The fate of polycyclic aromatic hydrocarbons in a model vegetated swale.

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Summary

Determining the fate of PAHs in SuDS is difficult due to the variability between storms and sites. This study developed a 10 m long model vegetated swale system and applied simulated storm events polluted with PAHs. Results from the storm runs show the distribution and fate of four indicator PAHs. Surface soil analysis showed significant reductions in pyrene and fluorene levels, from 1 m to 8 m sample points. Water analysis also showed reductions in PAH levels in the outflow water from the swale. The results show that the model is an effective simulation of environmental systems, allowing the ability to run simulations in controlled conditions.

Keywords

PAH contamination, SuDS, urban drainage, vegetated swale.

Introduction

Pollutants such as metals and polycyclic aromatic hydrocarbons (PAHs) are found in runoff from roads and urban areas. Increasing urbanization, with a dependence on road transport for transport and logistics, means that these releases are increasing. Developments on green field sites can increase flooding and pollution by increasing runoff (Bastien *et al.,* 2012). During the 'first flush' of a storm, the pollutant inputs are at their highest (Zhang *et al.,* 2010). It is during this first stage of a storm that the majority of pollutants are washed off impermeable surfaces and are transported into the immediate environment (Clozel *et al.,* 2006). Different pollutant groups found in stormwater runoff consist of suspended solids, heavy metals, nutrients and organic chemicals (Kayhanian *et al*., 2012). Build-up of these pollutants in the receiving waters can result in toxicity to organisms (Camponelli *et al.,* 2010). To help prevent flooding and pollution entering waterbodies, Sustainable Drainage Systems (SuDS) have been developed. SuDS mimic predevelopment hydrology using infiltration and storage (often in wetlands and ponds) as alternatives to sewer-based drainage (Fryd *et al.*, 2012). These systems trap pollutants from roads and other surfaces, where they can be exposed to remediation processes, providing protection for receiving rivers (Leroy et al., 2015).
Key PAH pollutant removal mechanisms in SuDS are sedimentation, photodegradation, volatilization and adsorption. Quantification of these pollutant removal processes would allow SuDS designs to be refined, and help realise the full potential of such Green Infrastructure. Swales are grassed or vegetated channels, with a slight gradient, normally built to run alongside roads or carparks. Most pollution studies refer to constructed wetlands, with few studies focusing on swales or retention ponds (Leroy *et al*., 2015; Lucke *et al*., 2014). Of those that focus on swales, few consider PAH pollution. Deletic & Fletcher (2006) created a swale for modelling purposes. This swale had no side slopes and focused on the removal of total suspended solids (TSS) in storm water. In a study of four different swales using simulation experiments, Lucke *et al*. (2014) demonstrated that 50 – 80 % of TSS in runoff was removed in the first 10 m of a swale. Their research further showed that swales were able to cope with the higher pollution levels found in the first flush of storms. Leroy *et al.*

(2015) developed swale mesocosms to assess the PAH dissipation process. This study returned positive results, but only looked at vertical filtration. Swales also enable horizontal filtration along the length of the swale, providing increased opportunity for the dissipation and remediation of pollutants.

In the 1970's, the US Environment Protection Agency identified 16 PAHs as representative of the whole family of PAHs, these are now used as standard, for monitoring purposes (Napier *et al.*, 2008). PAHs are considered key indicators for pollution, but can be difficult to quantify meaning that design guidelines, such as the UK SuDS manual (Woods Ballard *et al*., 2015), tend to treat pollutant removal as "black box" design components. PAHs are formed by both natural and anthropogenic sources. Natural sources include volcano emissions and forest fires (Manoli & Samara, 1999). Anthropogenic sources include vehicle emissions, coal fires and oil burning. Of these sources, the anthropogenic releases into the atmosphere are the most significant (Wilcke, 2000). PAHs that comprise of up to four benzene rings are termed 'Light PAHs' and those with more than four rings are known as 'Heavy PAHs'. Heavy PAHs are more stable, and have greater toxicity than the light PAHs. Light PAHs are more water soluble and as such are more likely to be found in an aquatic environment (Wenzl *et al.*, 2006).

Therefore this study has developed a model swale in a greenhouse where vertical and horizontal flow can allow pollutant removal processes to be quantified under controlled conditions.

