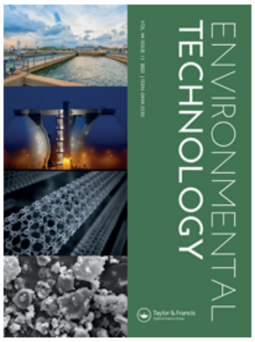

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Synthetic stormwater for laboratory testing of filter materials

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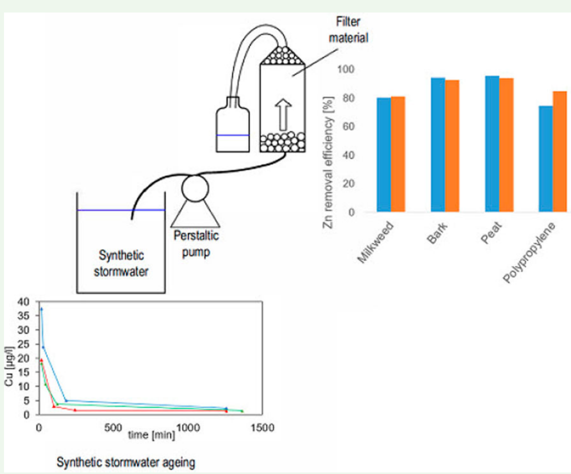
ABSTRACT
Synthetic stormwater was tested to determine the ageing effects on dissolved metal concentrations and used in a column experiment to determine efficiency of four different filter materials (milkweed, bark, peat, polypropylene) in removing total and dissolved metals. Synthetic stormwater was created by adding metal salts, oil and collected stormwater sediment to tap water. Two ageing experiments were performed to determine the change of synthetic stormwater quality over time. One experiment lasted for 11 days and another focused on rapid concentration changes one day after preparation. The one-day ageing experiment showed rapid decrease in dissolved concentration of certain metals, specifically Cu. To consider this change, correction coefficients for each metal were developed and used to estimate the average dissolved metal concentration in the synthetic stormwater during the experiment to determine filter treatment efficiency. During the 11-day experiment on metal concentrations, no noticeable quality changes were observed for at least six days after the preparation of synthetic stormwater. Furthermore, a column experiment was run with duplicate filter columns. Inflow and outflow samples were analysed for total and dissolved metals, turbidity, particle size distribution, and pH. High removal of total metal concentrations was noticed in all tested filter media (58–94%). Dissolved metal concentration removal varied among different filter media. In general, columns with bark and peat media were able to treat dissolved metals better than polypropylene and milkweed. The level of treatment of dissolved metals between the different filter media columns were bark > peat > milkweed > polypropylene.



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Stormwater filters; column test; metals; sediment; stormwater ageing

1. Introduction

Stormwater runoff from urban areas holds various substances and pollutants from sources that the runoff encounters and poses a potential threat to receiving waters. It is widely known that traffic related activities are among the largest sources of many of these substances, especially metals [1]. Metals were indentifed as posing a risk, both to human health and the status of the aquatic habitat of receiving water bodies [2]. The most important metals found in storwmater runnoff include chromium, cadmium, copper, nickel, and lead [1].

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In recent years, systems to remove pollutants from stormwater have received increased attention. These include systems such as sedimentation ponds and constructed wetlands. Stormwater treatment systems are largely based on the sedimentation of particles and as such, they are not efficient in the removal of pollutants present in the colloidal or dissolved phases. Therefore, there is a need to implement techniques to also remove metals not attached to particles. Filter systems, including filter materials with filtering and adsorption capabilities, can be implemented to remove not only particles, but also the dissolved and colloidal pollutants from the stormwater. These filter materials could be used in gully pot filters, or as an additive to filter materials in other stormwater treatment systems, such as bioretention cells [3]. Numerous laboratory studies on potential filter materials for stormwater and wastewater treatment have been performed, many of which have focused on dissolved metals or single metal removal efficiencies [4–7]. Few previous studies have used a mixture of metals commonly occurring in stormwater (Cu, Zn, Pb, Cd, Cr, Ni, etc.) as input solution [8–10], and even fewer have tried to simulate the complex composition of stormwater in the laboratory [11,12].

Synthetic or semisynthetic stormwater is often used in laboratory studies when the goal is to ensure good replicability, but also to try to simulate the quality of inflow more comprehensively. Approaches differ between different studies when it comes to producing a recipe for synthetic stormwater. For example, in a study by Blecken et al. [13], semisynthetic stormwater was used to evaluate the effect of intermittent wetting and drying conditions on heavy metal removal by stormwater biofilters. The influent was made by mixing natural stormwater sediment collected from a gully pot with tap water, and by adding metal salts to achieve target pollutant concentrations (154 mg L^{-1} total suspended solids (TSS) 6.7 µg L^{-1} Cd; 587 µg L^{-1} Zn; 181 µg L^{-1} Pb; and 95 µg L^{-1} Cu). In a study which examined the performance of bioretention systems for the treatment of heavy metals in stormwater [14], a solution was used, based on tap water mixed with the required metal salts, to achieve intended concentrations (80 µg/L Cu, 600 µg/L Zn, and 30 µg/L Pb). In a study that evaluated the potential of street sediment to release dissolved and particulate bound metals [15], synthetic stormwater was used as a testing medium. This synthetic stormwater was prepared using deionized water and different salts ($CaCl_2xH_2O$, KNO_3, $(NH_4)_2SO_4$, $NaNO_3$, Na_2SO_4, and $MgSO_4$) to achieve target concentrations. Another approach that has been used is to collect stormwater in the field and then add metal solutions in order to achieve target concentrations [11].

The aim of this study was twofold. Firstly, the changes in the properties of the synthetic stormwater over time were studied. Secondly, synthetic stormwater was used to compare four different filter materials for stormwater treatment using column tests.

2. Material and methods

2.1. Changes in properties of the synthetic stormwater over time

Two experiments were carried out to investigate how the properties of the synthetic stormwater changed over time. The first experiment focused on the long-term changes in quality and was run for 11 days (11-day ageing experiment), while and the second one focused on short-term changes in quality and lasted for one day (one-day ageing experiment). Highway runoff has been found to be a dominant source of metals in catchments [16]. For both experiments synthetic stormwater was prepared with relatively high pollutant concentrations, corresponding to those found in polluted runoff [17–22]. In the 11-day ageing experiment, synthetic stormwater was prepared by adding 110 g of sediment to 100 L of tap water, alongside metal solutions.

