

# The impact of macropores on heavy metal retention in sustainable drainage systems

Ruth Quinn and Alejandro Dussailant

## ABSTRACT

Numerous laboratory and field experiments have found that rain gardens exhibit excellent heavy metal retention (>88%). However, none examined the impact of macropore flow on this retention; this was established to be a key factor in heavy metal capture by previous landfill leachate experiments. Therefore, the aim of the experiments detailed in this paper was to investigate the effect of a single artificial macropore on heavy metal retention in a layered soil column (with a similar configuration to a rain garden). The findings of these experiments suggest that macropore flow does not impact the hydraulic performance or heavy metal retention of the columns with 99% of copper, lead and zinc captured. This indicates that macropores are not detrimental to heavy metal retention in rain garden systems with highly conductive soils; this was attributed to the high hydraulic conductivity of the media used and the depth of the system. However, in shallower systems, such as green roofs, the retention of heavy metals and other pollutants may be impacted by the existence of preferential flow, and more research into this area is needed.

**Key words** | heavy metals, macropores, sustainable drainage systems

**Ruth Quinn** (corresponding author)  
School of Engineering,  
University of Greenwich,  
Pembroke Building, Chatham Maritime,  
Chatham, Kent MW4 4TB,  
UK  
E-mail: [ruth.quinn@abdn.ac.uk](mailto:ruth.quinn@abdn.ac.uk)

**Alejandro Dussailant**  
Universidad de Aysén,  
Coyhaique, Patagonia-Aysén,  
Chile

## INTRODUCTION

Storm water runoff from impervious surfaces such as roads, highways, roofs and car parks contains a number of pollutants harmful to the environment (Klein 1979; Davis *et al.* 2001). The detrimental effects of these pollutants are visible in lakes and waterways throughout the United Kingdom with 11% of the total pollution in Scottish rivers attributed to it (Ellis & Mitchell 2006). In the United States, urban runoff is second only to agriculture as a source of river pollution (Ellis & Mitchell 2006). This pollution is caused by the transfer of contaminants present in urban storm water such as nutrients, hydrocarbons and heavy metals through storm drains and pipes into local waterways.

In order to prevent this pollution, alternatives to conventional drainage systems have been proposed in the form of sustainable drainage systems (SuDS). SuDS attempt to replicate natural systems and drain away urban runoff through collection, storage and filtration before releasing the water slowly back into the environment (Klein 1979).

There are numerous types of SuDS, such as green roofs, detention basins and swales. However, this paper focuses on an infiltration-based method known as a rain garden.

Rain gardens are vegetated depressions that have been specifically designed to collect and infiltrate the storm water. They are usually shallow depressions (less than 200 mm in depth) and much smaller than the impervious surface from which they receive runoff. Rain gardens consist of vegetation, a high permeability upper layer and lower storage zone; an underdrain may also be present to prevent overflow in cases of heavy precipitation (Dussailant 2002). Water is directed into these systems as opposed to conventional storm drains, travels through them and, depending on the subsoil, may replenish groundwater or slowly percolate into the drainage network. Therefore, it is of crucial importance to minimize contaminants released by these systems in order to maintain groundwater and waterway purity.

Heavy metals concentration levels in runoff are unlikely to affect human health but may induce ecotoxic effects (Brown *et al.* 2000). Thus, numerous laboratory and field experiments have examined heavy metal retention in rain garden devices and other infiltration systems (Davis *et al.* 2001; Hsieh & Davis 2005; Blecken *et al.* 2009; Paus *et al.* 2014; Lim *et al.* 2015; Trenouth & Gharabaghi 2015). It was found that in the majority of cases dissolved metals were removed almost completely in the first 200 mm of soil (Sun & Davis 2007). This is due to the high organic content of the upper layer, which has an increased capacity for metal removal (Li & Davis 2008). Sun & Davis (2007) observed that the majority of the heavy metals were removed via adsorption (88–97%), and the remainder were either accumulated in the vegetation (0.5–3.3%) or not captured (2–11.6%).

Experiments were also completed into the effects of changes in runoff pH, duration and pollutant concentrations, which were all found to have a minimal effect on the removal of heavy metals (Davis *et al.* 2003).

It was discovered that the single biggest contributing factor to reduced metal retention was flowrate. In the experiments completed by Farm (2002), the retention of cadmium (Cd), chromium (Cr) and copper (Cu) was high (>96%) at lower flow rates (2,500 mm/h); however, when the rate was increased to 4,000 mm/h results showed that the retention dropped dramatically (51%). This type of a high flowrate can occur in an actual rain garden due to a process called preferential flow.

Macropore flow is by far the most common preferential pathway in highly conductive homogenous soils such as rain gardens. Common macropores in SuDS include wormholes, root holes and fractures. Due to their high flowrate and capacity for bypassing the highly retentive upper layers of soil, macropores have been found to increase the movement of pollutants (Safadoust *et al.* 2012, 2016; Beven & Germann 2013). So although there are numerous experiments into heavy metal retention in homogenous rain garden soil (Davis *et al.* 2001; Hsieh & Davis 2005; Blecken *et al.* 2009; Gülbaz *et al.* 2015; Lim *et al.* 2015; Lucke & Nichols 2015), the influence of macropores has not been examined. This was established as a key factor in limiting heavy metal retention in a previous study completed into landfill soil by Camobreco *et al.* (1996). In their experiments, the heavy metal effluent concentration for two undisturbed and two homogenized soil columns of length 350 mm

were determined. They found that the undisturbed columns exhibited preferential flow and only retained between 70 and 75% of the influent Zn, Cu and Pb. In contrast, the homogenized columns retained all heavy metal input. The soil used in these columns was clay and consequently had a lower conductivity than rain garden soils, so it is unclear whether retention rates would differ in SuDS.

Macropores may also be a factor in explaining the findings of both Johnson & Hunt (2016) and Kluge *et al.* (2016), who studied heavy metal retention in operating rain garden devices. Both studies found substantial deposits of Cd, Cu, Pb and Zn at depths greater than 200 mm. These deposits may be caused by preferential pathways in the soil bypassing the upper retentive soil layer.

