



Removal of metals and hydrocarbons from stormwater using coagulation and flocculation

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ABSTRACT

As the understanding of how stormwater pollutants are fractioned and need for mitigation has increased, so has the investigation into more advanced treatment techniques. The present study investigated the treatment efficiency of coagulation/flocculation and sedimentation in semi-synthetic stormwater. Five coagulants were evaluated in terms of reducing particle content, organic carbon, total and dissolved metals, hydrocarbon oil index, and polycyclic aromatic hydrocarbons (PAHs). Changes in the resulting particle size distribution as a consequence of the coagulation treatment were also investigated. The pollutants in the semi-synthetic stormwater were predominantly in the particulate phase. The medium and longer chained hydrocarbons dominated the hydrocarbon oil index, while medium to high molecular weight PAHs were most abundant. Iron chloride was the only coagulant that affected particle size distribution post-treatment, shifting the distribution toward larger particles. In terms of total metal removal, the performance of the coagulants was similar, with over 90% removal on average. Concentration of dissolved copper, one of the metals found in the dissolved phase, was reduced by 40% via coagulation treatment. The iron chloride coagulant increased dissolved Zn, a change attributed to a considerable drop in pH resulting in higher ion mobility. Similarly, the reduction in organic content (total organic carbon, oil, and PAHs) was over 90% for most coagulants.

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1. Introduction

Elevated concentrations of highway-associated pollutants can frequently be found in stormwater runoff. Metals and hydrocarbons form two groups of these pollutants. Sources of metals are typically abrasion of tires, brake linings, and the car body itself. Many studies have reported on the concentration level of metals, such as cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn), in stormwater runoff (Brown and Peake, 2006; Davis et al., 2001; Helmreich et al., 2010). Exhaust gases from combustion engines are another source of pollutants (Brown and Peake, 2006), containing a mixture of substances such as soot particles and hydrocarbons, including polycyclic aromatic hydrocarbons (PAHs). PAHs found in stormwater runoff are typically associated with small particles (Albinet et al., 2008). In addition, asphalt

breakdown and leakages of motor oil or other lubricating oils and greases onto the road surface adversely affecting stormwater runoff quality (Khan et al., 2006).

In cold climate areas with frequent snow events in the winter seasons, pollutants accumulate in snowbanks alongside the roadways that are created by snow removal activities (Moghadas et al., 2015; Westerlund and Viklander, 2011, 2006), which physically move the pollutants from road surfaces into the snowbanks. Pollutants in the snowbanks are slowly released during the thawing period and are transported via the meltwater to stormwater conveyance systems (Oberts, 1994).

Several different treatment systems or stormwater control measures (SCM) are used to mitigate the effects that polluted runoff may have on the receiving waters. Often these SCMs are based on physical processes such as sedimentation and/or filtration (Starzec et al., 2005). Generally, sedimentation systems separate larger particle sizes efficiently while smaller size fractions stay in suspension longer (Li et al., 2006), sometimes even indefinitely in exposed open systems. This suspended particle fraction can range from colloidal-sized up to micrometer-sized, and its stability is

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attributed to stronger inter-particle forces compared to the gravitational force (Langmuir, 1997). Several studies have presented correlations between the metals and hydrocarbon and particles of smaller sizes ($<30\ \mu\text{m}$), indicating attachment or adsorption (Morquecho et al., 2005; Sansalone and Buchberger, 1997). These smaller particles are harder to remove and can escape SCMs based on sedimentation or physical filtration processes ending up in the receiving waters (Flanagan et al., 2019; Pettersson, 1998).

One way of enhancing the sedimentation process is adding a coagulant to destabilize the suspended smaller particle fraction, thereby causing particles to come together and form flocs that can readily settle (Bratby, 2016). While widely and extensively studied in wastewater and drinking water, stormwater presents a unique challenge for coagulation systems; i.e. because stormwater, unlike wastewater, exhibits considerable variability both in terms of flow and constituent pollutants (Göbel et al., 2007; Makepeace et al., 1995). Interestingly, several stormwater coagulation systems exist in operation. For example, the Swedish Transport Administration operates systems in Stockholm to treat road runoff in select places (Stockholms Miljöförvaltning, 2008). Another example is Florida, USA, with coagulation systems to treat phosphorus-laden urban runoff (Harper and Herr, 2015). However, only few previous research studies have investigated stormwater treatment with coagulation/flocculation (Kang et al., 2007; Sansalone and Kim, 2008). Despite promising initial results in those studies, coagulation as a treatment process for stormwater is under-investigated, and there is a clear need for more information regarding the effectiveness and optimum conditions for coagulation treatment to reduce stormwater pollutants. This information will prove useful when selecting appropriate treatment systems for severely polluted stormwater matrices, as for example highway runoff (Kayhanian et al., 2012), tunnel wash water (Hallberg et al., 2014), and reject water from dredging maintenance operations of stormwater ponds (Andersson et al., 2018).

In this paper, we present a laboratory study using a coagulation/flocculation process to assess the treatability of stormwater with respect to total and dissolved metals (Cd, Cr, Cu, Ni, Pb, and Zn), organic content, measured as total and dissolved organic carbon (TOC/DOC), hydrocarbon oil index (HOI), and PAHs.

2. Materials and methods

2.1. Study design

The treatability of stormwater by coagulation/flocculation and sedimentation was evaluated using semi-synthetic stormwater in coagulation jar test experiments using semi-synthetic stormwater. The experimental design was a randomized block design, where each block represented one batch of semi-synthetic stormwater consumed in two experiments. Five coagulants were tested in three replicates each, resulting in a total of 15 jar tests. Treatability was assessed via water quality analyses of the samples pre- and post-coagulation experiments and comparisons of pollutant concentrations. In the coagulation experiments, a mixture of polluted snow together with pristine snow was used as semi-synthetic stormwater, mimicking the meltwater reaching the urban drainage system in a catchment area. Due to the varying nature of the snowmelt mixture, each jar test included an untreated control to facilitate comparisons between sedimentation alone and coagulation/flocculation enhanced sedimentation.

2.2. Semi-synthetic stormwater

Semi-synthetic stormwater was used to ensure reasonably consistent water quality for the treatment experiments (Hatt et al.,

2007). For this study, the semi-synthetic stormwater was created by mixing equal-volume meltwater from traffic-impacted snow and pristine snow. The traffic-impacted snow was collected from a snowbank along the side of a road in downtown Luleå, northern Sweden, with an annual average daily traffic intensity of ~20,000 vehicles. The pristine snow was collected from a green area unaffected by traffic. Collected snow was stored in high-density polyethylene containers in freezer storage ($-10\ ^\circ\text{C}$) until used for the jar test experiments.

