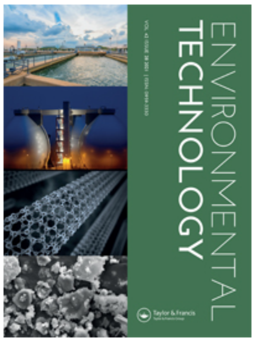

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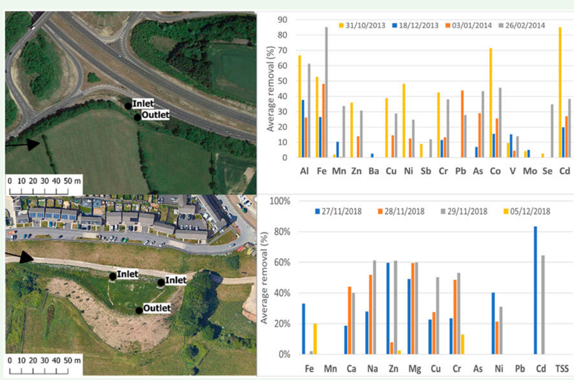
Are sustainable drainage systems (SuDS) effective at retaining dissolved trace elements?

Jasmine Humphrey, Chris Rowett, Jonathan Tyers, Mark Gregson and Sean Comber

Biogeochemistry Research Centre, University of Plymouth, Plymouth, UK

ABSTRACT

Sustainable drainage systems (SuDS) are increasingly deployed to mitigate against increased trace element contaminant loads associated with urban and road runoff. However, there is a lack of research on their capabilities in removing these trace elements, particularly from the dissolved phase. Water samples were taken, following various rainfall events, from three different SuDS in Devon; one wetland pond adjacent to a busy dual carriageway, a new SuDS serving a housing estate and an established SuDS draining a mixed housing/light industrial area. A total of 15 elements were studied over the course of six rain events including the first flush of runoff. Removal rates varied within and between rain events as well as between types of SuDS. Although there was a general (modest) removal of dissolved elements within any given SuDS, this was not the case for all of the elements studied. Highest observed element concentrations entering the SuDS occurred at the onset of a rain event (first flush), the intensity of which, was related to the antecedent dry period. During high flows associated with intense rainfall, the SuDS could also act as a source of trace elements associated with fine particulates (e.g. lead) owing to resuspension of fine particulate material. Mature ponds with an abundance of macrophytes help retain solids and particulate metals, however poor maintenance leading to successional growth of shrubs and trees, reduces the efficiency of metal removal. This study highlighted the importance of long-term management planning to be included within any SuDs scheme.



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SuDs; trace elements; metals efficiency; runoff; retention pond

1. Introduction

Urbanisation involves the significant use of impermeable surfaces, such as concrete and tarmac, which impedes rainwater infiltration [1]. Water that could previously be infiltrated now flows off surfaces, creating large volumes of runoff and therefore, generating increased flooding risks. This has been exacerbated by the threats of more intense rainfall events due to climate change [2], placing even further pressures on surface water systems.

Waterbodies are generally protect by the setting of Environmental Quality Standards for priority chemicals, including potentially toxic elements such as copper, zinc, cadmium, lead and nickel [3]. Surface runoff from urban areas and highways is a major source of pollution to waterbodies [4] from loading of sediment, trace elements, oxygen demanding substances and hydrocarbons [5–7]. The most commonly detected metals in urban runoff samples are copper (Cu), zinc (Zn), nickel (Ni), lead (Pb) and cadmium (Cd) related to sources

CONTACT Sean Comber sean.comber@plymouth.ac.uk Biogeochemistry Research Centre, University of Plymouth, Drakes Circus, Plymouth PL4 8AA, UK

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such as brake linings, tyre abrasion, road surface degradation, leaching from infrastructure, vehicle exhaust and spilt oil [8].

For other elements such as antimony, selenium, titanium, vanadium, molybdenum and aluminium little is known regarding their levels in runoff nor removal in sustainable urban drainage systems (SuDS). All of these elements come from industrial and residential buildings such as roofing, vehicle use and other everyday materials such as paints and oils or as naturally occurring impurities in products as well as from atmospheric deposition [5,9,10].

The degree of contamination can vary considerably between rainfall events due to the characteristics of the precipitation and the type of surface on which the rainfall passes over [11]. The antecedent dry period also affects the magnitude of the metal concentrations. For example, the longer the dry period the greater the dust and metal accumulation. Concentration can also vary even within the same rainfall event, a phenomenon known as 'first flush' [5]. This is where the concentration of the pollutant in run-off is highest during the initial period of the rainfall event as accumulated fine particulates, rich in metals, are mobilised [5]. For example, Chang et.al. [12] found that the first 6–8 mm of rainfall contained more than 60% of the pollutant loads from neighbouring industrial sites which may have acute impacts on receiving water [4].

Currently the best practices for water management in urban areas is sustainable drainage systems (SuDS) [1,13]. SuDS are designed on a relatively small scale to minimise flooding by either infiltrating the runoff into the ground or retaining the water within the system, in order to mimic the natural process of disposing surface water [14]. They help to improve water quality through chemical (e.g. precipitation), physical (e.g. sedimentation and adsorption), and biological (e.g. plant uptake) processes [15]. SuDS are also being increasingly recognised for providing amenity and recreation benefits, and are being incorporated in schemes to increase biodiversity [13]. Examples of different SuDS types are shown in Table 1.

Maintenance is crucial for SuDS effectiveness. Poor maintenance leads to sediment accumulation in SuDS over time [8,15], which reduces water storage capacity and flow attenuation [15], and can cause the SuDS to act as a source of pollution [16]. This is because pollutants tend to be associated with finer sediment particles (<63 μm) which are readily resuspended during intense rain events [8].

For SuDS to be effective against urban surface run-off contaminants, continuous maintenance and monitoring is required. However, it was found that 75% of Local Planning Authorities do not have a monitoring and/or reporting scheme in place to monitor SuDS implementation, and that 67% of adopted local plans do not have clear ongoing maintenance arrangements [17]. As a result of the processes occurring within the SuDS, without regular upkeep, sediment accumulation can occur over time [8,15]. This can reduce the water storage volume as well as flow attenuation [15]. Studies also suggest that poorly maintained SuDS can actually act as a source of pollution [16]. Pollutants can accumulate in sediment due to their high association with finer sediment particles [8]. Tedoldi et.al., [9] found that an accumulation of metals was found in the upper soil layers of the SuDS, with a concentration of which, in some cases, exceeded soil guidelines. These pollutants can also be remobilised during subsequent rain events [9]. Allen et.al. [18] found that contaminated sediment can actually continue to be remobilised and redeposited for up to a year after initial wash off.