Therefore, the aim of this paper is to investigate the effect of a single 10 mm diameter macropore on heavy metal retention in layered soil (with similar soil layout to a rain garden) under conditions specific to a temperate climate. This will establish whether macropores are of concern with regards to heavy metal removal in rain garden systems.

Soil column experiments in both the saturated and unsaturated regimes are widely used for applied and theoretical studies. In terms of heavy metal sorption studies, column experiments have inherent advantages over other approaches such as batch studies as they work at a high solid to solution ratio close to the one encountered in a natural rain garden device (Burgisser *et al.* 1993; Highways Research Agency 2010). Due to these reasons, column experiments were chosen as a suitable method for examining heavy metal retention in rain garden soil.

## METHODS

### Experimental design

Five biofilters were constructed from acrylic plastic columns (140 mm internal diameter, 1,200 mm in height). Transparent columns were used in order to observe the hydraulic efficiency of water filtration through the media. The inner walls of the columns were roughened using coarse sand paper to optimize soil-column wall adhesion, as recommended by Smajstrla (1985). Silicone rings were also installed at 300 mm intervals on the interior surface of the columns prior to the addition of soil to minimize sidewall flow (Cowin 2000).

The filter media consisted of two layers:

- top filter layer (600 mm): 50% compost/50% coarse sand mix by volume;
- drainage layer (300 mm): coarse sand.

An additional 300 mm was left clear at the top of the column to allow for ponding. This soil configuration was chosen as it reflects a typical rain garden design and the top layer mix of soil has proven to be an optimal choice for heavy metal retention and water infiltration (Morgan 2011).

Two of the columns contained artificially created macropores which extended through both upper and lower layers of soil. These were of 10 mm in diameter in accordance with previous solute transport experiments (Allaire-Leung *et al.* 2000). These macropores were created by inserting a metal rod through the length of the column from top to bottom, following the procedure of Kay *et al.* (2005). In order to prevent collapse, this insertion process was completed before each experimental run. It was observed that the rod was easily inserted into the substrate each time indicating that collapse did not occur.

Two sets of columns were created, three with normally packed homogeneous soil (matrix columns) and two with preferential pathways (macropore columns).

## Experimental procedure

In these experiments an excessive rainfall scenario was replicated; this is a relatively high water input rate for a relatively long period of time (5 hours). This input water rate was determined using data from a weather station located at Heathrow. The above average rainfall amount was decided at 10.9 mm/h (about 90% of total annual rainfall in the London area). This value is based upon total annual rainfall vs. intensity figures (Quinn 2015). This was determined to be an adequate reflection of a high average rainfall in temperate climates such as the UK. The average input into a rain garden is much higher than 10.9 mm/h however as it receives runoff from impervious surfaces surrounding it. The area ratio of rain garden to impervious surface was chosen as 10% as this was found to yield the most beneficial results in a climate such as that of the UK (Dussaillant *et al.* 2005). This resulted in a total maximum water input of 120 mm/h.

The metal contaminants Cu, Pb and Zn were chosen as the focus of this experiment as they are the most common metals present in urban storm water and also have the greatest detrimental effects on the environment (Brown *et al.* 2000; Davis *et al.* 2001).

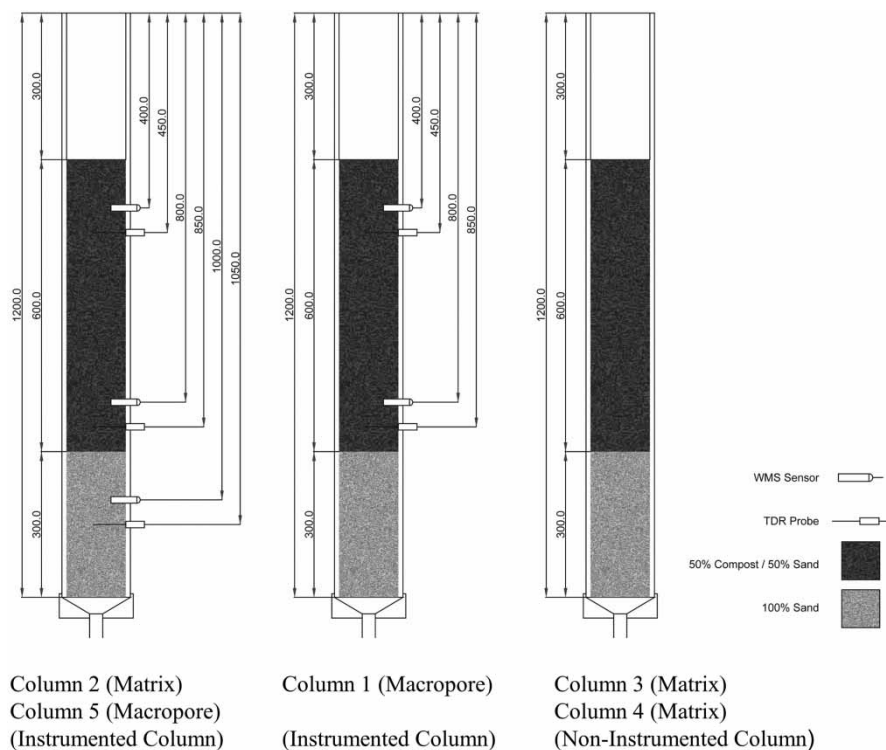
With regards to metal concentration, high values (compared with storm water heavy metal concentrations (Hares & Ward 1999) and those recommended for synthetic storm water runoff for the design of rain gardens (Davis *et al.* 2001)) were chosen: 10,000 µg/L Cu, 10,000 µg/L Pb and 30,000 µg/L Zn. These values are identical to those used by the Highways Research Group (2010) and were chosen as it allowed the examination of a large quantity of heavy metal inflow in a short period of time.

A 20-L container was used to deliver the metal solution to the columns via adjustable sprinklers to control flow and distribute the inflow uniformly across the surface of the soil. The flow rate was measured by determining the time required to fill up a fixed volume in a volumetric flask.