Before treatment experiments, the snow was left to thaw for 24 h. The melted snow from the snowbank and the park area were then mixed in equal-volume parts and left for 1 h, allowing coarser particles to settle. The resulting batch sample was characterized by a high amount of total suspended solids (TSS, mean 990 mg/L) and high turbidity (mean 800 NTU), similar in magnitude to previously sampled meltwater reaching the urban drainage system (Westerlund et al., 2003). Snow collection was carried out at the end of the winter season, before the thawing season; any pollutants in the snow were the result of seasonal accumulation.

2.3. Coagulants

A screening study of coagulants for the semi-synthetic stormwater was previously conducted (Nyström et al., 2020). Based on those results, five coagulants were selected for this study: alum, two pre-hydrolyzed aluminum coagulants (PAX-215, relative basicity of 30% and PAX-XL360, amended with an organic polymer), an iron chloride (PIX-111), and chitosan, a cationic biopolymer with a molecular weight between 600,000 and 800,000 Da. Alum and chitosan solutions were prepared in the laboratory. A 5% w/v alum solution was obtained by dissolving 5 g of aluminum sulfate hexahydrate ($\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$) (BDH, London, United Kingdom) in 100 ml of water. A 5% w/v chitosan solution was prepared by dissolving 5 g of chitosan in 5% HCl. The PIX/PAX products are commercially available water treatment products (Kemira, Helsinki, Finland), and were diluted to working solutions by a factor of ten (0.38 M for PAX-215 and 0.34 M for PAX-XL360).

2.4. Coagulation experiments

Coagulation/flocculation and sedimentation were carried out using jar tests. The jar testing apparatus consisted of six 1 L beakers and detachable impellers connected to a central control unit with programmable settings for rotational speed and time. The program used was rapid mixing at 200 rpm for 60 s ($G = 190\ \text{s}^{-1}$), followed by slow mixing at 30 rpm for 15 min ($G = 15\ \text{s}^{-1}$), and sedimentation for 30 min. The coagulant was injected at the beginning of the rapid mixing phase to ensure complete dispersion. In each experiment, a set of two jar tests was performed. The first jar test was intended to determine the optimal coagulant dose for the stormwater samples in reducing turbidity. The first jar test included an untreated control and five increasing coagulant concentration steps. In a second jar test, the optimum dose was then tested in triplicate. For each run, stormwater in three beakers was used as controls and in three beakers with the optimal coagulant dose. These sets of three beakers were post jar test mixed together to generate enough volume for the following water quality analyses: turbidity, pH, and concentrations of total/dissolved organic carbon (TOC/DOC), total and dissolved metals (Cd, Cr, Cu, Ni, Pb, and Zn), HOI and 16 PAHs. The untreated control (hereafter termed sedimentation control) was only subjected to the mixing energy in the jar test and the settling phase. The water phase was separated from the settled flocs by decantation.

2.5. Water quality analyses

Turbidity was used to determine optimal coagulant concentration and was measured on a Turbidimeter 2100N (Hach, Loveland, Colorado) using signal average and ratio calculation settings. A WTW SenTix 41 pH electrode connected to a WTW pH 330 device (WTW, Weilheim, Germany) was used for pH measurements. TOC and DOC concentrations were measured using IR detection after oxidation (EN 1484:1997) with a reporting limit (RL) of 0.5 mg/L. Metal concentrations were determined using ICP-SFMS (ISO 17294:2004) for Cd (RL of 0.05 µg/L), Cr (RL of 0.9/0.5 µg/L for total/dissolved), Cu (RL of 1 µg/L), Ni (RL of 0.6/0.5 µg/L for total/dissolved) and Pb (RL of 0.5/0.2 µg/L for total/dissolved), and ICP-AES (ISO 11885:2007) for Zn (RL of 4/2 2 µg/L for total/dissolved). Both total and dissolved metal concentrations were determined. For dissolved metal concentrations, the samples were passed through a 0.45 µm polyethersulfone filter before acid digestion and analysis. The standard 16 PAH compounds identified by the U.S. Environmental Protection Agency (Keith, 2015) were analyzed and grouped by the number of ring structures as low, medium, and high molecular weight (LMW, MMW, HMW). The concentrations for the 16 priority PAHs (RL of 0.03 µg/L for naphthalene, 0.02 µg/L for phenanthrene, and 0.01 µg/L for the rest) were analyzed using GC-MS (ISO 6468:1996). HOI (RL of 5 µg/L for C10–C12 & C12–C16, 30 µg/L for C16–C35 and 10 µg/L for C35–C40) was determined using GC-FID (ISO 9377–2:2000). Particle size distributions (PSDs) were obtained using laser diffraction on a HORIBA LA-960 (HORIBA, Kyoto, Japan).

Analyses for TOC/DOC, total and dissolved metals, PAH, and oil index were carried out by an accredited laboratory (ALS Scandinavia, SWEDAC Accreditation no: 2030). Uncertainty in external analyses was reported with a coverage factor of 2, approximating a 95% confidence interval (JCGM 100:2008, 2008).

2.6. Statistical analyses

Differences between coagulation treatments were tested using one-way ANOVA. Post hoc pairwise t-testing (using Bonferroni correction) was used to compare means between different coagulants. Measurements below the reporting limit were set as half the reporting limit for all statistical tests (US EPA, 2000). All tests were performed with a significance level of 0.05.

3. Results and discussion

3.1. Semi-synthetic stormwater quality

The semi-synthetic stormwater was characterized by high variability in water quality parameters between batches. The particle content, measured as turbidity (mean 800 NTU, range 260–1800 NTU) and TSS (mean 559 mg/L, range 237–990 mg/L), varied considerably. The pH measured in the batches was slightly basic (mean 7.9) and the alkalinity low (mean 30 mg/L as CaCO₃).