Owing to SuDS being predominantly engineered to retain suspended solids, there is less data available for dissolved metal concentrations and removal efficiencies. The ability of a SuDS to retain dissolved elements will be largely dependent on the partitioning characteristics of the specific elements along with the ambient water quality and flow regime. For example, zinc and cadmium have been reported to be predominantly in the particulate form [19]. Copper, by comparison has a strong affinity for any dissolved organic carbon present in the dissolved phase [20–22] and Ni is classed as one of the most mobile metals [21]. Few studies, however report removal from the dissolved phase and where they do, removal rates can be low and highly variable [16,23,24].

Even though the implementation of SuDS in the UK is growing, the research behind them is still very much in its infancy. This was highlighted in a very recent literature review by [25]. During their 19 year search they only found 80 scientific papers on the implementations of SuDS within the European Union. From these only 29 papers had conducted real-world tests of SuDS performance, only 11 of which were based on experimental sites.

There is a clear gap in understanding regarding the effectiveness of SuDS based on their location, type and longer term maintenance regimes. The reported research here seeks to provide pressing empirical evidence on the effectiveness SuDS in different bio-physical scenarios, particularly in terms of their effectiveness for reducing dissolved metals discharged to watercourses as this is the form the EQS are based upon. Without this sufficient evidence, advances cannot be made on the management and maintenance of SuDS facilities.

Table 1. The description and the relative importance of contaminant mitigation processes of different SuDS type.

SuDS Type	Description	Contaminant mitigation processes Adsorption to substrate	Filtration	Settling	Microbial degradation	Plant uptake
Filter drains	Gravelled trench structures where stormwater can drain through the gravel and collected in a pipe; unplanted but host to algal growth	Medium/high	Medium	Low/ medium	Medium	Low
Porous paving	Continuous surface or porous blocks with adjoining infiltration spaces; an associated reservoir structure provides storage; host to algal growth	High	High	Low/ medium	Medium	Low
Swales	Vegetated broad shallow channels for transporting stormwater	Medium	Medium	Low/ medium	Low/medium	Medium
Infiltration basin	Detains stormwater above ground which then infiltrated into the ground through a vegetated or rock base	High	Medium/ high	High	High	Low/ medium
Retention ponds	Contains a volume of water at all times and retains incoming stormwater; frequently with vegetated margins	Low/medium	Low	High	Medium	Low
Detention basins	Dry most of the time and able to store rainwater during wet conditions; often possess a grassed surface	Medium	Low	Medium/ high	Low/medium	Low
Constructed wetlands	Vegetated system with extended retention time; contains either a soil or gravel substrate, planted with reeds, through which the water flows	Medium/high	Medium/ high	Medium	High/medium	Medium/ high

Source: Adapted from Scholes et.al. (2008) [56]

2. Methods

2.1. Study sites

This study focusses on three retention ponds of differing characteristics located in the South West of England in the county of Devon, UK (Figure 1). One that has formed into a wetland, is situated south of the A30 Whiddon Down junction, grid reference SX 69728 92749 (Figure S1 and S2 of the Electronic Supping Information) and the other two are located in Derriford, Plymouth, grid reference SX 49841 58683 (Figures S3 and S4).

The wetland attenuation pond at Whiddon Down discharges into the Fingle Brook. It was chosen to investigate the effect of road runoff, due to the fact 5600 motor vehicles flow through the junction each day [26].

The two retention ponds in Derriford are situated within the Forder Valley catchment. The Forder Valley stream is a tributary of the River Plym, with a total length of 7 km and drains a catchment of 4,664,706 m^2. The catchment is primarily urban, with 6500 new homes being constructed between 2006 and 2021, but also contains, a business park, parkland, and busy commuting road. The two retention ponds are of different ages. The newer pond (SuDS1) was built in 2017 to mitigate the increased surface runoff from the new housing estate and has two inlets from different parts of the estate and a single outlet. The older, more mature pond (SuDS2) was built in 2002 as part of the neighbouring business park development. It is shallower, dries out in the summer and has been planted or colonised with vegetation such as grey willow (*Salix cinereal*) and bulrush (*Typha latifolia*), and discharges into Bircham stream. The sites were chosen to provide a comparison of effectiveness based on different catchments and maturity of the SuDS.

Samples at the Forder Valley SuDS were taken at various times in May 2018 and November 2018 to capture rain events. During the May 2018 rain event one sample was taken at the inlet and outlet at both SuDS1 and SuDS2. The focus, however, was on the newer SuDS1, where two or three samples were taken on four occasions during rain events between the end of November to the start of December 2018. At Whiddon Down, four samples were taken from both the inlet and outlet over the duration of rain events in December 2013 and January 2014 (see Table 2).

2.2. Sampling and analysis

The description of the sampling sites is provided in Table 2. Prior to sampling, the equipment, including polythene sample bottles were cleaned in a 10% hydrochloric acid bath for 24 h before being washed with deionised water. Filters were soaked in 0.01% hydrochloric acid for 24 h and washed with Milli-Q water, this was repeated three times to ensure they were trace element clean.

At each sampling site, on each occasion, samples were collected in acid cleaned buckets and filtered using 60 ml syringes fitted with a sterile 25 mm 0.45 µm cellulose acetate filters (Sartorius) then preserved with the equivalent of 2 ml/l high purity concentrated nitric acid (Primar Plus, Fisher Chemicals) prior to analysis. pH was measured using an Oakton Acorn series pH monitor with a sensitivity of ±0.01. Dissolved organic carbon (DOC) samples used to provide an indication of the bioavailability of copper, zinc and nickel, were taken at Whiddon Down for the December 2013 and