A number of sensors were installed throughout the columns. In order to measure soil water content eight Campbell Scientific S645-L 3-Rod 75 mm time domain reflectometry (TDR) probes were installed through three of the columns (Column 1 (macropore column), Column 2 (matrix column) and Column 5 (macropore column)). To measure water head, eight Campbell Scientific 229-L water matric potential (WMP) sensors were installed throughout three of the columns (Column 1 (macropore column), Column 2 (matrix column) and Column 5 (macropore column)), as close as possible to the TDR probes to obtain values at consistent locations. A diagram of the columns and sensor positions is given in Figure 1.

The water outflow rate from the base of each column was measured using a tipping bucket rain gauge (Two Environmental Measurement Ltd. Golden River 2 mm tip rain gauges, one Texas Instrumentation TR-525M rain gauge, one ADCON RG1 rain gauge and one ONSET 2 mm tip rain gauge). The TDR probes, WMP sensors and rain gauges were connected to a Campbell Scientific CR10X datalogger where their measurements were stored.

To determine whether preferential flow occurred, a tracer (bromide) of concentration 10,000 µg/L was included in the inflow. Its outflow concentration was monitored using a Cole-Parmer Bromide Ion Combination Epoxy Electrode



**Figure 1** | Diagram of column experiments. All units in mm.

and from the breakthrough curves the degree of macropore flow was ascertained (Cole-Parmer 2008).

Three 20 mm<sup>3</sup> samples of water outflow were taken on breakthrough from the base of each column and every hour subsequently. The samples were filtered through 0.45 µm filter paper. The concentration of Br and the pH of the sample were also measured at this time. Nitric acid was then added to the outflow samples to preserve them for analysis.

All samples were sent to the Consultancy Laboratory at the University of Greenwich for analysis. Determinations were made by ICP-MS (Thermo X series II). Calibration was via synthetic standards. The magnitude of error for this equipment is 5% of result concentration given and the level of detection was 0.03 µg/L for Cu, 0.01 µg/L for Pb and 0.1 µg/L for Zn.

Three experimental sets were completed, each consisting of four runs. Each of these runs lasted for 300 min (5 hours) of water input. Following the completion of each experimental set (4 runs), the media in each column were removed and replaced with new material. This process was completed to ensure the repeatability and accuracy of experiments. A summary of experimental design is given in Table 1.

A preliminary run was completed in order to obtain a sizeable number of blank samples and a meaningful representation of background heavy metal concentration for each set of experiments. This run was identical in duration and sampling times to the experimental runs but the input was pure distilled water without additional heavy metals.

## RESULTS

### Hydrological results

In order to determine whether preferential flow occurred, the results of soil moisture content, tracer analysis and breakthrough times were examined. Water breakthrough refers to the point at which water begins to flow from the column. If a preferential channel exists in the soil, the water should typically travel quickly through it and thus have a shorter breakthrough time than a matrix column.

The basic hydrological parameters of the columns are shown in Table 2. The saturated soil moisture content was determined using the TDR probes and the hydraulic conductivity with a hydraulic permeability test.

**Table 1** | Summary of experimental design

Column no.	Column title	Diameter of column		Upper boundary flow condition	Lower boundary flow condition	Upper boundary metal concentration condition	Column composition	Length of run	Description of set
		Internal	External						
1	Macropore	0.14 m	0.15 m	Average flow: 10 cm/h	Free flow	10,000 µg/L Cu;	Top filter layer (600 mm): 50% compost/50% coarse sand mix. Drainage layer (300 mm): coarse sand. Total column length: 1,200 m	300 min	Each set comprised 4 runs. There were 3 sets in total
2	Matrix					10,000 µg/L			
3	Matrix					Pb;			
4	Matrix					30,000 µg/L			
5	Macropore					Zn			

The saturated hydraulic conductivity for the upper compost/sand layer was 770 mm/h. This is significantly higher than the value of 100 mm/h recommended for a rain garden in order to protect groundwater (Prince George's County Maryland, Department of Environmental Resources 1999). It was decided that this soil be examined despite this finding in order to assess whether its capacity for heavy metal retention is limited by its high permeability. There are numerous advantages to using a highly conductive soil such as reduced ponding and increased plant survival.

### Soil moisture content

Figure 2 shows the variation in soil moisture between the matrix and macropore columns for Experimental Set 1, Run 1. Similar soil moisture content results were obtained for all runs.

In Figure 2 water input occurred between 0 and 300 minutes (5 hours) and a clear wetting and drying front are observable.

If the soil moisture content values in Figure 2 are compared to the  $\theta_{sat}$  values contained in Table 2, it can be seen that the soil moisture content is not close to saturation, thus macropore flow should not be expected to occur in accordance with the findings of other column experiments (Lamy *et al.* 2009).

However, Nimmo (2012) detailed a number of cases where preferential flow occurred in unsaturated field conditions.

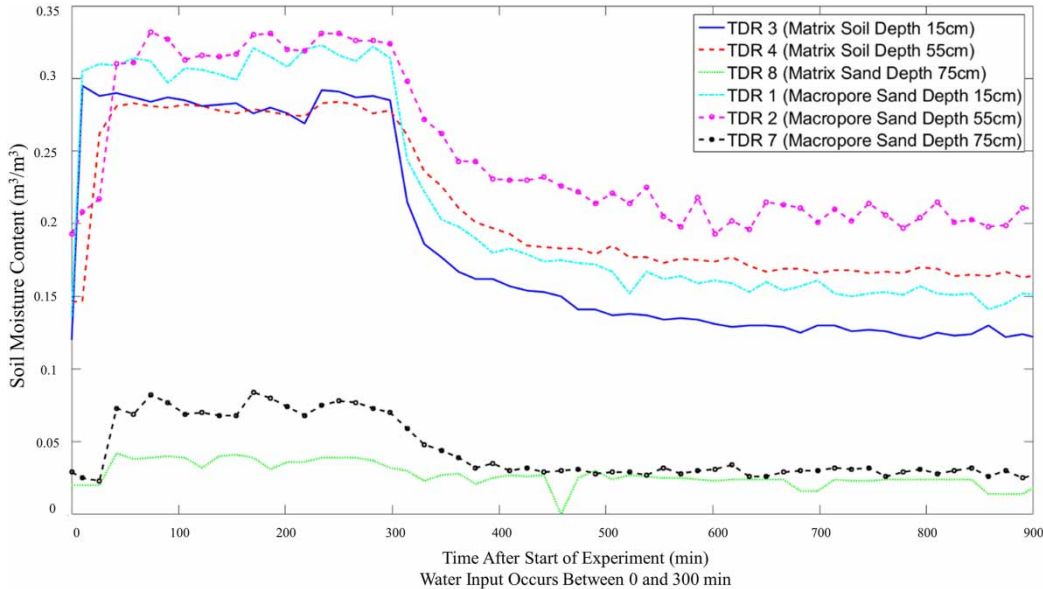
From Figure 2 at a depth of 15 cm and 55 cm the soil moisture contents in the columns are comparable differing, on average, 11 and 14%, respectively. It is noted that at 75 cm there is a distinct difference in water content values with Column 5 (macropore) having a considerably larger value than Column 2 (matrix) during water input. This difference was, on average, 35%. This may be due to macropore flow occurring in the upper layer and transferring water from the surface directly to the drainage layer. There is no clear proof that preferential flow has occurred however as this could be due to soil heterogeneity so the tracer and breakthrough results are also analysed.