Metal concentration analyses revealed that most of the metals were in the particulate fraction, and a small part in the dissolved fraction (Table 1). In particular, Zn and to some extent Cu, were the only metals quantifiable after filtration through 0.45 µm filter. The metal concentrations in the semi-synthetic stormwater were one order of magnitude lower, on average, compared to results from a previous study in the same geographical area that investigated metals concentrations (<1 mm fraction) in traffic-impacted snowpacks (Moghadas et al., 2015). Likely, the mixing process, combined with the initial sedimentation, accounted for most of this discrepancy. Previous measurements of total metal concentrations in urban snowmelt (Westerlund and Viklander, 2006) and urban snow

Table 1

Total and dissolved concentrations of metals in the semi-synthetic stormwater as mean and standard deviation (SD).

| Metal | Total concentration (µg/L) | | Dissolved concentration (µg/L) | |
|-------|----------------------------|------|--------------------------------|------|
| | mean | (SD) | mean | (SD) |
| Cd | 0.13 | 0.06 | <0.05 | – |
| Cr | 33.4 | 12 | <0.5 | – |
| Cu | 98.5 | 32.9 | 3.7 | 1 |
| Ni | 13.5 | 4.8 | <0.5 | – |
| Pb | 14.6 | 5.2 | <0.2 | – |
| Zn | 257 | 91.6 | 5.1 | 4.5 |

(Viklander, 1999a) from the same area, were in the same order of magnitude compared to the results in this study.

The metal with the highest concentrations in the semi-synthetic stormwater was Zn, followed by Cu (Table 1); this result is in line with previous findings (Viklander, 1999b; Westerlund and Viklander, 2006) in the study area (for both snow and snowmelt) as well as in snowmelt studies elsewhere (Bäckström et al., 2003; Helmreich et al., 2010). The metal concentrations were on average similar to those of event mean concentrations of highway runoff (Kayhanian et al., 2012), but much lower than first flush events (Mangani et al., 2005).

The concentrations of organic compounds were measured as three compositionally different parameters: TOC/DOC, HOI, and PAHs (Table 2). Few studies have investigated TOC and DOC in snowpack or snowmelt, but the TOC concentrations presented here were in line with previous results (Glenn and Sansalone, 2002). The DOC content was only 8.6% of the TOC in this study compared to 85% found in snow in another study (Sempère and Kawamura, 1994). The HOI includes the combustible non-polar organic substances and is divided into different fractions depending on the oil standard used; here, the linear alkanes C_{10–12}, C_{12–16}, C_{16–35}, and C_{35–40}. In the semi-synthetic stormwater, hydrocarbons that eluted between the linear alkanes C₁₀ and C₁₆ constituted less than 1% of the total hydrocarbon load, and the composition was instead characterized by hydrocarbons eluting between the longer-chain alkanes C₁₆–C₄₀ (98%) (Table 2). The total average concentration for the HOI was just above 1 mg/L, but with substantial differences between different batches. The PAH composition was characterized by mostly medium and high molecular weight compounds, with

Table 2

The concentrations of organic substances, measured as organic carbon, PAHs, and hydrocarbon fractions, in the semi-synthetic stormwater presented as mean and standard deviation.

| Organics | Concentration | | Fraction of total (%) | |
|--|---------------|------|-----------------------|------|
| | mean | (SD) | | |
| TOC | 37.4 | 13.3 | mg/L | 8.6 |
| DOC | 3.2 | 1.7 | mg/L | |
| Oil index C ₁₀ –C ₄₀ | 1060 | 1197 | µg/L | 0.3 |
| C ₁₀ –C ₁₂ | 2.77 | 1.03 | µg/L | |
| C ₁₂ –C ₁₆ | 5.29 | 4.05 | µg/L | |
| C ₁₆ –C ₃₅ | 771 | 882 | µg/L | |
| C ₃₅ –C ₄₀ | 276 | 315 | µg/L | |
| PAH EPA 16 | 1.64 | 0.95 | µg/L | 59.8 |
| PAH LMW ^a | 0.03 | 0.02 | µg/L | |
| PAH MMW ^b | 0.98 | 0.55 | µg/L | |
| PAH HMW ^c | 0.64 | 0.4 | µg/L | |

^a LMW = Low molecular weight.

^b MMW = medium molecular weight.

^c HMW = high molecular weight.