The sediment was collected from an underground sedimentation basin receiving runoff from a heavily trafficked road (annual daily traffic = 71,000 vehicles per day) in Stockholm, Sweden (further described by [23]), and passed through a 200 µm sieve using three pre-sieves (0.8, 0.5, 0.4 mm). The sieved slurry was collected in a plastic container; while stirring, samples were taken out for analyses. The TSS and loss on ignition residue were determined to 156 and 130 mg/g of slurry, respectively. Concentration of metals in sediment as well as total organic carbon is presented in Table 1.

Metal solutions were further prepared using $CdCl_2$, $K_2Cr_2O_7$, $CuSO_4 \times 5H_2O$, $HgSO_4$, $NiCl_2$, and $(CH_3COO)_2$-$Pbx3H_2O$ and $ZnCl_2$, and added to a mixture of 110 g of sediment and 100 L of tap water, to spike the synthetic stormwater with dissolved metals (Table 2). The synthetic stormwater was then kept in a tank and

Table 1. Concentration of metals and total organic carbon (TOC) in the collected sediment from the sedimentation basin.

	Ba	Cd	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn	TOC
mg/kg	159	0.35	69.7	239	37,600	380	32.3	35.4	89.5	1170	78,700

Table 2. Synthetic stormwater characteristics (means with standard deviations in brackets) for stormwater ageing and column experiments.

	11-days ageing experiment ($n = 6$)		Column experiment ($n = 24$)	
Metal	Total concentration	Dissolved concentration	Total concentration	Dissolved concentration
Cd [µg L-1]	1.06 (0.63)	0.2 (0.1)	0.96 (0.08)	0.6 (0.1)
Cr [µg L-1]	15.88 (7.82)	3.6 (0.2)	14.57 (1.71)	5.3 (0.4)
Cu [µg L-1]	94.55 (45.04)	1.7 (0.6)	117.24 (20.22)	17.8 (9.1)
Ni [µg L-1]	13.19 (5.23)	5.6 (0.8)	11.61 (1.00)	7.1 (0.5)
Pb [µg L-1]	27.73 (15.34)	0.5 (0.2)	23.89 (2.01)	4.8 (2.1)
Zn [µg L-1]	459.25 (241.78)	59.4 (9.2)	374.96 (21.03)	161.4 (16.5)
pH	7.8	–	7.6	–
Conductivity [µS/cm]	421	–	154.1	–

pH is given as geometric mean and geometric standard deviation.

continuously stirred using an electrical stirrer to avoid sedimentation of particles.

Samples were extracted from the synthetic stormwater using a valve at the bottom of the tank and collected in glass beakers. For the first experiment, samples were taken the same day as preparation (three hours after mixing), and the following days (day 2, day 3, day 5, day 8 and day 11).

A one-day ageing experiment was conducted during the filter column experiments. The synthetic stormwater solution was prepared from 150 l of tap water, the same batch of stormwater sediment (165 mg) and metal solutions as in the 11-day ageing experiment, and used mineral oil (0.3 g) from the car engine. The synthetic stormwater was kept in a tank where it was continuously stirred. In order to observe changes in the dissolved fractions of metals during the period of one day, samples were taken immediately after preparation of synthetic stormwater, 15, 100 min and 1200 min after preparation. This was repeated for three synthetic stormwater batches. The samples were analysed with respect to total and dissolved metal concentrations. The synthetic stormwater characteristics for both the 11-day ageing experiment and the column experiment are presented in Table 2.

2.2. Use of synthetic stormwater in column experiment

The synthetic stormwater was used to investigate four filter materials in the column experiment. The filter materials tested included both previously investigated materials, i.e. bark (B) [24] and peat (P) [25], as well as novel materials, i.e. airblown polypropylene (PP) and common milkweed (Asclepias syriaca) (M).

Polypropylene is a thermoplastic polymer used for oil-spill recovery due to its low density, low water uptake, and good physical and chemical resistance [26] and has also shown to have a good potential as a stormwater treatment material [27]. In batch tests, polypropylene was shown to have good sorption capacity and relatively fast removal for the organic pollutants [28]. Milkweed has been shown to be efficient in removing oil, due to its oleophilic and hydrophobic nature [29], but it has not yet been considered for stormwater filters.

For the column experiment, the filter materials were inserted into acrylic plastic columns with an inner diameter of 74 mm (Figure 1). Each material was tested in duplicate, resulting in eight filter columns. The filter volume of each of the columns was approximately 0.3 L and the depth of filter media was approximately 60 mm. The amount of filter material added varied between the materials due to their different densities; 9 and 13 g of milkweed, 50 and 45 g of bark, 51 and 64 g of peat, and 22 and 24 g of polypropylene were added to the first and second duplicate, respectively. To keep the filter material from dispersing, it was covered with a round piece of geotextile, which is also used in the full-scale application of gullypot filters. In order to create an even flow distribution for both the inflow and outflow, glass beads (4 mm in diameter) were placed below and above the filter material (Figure 1). Plastic containers and tubing were used throughout the experiment.

Synthetic stormwater was prepared (as described above), continuously stirred, and pumped through the

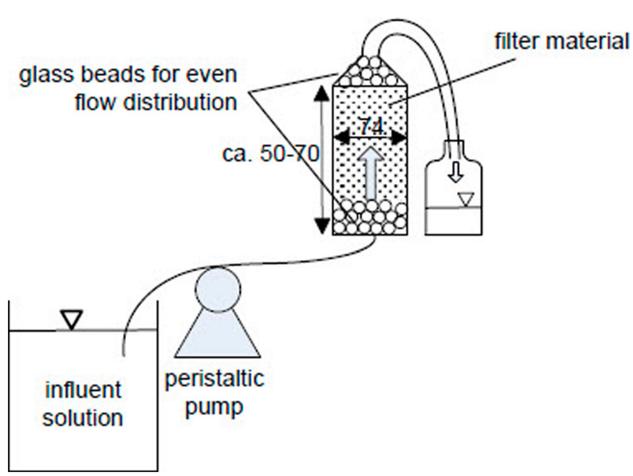

Figure 1. Experimental set-up. Dimensions are given in mm.

columns in up-flow mode, with a flow of 0.005–0.008 L min^{-1}, which corresponds to 0.07–0.11 m^3 m^{-2} h^{-1}. The experiment was run in batches; synthetic stormwater was freshly prepared at the beginning of each day and pumped in the up-flow mode for three days, followed by four days of break. After three weeks, the experimental set-up was left to rest for six months during which the columns were left to dry. Upon restart, the columns were run with the same flow as before for one week, after which the flow was increased to 0.012–0.014 L min^{-1}, corresponding to 0.16–0.20 m^3 m^{-2} h^{-1}, for three more weeks to obtain a more rapid saturation of the filter materials.