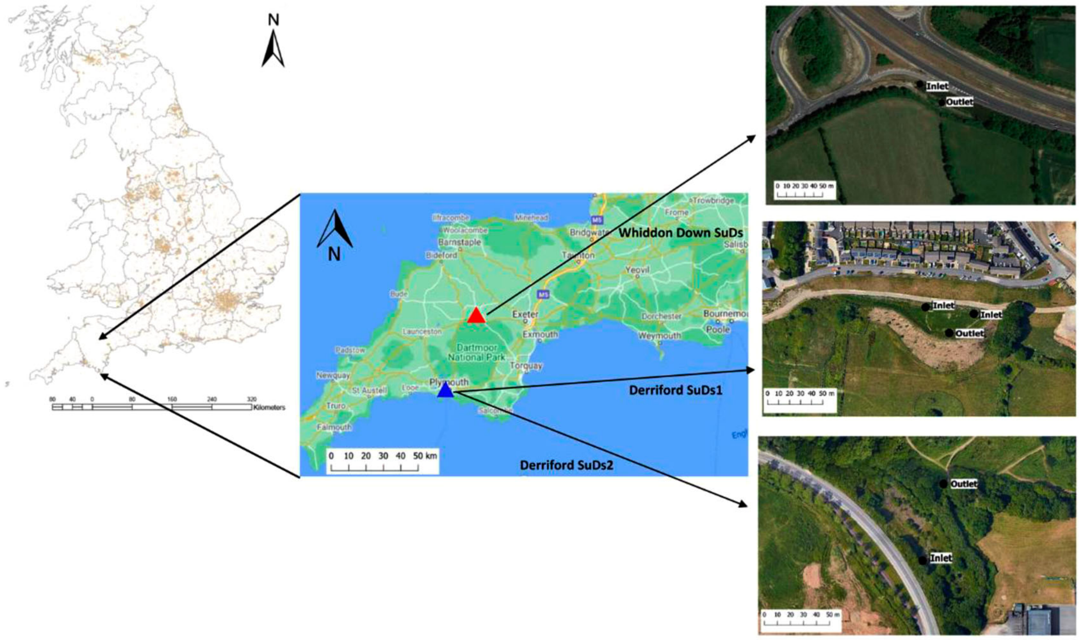

Figure 1. Map of the South West England showing the location of the Whiddon Down and the Derriford sample sites.

January 2014 rain events. These were collected in a similar way to the metal samples but collected in glass bottles (combusted at 450°C for six hours to remove any organic carbon residues). After preservation with 20 µl of 6M hydrochloric acid, DOC was determined using a Shimadzu TOC analyser [27,28]. A DOC average value of 3.5 mg/l for inlet and outlet DOC for the Whiddon Down SuDS was used for bioavailability estimates for Derriford SuDs discharges.

Trace metal analysis was undertaken using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) (Thermo Scientific, X Series 2) or Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) for the major ions, specifically calcium. Calibration was carried out using standards prepared by serial dilution of mixed stock solutions (LabKings) in 2% nitric acid, with EnviroMat Drinking water reference material analysed within each batch.

2.3. Modelling and statistics

Biotic Ligand Modelling was used following the Bio-met manual (available at Bio-Met-net), by inputting the site-specific levels of pH, calcium, and DOC, as well as site-specific concentrations of copper, nickel, zinc and lead. This was to determine the bioavailability of these trace metals and therefore providing an indication of their potential impact on receiving waters.

Due to the data having different sized groups, a Kruskall–Wallis test was used to find a statistically significant difference between the concentration of each metal and the sample site location, as well as between rain events. Where appropriate One-Way ANOVA was used to determine any statistically differences between sites based on a 95% confidence interval. All data manipulation and analysis was carried out using commercially available software (Microsoft Office, Excel).

Table 2. Sample site number and description of site at Whiddon down and Derriford.

Site description	Sampling dates	Sites	Rainfall (mm)	Antecedent dry period (days)	Samples per event
Whiddon Down road runoff	31/10/13	All sites	0.3	2	1
Whiddon Down road runoff	18/12/13	All sites	40.4	2	4
Whiddon Down road runoff	03/01/14	All sites	15.0	2	4
Whiddon Down road runoff	26/02/14	All sites	1.0	1	1
Derriford housing/industrial estate	30/05/18	SuDs1 & 2	4.8	2	1
Derriford housing estate	27/11/18	SuDs1	22.2	2	3
Derriford housing estate	28/11/18	SuDs1	4.4	2	2
Derriford housing estate	29/11/18	SuDs1	9.8	2	2
Derriford housing estate	05/12/18	SuDs1	7.2	2	2

3. Results and discussion

3.1. SuDS trace metal concentration and bioavailability

Rainfall data for the sampled events exhibited a range of 5–40 mm (Table 2 and Figure S5). Due to minimum rainfall in May 2018 (4.8 mm), the water quality in and around SuDS1 could only be sampled once. Rainfall data are important as it has a significant impact on the quantity of material carried from the surface of the road into the aquatic environment.

Data used to calculate the bioavailability of copper, nickel, lead and zinc in the surface runoff are shown in Table 3. Bioavailability varied according to the ambient pH, Ca and DOC. Mean pH values at Whiddon Down sites were similar (pH 7.3–7.5), with DOC between 2.8 and 4.0 mg/l and calcium being relatively low (20–30 mg/l) reflecting the non-calcareous underlying geology. For the Derriford sites pH was generally higher (7.69–8.45) with calcium in a similar range to Whiddon Down (27–28 mg/l). Under these ambient conditions of alkaline pH, low to moderate DOC (compared with typical river values) and relatively low calcium concentration, bioavailability of the metals was quite variable between the sites. Owing to the high pH recorded at the Derriford sites bioavailability was predicted to be higher due to the presence of carbonate and soluble hydroxyl species. Copper complexes strongly with dissolved organic carbon, thus reducing bioavailability. There was sufficient DOC present in solution to reduce the percentage of copper bioavailable to between 5–23%, lower than zinc, nickel or lead (Table 3). Lead bioavailability across sites and sampling occasions was similar with a range of 10–19% of the dissolved lead present in any samples likely to be bioavailable. Zinc bioavailability was predicted to be between 36% and 48%, with nickel up to 100% bioavailable for the samples with the highest pH. These values tended to reflect the typical bioavailability of copper and zinc in low alkalinity lowland rivers [29,30]. Based on these numbers threshold concentrations of dissolved metal concentrations potentially causing harm would be 5–22; 3–10; 23–26 and 8–12 μg/l for copper, nickel, zinc and lead respectively.