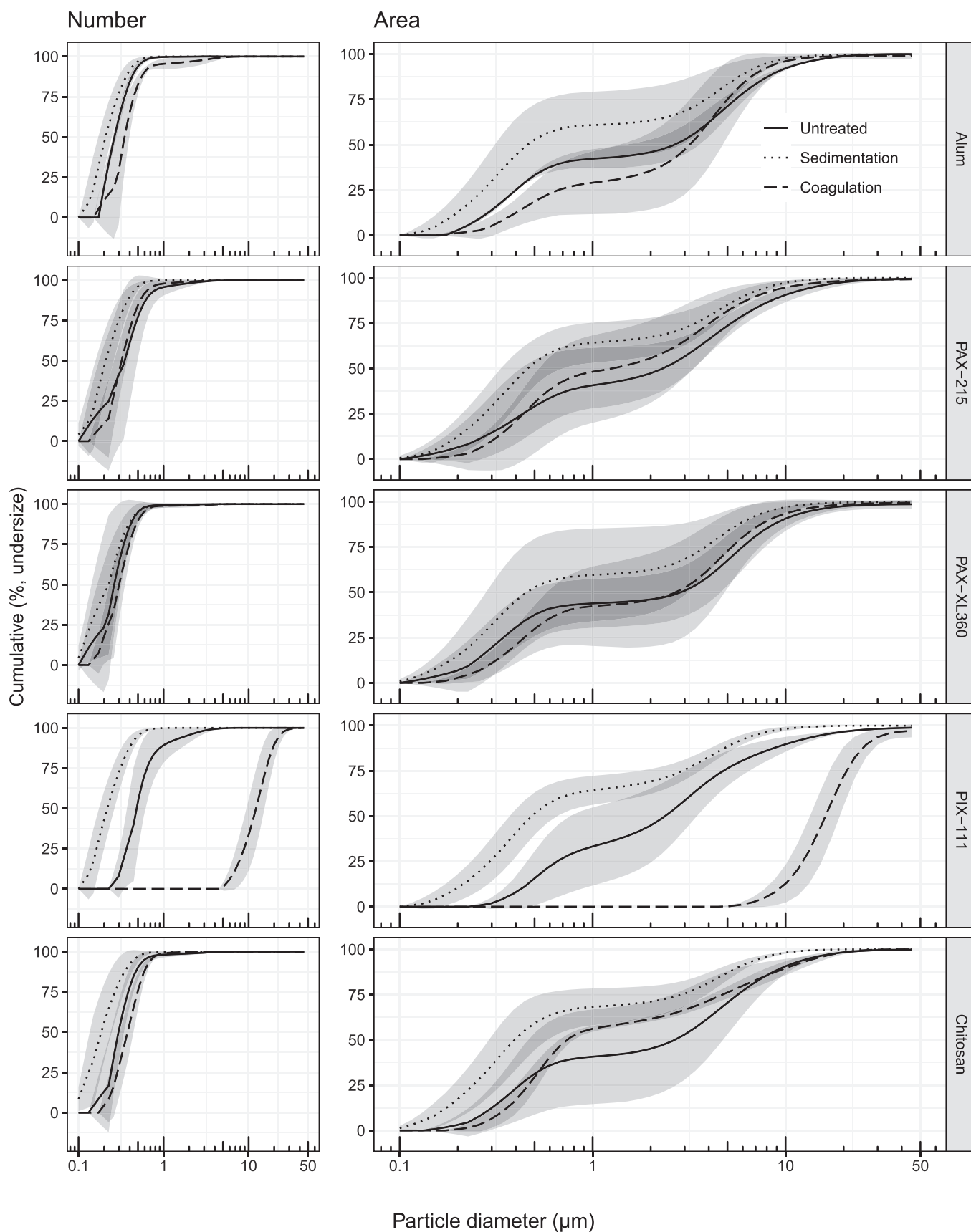


Fig. 1. Cumulative particle size distribution in the semi-synthetic stormwater, the sedimentation control, and the coagulation treatment, calculated using the number of particles (left column) and the surface area (right column) the basis. The effects for each coagulant are displayed by the row. The shaded areas represent the interval (mean \pm SD) as calculated for the replicates ($n = 3$).

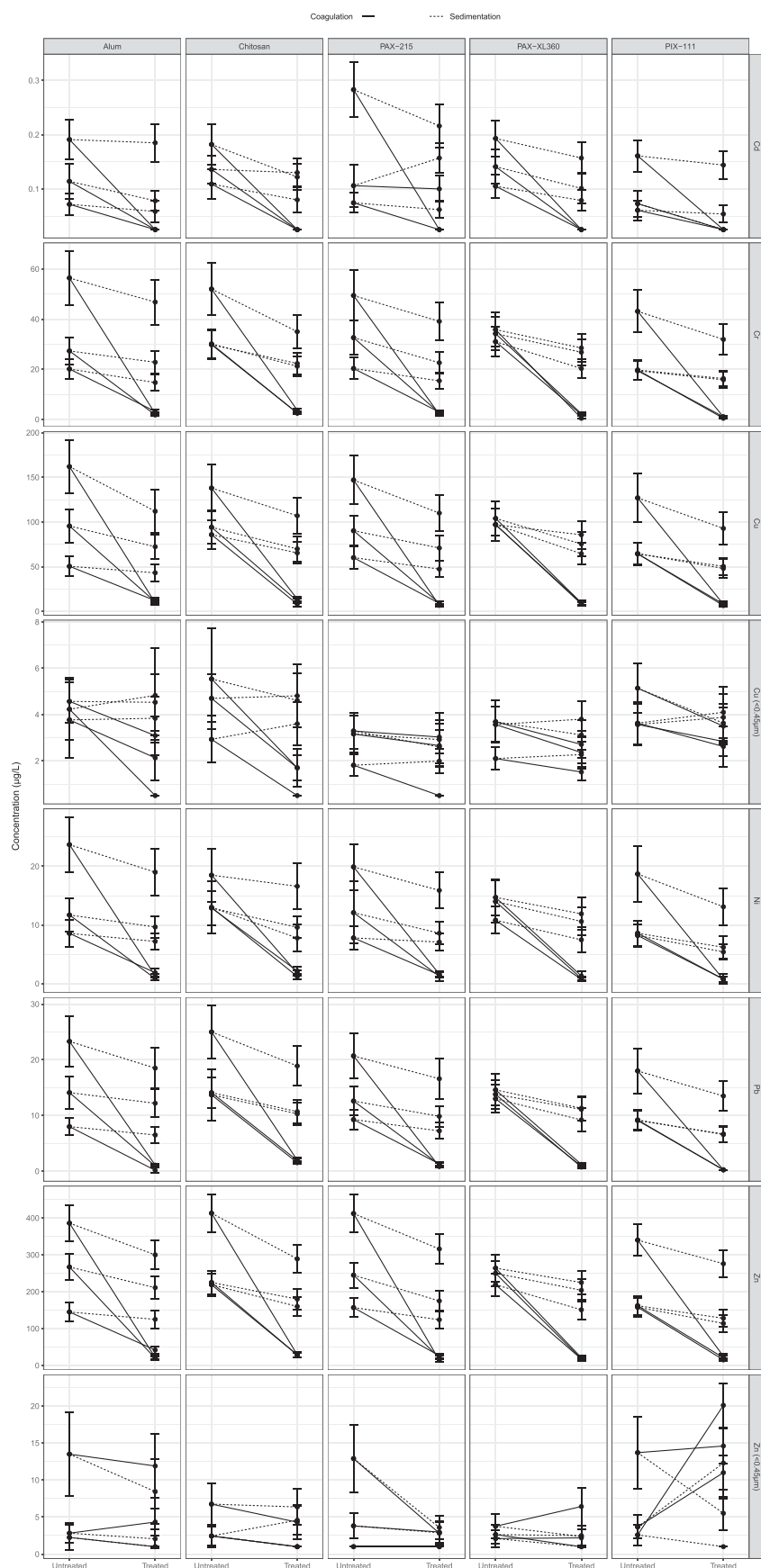


Fig. 2. Removal of total and dissolved metal fractions of Cd, Cr, Cu, Ni, Pb, and Zn by coagulation and sedimentation (solid lines) and only sedimentation (dotted lines). Error bars cover two standard deviations from the mean (see method section).

very few low molecular weight compounds.