In total, 28 batches of synthetic stormwater were prepared. The synthetic stormwater was sampled directly after preparation and after one day of run time – before the next batch of influent solution was prepared. Samples of the effluent water were taken during the preparation of the next batch of influent solution. For the first three weeks of the experiment, influent and effluent samples were taken three days a week. After the experiment break, samples from the influent were continued to be taken daily, while samples from the effluent were taken once a week. For sampling and change of the synthetic stormwater batch, the pump was stopped for approximately 2 h.

After each three-day flow cycle, the synthetic stormwater was emptied from the columns using a valve at the bottom inlet hose. The samples taken from the influent and effluent solutions were analysed with regard to TSS, turbidity, pH, electrical conductivity, and total and dissolved metals (Ca, Fe, K, Mg, Al, As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, V, Zn). During the first week of the experiment, the particle size distribution of the samples was also determined.

2.3. Analyses

Electrical conductivity and pH were measured using a MeterLab CDM210 conductivity metre (Radiometer Copenhagen) and a WTW pH 330 / SET-1 pH-metre, respectively. TSS was analysed according to the Swedish standard SS-EN 872:2005 [30]. Particle size distribution (PSD) was analysed with a laser scattering particle size distribution analyser, Horiba LA-960. Prior to the analyses of dissolved metals, the samples were filtered using a 0.45 µm polyethersulfone (PES) membrane filter. Metal analyses were carried out by an accredited commercial laboratory, using inductively coupled plasma-sector field mass spectrometry (ICP-SFMS) and atomic emission spectrometry (ICP-AES). Sediment metal concentration analysis was carried out by the same laboratory using inductively coupled plasma mass spectrometry (ICP-MS).

Handling of values below the detection limit (TSS, total and dissolved metal concentrations), was performed in accordance with [31]. In cases where the concentrations were below the detection limit, a check was made to see if this occurred for less than 15% of samples for that parameter (e.g. dissolved Pb). If this was the case, that sample was assigned the value of half of the detection limit. If a parameter was under the detection limit more frequently, the sample was assigned the value of the detection limit, as this would be the 'worst case scenario' when analysing filter performance.

In order to test if there were significant differences between the metal concentrations between the first and the second phase of the column experiment, a statistical test, Two-Sample t-Test, was used.

In order to estimate the effectiveness of filters, it was necessary to calculate an average influent concentration of the metal in question. Time-weighted averages of dissolved metal concentration during the one-day ageing experiment in the synthetic stormwater mixture was calculated according to (Equation (1)):

$$C_{avg} = \frac{\sum_{i=1}^{3} \frac{(C_i + C_{i-1})}{2}(t_i - t_{i-1})}{T} \quad (1)$$

where C_{avg} is the average influent dissolved concentration, C_i is dissolved concentration of the element in question at the time step $t_{i,}$ and the total experiment time is T. Essentially, this formula integrates the area below the dissolved concentration curve using the trapezoidal method. This was repeated for the following two run days of testing, and a coefficient was established that determined the relationship between the starting concentration and the average according to Equation (2)

$$k_c = \frac{\sum_{j=1}^{3} \left(\frac{C_{avg,j}}{C_{0,j}}\right)}{3} \quad (2)$$

Table 3. Time-weighted average coefficient (kc, according to Equation (2)) and standard deviation (σ) for dissolved concentrations of metals in synthetic stormwater mixture ($n = 3$).

	metals															
	Cu	Zn	Cd	Cr	Ni	Pb	Ca	Fe	K	Mg	Na	Al	Ba	Co	Mn	V
kc	0.15	0.61	0.34	0.94	0.86	0.34	0.98	0.63	0.99	0.98	0.98	1.09	1.16	1.78	1.14	1.65
σ	0.03	0.01	0.05	0.08	0.02	0.09	0.01	0.13	0.02	0.02	0.03	0.12	0.04	0.08	0.07	0.24

where, $C_{0,j}$ was initial dissolved concentration for the cycle j and $C_{avg,j}$ the time weighted average concentration for cycle j. In Table 3, coefficient k_c and standard deviation (σ) of k_c for different days are presented. Coefficients for total metals were also calculated, but since their values were found to be in the range of 1.01–1.13 they were not used to calculate influent concentrations.

The concentration for the synthetic stormwater batch was then obtained by multiplying the initial concentration with the coefficient corresponding to the metal for which it was calculated, kc.

Metal removal efficiencies were then calculated by comparing the time-weighted average influent synthetic stormwater concentrations and effluent concentrations throughout the experiment.

$$R_m = \frac{\sum_{i=1}^{n}\left(\frac{C_{avg,i}-C_{e,i}}{C_{avg,i}}\right)\times 100}{n} \quad [\%] \tag{3}$$

Where, R_m was the removal efficiency for metal m, $C_{avg,i}$ was corrected influent concentration, ($C_{avg,i} = C_{in,i} * k_c$) was the effluent concentration, i represents the day of the experiment, and n the total number of experiment days.

3. Results

3.1.1. Changes in properties in the synthetic stormwater over time

When evaluating the properties of the synthetic stormwater over time, there was a general decrease of the total concentrations of Cd, Cr, Cu, Ni, Pb, and Zn during an evaluation period of 11 days (Figure 2). The starting concentrations for total metals were 0.8, 14, 81, 12, 24 and 440 µg L^{-1} for Cd, Cr, Cu, Ni, Pb, and Zn, respectively. On the last day, total concentrations were reduced to between 38% (Zn) and 64% (Ni), compared to the starting value. One deviation was noticed, on the eighth sampling day, where the total concentrations were at least doubled as compared to the previous sampling. This was likely caused by sediment accumulation and a non-representative sample for that specific day of the sampling. The dissolved metal concentrations were more stable in the synthetic stormwater, where values on the final day of the experiment remained at 70-110% of the value for the first day.