### Water breakthrough times

Figure 3 shows the breakthrough times for each of the columns for the four runs in all experimental sets. Water breakthrough time refers to the point at which water begins to flow from the column. If there is a preferential channel through the soil, the water should typically travel quickly through it and thus will have a shorter breakthrough time than a matrix column (Jury & Horton 2004).

**Table 2** | Hydrological parameters of the columns

Parameter	Sand/Soil mix			Sand	
	Column 1 (macropore column)	Column 2 (matrix column)	Column 5 (macropore column)	Column 2 (matrix column)	Column 5 (macropore column)
$\theta_{sat}$ ( $m^3/m^3$ ) (saturated soil moisture content)	0.466	0.491	0.467	0.306	0.343
$K_{sat}$ (mm/h) (saturated hydraulic conductivity)	770	770	770	1,100	1,100



**Figure 2** | Soil moisture content for a matrix and macropore column for Experimental Set 1, Run 1.

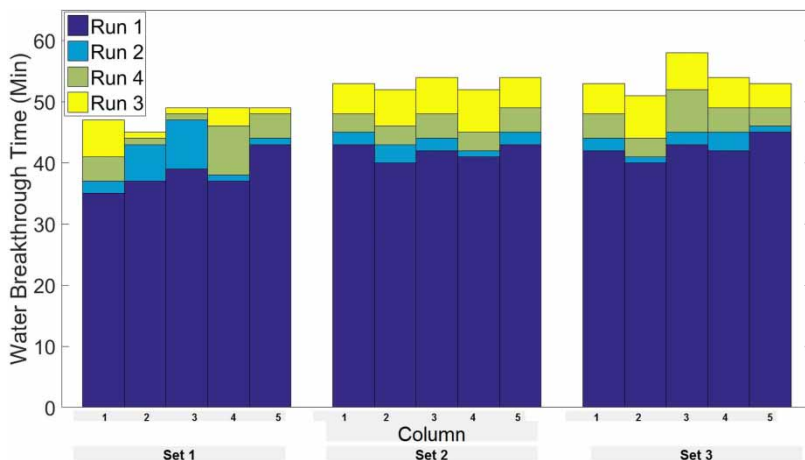
Figure 3 shows that there is no considerable difference in breakthrough times between the columns. On average, they fall within 10% difference of one another. Run 1 consistently has the lowest breakthrough times, and this was attributed to the initial higher water content of the columns (Quinn 2015).

The slight differences between the breakthrough times of the runs are attributed to the preceding periods of dryness. There was a period of 48 hours between Run 1 and Run 2, 96 hours between Run 2 and Run 3, and 48 hours between Run 3 and Run 4. However, soil initial conditions

remained similar with a maximum decrease in soil moisture content of 21%. The 96 hour break between Runs 2 and 3 resulted in a longer time to water breakthrough as the columns were considerably drier than for the other runs.

### Tracer results

It was found that in all runs at breakthrough the tracer inflow concentration was equal to the tracer outflow concentration. This indicates that piston flow has occurred and that tracer and water move at the same velocity and the front arrives as



**Figure 3** | Breakthrough times for columns for all experimental sets.

one discontinuous jump to the final concentration (Jury & Horton 2004). This gives a preliminary indication that no surface macropore flow occurred. However, there is still a possibility of subsurface initiated preferential flow which would influence metal retention. This will be ascertained by examining the heavy metal outflow results.

### Heavy metal outflow results

Figure 4 shows the range and average of the blank sampling procedure. It is evident that the upper layer of soil contained a low concentration of heavy metals (Quinn 2015). Thus, it was important to differentiate between this background concentration and increased outflow concentration due to the input of additional heavy metals. Figure 4 indicates that for all sets the blank concentration of heavy metals fell within the same range. It is clear that the initial Cu and Pb outflow concentrations for all experimental sets is comparable. The initial concentration for Zn varies between the sets from 3 to 42  $\mu\text{g/L}$  but in all cases it is far less than the input concentration of 30,000  $\mu\text{g/L}$ .

In Figure 5 the results of the four experimental runs are shown; heavy metal outflow concentration is displayed as a

function of experimental time (along the four runs) for each of the experimental sets. For Set 1, one sample was taken at water breakthrough and every hour afterwards. This resulted in numerous spikes in the outflow concentration of Pb and Zn which was attributed to their tendency to remain in particulate rather than dissolved form. This leads to abnormally high values upon analysis. The samples were filtered through 0.45  $\mu\text{m}$  filter paper; however, this has been found to be insufficient at removing particulate matter and in future 0.1  $\mu\text{m}$  should be used (Chen *et al.* 2016). For Sets 2 and 3, three samples were taken at every sample time to temper these large values. The trend line for each column represents the median values and the error bars represent the maximum and minimum concentration values of the three samples.

It is evident from Figure 5 that in all cases the heavy metals were retained almost completely with the rates of >99%.