3.2. Coagulation impact on the particle size distribution

Particle size distributions (Fig. 1) were determined to investigate whether the composition of particles changed due to coagulation treatment as compared to the sedimentation control. The particle size distributions were determined using both number and surface area as the underlying basis. In terms of particle number counts, the semi-synthetic stormwater was characterized by particles with a diameter between 0.1 and 1 μm in a unimodal distribution (Fig. 1). After transformation to a surface area basis, the distribution was bimodal (with a plateau in the cumulative distribution) with modes around 0.5 μm and 5 μm (Fig. 1). These contributed roughly equal to the total surface area of the particles. Comparing the sedimentation control to the treated samples revealed a slight shift toward smaller particles both in terms of numbers and surface area, which was consistent with larger particles being removed by sedimentation.

On the other hand, comparing the particle size distributions pre- and post-coagulation treatment, showed little to no change for almost all coagulants (except the iron chloride product, PIX-111), indicating that coagulation treatment affected all particle size ranges equally. In the PIX-111 experiments, there was a rightward shift toward particles with a larger diameter both in terms of numbers and surface area. The surface area distribution changed from a bimodal distribution into a unimodal distribution, implying that coagulation treatment using PIX-111 reduced the smaller

particle fraction more efficiently, shifting the composition of the particle size distribution towards larger particle sizes. Previous investigations into particle size distributions in stormwater after coagulation/flocculation treatment (Sansalone and Kim, 2008), have shown resuspension events of 5 μm particles when overdosing coagulant.

3.3. Coagulation treatability of total and dissolved metals

Treatability was assessed by comparing concentrations of total and dissolved metals pre- and post-treatment. Comparisons were made with the coagulation treatment and sedimentation control. The coagulation treatment was highly effective in reducing the total metal content (Fig. 2), mainly because the metals present were associated with the particulate fraction, which was removed during the coagulation treatment process. Coagulation treatment resulted in significantly higher removal efficiency of total metal content than the sedimentation control (Table 3), with 90% average removal for the coagulation treatment, and 24% for the sedimentation control. There was no significant difference between coagulants in terms of removal of total metals.

Comparisons for the dissolved fractions could only be made for dissolved Cu and dissolved Zn, since there were no quantifiable levels of dissolved Cd, Cr, Ni and Pb in the semi-synthetic stormwater. Concentrations of dissolved Cu were reduced by 72% using Chitosan, 32% using PAX-215, 29% using PAX-XL360, 27% using PIX-111, and 55% using Alum, showing considerable differences

Table 3

Treatment effect in percent removal (bold) and absolute units calculated as the arithmetic mean reduction with one standard deviation.

| | | Sedimentation | Alum | PAX-215 | PAX-XL360 | PIX-111 | Chitosan |
|----------------------------------|-----------------|------------------|----------------|------------------|----------------|-------------------|------------------|
| <i>Total metal</i> | | | | | | | |
| Cd | % | 18 ± 12 | 77 ± 11 | 54 ± 44 | 82 ± 5 | 70 ± 13 | 82 ± 5 |
| | $\mu\text{g/L}$ | 0.024 ± 0.028 | 0.1 ± 0.06 | 0.1 ± 0.13 | 0.12 ± 0.044 | 0.073 ± 0.055 | 0.12 ± 0.037 |
| Cr | % | 24 ± 4 | 91 ± 6 | 91 ± 5 | 95 ± 3 | 97 ± 2 | 92 ± 1 |
| | $\mu\text{g/L}$ | 8.1 ± 3.6 | 32 ± 19 | 32 ± 15 | 32 ± 3.1 | 27 ± 13 | 34 ± 12 |
| Cu | % | 24 ± 1 | 86 ± 9 | 90 ± 5 | 91 ± 1 | 90 ± 3 | 89 ± 2 |
| | $\mu\text{g/L}$ | 24 ± 12 | 92 ± 57 | 91 ± 45 | 90 ± 3.7 | 78 ± 36 | 95 ± 26 |
| Ni | % | 24 ± 5 | 89 ± 9 | 88 ± 6 | 93 ± 1 | 93 ± 3 | 88 ± 4 |
| | $\mu\text{g/L}$ | 3.1 ± 1.4 | 13 ± 8.1 | 12 ± 6.1 | 12 ± 1.8 | 11 ± 6 | 13 ± 3.2 |
| Pb | % | 23 ± 3 | 96 ± 2 | 91 ± 5 | 93 ± 2 | 98 ± 1 | 89 ± 3 |
| | $\mu\text{g/L}$ | 3.3 ± 1.2 | 14 ± 7.3 | 13 ± 6.1 | 13 ± 0.67 | 12 ± 5.1 | 16 ± 6.3 |
| Zn | % | 23 ± 3 | 86 ± 13 | 90 ± 7 | 92 ± 1 | 90 ± 3 | 89 ± 3 |
| | $\mu\text{g/L}$ | 59 ± 27 | 240 ± 130 | 250 ± 140 | 230 ± 22 | 200 ± 100 | 260 ± 110 |
| <i>Dissolved metal</i> | | | | | | | |
| Cu | % | 0 ± 4 | 55 ± 30 | 32 ± 35 | 29 ± 4 | 27 ± 6 | 72 ± 10 |
| | $\mu\text{g/L}$ | 0.078 ± 0.61 | 2.3 ± 1.3 | 0.69 ± 0.55 | 0.92 ± 0.32 | 1.1 ± 0.47 | 3.1 ± 0.71 |
| Zn | % | 12 ± 33 | 5 ± 55 | 33 ± 40 | -4 ± 67 | -294 ± 345 | 51 ± 13 |
| | $\mu\text{g/L}$ | 1.4 ± 4.1 | 0.45 ± 1.7 | 3.6 ± 5.6 | -0.37 ± 2.2 | -8.6 ± 8.4 | 1.8 ± 0.57 |
| <i>Organic content</i> | | | | | | | |
| TOC | % | 28 ± 3 | 86 ± 7 | 89 ± 4 | 90 ± 3 | 88 ± 4 | 89 ± 3 |
| | mg/L | 10 ± 4.2 | 36 ± 20 | 35 ± 15 | 33 ± 4.9 | 29 ± 18 | 34 ± 12 |
| DOC | % | 6 ± 19 | -1 ± 7 | 21 ± 33 | -11 ± 4 | 30 ± 15 | 0 ± 7 |
| | mg/L | 0.44 ± 1.4 | -0.067 ± 0.23 | 1.6 ± 2.7 | -0.23 ± 0.16 | 1.1 ± 0.87 | 0 ± 0.17 |
| <i>Oil index</i> | | | | | | | |
| C ₁₆ -C ₃₅ | % | -16 ± 80 | 89 ± 11 | 79 ± 11 | 64 ± 52 | 88 ± 8 | 94 ± 4 |
| | $\mu\text{g/L}$ | 380 ± 860 | 2100 ± 880 | 140 ± 32 | 660 ± 940 | 1300 ± 2000 | 700 ± 730 |
| C ₃₅ -C ₄₀ | % | -65 ± 135 | 89 ± 11 | 81 ± 12 | 64 ± 53 | 49 ± 74 | 93 ± 6 |
| | $\mu\text{g/L}$ | 170 ± 380 | 1600 ± 660 | 110 ± 26 | 480 ± 670 | 890 ± 1500 | 500 ± 510 |
| PAH EPA 16 | % | 25 ± 85 | 89 ± 12 | 79 ± 13 | 66 ± 50 | 89 ± 7 | 95 ± 4 |
| | $\mu\text{g/L}$ | 73 ± 140 | 550 ± 220 | 30 ± 7 | 180 ± 260 | 320 ± 510 | 190 ± 220 |
| PAH LMW | % | -20 ± 62 | 84 ± 15 | 87 ± 4 | 85 ± 9 | 91 ± 6 | -13 ± 182 |
| | $\mu\text{g/L}$ | 0.21 ± 0.62 | 1.5 ± 0.98 | 1.7 ± 0.77 | 1.4 ± 1 | 1.6 ± 1.2 | 1.1 ± 1.3 |
| PAH MMW | % | -70 ± 90 | 12 ± 60 | -32 ± 108 | 21 ± 64 | 48 ± 29 | 32 ± 41 |
| | $\mu\text{g/L}$ | 0.00047 ± 0.035 | 0.01 ± 0.021 | -0.005 ± 0.038 | 0.014 ± 0.023 | 0.021 ± 0.021 | 0.02 ± 0.029 |
| PAH HMW | % | 3 ± 25 | 77 ± 20 | 86 ± 5 | 77 ± 13 | 86 ± 9 | 54 ± 58 |
| | $\mu\text{g/L}$ | 0.18 ± 0.37 | 0.8 ± 0.55 | 1.2 ± 0.4 | 0.76 ± 0.57 | 0.92 ± 0.73 | 0.58 ± 0.68 |
| PAH HMW | % | 0 ± 10 | 91 ± 10 | 93 ± 4 | 95 ± 2 | 96 ± 2 | 89 ± 11 |
| | $\mu\text{g/L}$ | 0.043 ± 0.23 | 0.72 ± 0.47 | 0.54 ± 0.48 | 0.62 ± 0.44 | 0.68 ± 0.43 | 0.47 ± 0.55 |