Methods

Model swale

In order to accurately assess the potential of swale systems to remove pollutants a model swale was designed to mimic a field system. The swale was built, guided by the dimensions recommended in the CIRIA SuDS manual (Woods Ballard *et al.,* 2015). Design was based on a hypothetical catchment of a small car park, 40 m x 10 m. Built to these dimensions the swale is 9.8 m in length, 0.6 m wide with a soil depth of 0.3 m after compaction (Fig. 1.). In cross section the swale has a 0.3 m base and sloping sides of 0.15 m (1 in 3 slope). Longitudinally the slope is 1 in 100, giving a height difference of 0.4 m from inflow to outflow. Soil used in the swale was top soil sourced from a local supplier (Rolawn Blended Loam Topsoil). Soil was uniformly compacted to the specified depth, before a specific SuDS turf, provided by Wildflower Turf UK, was laid on the surface.

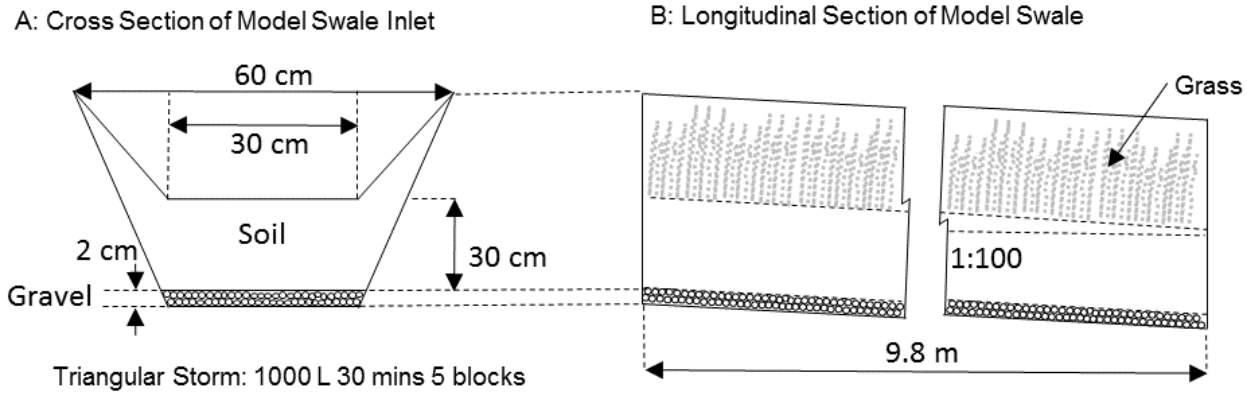

Fig. 1. *Schematic of model swale dimensions A: cross section, B: longitudinal section (not drawn to scale).*

Ten simulated storm events were run over twenty weeks, between November 2016 and April 2017. Over half an hour, 1000 L of water was pumped onto the swale at varying flow rates to mimic a triangular storm hydrograph. Flow rates were: 18.5 l/min for 0 – 6 mins, 37 l/min for 6 – 12 mins, 55.6 l/min for 12 – 18 mins, 37 l/min for 18 – 24 mins and 18.5 l/min 24 – 30 mins (Fig. 2.).

During the first 15 minutes, simulated contaminated road runoff particulates were mixed with the water as it was pumped onto the swale. To create the simulated road runoff, soil used to construct the swale was ground down and sieved into three fraction sizes to best resemble those found in runoff (<63 um, 63 – 150 um and 150 – 450 um). The % of the simulated runoff particulates were <63 um- 80%, 63 – 150 um 14% and 150 – 450 um 6 %. For each simulation 120 g of sieved soil was dosed with 40 ml creosote in 800 ml acetone left to evaporate to give a mean of 200,596, 3,438,354, 7,957,572 and 50,240 ng/g (naphthalene, fluorene, pyrene and benzo(a)pyrene respectively). This is approximately 4 times that seen in background environmental samples (Waterlooville, Hampshire, Roinas *et al.*, 2014) to allow detection of the contaminated particles once diluted and flushed onto the model swale. Contaminated soil was added to the swale during the storm simulation by suspending contaminated soil in tap water (40 g/L) and pumping 2.1 L of contaminated solution at 140 ml/min into the simulated storm water just before it entered the swale.

Experimental methods

Water samples were collected at specific intervals from both inflow and outflow, stored in glass amber bottles at 2 – 8^{o}C. Standard water quality tests for: pH, temperature, conductivity were measured in situ with a field probe (PCTestr 35) to manufacturer's instructions, and chemical oxygen demand (COD) was tested using Hach^{TM} mercury- free vials. The samples were acidified to pH 2 with 6N hydrochloric acid to inhibit biological activity and 5 ml of methanol was added to prevent hydrocarbons in the water attaching onto the glass surface of the bottles (EPA method 550.1). PAHs were extracted from the water samples using solid phase extraction Empore C18 Discs (3 M) described in the EPA method 550.1 and application note 54 for C18 discs.