In order to evaluate how the concentration of total and dissolved metals changed over time in batches of synthetic stormwater, more frequent samples of the synthetic stormwater were taken from three batches. The change of concentrations of total and dissolved Zn, Cu, Cd and Cr are shown in Figure 3.

The change of the concentration of dissolved metals differs for different metals. For some, like Cu and Zn, there is a clear decrease in dissolved concentration during the evaluation period of 1200–1400 min, where the concentration of dissolved Cu and Zn decreased by 85% and 28%, respectively. By contrast, the concentration of dissolved Cr and Mg decreased by only 1 and 2%, respectively. The observed changes in metal concentrations occurred quite rapidly after the synthetic stormwater batches were created, i.e. within the first two hours.

3.1.2. Column test to evaluate filter materials for stormwater treatment

3.1.2.1. Change in particle size distribution, turbidity and pH after filtration

In the evaluated effluent samples from the different columns, median particle size distribution (d50) ranged from 0.52 µm for bark to 2.45 µm for polypropylene over the experiment period. However, the particle size distribution (d50) varied between the duplicate columns, e.g. the two columns with bark showed a relative difference of 9.3%, while that value for polypropylene was 76%, the same day (data not shown). It could

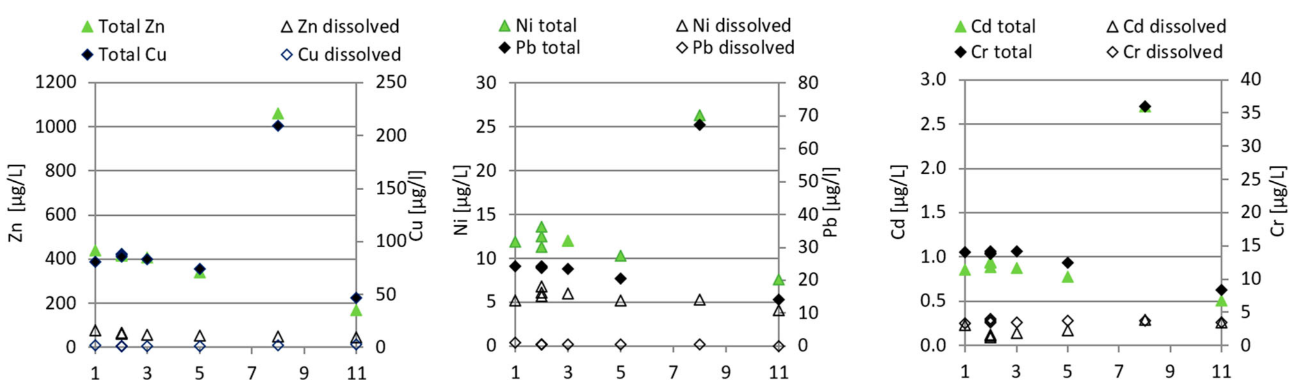

Figure 2. Total and dissolved concentrations of Zn, Cu (left), Ni and Pb (middle) and Cd and Cr (right) during 11-day evaluation period.

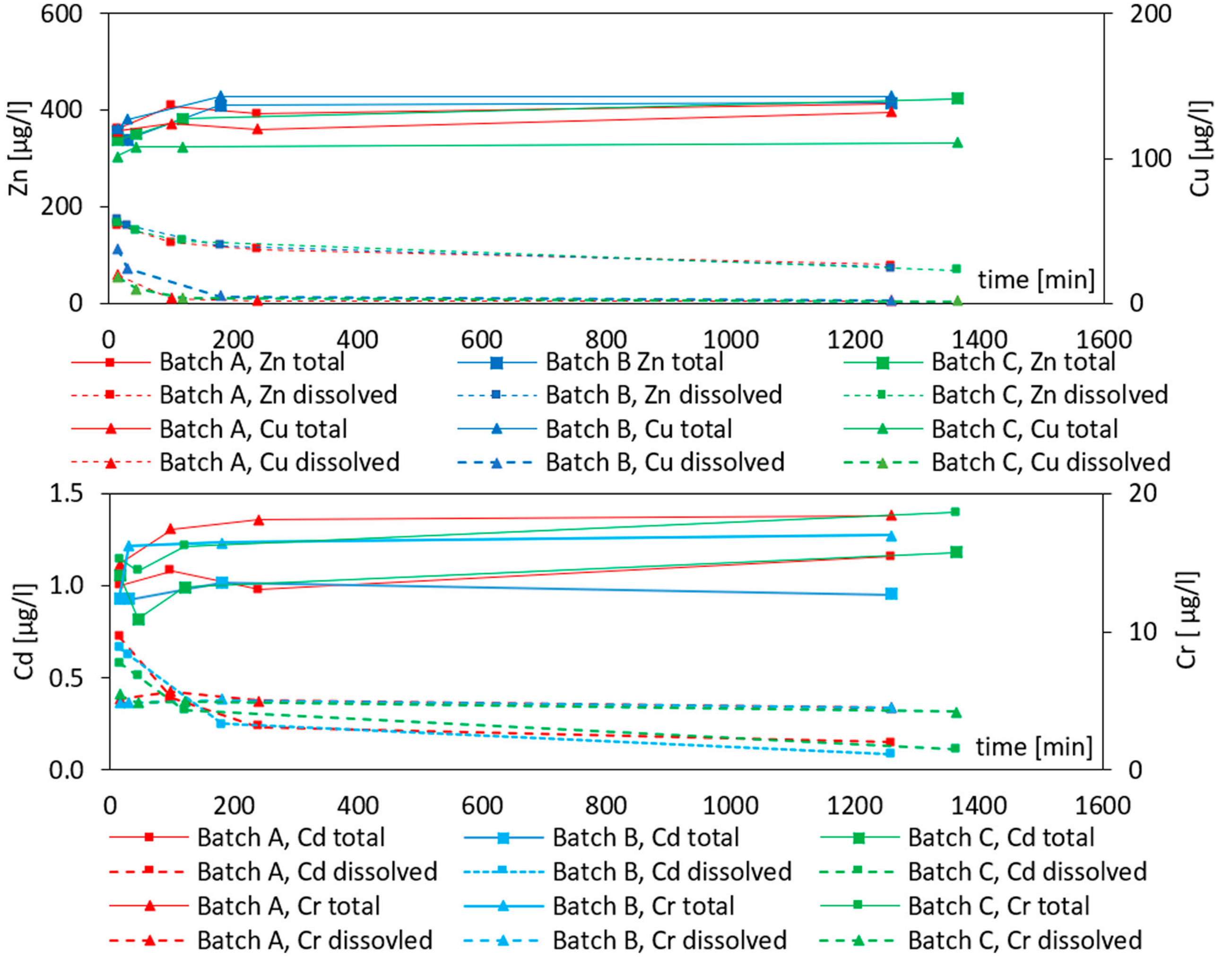

Figure 3. Change in total and dissolved Cu and Zn (top) and Cd and Cr (bottom) concentration in the inflow batches during the short-term ageing experiment.