The observed variability in SuDS inlet trace element concentrations (Table S3) has previously been attributed to variability in roads, traffic and weather conditions [31]. Average daily traffic density and the type of road have been seen to affect the concentrations of metals in some studies, particularly copper and zinc [32,33]. However, samples for this current study were collected at the same sites, in the same season. Therefore, traffic variability is thought not to play a major role. The antecedent dry weather periods (Tables S1 and S2) were only two days for both of the full rain events at Whiddon Down and Derriford (there was 0.2 mm on the day before the May sample was taken (Table S1), but this was considered insignificant), and should therefore have had minimal impact of pollution build up (Figure S5, Table S1). With these variables remaining relatively constant, the variation in metal concentration was suspected to be due mainly to the differences in rainfall intensity, which is discussed in more detail below.

Overall dissolved concentrations of trace elements in the inlet and outlets of all of the SuDS reflected a combination of degradation of road surface (reflected in high levels of calcium, magnesium, aluminium and sodium) along with abrasion of tyres (rich in zinc) brake linings (rich in copper) [32,34]. Other elements such as chromium, arsenic, nickel, lead and cadmium and minor elements such as cobalt, vanadium, molybdenum and selenium are likely to reflect impurities from sources including rainwater deposition, roof and road materials, brakes and tyres, oil and exhaust emissions [35].

Mean runoff trace element concentrations in inlet and outlets from the SuDS unsurprisingly varied across the sites and occasions. For an example of the trace elements (compared with major ions such as iron, aluminium, calcium, sodium and magnesium) copper and zinc exhibited highest concentrations at the A30 Whiddon Down site (Figure 2) reflecting the high volume of road traffic linked to obvious sources of

Table 3. Mean pH, DOC and Ca concentrations and estimated bioavailability of Cu, Ni, Zn and Pb based on the measured ambient conditions using the BioMET tool.

					Bioavailable fraction %			
Sample Site	Date	pH	DOC (mg/L)	Ca (mg/L)	Cu	Ni	Zn	Pb
Whiddon Down inlet	18/12/13	7.50	3.78	20.0	6	49	48	10
Whiddon Down inlet	03/01/14	7.30	3.21	30.0	7	45	48	19
Whiddon Down outlet	18/12/13	7.50	4.05	20.6	5	40	36	10
Whiddon Down outlet	03/01/14	7.30	2.81	29.9	7	45	48	19
Derriford site SuDS1 inlet 1	30/05/18	7.69	3.5	26.7	8	58	45	17
Derriford site SuDS1 outlet	30/05/18	8.39	3.5	26.7	23	100	43	15
Derriford site SuDS2 inlet	30/05/18	7.98	3.5	27.8	11	69	43	15
Derriford site SuDS2 outlet	30/05/18	8.45	3.5	27.8	23	100	43	15

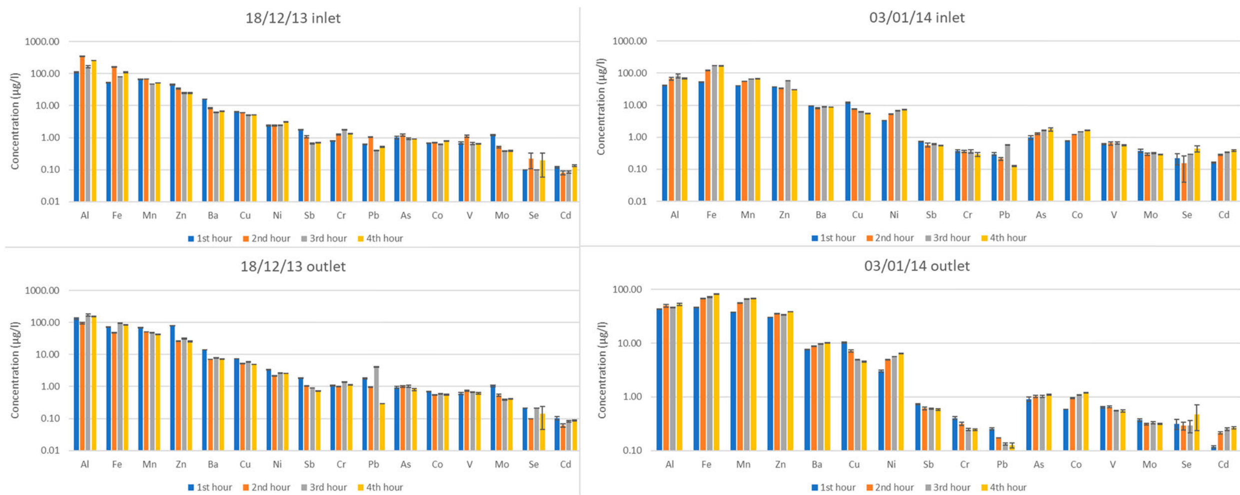

Figure 2. Dissolved trace element concentration data across the two rain events at the A30 Whiddon Down dual carriageway site (error bars represent standard deviations).

these elements. Where comparisons were available for the other metals, nickel, iron, manganese and lead were also elevated at the Whiddon Down site compared with the industrial/residential site at Derriford potentially also associated with transport [32,34]. Mean dissolved concentrations of arsenic and chromium were similar, potentially reflecting ubiquitous sources, including background geology contributing low µg/l concentrations [35].

For SuDS1 at Derriford (Figures 3 and 4) there are two inlets draining the housing development which exhibited slightly different concentration profiles. For example, iron and zinc tended to be higher in Inlet 1 on two of the four occasions (although not statistically significant at 95% confidence); whereas magnesium was higher in Inlet 2 on all occasions and significantly so on all but one rain event. It is not clear as to the reasons for this, but may be a result of the fact that the two inlets entering the pond are draining different parts of the housing estate which were under different stages of development. For example, where houses had been completed and were occupied, there is more residential car traffic compared with construction traffic. Furthermore, there is generally greater bare ground exposed during construction, providing the opportunity of soil runoff. Of the trace elements, again, copper and zinc were found at highest concentrations in the runoff, associated with high/medium traffic density and its 'stop/start' nature resulting in increased brake and tyre wear, respectively [36] as well as the range of building material commonly found in residential areas and roads [37]. For the mature SuDS2 collecting runoff from housing and commercial/light industrial land use trace element concentrations were of a similar magnitude to the other sites (Figure 4).