between coagulants (Table 3). On average, concentration of dissolved copper was reduced by 40% using coagulation treatment. Concentrations of dissolved Zn were only reduced when using chitosan (by approximately 51%). Coagulation using PIX-111 showed a reverse effect by increasing the levels of dissolved Zn. This may be explained by increased mobility (Stumm and Morgan, 1996) due to the pH caused by hydrolysis reactions. The resulting pH was 6.4 for PIX-111 compared to 7.6 for chitosan, for example. Industrial wastewaters with a high metal content, for example in the electroplating industry, often utilize coagulation/flocculation to remove the metals from solution with very good effect (Kurniawan et al., 2006). However, they are often performed at a high pH level to promote precipitation reactions together with the use of lime or polymers as a flocculant aid.

3.4. Treatability of organic content using coagulation

The reduction of TOC and DOC was assessed analogous to the treatability of metal (Fig. 3). On average, the coagulation treatment effects were significantly higher (93%) for TOC than the sedimentation control (20%). There was no significant difference in the reduction of DOC between the coagulation treatments and the sedimentation control.

The removal of oil content – measured as HOI (Fig. 4) – varied across the coagulants, mainly due to a considerable variation in initial HOI concentrations. Despite the randomized experiment design, all three replicates for alum treated samples with an HOI of 1000–3500 µg/L, whereas PAX-215 treatment was only subjected to samples with an initial HOI of around 500 µg/L. In terms of the sedimentation control, there were cases in which sedimentation alone showed a strong removal effect (PAX-XL360 and Chitosan), but also cases in which the HOI increased (PAX-215). These varying

results for sedimentation control make a comparison of the different coagulants difficult. However, the treatment effect of all coagulants on the oil fractions C₁₆₋₃₅ and C₃₅₋₄₀ was significantly greater than zero (Table 3), and greater than the effect for the sedimentation control.

Fig. 5 illustrates that the removal efficiency for PAH follows a similar trend to that for the removal of the constituents that make up the oil index measurement (of which PAH represents around 0.15%). The treatment effect for all coagulants in terms of the MMH and HMW PAH was significantly higher than zero; concentrations of the LMW PAHs were too low to make any assertions regarding treatment effect. PAH removal in both the sedimentation controls and across the replicates varied. Using chitosan in one coagulation replicate (with low initial PAH content) increased PAH concentrations while they decreased considerably in the other two, offsetting the overall result for the chitosan treatment.

In general, the HMW PAH fraction was reduced (93% on average) to below or near the reporting limit in all coagulant treatments (Table 2). However, the same effect was not found for the MMW PAH fraction (reduction of 76%), which was present in residual concentrations that were well above the reporting limit in all experiments. Thus, there was an evident difference in treatment effect for coagulation on PAH MMW and PAH HMW.

The treatment effect for PAHs in this study is similar to what has reported in previous investigations into coagulation treatment and PAHs with spiked water (Nowacka et al., 2016). The major difference is that they reported on the treatment effect for LMW PAHs (e.g., naphthalene), which was significantly lower than MMW and HMW PAHs. The hydrocarbons, measured as oil index and PAH in this study, have a general affinity to adsorb onto carrier particles, predominantly small particles up to 2 µm (Baek et al., 1991; Kaupp and McLachlan, 2000). In the context of stormwater, previous