Soil samples were collected 24 hours after the storm event. A quadrat was used to establish a grid pattern from which to collect samples at each of the sampling points: 1 m, 2 m, 3 m, 5 m and 8 m. A random number generator was used to obtain random sampling grid points. Soil cores were extracted with a 2 cm diameter stainless steel corer, and separated into 5 cm sections; surface 0 – 5 cm, mid 5 – 10 cm and lower 10 – 15 cm. Once separated the samples were frozen until analysis.

Soil PAHs were extracted using accelerated solvent extraction (ASE 200 Dionex) following the manufacturer's application note 313, and EPA method 3630C clean-up process. All samples were concentrated to 1 ml at 40^{o}C in a stream of N_2 before analysis via GC-MS (Agilent 6890N - 5973) in SIM mode (method adapted from Roinas *et al*., 2014) .

Four PAHs: benzo(a)pyrene (BaP), pyrene (Pyr), fluorene (Flu) and naphthalene (Nap) were selected for detailed analysis in this paper. Each of which represent PAHs of interest and cover both low and high molecular weight compounds. All are considered as priority pollutants by regulatory organisations around the world (e.g. USEPA, UK EA).

Statistical analysis was performed using Minitab 17. Data was tested for normality and Log_{10} transformed where necessary.

Results

Water

Hydraulically the swale performed consistently under the designed experimental inflow conditions. Fig. 2. is a hydrograph from Run 7, showing both inflow with the stepped flow rate, and the lag time of the outflow (7 to 8 mins in all runs), giving a reliable indication of the swales performance of delaying storm flows. Peak outflow was reduced compared to the peak inflow, demonstrating proving the attenuation of flow by swale systems (Woods Ballard *et al.*, 2015).

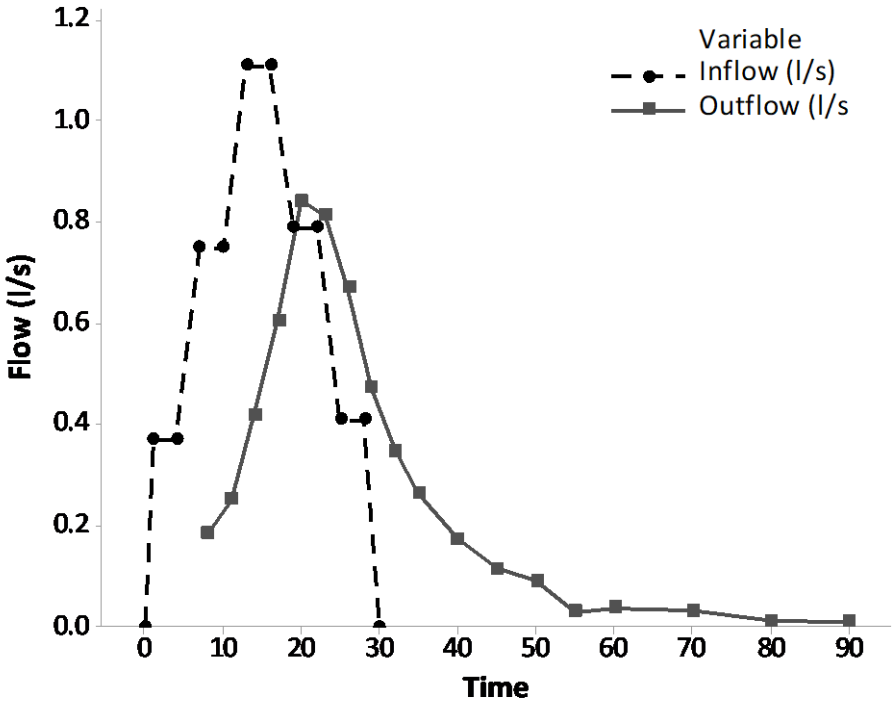

Fig. 2. *Hydrograph from Run 7 showing both inflow and outflow from the swale.*

Water samples showed reduction in pollutant concentrations in the outflow samples (Fig. 3.) for all PAHs. Significant decreases were found in all PAHs, except BaP (ANOVA $F(7, 42) = 0.35$, $P = 0.927$) in the outflow samples compared to the inflows (Tukey pairwise $P < 0.04$ in all cases). The pollutant concentrations progressively decreased over the inflow as the dosed contamination was diluted and then stopped (Fig. 3.).

