direct deposition of copper from a greater presence of heavy vehicles at the Heathcote site, compared to the Addington site.

4.2. Implications for stormwater treatment approaches

The old uncoated galvanized roof produced FF zinc concentrations of up to 56,000 μg/L, higher than anything previously reported in literature (e.g. review in Charters et al. (2016)). Current assumptions of zinc concentrations in roof runoff may be substantially underestimating the amount of zinc being contributed to urban waterways from these types of surfaces, and suggests that more urgent action is needed to address such sources of ecotoxic zinc in our urban environments. Any treatment system also needs to account for the vast majority of that zinc being in dissolved forms, which are more difficult to remove.

The copper roof produced FF and SS copper concentrations orders of magnitude higher than any other surface. If copper roofs are present in a catchment, these need to be prioritised for runoff management. Copper is the most ecotoxic heavy metal in urban environments as it can be very toxic at concentrations only marginally above what is required for growth and reproduction (Hall Jr et al., 1998). While modern copper roofs are typically reserved for bespoke architectural features, there is a historic legacy of copper roofs in many old city centres around the world, particularly in Europe (Athanasiadis et al., 2010; Hedberg et al., 2014). As seen with the concrete roof with zinc guttering, even limited copper features on a roof (e.g. guttering, decorative sheeting) could contribute a substantial amount of copper into roof runoff.

Of second priority for copper management are higher trafficked roads and any carparks. Like TSS, the copper concentrations from these surfaces did not substantially differ from FF to SS, indicating that the treatment approach for copper management in runoff from these surface types should incorporate flows throughout the runoff event. Copper from these surfaces is also a mix of particulate and dissolved form, with substantial variation between sites of the same type and function. Therefore effective management would require a combination of treatment processes that can address both forms. Likewise, the proportion of zinc in dissolved form varied widely for road and carpark surfaces (average percent dissolved for each road or carpark surface type ranged from 40 to 62%), indicating that both dissolved and particulate forms need to be considered when treating zinc pollution from these surfaces if a reasonable zinc reduction is to be achieved.

Variation in untreated runoff quality is a key factor in the ability of any stormwater treatment system to achieve its design treatment performance. The substantial variation seen in the surfaces with the corresponding highest loads for TSS, total copper or total zinc suggest that designing a system with an ability to treat a wide range of influent concentrations is necessary to achieve the intended pollutant reduction.

Avoiding the use of metal materials is the optimal approach to reducing heavy metal pollution of urban waterways. This highlights the source reduction role that strong policy can contribute to prevent generation of such pollutants in the first place. For example, policy could require selecting non-metallic roof surfaces or coating and frequent maintenance of metal roofs. In the case of road and carparks, policy can require non-copper brakepads and maintenance of adequate tyre tread that reduces the amount of zinc derived from vehicle tyre wear. When avoiding metal components is not possible, at source metal treatment is the next best option. For roofs, the treatment system needs to focus on removing dissolved metals (e.g. enhanced media in bioretention or proprietary systems). For roads and carparks, the treatment system needs to address both particulate and dissolved metals. This could include on-site infiltration systems (potentially with enhanced media) where runoff is treated at the source before being conveyed to the local receiving waterway.

At source management should be prioritised rather than allow runoff from different surface types to mix as they have different water quality signatures and treatment needs. Much like dealing with combined sewer systems, allowing runoff to combine can end up with a large volume with diluted amounts of many different pollutants. In comparison, targeted at source treatment may limit the range of pollutants to be dealt in by a particular treatment system and could also expect to achieve higher removal rates with more concentrated pollutants (Clark and Pitt, 2012).

Overall, these findings reinforce the need for a treatment train approach which provides a sequence of targeted pollutant removal processes that can address the variety of pollutant types and forms observed in this data (particularly particulate and dissolved metals).

5. Conclusions

The untreated runoff quality sampling programmes have produced a comparative dataset of eight different roof types, four road types and three carpark types, all within the same geographical area (and therefore exposed to the same climatic conditions). Substantial differences in pollutant concentrations were found between the different surface types, regardless of the surrounding land use.

The highest zinc producing surfaces are uncoated zinc-based roofs, with observed concentrations several orders of magnitude higher than local instream water quality guideline values for zinc. Any treatment approach on zinc-based roof surfaces needs to account for: a) majority of the zinc being in dissolved form; b) a wide range in zinc concentrations across multiple rain events; c) even small areas of uncoated zinc (e.g. guttering only) can elevate zinc concentrations above that of coated zinc roofs; d) even new, but uncoated, zinc-based roofs have zinc concentrations greater than older coated roofs; and e) any zinc-based roof surfaces, even if brand new and coated, leach high zinc levels. Higher traffic roads zinc levels are comparable to older coated zinc-based roofs, while lower trafficked roads are comparable to new coated zinc-based roofs. If copper roofs are present in a catchment, these need to be prioritised for runoff management to reduce ecotoxic effects from copper, followed by higher trafficked roads and any carparks. Higher trafficked roads and carparks with heavy vehicle traffic were the highest producers of TSS. Even though FF concentrations were consistently higher than SS concentrations, SS concentrations were still substantially elevated above receiving environment guidelines, suggesting that a focus on FF treatment only may not achieve pollution reduction goals.

To further enhance the knowledge gained from this dataset, additional sampling of the same surface types in a different geographical location would provide a valuable comparison between the influence of climate and the influence of surface type on the resultant runoff quality. Knowledge of the relative influence of factors such as climatic conditions, surrounding land use, surface type, surface material and surface condition allows more targeted stormwater management planning. It also enables more appropriate design of treatment systems, ensuring that the systems incorporate treatment processes that match the pollutant characteristics.

CRediT authorship contribution statement

Frances J. Charters: Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing, Visualization. **Thomas A. Cochrane:** Conceptualization, Methodology, Writing - review & editing, Supervision. **Aisling D. O'Sullivan:** Conceptualization, Methodology, Investigation, Writing - review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We would like to thank Fabio Cabral Silveira for his sampling assistance on the Heathcote programme, and Peter McGuigan from the University of Canterbury for his technical support in the field and in the lab for the Okeover programme. Funding support was provided by Environment Canterbury (Addington programme; Grant No. 16-06-010) and Christchurch City Council (Heathcote programme; Grant No. 16-09-017).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.142470.

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