For six rain events, samples were collected on more than one occasion in an attempt to assess the impacts of any 'first flush' effects leading to elevated concentrations caused by immediate wash off of trace elements from roof and road surfaces at the start of a rain event (Figures 2 and 3). At Derriford sampling was undertaken during a number of days of initially heavy followed by sustained rainfall. Unsurprisingly the first event on the 27th of November (22 mm of rain over the 24 h period) provided evidence of a first flush effect for iron (both inlets), zinc, nickel, cadmium and copper although only for inlet 1. Owing to variability in the sample replicates, the effects were not significant at 95% confidence. For the rain events that followed, there were little differences between the two samples taken on each occasion, reflecting rain falling on increasingly clean surfaces. There was a single sample collected at the inlet and outlet from SuDS1 in May 2018 which showed similar concentrations for a variety of trace elements (Figure 4).

For Whiddon Down 40 mm of rain fell on the 18th of November and 15 mm on the 6th of January. For the first rainfall event, there was only a clear (statistically significant) first flush effect for barium, zinc, copper, antimony and molybdenum all of which are associated with transport [38,39]. For the January event other than for copper and to a degree, antimony there was no clear first flush effect; indeed, for aluminium, iron, manganese, nickel, arsenic and cobalt concentrations of dissolved metal rose over the course of the first three hours at least; reflecting a rising intensity of rainfall over the sampling period.

Outlet concentrations largely correlated to inlet concentrations but in most cases concentrations were lower reflecting some form of removal (discussed further below). In terms of potential environmental impact for

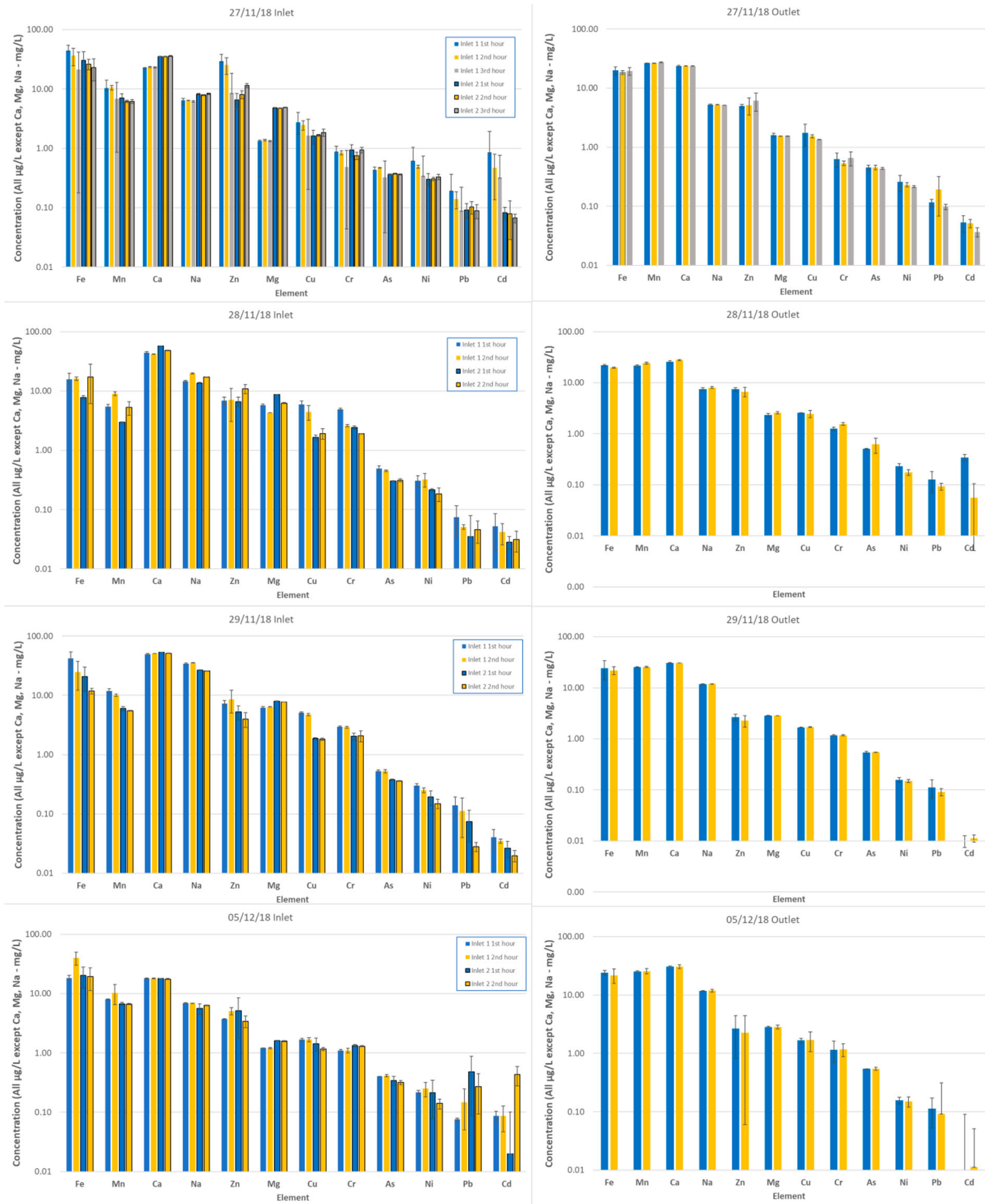

Figure 3. Dissolved trace element concentration data across the four rain events at the Derriford SuDs1 from a new housing estate (error bars represent standard deviations).

metals where bioavailability estimates were available, for Whiddon Down, zinc levels in the outlet for the January samples were slightly above the threshold concentration for potential impacts for the first flush in December and for all samples in January, by up to a factor of around three. Copper, nickel and lead were lower than the threshold concentration for all samples across both events. Given the dilution of the road runoff into the receiving water, for this particular site on these there was not an exceedance of the in-river EQS (data not shown). For the Derriford sites, there were no outlet runoff concentrations greater than the