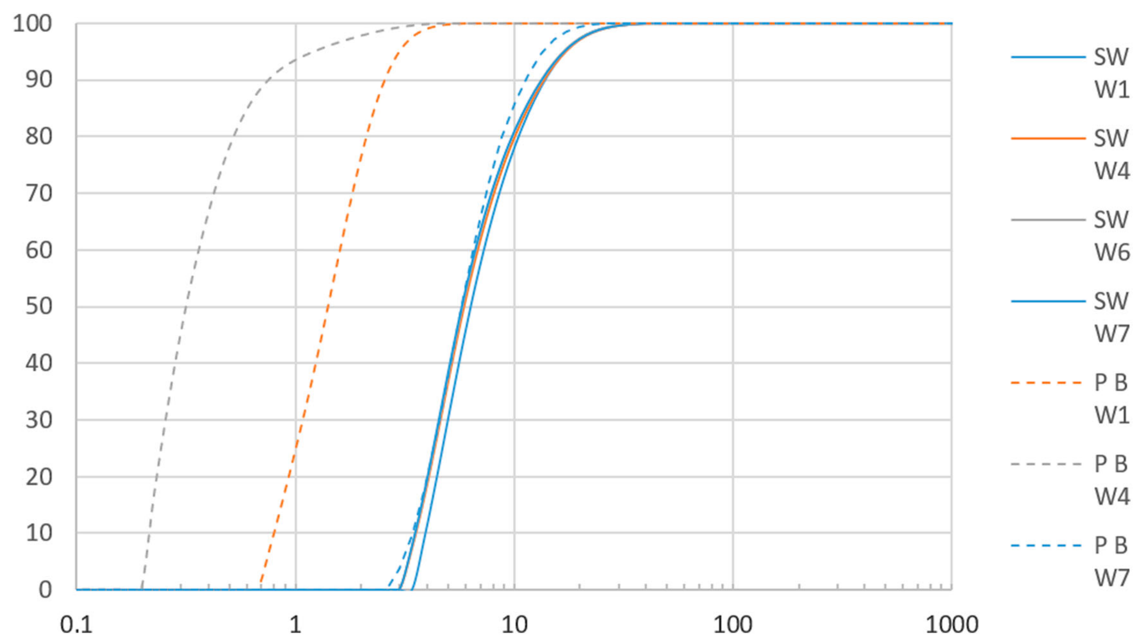

Figure 4. Particle size distribution in synthetic stormwater (SW) samples and effluent samples from one of the two peat columns (P B). The legend presents the week of the cycle for which PSD graph is presented (e.g. (W1) Week 1).

also be seen that effluent from all the columns showed smaller particle size distribution (d50) than the influent synthetic stormwater.

For the synthetic stormwater, the median particle size distribution in the influent (d50) did not vary between the analysed batches, and d50 ranged from 7.6 to