In order to demonstrate the repeatability of the experiments, Figure 6 shows a comparison between sets for individual columns for each of the heavy metals Cu, Pb and Zn. Overall, each column exhibits the same heavy metal outflow behaviour irrespective of set, proving that the results are consistent despite different batches of soil being used for each set.

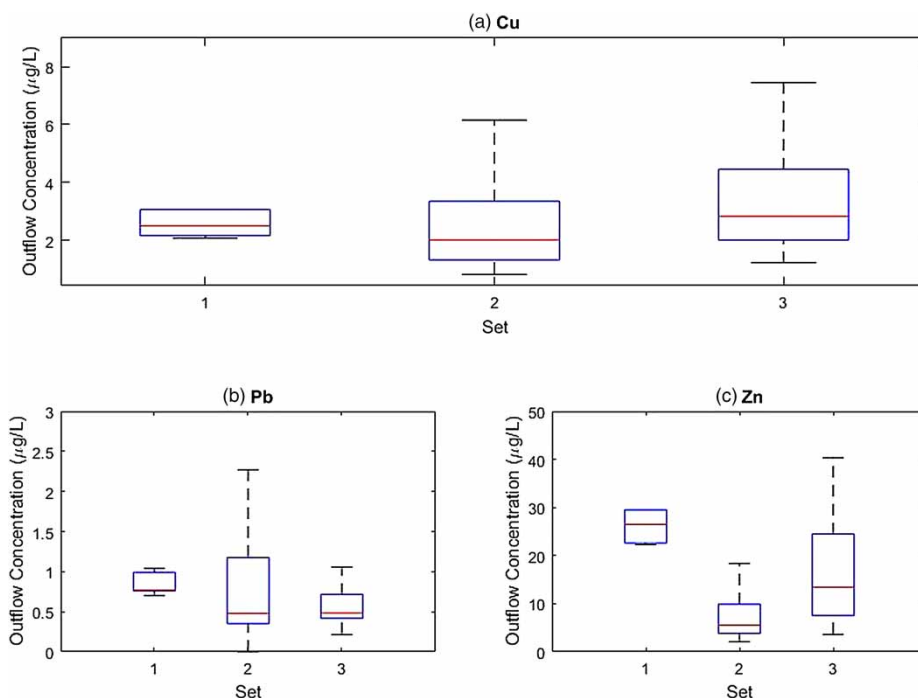


Figure 4 | Blank sample ranges of the columns.

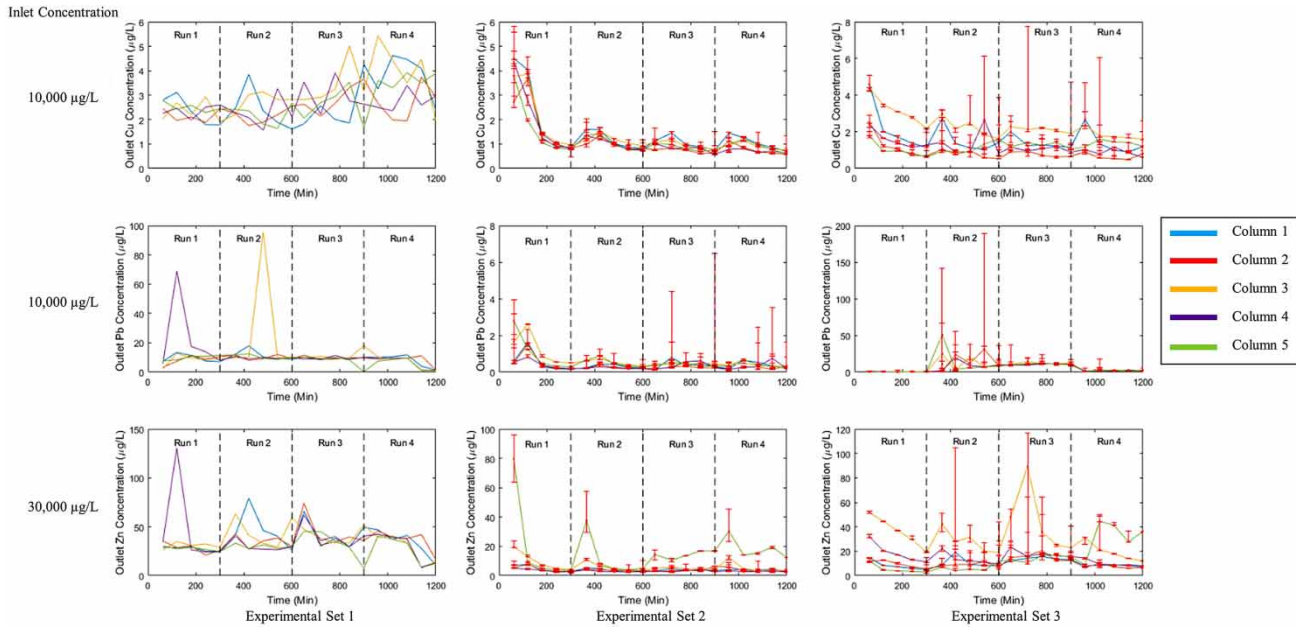


Figure 5 | Heavy metal outflow concentrations for all experiment sets.

The small variations between the sets are attributed to differences in background concentration (Figure 4).

From Figure 5 there appears to be no significant difference between the outflow concentrations from the matrix and macropore columns. This indicates that the presence of

a macropore in highly conductive rain garden soil does not decrease heavy metal retention. Statistical analysis in the form of a t-test was performed to further confirm this finding.