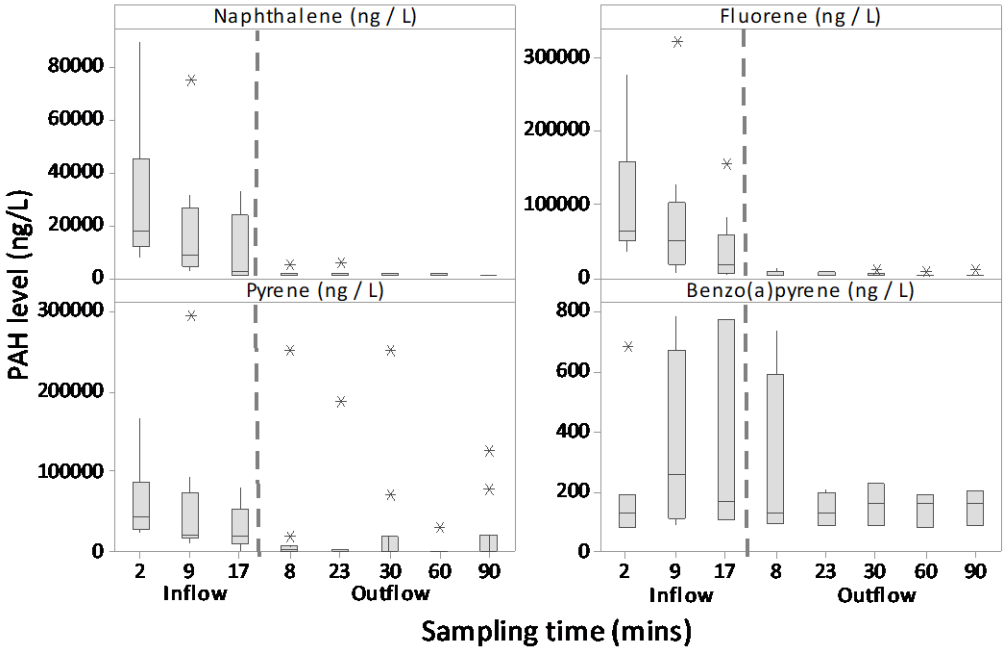

Fig. 3. *Cumulative PAH levels in water samples over ten runs. Four PAHs were analysed, Naphthalene (Nap), Fluorene (Flu), Pyrene (Pyr). Outliers are shown by stars. Vertical dotted line separates inflow and outflow results*