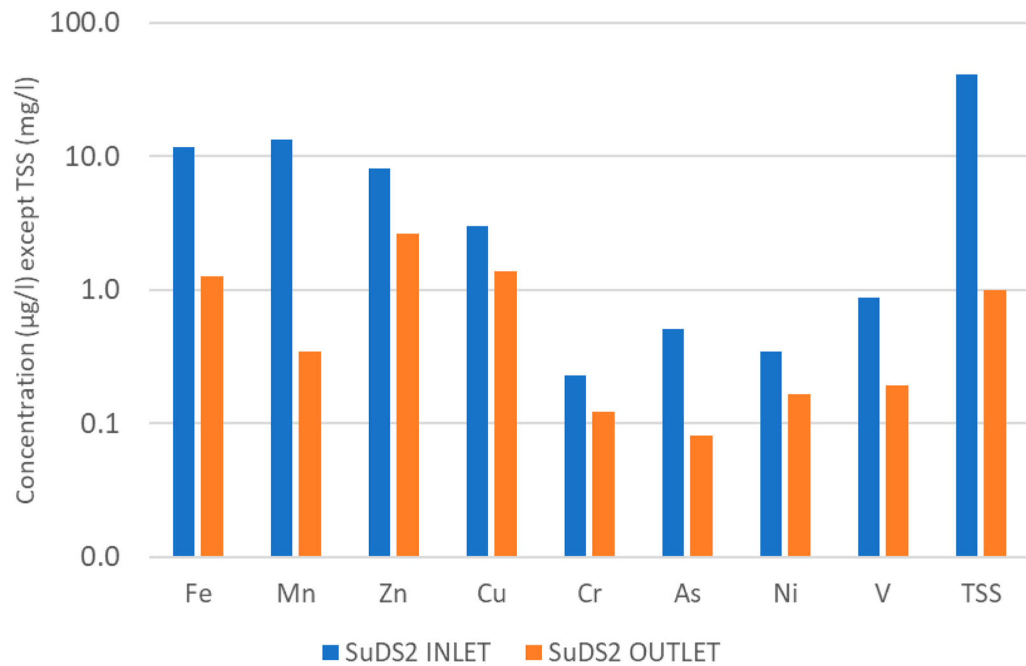

Figure 4. Dissolved trace element concentration data across the single rain event at the Derriford SuDS2 site (mixed housing/light industry).

threshold values based on the average DOC concentration applied to the BioMet tool. However, it should be noted that the antecedent dry periods for all of these events were only 2 days and so there was little opportunity to build up trace elements on roof and road surfaces prior to the sampled rain events.

3.2. SuDS removal efficiency

The objective of these SuDSs is to intercept urban runoff from the A30 Whiddon Down Junction, or from new housing developments and industrial areas within the Forder Valley, and control the rate of discharge into their corresponding waterbodies. To assess how effective the SuDS are at mitigating runoff element contaminants, the difference in the dissolved metal concentrations recorded at the inlet and the outlet were calculated and expressed as a percentage removal (Figures 5, 6 and 7; Tables S6 to S9). The removal of trace elements will be controlled by a number of factors including their partitioning between the dissolved and particulate phases, the amount of suspended solids present (and its nature), chemical reactions (particularly precipitation) that may occur and their speciation, largely controlled by pH, hardness/Ca and dissolved organic carbon concentrations [40]. This final aspect of speciation is particularly pertinent for copper, zinc, cadmium and to a degree, nickel. Consequently, removal from the dissolved phase is likely to vary within and between rain events where all these parameters vary considerably as much as between elements.

For Whiddon Down (Figure 5) it can be seen that in December at the outset of the rain event a number of the metals (aluminium, iron, zinc, copper, nickel, chromium, lead and selenium) were actually mobilised from the SuDS within the first hour. Lead showed the greatest mobilisation likely to be a combination of its strong association with the fine particulate material [41] and the fact that concentrations were typically low and close to the limit of detection, leading to high percentage values resulting from small differences in inlet and outlet concentrations. There was a net removal of metal over the 2nd hour before another net loss of metal in the 3rd hour before finally in the 4th hour removal was once more observed. This pattern was put down to the heavy bursts of rain remobilising fine sediment trapped within the poorly maintained wetland SuDS leading to dissolution of metal concentrated in the finer fractions. Such occurrences have been reported previously [42]. The wide variability of the removal rates over a rain event leads to significant confidence intervals when calculating a mean removal rate. The January rain event showed a significantly different pattern, with almost the whole event showing a net removal of dissolved metal from the runoff passing through the SuDS. This was postulated to be a result of the rain event being less intense (15 mm compared with 40 mm). Taking the overall event mean concentrations (EMC) and comparing outflow to