The p-values from t-tests were used to compare macropore (Column 1 and 5) and matrix (Column 2 and 4)

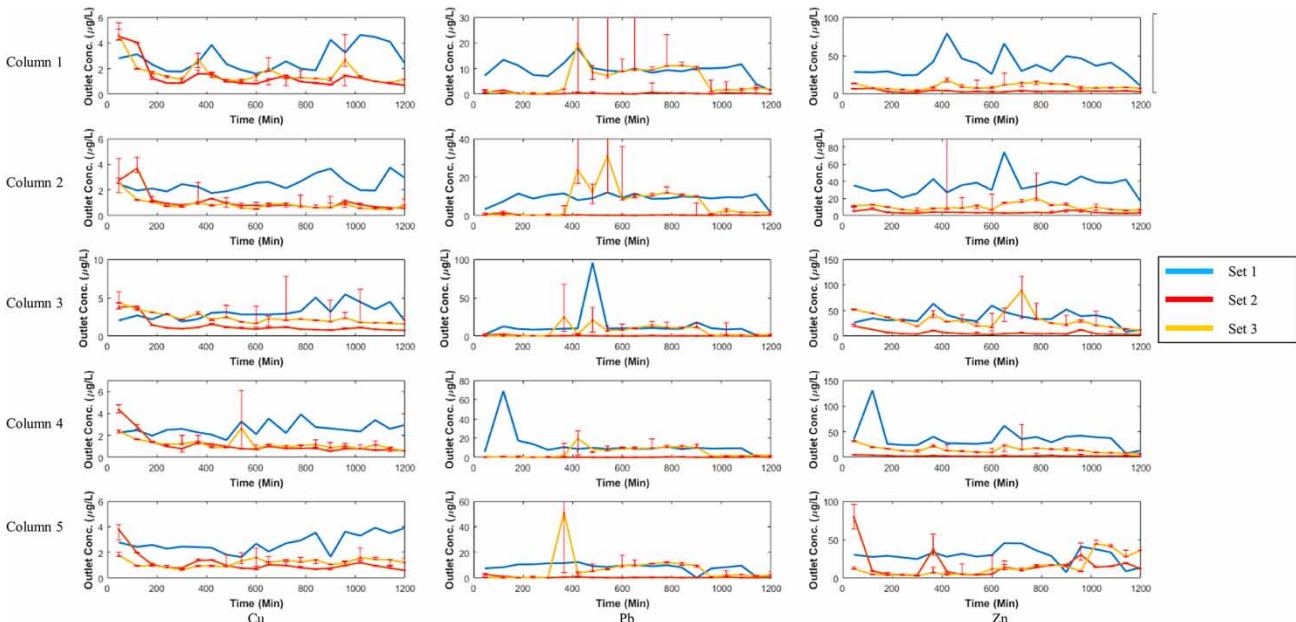


Figure 6 | Comparison of experimental sets for each column.



columns. Column 3 was excluded from statistical analysis, as during the experiments, sidewall flow was consistently observed resulting in erratic outflow concentration values.

It was found that there were two cases with a consistent statistical difference between macropore and matrix columns (one case for Cu, Set 3 (0.0082) and two cases for Zn, Set 2 (0.003 and 0.0017)). These cases correspond to sets which had large ranges of outflow concentration, as illustrated by the error bars in Figure 5.

## DISCUSSION

In this study, column experiments were performed to investigate the heavy metal retention in rain garden soil with and without macropores under English climatic conditions. A preliminary analysis of the soil moisture content, breakthrough times and tracer results indicated that there was no significant hydrological difference between the macropore and matrix columns.

It should be noted that the hydraulic conductivities of both the upper (soil/sand mix) and lower (sand) layers are very high with a saturated hydraulic conductivity value of 770 mm/h and 1,100 mm/h, respectively. These values are properties of the soil and were calculated by examining the velocity of the wetting wave using the instantaneous profile method (Quinn 2015). Nimmo (2007) proposed that macropores in soils have a 'natural speed limit' in unsaturated soils. This limit varies depending on soil type but has been found to range from 41.6 mm/h to 2,500 mm/h. The minimum breakthrough times for the columns (Experimental Set 1, Run 1: 35 minutes Column 3) indicate that the water velocity through the columns was 1,100 mm/h. This is within these speed limits. Thus, water could be active in the macropores, yet have the same speed as flow in the matrix region; this would explain the similar breakthrough times and tracer results despite the deviation in soil moisture content between the two types of column.

These findings also support the possibility of complete water transfer from the macropore to matrix region. Water transfer has been found to occur between the regions in grassland soil but has never been examined in the context of a rain garden (Weiler & Naef 2003). It has been proposed that due to the high hydraulic conductivity of the soil used in

some SuDS, all of the water contained in the macropores transfers directly to matrix region instantaneously due to the conductivity of the media (Morgan 2011; Quinn 2015). These experiments support this conclusion.

With regards to heavy metal retention, it was found that there was a statistically significant difference between macropore and matrix columns for Cu and Zn concentration outflow. Cu and Zn are the most mobile of heavy metals so if a small concentration was present in the macropores it would not be retained to the same extent as in the matrix region as macropores have a lower heavy metal retentive capacity (Knechtenhofer *et al.* 2003). This result has been found by previous field studies, that macropores can adsorb heavy metals but that their adsorption sites decrease over time as they reach retention capacity (Knechtenhofer *et al.* 2003). This is supported by the retention of Pb in these column studies which was unaffected by macropore flow due to its immobility in soil.

However, there is a possibility that due to the low concentrations involved, these statistical findings are simply anomalies. This is supported by the findings of the other sets where there was no difference between macropore and matrix columns.

From the raw data for all experimental sets, it was clear that for all heavy metals (Cu, Pb, Zn) excellent retention was seen (>99%) for both macropore and matrix columns. This result correlates with previous findings (Davis *et al.* 2001; Sun & Davis 2007; Li & Davis 2008; Blecken *et al.* 2009).

These results differ from the macropore column findings of Camobreco *et al.* (1996), who found that columns exhibiting preferential flow only retained 70–75% of the influent Cu, Pb and Zn. This is attributed to the length of the columns; the columns in this paper were packed with a depth of 600 mm of optimized soil and 300 mm coarse sand as opposed to the 350 mm of soil used by Camobreco *et al.* (1996). This indicates that in deeper SuDS devices, macropore flow is not of paramount concern with regards to the retention of heavy metals and may be beneficial in terms of increased hydraulic conductivity over time (Dussaillant 2002). However, in shallower systems such as green roofs, their retention may be impacted by the existence of preferential flow, and more research into this area is needed. The difference in retention may also be attributed to the level of soil saturation. The soil moisture contents observed by

Camobreco *et al.* (1996) were similar to those observed in the experiments presented in this paper. However, they did not record the saturated soil moisture content so the degree of column saturation is unclear.