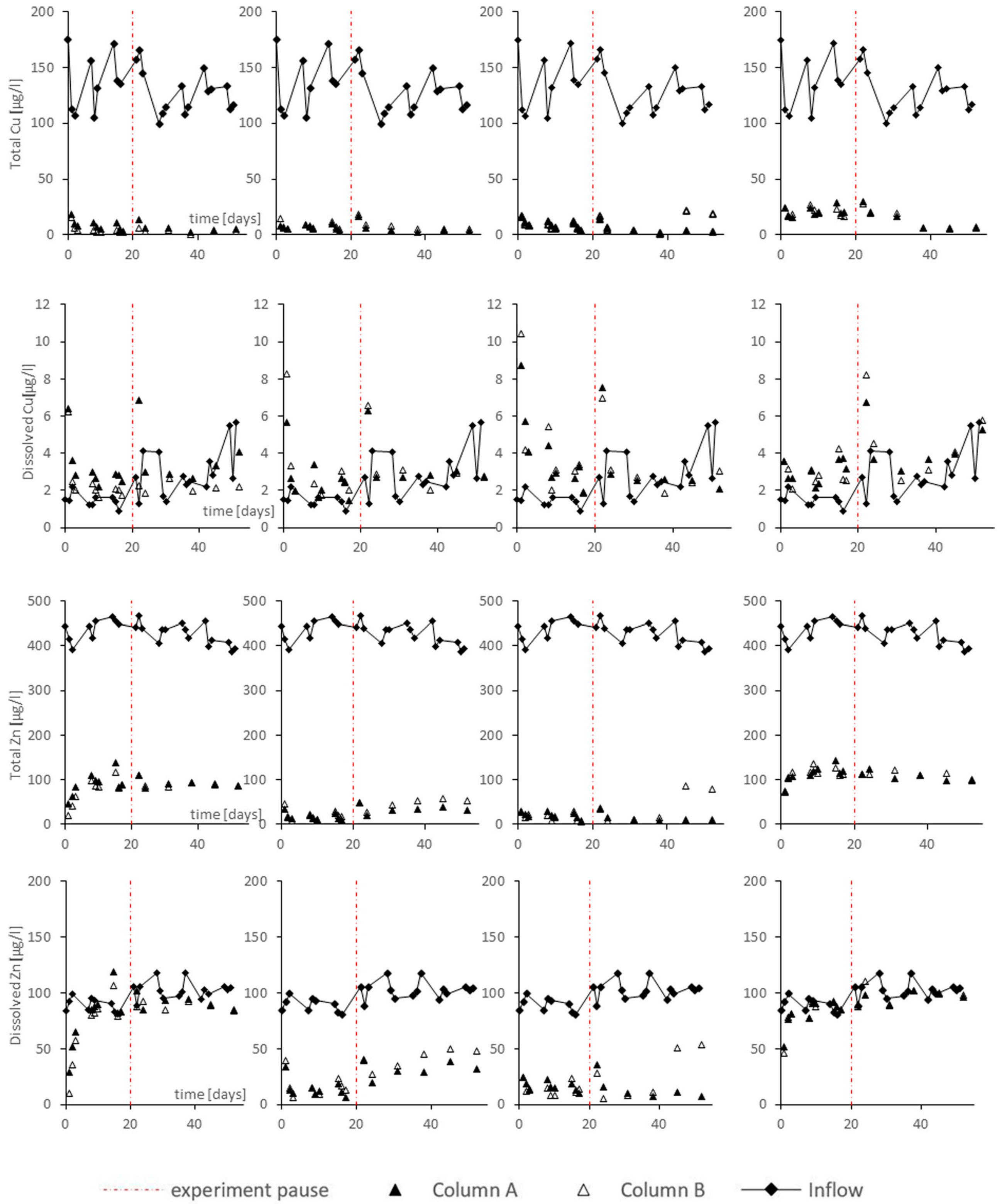

Figure 5. Total and dissolved concentration of Cu and Zn in the column experiment in the inflow and the outflow from duplicate columns. The red line indicates the break in the experiment. Order of charts from left to right: Milkweed, Bark, Peat, Polypropylene.

7.8 µm with standard deviation of 0.4 ($n = 28$). While there was no noticeable change in particle size distribution over time in the influent synthetic stormwater samples (Figure 4), the particle size distribution in the effluent varied over time. There was a noticeable increase of particle size in the outlet samples, as the experiment progressed.

The PSD of other filters behaved similarly, with an increase in particle size as the experiment progressed.

The initial turbidity in the synthetic stormwater ranged from 32 to 60 NTU. Milkweed (excluding the outlier on the second day), bark and peat filters were able to reduce the turbidity by more than 90% throughout the duration of the experiment, and the average effluent turbidity was 2.3, 4.0 and 3.6 NTU for those three filters, respectively. Turbidity in the samples taken from the polypropylene filter columns was higher (average 7.8 NTU).

The average pH value in the synthetic stormwater was 7.6 over the duration of the column experiment. In the effluent, pH values were 7.2–7.8, 6.2–7.7, 6.0–7.8 and 7.4–7.8 for milkweed, bark, peat, and polypropylene effluent samples, respectively. No trend of increase or decrease was noticed over the duration of the experiment.

3.1.2.2. Reduction of total and dissolved metal concentrations

Figure 5 shows the total and dissolved Cu and Zn concentrations in the influent solution and in the effluent from the duplicate columns during the experiment, respectively. There was a statistically significant increase in the dissolved metal concentrations in the synthetic stormwater after the break for the Cd, Cu, Pb and Zn. Effluent from the peat columns showed a significant increase in total Zn, Ni and Pb concentrations, as well as dissolved Cd, Pb and Zn concentrations. Effluent from milkweed columns showed no significant increase in concentrations, other than the dissolved Pb. No noticeable trend was identified for the peat and polypropylene columns.

The average influent total and dissolved Cu concentrations were 100–175 µg L^{-1} and 0.9–5.7 µg L^{-1}, respectively. The corresponding total and dissolved Zn concentrations were between 380 and 460 µg L^{-1} and 80 and 118 µg L^{-1}, respectively. For example, the average dissolved Zn in the influent before the experiment break was 89.1 µg L^{-1} and the concentration increased to 102.6 µg L^{-1} after the break. In the effluent, total Cu concentration ranged from 2.6 µg L^{-1}–18 µg L^{-1} for milkweed, 1.4 µg L^{-1}–6.3 µg L^{-1} for bark, 1.8 µg L^{-1}–8.7 µg L^{-1} for peat, and 2.2 µg L^{-1}–6.7 µg L^{-1} for polypropylene filtrated samples. Total and dissolved average concentration and with standard deviations for Cd, Cr, Cu, Ni, Pb and Zn are presented in Table 4.

In general, the total metal removal was high (over 70%) for all of the tested filter materials, with the only exception being total Ni removal in case of the milkweed (59%, Table 5). All filter materials reduced total Zn in synthetic stormwater in the range of 74% (PP) to 96% (P). Similarly, all four materials showed high removal potential for total Cu, where efficiencies ranged from 87% (PP) to 95% (B). Looking at dissolved Zn, bark and peat achieved a higher removal efficiency when treating the synthetic stormwater (75% and 82%). Milkweed and polypropylene treated dissolved Zn inefficiently (16% and 8%, Table 5). The removal efficiency of dissolved Cu was negative for all four filter materials, meaning that either leaching occurred, and there was more dissolved Cu fractions in the effluent than in the synthetic stormwater, or the inlet concentrations of dissolved Cu were underestimated.

The bark and peat filters had significantly higher removal efficiency in removing dissolved Cd, Cr, Ni, and Zn from synthetic stormwater. Less difference was noticed for the total metal concentrations, likely

Table 4. Average total and dissolved concentrations of metals in the effluents of the filter columns during the experimental runtime of eight weeks ($n = 15$).

	Total concentrations				Dissolved concentrations			
	M	B	*P*	PP	M	B	*P*	PP
Cd	0.23	0.11	0.06	0.25	0.2	0.1	0.1	0.2
	(0.07)	(0.04)	(0.03)	(0.06)	(0.1)	(0.1)	(0.0)	(0.1)
Cr	4.68	4.08	4.62	5.10	4.5	3.2	3.5	4.6
	(0.39)	(0.39)	(3.78)	(0.52)	(0.4)	(0.3)	(0.5)	(0.3)
Cu	5.23	6.74	7.85	15.78	2.8	3.0	3.4	3.7
	(3.30)	(3.42)	(5.28)	(7.50)	(1.0)	(1.3)	(1.8)	(1.2)
Ni	5.28	1.61	1.39	5.99	5.1	1.5	0.8	5.9
	(0.97)	(0.64)	(2.61)	(0.56)	(0.9)	(0.8)	(0.5)	(0.4)
Pb	1.24	1.67	1.72	3.75	0.5	0.3	0.6	0.9
	(0.77)	(0.74)	(1.04)	(1.71)	(0.3)	(0.3)	(0.4)	(0.4)
Zn	88.3	32.2	23.0	111.0	83.4	28.1	17.6	91.0
	(18.4)	(13.5)	(17.7)	(11.9)	(18.6)	(12.6)	(11.6)	(111.9)

All values are presented in µg L-1 and standard deviation is presented in brackets. (M: milkweed; B: bark; *P*: peat; PP: polypropylene).