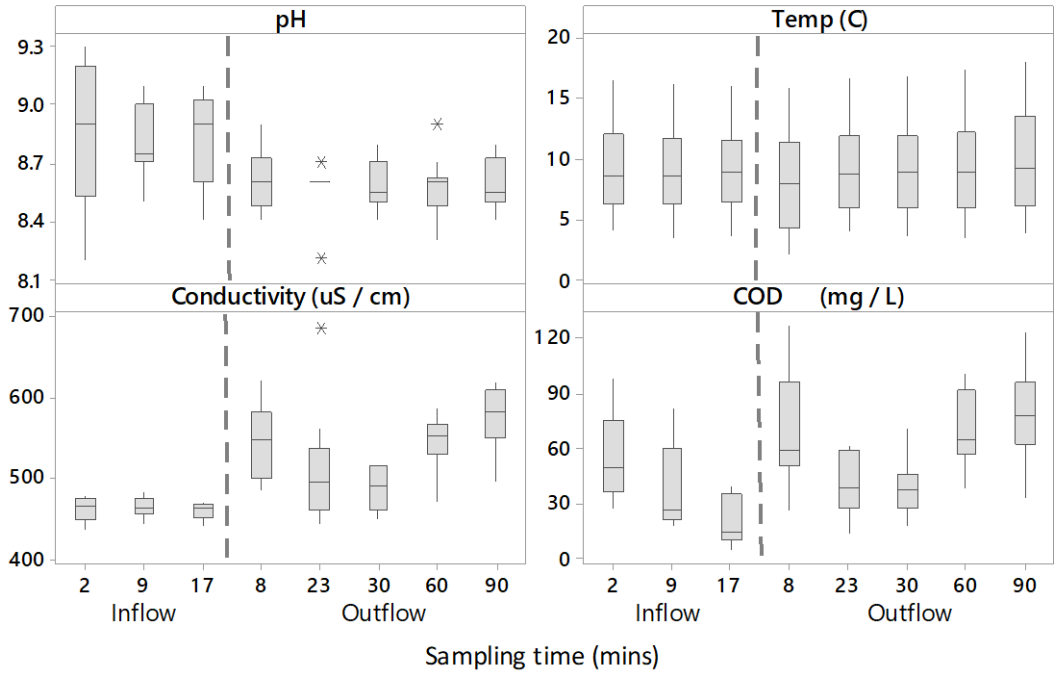

Fig. 4. *Water quality parameters taken at the time of sampling, based on readings taken over ten experimental runs. Outliers are shown by stars. Vertical dotted line separates inflow and outflow results.*

Fig. 4. shows the changes in water quality characteristics. Inflow pH readings were higher than those taken from the outflow samples, however no significant difference was detected ($p > 0.05$). Inflow pH variation was greater than that seen in the out flow waters. Inflow at 2 minutes had a minimum pH of 8.2 and a maximum of 9.3. Conductivity results were significantly higher in the outflow compared to the inflow levels, and also showed a greater range than that seen in the inflow water (inflow 435 – 482 µS/cm, outflow 444- 685 µS/cm).

Temperatures measured remained consistent around a mean of 9°C. The lowest mean temperature was recorded at the first flush outflow (8°C). Run 5 had the lowest recorded temperatures at all sample points, lowest temperature 2.1°C (1st flush at 7 minutes), highest temperature 4.1°C (inflow 2 minutes).

A one-way ANOVA of COD levels showed that there was a significant difference between water samples taken at the different sampling times, $F(7, 72) = 14.32$, $P = <0.001$, Tab. 1. Shows the significant comparisons (Tukey pairwise comparisons). However all median values in outflow samples were higher than those of the inflow at 9 and 17 minutes.

Tab. 1. *COD significant differences (p- value) at various sampling points*

Location/time	Inflow 9 mins	Inflow 17 mins	Outflow 23 mins	Outflow 30 mins
Inflow 2 mins	-	0.009	-	-
Outflow 1st Flush	0.049	<0.001	-	0.045
Outflow 60 mins	0.042	<0.001	-	0.036
Outflow 90 mins	0.003	<0.001	0.005	0.003

Soils

When comparing PAHs across the sampling location, there was significant differences seen for fluorene and pyrene (One way ANOVA $F(4, 137) = 3.78$, $P = 0.006$). Detailed analysis shows the key differences occur between 1 m and 8 m (Tukey pairwise $P = 0.023$ and $P = 0.013$ respectively).