There were several limitations to this study. The water loading rate of 120 mm/h was significantly inferior to the saturated soil conductivity (770 mm/h). Thus, the soil matrix remained unsaturated and no ponding occurred, which is not the usual mode of operation of a rain garden. The chosen soil conductivity is also far superior to recommended values which limits its capacity to filter suspended solids. Therefore, it is recommended that future experiments examine soils with lower hydraulic conductivity under ponded conditions. In addition, further parameters such as humidity should be measured and smaller mesh of filter paper used to prevent particulate matter in the analysed samples.

Macropore flow has never been examined in the context of green roofs but it is of vital importance to consider due to the shallow nature of these systems and could possibly partially explain the large variance in retention between green roofs. It has also been observed by Getter *et al.* (2007) that over a period of five years, the pore space in an intensive roof increased from 41.41% to 81.84%, which increased water holding capacity but could have an impact on metal retention if part of this was macropore space; since this was not examined, more work needs to be completed.

In addition to depth, other factors play a key role in pollutant retention such as adsorption isotherm constants of the soil media, average residence time, event mean pollutant concentration statistics, the long-term mean annual heavy-metal loads per unit area of the system and the age of the system reflected as diminished treatment capacity. These need to be examined further and the influence of macropore flow on these parameters quantified.

## CONCLUSIONS

In conclusion, under temperate climatic conditions macropores are not a dominant factor in either the movement of water or pollutant through a rain garden with highly conductive soil. There were some statistical differences between macropore and matrix columns' outflow concentrations of Cu and Zn in two individual sets. However, as this behaviour

does not occur in other sets it is attributed to anomalous values caused by low outflow concentrations.

The above results were then compared to other macropore retention experiments and it was observed that macropore flow may not impact rain gardens due to their depth. However, in shallower systems, such as green roofs, heavy metal and other pollutant retention may be impacted by the existence of preferential flow and more research into this area is needed.

## REFERENCES

- Allaire-Leung, S., Gupta, S. & Moncrief, J. 2000 [Water and solute movement in soil as influenced by macropore characteristics 2. Macropore tortuosity](#). *J. Contam. Hydrol.* **41** (3–4), 303–315. Doi:10.1016/S0169-7722(99)00074-1.
- Beven, K. & Germann, P. 2013 [Macropores and water flows in soils revisited](#). *Water Resour. Res.* **49** (6), 3071–3092. Doi:10.1002/wrcr.20156.
- Blecken, G. T., Zinger, Y., Deletic, A., Fletcher, T. D. & Viklander, M. 2009 [Influence of intermittent wetting and drying conditions on heavy metal removal by stormwater biofilters](#). *Water Res.* **43** (18), 4590–4598. Doi:10.1016/j.watres.2009.07.008.
- Brown, P., Gill, S. & Allen, S. 2000 [Metal removal from wastewater using peat](#). *Water Res.* **34** (16), 3907–3916. Doi:10.1016/S0043-1354(00)00152-4.
- Burgisser, C. S., Cernik, M., Borkovec, M. & Sticher, H. 1993 [Determination of nonlinear adsorption isotherms from column experiments: an alternative to batch studies](#). *Environ. Sci. Technol.* **27** (5), 943–948. Doi:10.1021/es00042a018.
- Camobreco, V., Richards, B., Steenhuis, T. & Pevery, J. M. M. 1996 [Movement of heavy metals through undisturbed and homogenized soil columns](#). *Soil Sci.* **161** (11), 740–750. Doi:10.1097/00010694-199611000-00003.
- Chen, J. P., Wang, L. K., Wang, M. S., Hung, Y. & Shammas, N. K. 2016 [Remediation of Heavy Metals in the Environment](#). CRC Press, Boca Raton, FL.
- Cole-Parmer 2008 [Cole-Parmer Laboratory Bromide Ion Electrode Instruction Manual](#). Cole Palmer Instrument Company, Vernon Hills, IL, USA.
- Cowin, D. L. 2000 [Evaluation of a simple lysimeter-design modification to minimize sidewall flow](#). *J. Contam. Hydrol.* **42** (1), 35–49. Doi:10.1016/S0169-7722(99)00088-1.
- Davis, A., Shokouhian, M., Sharma, H. & Minami, C. 2001 [Laboratory study of biological retention for urban stormwater management](#). *Water Environ. Res.* **73**, 5–14. Doi:10.2175/106143001X138624.
- Davis, A. P., Shokouhian, M., Sharma, H., Minami, C. & Winogradoff, D. 2003 [Water quality improvement through bioretention: lead, copper, and zinc removal](#). *Water Environ. Res.* **75** (1), 73–82. Doi:10.2175/106143003X140854.
- Dussailant, A. R. 2002 [Focused Groundwater Recharge in A Rain Garden: Numerical Modeling and Field Experiment](#). PhD thesis, University of Wisconsin, Madison, WI, USA.