Table 5. Total and dissolved metal removal efficiency for milkweed (M), bark (B), peat (*P*) and polypropylene (PP) filters.

		Dissolved								Total			
		M		B		*P*		PP		M	B	*P*	PP
		%	μg/g	%	μg/g	%	μg/g	%	μg/g	%	%	%	%
Cd	A	−15	−1	52	1	72	1	−9	0	75	90	95	75
	B	0	0	50	1	69	1	−18	0	79	89	93	71
Cr	A	7	15	25	7	33	8	7	7	74	78	67	71
	B	12	15	28	10	34	0	7	6	74	77	80	75
Cu	A	−91	−25	−62	−2	−118	−4	−92	−17	94	95	95	87
	B	−40	9	−76	−2	−122	−3	−91	−16	97	94	93	87
Ni	A	17	29	83	30	91	38	5	2	58	90	83	52
	B	22	23	79	31	85	26	4	4	60	88	92	87
Pb	A	47	45	60	9	36	8	28	12	93	95	94	84
	B	58	32	51	10	29	6	26	12	96	92	93	74
Zn	A	13	435	78	471	83	575	9	105	80	94	96	74
	B	20	398	73	478	80	409	8	80	81	93	94	85

A and B represent duplicate columns. For the dissolved metals, removal is presented in both percentage removed and μg/g of pollutant removed.

because mechanical filtering was the process that contributed to the removal of the particles from the synthetic stormwater. While milkweed showed only slightly higher efficiency in treating dissolved Zn (M – 16%, PP – 8%), it should be noted that the performance increased substantially when looking at the removal per gram of filter material, where it showed comparable numbers to bark and peat.

4. Discussion

4.1. Synthetic stormwater ageing

Although there was no drastic change of the dissolved metal concentration during the 11-day experiment, a change of dissolved metal concentrations occurred in the synthetic stormwater batches shortly after synthetic stormwater preparation, likely due to the sorption of metal ions to the surface of the added sediment [32]. Directly after mixing the water, metal salts, and sediment, there was a decrease of dissolved metal concentration. Within 240 min, for instance, the concentrations of Cu, Zn, and Cd decreased by 58, 85 and 29%, respectively. However, after about three hours the concentrations of dissolved and total metal concentrations were stable and only minor decreases of dissolved metals were observed for the rest of the study period (total 22 h) (Figures 2 and 3).

The influent concentration change in the influent synthetic stormwater needs to be considered when calculating the treatment efficiency of the filters. In this study, corrected influent values for the metal concentrations were used in order to account for this quality change in stormwater. If this had not have been done, the reported level of treatment would have been significantly different.

In the case of Cu, the filter effectiveness was −65.9%, −69.0%, −120.1% and −91.5%, for milkweed, bark, peat, and polypropylene columns, respectively. The negative values for treatment could be explained either by leaching of copper or by the overestimation of inlet concentration of Cu in the inlet. Depending on calculation method to estimate removal efficiency, the results varied significantly. To demonstrate this, a comparison of three different methods to consider the influent value estimation is presented in Figure 6. The first method assumed that the initial concentration of dissolved metals is representative for the whole loading cycle (start). The second method calculated an average based on the initial start concentration and the measured influent concentration at the end of experiment (mid). Finally, the third method adjusted the initial concentration by applying the time-weighted coefficient described in Section 2.3 (integral).

The difference between the filter efficiency was less noticeable for pollutants that did not show this significant change over time, such as Zn (Figure 6 right). The implication of this could be significant when performing experiments with dissolved metals and sediment particles. In studies where the purpose of the experiment is to estimate how effective a filter material would be in treating stormwater from a site that has mostly dissolved metal fractions, such as runoff from copper roofs [33], field performance of the filter could significantly differ from the one determined in the laboratory. In order to remedy the volatility of dissolved metal concentration, the authors suggest that in future experiments containing synthetic stormwater with dissolved metal fractions and sediment, the mixture is prepared at least three hours before the start of the experiment to ensure stable metal concentration in the influent. When prepared in this manner, stormwater could be used for the following six days at least, as seen in the 11-day ageing experiment. Further studies would be needed to see how different characteristics of the sediment (TSS, PSD, sediment origin) or different metal

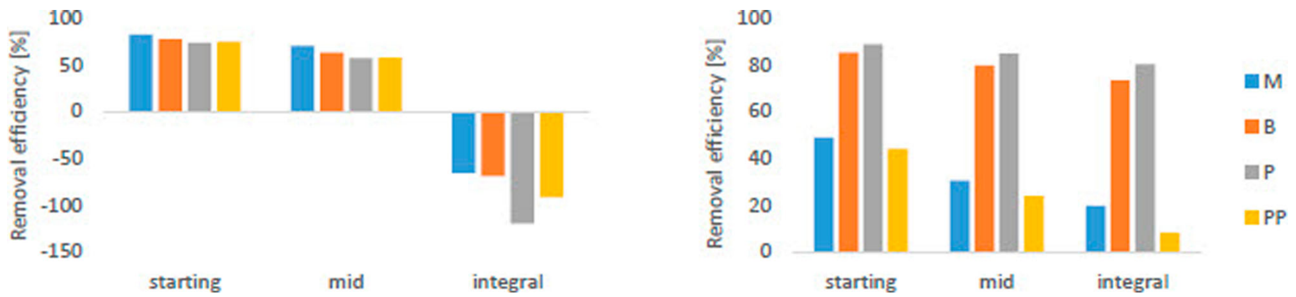

Figure 6. Impact of different correction methods of inlet concentrations on dissolved Cu (left) and Zn (right) treatment efficacy. Starting – initial concentration of dissolved metals; Mid – mean of the initial concentration of dissolved metals and the measured concentration after one day; and integral – adjusting the initial concentration with coefficients from Table 3.

concentrations affect the behaviour of dissolved metals in synthetic stormwater.