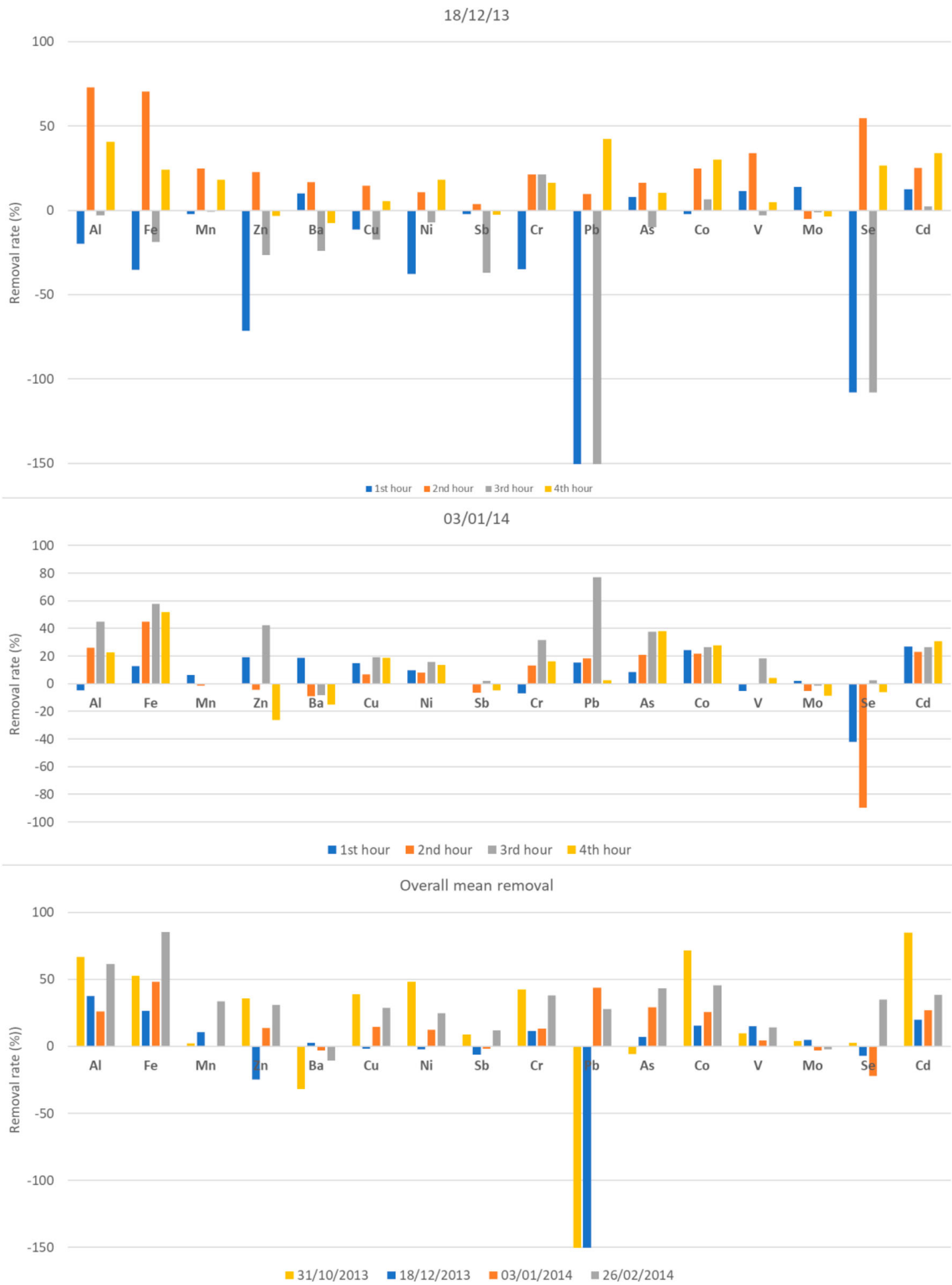

Figure 5. Whiddon Down trace element removal by the SuDS over time and overall mean (bottom figure).

inflow generated variable removal rates for the elements between rain events. Aluminium and iron showed removal between 25% and 50% likely to be linked to precipitation reactions as much as sorption and settlement of solids [43]. Two other rain events were monitored in October 2013 and February 2014 based on inflow and outflow from the SuDS to provide a background removal rate based on low flow and low rainfall conditions. Figure 4 shows that for these cases removal rates (up to 50%) for most of the metals are higher than

Figure 6. Removal of elements from Derriford SuDS1.

under more intense rainfall occasions, which indicates the lack of retention associated with highway SuDS. Low rainfall events have been reported to cause lower concentrations of metals in runoff [44,45], due to the total load being influenced by the rainfall intensity [46]. However, the results from this study show that the road runoff in the lower rainfall event had higher concentrations of most metals. This could be due to a weaker flow rate during low rainfall, resulting in the sediment being unable to be remobilised. It also suggested

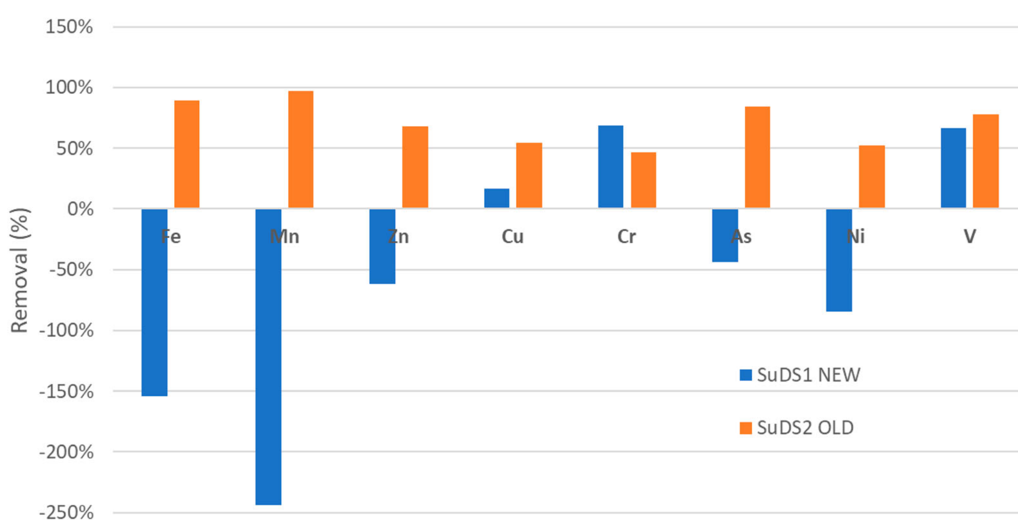

Figure 7. Comparison of removal of elements from Derriford SuDS1 and SuDS2 across an identical rain event.

that lower rainfall has less of a dilution effect on metals in runoff, causing increased concentrations [47].

The Derriford newly developed housing estate SuDS1 showed clear patterns of removal across all of the rain events from May 2018 to November 2018 (Figures 6 and 7). Removal rates were similar for the samples taken over the individual rain events (2 or 3 occasions) and more consistent than observed at the highway SuDS, likely to be related to it being a newly installed SuDS feature with better retention capacity and with less propensity to mobilise fine sediment during more intense rainfall events. Dissolved element removal was observed for most metals with the exception of manganese which showed a significant increase in concentrations in the outflow compared with the inflow. One explanation for this could be that metals associated with particles such as manganese would only be mobilised in high-intensity rainfall [48], whereas dissolved metals may not require a minimum runoff velocity in order to be mobilised [49]. Thus suggesting that overtime during less intense rain events the SuD accumulates manganese, and then becomes a source during heavy rainfall. Supporting data (temperature, pH, conductivity, dissolved oxygen – see Tables S4 and S5) were reasonably consistent, although pH was alkaline (up to 8.45 – Table 3) which would promote the formation of Mn(OH)2 which in a colloidal form may result in loss from the system within suspended solids. Given the oxygenated systems under a similar pH iron might be expected to form more insoluble oxyhydroxides [50]. The same pattern was not observed at the Whiddon Down road runoff site, but the pH was lower (7.3–7.5) favouring Mn2+ formation which may have an affinity for settling particulates or co-precipitation with iron. Further work would be required to elucidate these complex physico-chemical interactions.

The 5th of December event showed a different pattern for a number of elements (calcium, sodium, magnesium, copper, arsenic and cadmium) with the elements being mobilised and lost from the SuDS1. Total suspended solids concentrations in the outlet were of similar order and so mobilisation of material cannot be attributable to the observed increase. It should be noted that for elements present at very low concentrations, subtracting outflow from inflow to derive a percentage removal can lead to large values, likely to reflect analytical variability rather than extreme removal/mobilisation.