- Dussaillant, A. R., Cuevas, A. & Potter, K. W. 2005 Raingardens for stormwater infiltration and focused groundwater recharge: simulations for different world climates. *Water Sci. Technol.: Water Supply* **5** (3–4), 173–179.
- Ellis, J. & Mitchell, G. 2006 Urban diffuse pollution: key data information approaches for the Water Framework Directive. *Water Environ. Res.* **20** (1), 19–26. Doi:10.1111/j.1747-6593.2006.00025.x.
- Farm, C. 2002 Metal sorption to natural filter substrates for storm water treatment-column studies. *Sci. Total Environ.* **298** (1–3), 17–24. Doi:10.1016/S0048-9697(02)00142-0.
- Getter, K. L., Bradley Rowe, D. & Andresen, J. A. 2007 Quantifying the effect of slope on extensive green roof stormwater retention. *Ecol. Eng.* **31** (4), 225–231. Doi:10.1016/j.ecoleng.2007.06.004.
- Gülbaz, S., Kazezyilmaz-Alhan, C. M. & Coptý, N. K. 2015 Evaluation of heavy metal removal capacity of bioretention systems. *Water Air Soil Poll.* **11**, 376. Doi:10.1007/s11270-015-2640-y.
- Hares, R. & Ward, N. 1999 Comparison of the heavy metal content of motorway stormwater following discharge into wet biofiltration and dry detention ponds along the London Orbital (M25) motorway. *Sci. Total Environ.* **235** (1–3), 169–178. Doi:10.1016/S0048-9697(99)00210-7.
- Highways Research Group 2010 *Fate of Highway Contaminants in the Unsaturated Zone*. Highways Agency, Nottingham, UK.
- Hsieh, C. H. & Davis, A. 2005 Multiple event study of bioretention for treatment of urban stormwater runoff. *Water Sci. Technol.* **51** (3–4), 177–181.
- Johnson, J. P. & Hunt, W. F. 2016 Evaluating the spatial distribution of pollutants and associated maintenance requirements in an 11 year-old bioretention cell in urban Charlotte, NC. *J. Environ. Manage.* **184**, 363–370. Doi:10.1016/j.jenvman.2016.10.009.
- Jury, W. A. & Horton, R. 2004 *Soil Physics*. John Wiley & Sons, Inc., Hoboken, NJ, USA.
- Kay, P., Blackwell, P. A. & Boxall, A. B. 2005 Column studies to investigate the fate of veterinary antibiotics in clay soils following slurry application to agricultural land. *Chemosphere* **60** (4), 497–507. Doi:10.1016/j.chemosphere.2005.01.028.
- Klein, R. 1979 Urbanization and stream quality impairment. *J. Am. Water Resour. Assoc.* **15** (4), 948–963. Doi:10.1111/j.1752-1688.1979.tb01074.x.
- Kluge, B., Markert, A., Facklam, M., Sommer, H., Kaiser, M., Pallasch, M. & Wessolek, G. 2016 Metal accumulation and hydraulic performance of bioretention systems after long-term operation. *J. Soil. Sed.* 1–11. Doi:10.1007/s11368-016-1533-z.
- Knechtenhofer, L. A., Xifra, I. O., Scheionost, A. C., Fluhler, H. & Kretzschmar, R. 2003 Fate of heavy metals in a strongly acidic shooting-range soil: small-scale metal distribution and its relation to preferential water flow. *J. Plant Nutr. Soil Sci.* **166** (1), 84–92. Doi:10.1002/jpln.200390017.
- Lamy, E., Lassabatere, L., Bechet, B. & Andrieu, H. 2009 Modeling the influence of an artificial macropore in sandy columns on flow and solute transfer. *J. Hydrol.* **379** (3–4), 392–402. Doi:10.1016/j.jhydrol.2009.07.048.
- Li, H. & Davis, A. P. 2008 Heavy metal capture and accumulation in bioretention media. *Environ. Sci. Technol.* **42** (14), 5247–5253. Doi:10.1021/es702681j.
- Lim, H., Lim, W., Hu, J., Ziegler, A. & Ong, S. 2015 Comparison of filter media materials for heavy metal removal from urban stormwater runoff using biofiltration systems. *J. Environ. Manage.* **147**, 24–33. Doi:10.1016/j.jenvman.2014.04.042.
- Lucke, T. & Nichols, P. W. 2015 The pollution removal and stormwater reduction performance of street-side bioretention basins after ten years in operation. *Sci. Total Environ.* **536**, 784–792. Doi:10.1016/j.scitotenv.2015.07.142.
- Morgan, J. G. 2011 *Sorption and Release of Dissolved Pollutants Via Bioretention Media*. MSc thesis, University of Minnesota, Minnesota, MN, USA.
- Nimmo, J. R. 2007 Simple predictions of maximum transport rate in unsaturated soil and rock. *Water Resour. Res.* **43** (5), W05426. Doi:10.1029/2006WR005372.
- Nimmo, J. R. 2012 Preferential flow occurs in unsaturated conditions. *Hydrol. Process.* **26** (5), 786–789. Doi:10.1002/hyp.8380.
- Paus, K. H., Morgan, J., Gulliver, J. S., Leikes, T. & Hozalski, R. M. 2014 Assessment of the hydraulic and toxic metal removal capacities of bioretention cells after 2 to 8 years of service. *Water Air Soil Poll.* **225** (1), 1801. Doi:10.1007/s11270-013-1803-y.
- Prince George's County, Maryland. Department of Environmental Resources 1999 *Low-Impact Development Hydrologic Analysis*. US Environmental Protection Agency, Maryland, USA.
- Quinn, R. 2015 *Evaluation of Flow Models and Pollutant Retention Isotherms for Their Application to Rain Gardens*. PhD thesis, University of Greenwich, London, UK.
- Safadoust, A., Mahboubi, A. A., Mossaddeghi, M. R., Gharabaghi, B., Unce, A., Voroney, P. & Heydari, A. 2012 Effect of regenerated soil structure on unsaturated transport of *Escherichia coli* and bromide. *J. Hydrol.* **430–431**, 80–90.
- Safadoust, A., Amiri Khaboushan, E., Mahboubi, A. A., Gharabaghi, B., Mosaddeghi, M. R., Ahrens, B. & Hassanpour, Y. 2016 Comparison of three models describing bromide transport as affected by different soil structure types. *Arch. Agronomy Soil Sci.* **62** (5), 674–687.
- Smajstrla, A. 1985 A field lysimeter system for crop water use and water stress studies in humid regions. *Proc. Soil Crop Sci. Soc. Florida* **44**, 53–59.
- Sun, X. & Davis, A. P. 2007 Heavy metal fates in laboratory bioretention systems. *Chemosphere* **66** (9), 1601–1609. Doi:10.1016/j.chemosphere.2006.08.013.
- Trenouth, W. R. & Gharabaghi, B. 2015 Soil amendments for heavy metals removal from stormwater runoff discharging to environmentally sensitive areas. *J. Hydrol.* **529** (3), 1478–1487.
- Weiler, M. & Naef, F. 2003 An experimental tracer study of the role of macropores in infiltration in grassland soils. *Hydrol. Process.* **17** (2), 477–493. Doi:10.1002/hyp.1136.