4.2. Synthetic stormwater quality

The synthetic stormwater used in this study was created in order to mimic a polluted highway runoff. When compared to other studies, the target values for Cu and Zn fall within the ranges that are commonly used for synthetic stormwater. Achieved synthetic stormwater concentrations of total Cu and Zn in this column study were 127 and 386 μgL^{-1}, respectively. In other laboratory studies [8,11,14,34–39], reported values of total Cu concentration ranged from 10 μg L^{-1} to 2500 μg L^{-1}, and reported values for total Zn concentration were in the range of 20 μgL^{-1}–5,000 μg L^{-1}, with one study [8] using 52,300 μg L^{-1} for a heavily polluted runoff. The concentrations of metals in this study fell in the middle of the range compared to the studies of other researchers.

Few of the studies cited above [15,38,40] used sediments in their synthetic stormwater. The advantage of including sediment in the synthetic stormwater to be used in laboratory experiments is that the synthetic stormwater would be a closer approximation of real stormwater, and it is possible to account for phenomena encountered in situ. Suspended solids have been identified as one of the key pollutants in stormwater due to numerous sources, and the adsorption of other pollutants to the particles [15,41]. Suspended Solids in the stormwater could also cause clogging in filtration systems, which can lead to the reduction of treatment capacity of the installation [42].

The benefit of using synthetic stormwater in laboratory studies is that it ensures relatively constant and controllable influent characteristics, which allows for both comparisons in factorial experimental designs and repeatablity of the experiment by future researchers and its advancement. Furthermore, the use of synthetic stormwater facilitates long-lasting experimental runs since it can be created at any time, in the volumes needed. However, there are drawbacks to this approach, as this study has shown, one being that there were difficulties with maintaining the desired dissolved metal concentrations. Synthetic stormwater, however complexly made, remains a simplified model of the stormwater encountered insitu, with the advantages and disadvantages that modells offer. The assumption is that the most important characteristics are replicated in the synthetic stormwater experiment, but this does not have to be correct. Unkown, or overlooked, interactions may cause the result of the experiment to not be applicable in the field. The prefered level of the approximation depends on the objective of the study. If the aim or one of the aims of the study is to simulate the preformace of the filter facility, inclusion of sediment helps to achieve that objective. However, if the aim of the study is to compare adsorption capacities of different filter materials, a single metal sollution or mixture of dissolved metals could be an appropriate choice.

4.3. Effectiveness of filter materials

Guidelines that specify allowed concentration of metals in stormwater are sparse. When compared to the city of Gothenburg's recommendations for the maximum concentration of metals in discharge, some of the values cross the threshold. The suggested limit for Zn was 30 μg L^{-1} [43], which was exceeded by the average concentration of effluent from milkweed and polypropylene filled columns. Similarly, for Cu, the limit was 10 μg L^{-1}, which was exceeded by the effluent concentration from polypropylene columns. Other metals were below the specified guidelines.

When comparing treatment of the four filter materials, it is important to note that the performance of filter materials may vary in different types of filter installations, such as bioretention filters, catch basin inserts or commercial filter units [44,45]. In addition, the stormwater quality will also impact the treatment level. Due to practical reasons, the filter depth in the column experiments was 60 mm, which is approximately the filter length of a lateral-flow catch basin insert but less than the filter depth bioretention systems where the minimal recommended depth is 400–600 mm [46]. Therefore, the main findings of the column experiment should serve as comparison between the efficiency of the filter materials, rather than a direct approximation of the removal of full-scale treatment systems. While total metal treatment levels were relatively high (59–95%), dissolved metal treatment varied greatly by the metal and by the filter in question. On average, bark and peat filters reduced the dissolved metals to a higher extent than milkweed and polypropylene (excluding Cu treatment, discussed above). Total level of metal treatment for bark was similar to the values found in previous studies [9,47]. Similarly, peat filters had been previously found efficient in removing Cu, Zn and Cd from multi-metal solutions [48], which was confirmed in this study (94%, 95% and 94% for Cu, Zn and Cd, respectively).

Dissolved Zn removal for polypropylene and milkweed was low: −13% to 27% and −7% to 51%, respectively. These results indicate that the dominant treatment mechanism was mechanical filtration, and that the removal of sediment particles with pollutants attached accounted for most of the treatment. This would explain the high total metal removal across the filter media. Milkweed columns showed a slightly higher removal efficiency than polypropylene, e.g. removing 16% of dissolved Zn, compared to 8.4% for the polypropylene columns and 19% of dissolved Ni, compared to 4% treatment achieved by polypropylene filter. It should also be noted that when comparing filter effectiveness per mass of the filter media, milkweed showed a substantially more efficient treatment of dissolved metals then polypropylene. The findings of the experiment indicated which materials would be suited for dissolved metal removal from urban stormwater. However, further testing with other stormwater pollutants would be required before implementation of the filters in stormwater treatment systems.

5. Conclusions

- The 11 -day ageing test showed no change in dissolved metal concentration over the duration of the experiment. The shorter (one day) ageing experiment, with multiple samples taken in the first hours, showed that there was a rapid change in dissolved metal concentration for some of the studied metals, particularity Cu. In order to account for this quite rapid change in dissolved concentrations, a time-weighted coefficient was suggested and applied. These time-weighted coefficients were individually calculated for all dissolved metals based on the data from the one-day ageing experiment.
- The inclusion of sediment particles in synthetic stormwater mixture is important when analysing the effectiveness of a filter system, as the interaction between the sediment particles and pollutants cannot be neglected. The results showed that the synthetic stormwater should be prepared at least three hours before the experiment to ensure a stable dissolved metal concentration. After preparation, stormwater could be used for the following six days. Further studies would be required to investigate if these recommendations are valid for different sediment compositions, different metal concentrations, as well as the impact of stormwater ageing on other compounds such as organic pollutants or nutrients.
- Total metal removal was high (58–98%) across all the filter materials tested, likely due to mechanical filtration of particle bound metals. In order to assess the removal rates in full-scale applications, further experiments are needed at pilot or full scale.
- Peat and bark filters achieved higher removal rates for dissolved metals (76 and 82% for dissolved Zn) than polypropylene and milkweed (16 and 8%). However, when taking into account the mass of filter material investigated, milkweed had a comparable removal rate to bark and peat (M – 416 µg/g, B – 475 µg/g, P – 492 µg/g).

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Data availability statement

Data is available on request from the authors.

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