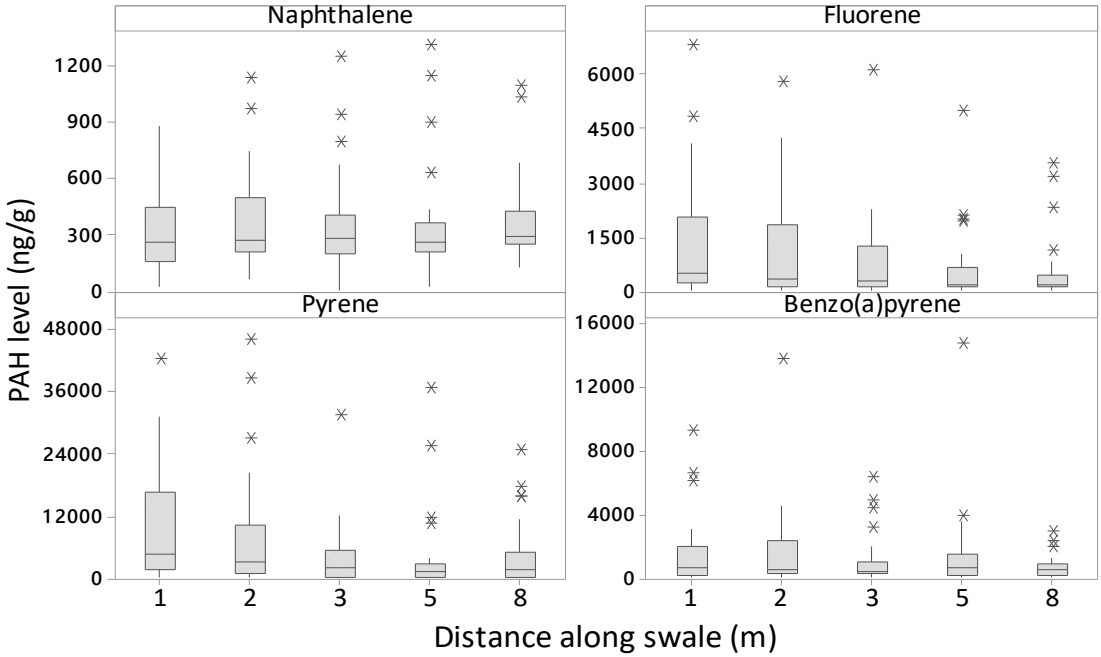

Fig. 5. *Cumulative PAH levels (ng / g) in sediment samples along the length of the swale from ten runs. Samples were collected 24 hours after each run. Outliers are shown by stars. Note: fluorene (73605 ng/g) and pyrene (798259 ng/g and 171940 ng/g) extreme outliers were omitted from Run 6 samples at 1 m for clarity.*

Pyrene levels in 5 m samples were also significantly different to 1 m levels (Tukey pairwise $P = 0.028$). Quartile ranges for the PAHs decrease in size the further along the swale the samples were taken (Fig. 5.), with the greatest reduction occurring in fluorene.

Discussion

Levels of PAHs in the outflow, particularly fluorene and pyrene, demonstrates these heavier PAHs were retained in the system (Wenzl *et al.*, 2006). Adsorption onto particulates increases the likelihood of these PAHs being filtered out of the water column by sedimentation and filtration in the vegetation (Simon & Sobieraj, 2006; Stagge *et al.*, 2012). Reduced levels of PAHs in both water and soil samples (Fig. 3. & Fig. 5.) indicate that a range of removal processes appear to be occurring in the system.

Median values of the individual PAHs across all runs for inflow and outflow show there was an 86 – 94 % reduction seen in the outflow for Nap, Flu and Pyr. BaP showed no decrease. Leroy *et al.* (2015) also observed that mesocosm outflow water was dominated by BaP (58 – 88 % of total PAHs).

Results from the top layer of soil, 0 – 5 cm, were highly variable. During the storm runs, at peak flow, 12 – 18 mins, surface water was reaching the 9 m mark. Due to this coverage, pollution was seen along all samples (Fig. 5.) showing the sediment movement in storm events, as reported by Allen *et al.* (2017). For the heavier PAHs (Flu, Pyr and BaP) there was a reduction in levels found. Similar reduction patterns were shown in the Waterlooville field study (Roinas *et al.*, 2014), where Pyr levels were reduced significantly along the swale and nap showed only slight reductions. Due to their hydrophilic nature the heavier PAHs will adsorb onto particles and are therefore more likely to settle out of the water column. Conversely the lighter PAHs are hydrophobic and are more mobile in the water as it flows down the swale.

Water quality results show that passage through the swale is causing changes to the water. The pH results show that the water is alkaline and falls within the good to high range (pH ≥6 to ≤9) for water quality in rivers for England (www.wfduk.org). The water used for the experimental runs was tap water, in a hard water area. Tests performed in triplicate on each run showed the pH levels of this tap water to have a mean pH 9 across all runs. Outflow results show that passage through the swale

system has reduced and buffered pH. COD levels showed significant changes when comparing inflow and outflow samples. A significant increase was seen in the outflow samples, 1st flush, 60 and 90 minutes compared to the inflow samples at 9 and 17 minutes (Tab. 1.). As the water filters through the swale, organic material is re-suspended in the water column. Pontier *et al.* (2004) reported an increase in COD levels over time in a wetland system receiving road runoff. COD was also reduced in the inflow water again due to the dilution effect of the pollutants.

Based on evidence so far collated it is clear that vegetated swales show significant improvement in water quality, however it is not currently possible to determine exactly where this occurs and the relative importance of each removal process. To further investigate and quantify these processes the next steps for this study are to quantify the vertical dispersion of PAHs and undertake a mass balance to allow the balance of retention and degradation processes to be assessed. This will then inform the future design of swales for PAH removal.

Conclusions

This study aimed to create an effective simulation of results found in the field in a controlled environment:

- The model effectively simulated environmental SUDS swale system.
- Reductions in PAH levels was shown in both water and soil samples.

Further work will now use this system to model the fate processes that occur in swale systems, looking at both infiltration and transportation of PAHs. These will then provide data for environmental risk assessments and future design codes.

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