Concurrent sampling of SuDS1 and SuDS2 in May 2018 for the same rain event showed how different the removal characteristic of SuDS can be (Figure 6), with SuDS1 generating a net loss of elements from the SuDS for iron, manganese, zinc, arsenic and nickel; compared with the more mature SuDS2 exhibiting removal for all elements. This reflected the design and age of the SuDS. SuDS1 was newly established with no vegetation present, thus only providing retention of runoff. SuDS2 was much more mature and more wetland-like as well as longer and therefore provides both volume retention but also the ability to trap particulates via the presence of wetland species such as Typha which can also take up bioavailable, soluble

Table 4. Comparison of mean dissolved metal removal rates for retention ponds in the literature.

Element	Mean (median) reduction (%)	Reference
Copper	81	[23]
	23	[16]
	58	[24]
	20	Current study: Derriford SuDS1 (housing)
	55	Current study: Derrifed SuDS2 (housing/industrial)
	20 (22)	Current study: Whiddon Down (highway)
Zinc	82	[23]
	41	[16]
	64	[24]
	−29	Current study: Derriford SuDS1 (housing)
	51	Current study: Derrifed SuDS2 (housing/industrial)
	14 (22)	Current study: Whiddon Down (highway)
Nickel	1	[16]
	8	[24]
	−8	Current study: Derriford SuDS1 (housing)
	68	Current study: Derrifed SuDS2 (housing/industrial)
	21 (19)	Current study: Whiddon Down (highway)
Lead	41	[16]
	50	[24]
	18	Current study: Derriford SuDS1 (housing)
	−25	Current study: Derrifed SuDS2 (housing/industrial)
	−379 (−73)	Current study: Whiddon Down (highway)
Cadmium	63	[24]
	−107	Current study: Derriford SuDS1 (housing)
	100	Current study: Derrifed SuDS2 (housing/industrial)
	43 (33)	Current study: Whiddon Down (highway)

metals [51]. This is in contrast to the Whiddon Down road runoff site dominated by willow, some grasses and bare ground, therefore providing less retention. Owing to only intermittent flow, the habitat cannot support wetland plants such as Typha and so is more susceptible to fine sediment mobilisation during intense rainfall events. Plants can heavily influence the removal of metals through uptake, stabilising flow, increasing detention time, and increasing the organic carbon content in sediments [42]. Different species of plants are also better at removing metals than others, for example, *Phragmites australis,* the most common species found in wetland systems and are associated with metal removal rates of more than 70% [52]. This is also the case for the maturity of the plants within the wetland; it was found that more mature plants accumulate higher metal concentrations [47]. However, other studies have suggested that the biological processes of reducing metals within wetlands is minor compared to filtration and sedimentation processes [45,52,53].

For metals typically measured and regulated for, it was possible to compare removal rates with literature data (Table 4). Literature on the removal rates for retention ponds is more limited. The SuDS studied here were in a similar range of efficiency to reported data. Other than copper, the rest of the element's removal rates for the retention ponds in this current study are very variable compared with the literature. In general, SuDS2 best reflected reported literature removal efficiencies, whereas SuDS1 and the Whiddon Down highway runoff SuDS had lower efficiency than the literature, likely to reflect a combination of immaturity of the pond and lack of vegetation (Derriford SuDS1) and poor maintenance and plant type (Whiddon Down highway runoff).

Sedimentation is considered to be the main removal process of contaminants in retention ponds; therefore, they have a low capacity to remove dissolved metals [54]. For dissolved metals, this process will be driven by their partition coefficients and is seen in the retention ponds in the current study. Concentration of copper, nickel and lead were found in higher concentrations during the May rain event, where only 4.8 mm of rain fell, whereas zinc and cadmium were higher during the December rain event, where 71.6 mm of rain fell. This may be because zinc and cadmium are dominant in particulate form, where they are mainly bound to particles in soil [19], therefore, they need higher intensity rain events to allow for remobilisation. Copper on the other hand has a strong affinity to the dissolved phase [22] and nickel is classed as one of the most mobile metals [21]. In general, SuDS1 was more effective at reducing dissolved metal contamination during the heavier rain event in November, except for lead and cadmium, where the SuDS was acting as a source of these metals (albeit allowing for the low observed concentrations potentially biasing the removal data).

Overall, SuDS2 was much more effective at reducing metal concentrations, with concentrations of above 50% for most elements, albeit only sampled on one occasion under relatively low-intensity rainfall. However, retention ponds in the literature have been shown to reduce removal efficiency over time due to the sedimentation process [19]. This was evidenced by the reduction in total suspended solids from 41 to 1 mg/l between the inlet and outlet of the SuDS; compared with 313 and 75 mg/l, respectively, for SuDS1 for the same rain event. The sediment accumulation reduces the water holding capacity of the pond, increasing the risk of resuspension and lowers residence times [19]. This illustrates the necessity for periodic maintenance and potentially dredging of material. It should also be noted that sampling of discrete rain events has been proven to not be a good reflection of the long-term removal efficiency [55], therefore, this study only acts as a snapshot into the efficiency of these retention ponds.

4. Conclusions

The widely variable removal rates observed in these studies and reported in the literature are a product of changing flows through the SuDS, physico-chemical processes, rainfall intensity as well as loading from the roads based on the antecedent dry period. The complexity of these processes combined with variation in design and maintenance of the ponds would make prediction of removal rates almost impossible.

Measurement of removal rates for SuDS therefore needs to be considered on a site-by-site basis in most cases. This study has illustrated the complexity in monitoring the efficiency of dissolved element removal within SuDS and explains why there are so little data relating to their efficiency for trace element removal. As regulators strive to improve surface water quality, based on dissolved element environmental quality standards this study has shown the importance of monitoring a variety of SuDS types across different rainfall regimes and associated antecedent dry periods.

Ideally, it would be beneficial for developers and environmental managers to be able to predict the removal of elements under specific environmental conditions, thus allowing the optimum design and maintenance programme to be implemented. However, owing to the variation associated with antecedent dry period, traffic, rain intensity, pond dimensions, pond design and planting, pond maturity, there are too many factors impacting on the observed metals concentrations to allow any form of prediction to be achieved. Therefore it is evident that ongoing chemical monitoring of SuDS is required to optimise their effectiveness, particularly the water holding capacity, planting to allow uptake and retention of metals and most importantly, long-term maintenance to remove any build-up of fine material and manage plant growth.

Data availability statement

The authors confirm that the data supporting the findings of this study are available within the article [and/or] its supplementary materials.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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