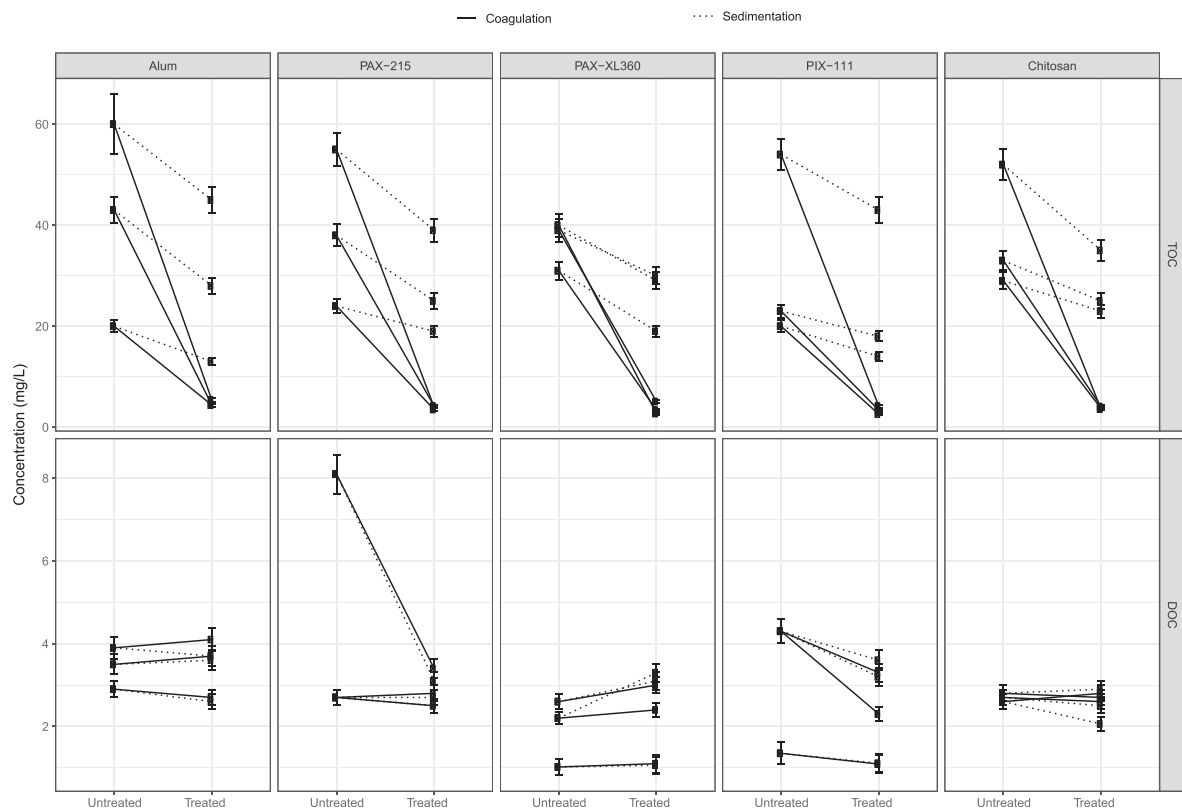


Fig. 3. Removal of organic content measured as TOC and DOC by coagulation and sedimentation (solid lines) and only sedimentation (dotted lines). Error bars indicate an approximate 95% confidence interval.

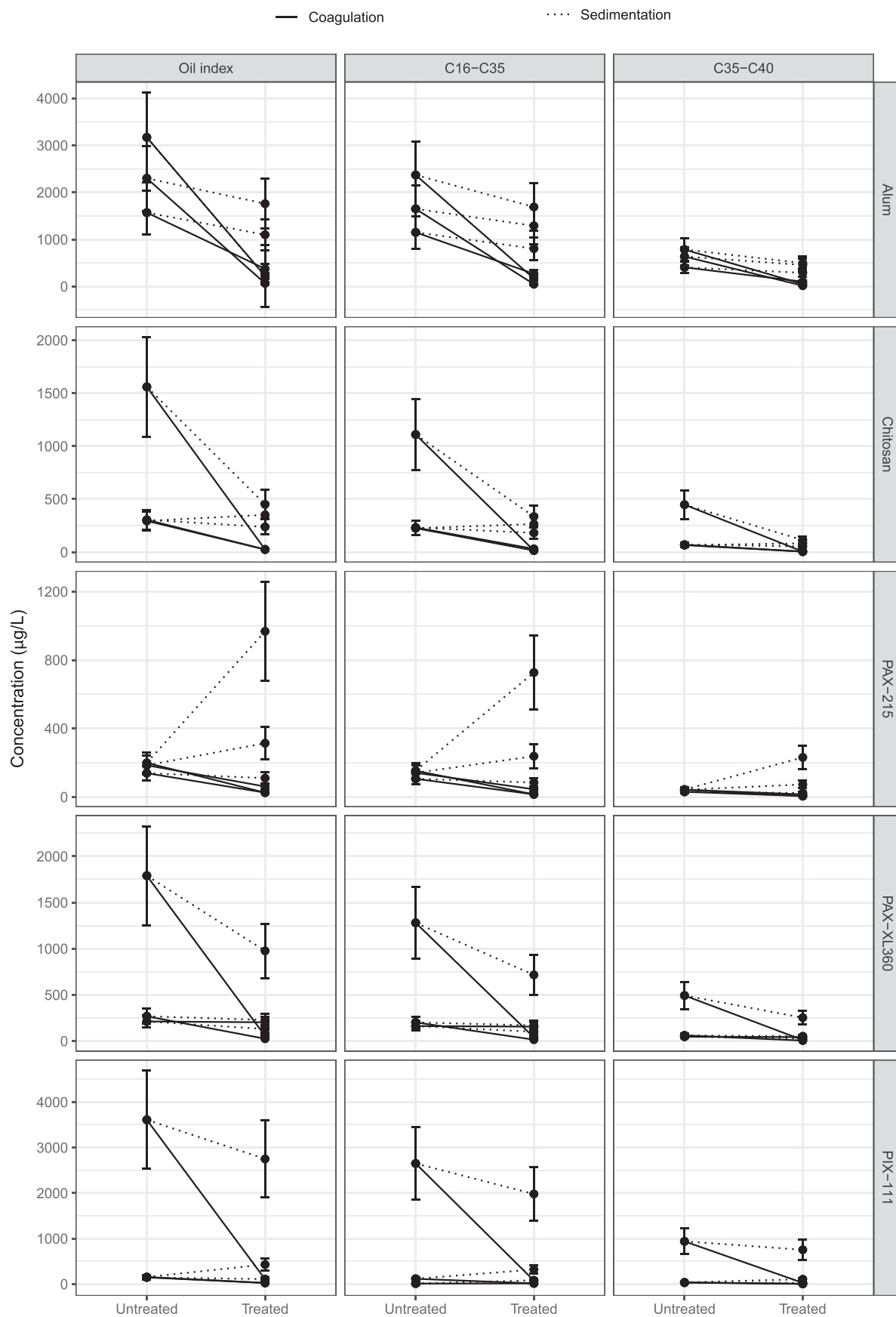


Fig. 4. Removal of hydrocarbon compounds, measured as HOI, by coagulation and sedimentation (solid lines) and only sedimentation (dotted lines). Error bars indicate an approximate 95% confidence interval.

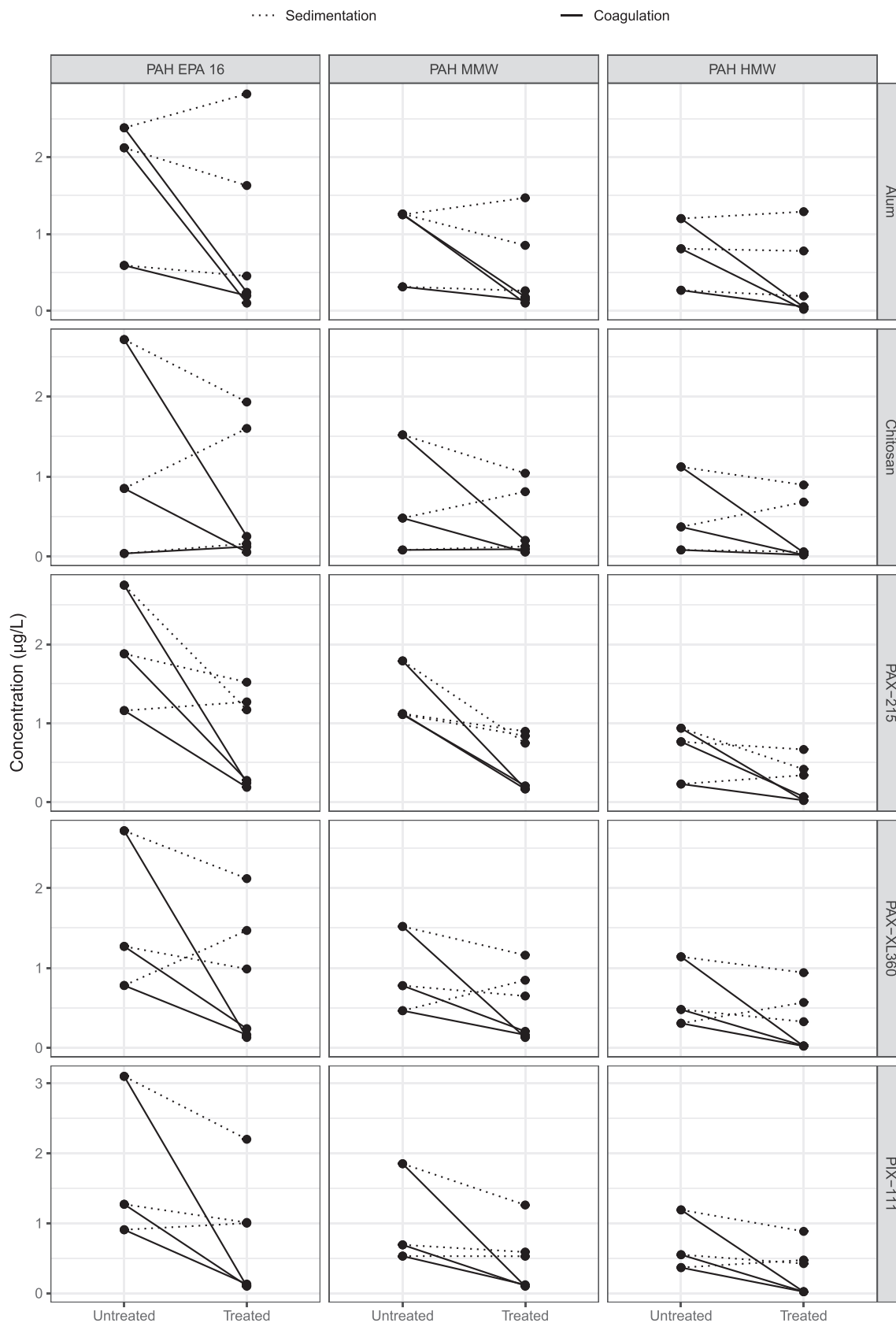


Fig. 5. Removal of PAH measured as the aggregate polycyclic aromatic hydrocarbons PAH EPA 16, PAH MMW (low molecular weight), PAH MMW (medium molecular weight), and PAH HMW (high molecular weight) by coagulation and sedimentation (solid lines) and only sedimentation (dotted lines). Error bars indicate an approximate 95% confidence interval.

studies have shown that both LMW and MMW PAH are typically found in the dissolved fraction, and HMW PAH in the particulate fraction (Nielsen et al., 2015). However, the effect of coagulation treatment on the PAHs found in the dissolved fraction was not tested in this study, as samples were not filtered before the PAH analysis, and only total content was measured.

4. Conclusions

In this study, we evaluated the treatment effect of a coagulation/flocculation treatment on semi-synthetic stormwater. The treatment effect was measured as the removal of total and dissolved metals (Cd, Cr, Cu, Ni, Pb, and Zn), organic content, measured as total and dissolved organic carbon (TOC/DOC), hydrocarbon oil index (HOI), and polycyclic aromatic hydrocarbons (PAHs). All tested coagulants removed particulate-associated pollutants by over 90% on average as measured by the total metal fraction, PAH, HOI, and TOC. Dissolved cadmium, chromium, lead, and nickel were below the reporting limit for their concentrations, and therefore, no assessment of the treatment effect on these was performed. The removal of dissolved copper varied between the coagulants tested, with chitosan showing a considerably higher removal effect of 72% compared to the other coagulants. Chitosan was the only coagulant with an apparent removal effect (51%) for the dissolved fraction of zinc, whereas treatment using iron chloride increased the dissolved concentration of zinc. This effect was accounted for by a lower final pH, which favored the ionic zinc species. Our analysis of the particle size distributions showed that sedimentation alone shifted the distributions towards dominance of smaller particles, by removing settleable particles from the suspension. The coagulation treatment decreased this dominance noticeably by shifting the distribution away from the smaller particle sizes. This effect was considerably stronger for particles smaller than 10 µm in diameter when iron chloride was the coagulant.

Declaration of competing interest

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

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