Treatment of road runoff by coagulation/flocculation and sedimentation

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ABSTRACT

A laboratory investigation of the treatment potential of a coagulation process in the context of stormwater treatment was undertaken. The initial 25 L road runoff generated from four rain events was collected and subjected to a jar-testing regime with two commercial coagulants. The treatment effect was assessed by analysing the runoff before and after treatment for turbidity, suspended solids and metal content. The coagulation process resulted in particle and total metal reduction of more than 90% compared to 40% for only sedimentation. Up to 40% reduction of dissolved Cr, Cu and Pb was also observed compared to 0% for sedimentation. This study shows that coagulation may be a useful process for stormwater treatment systems when the treatment requirements are high.

Key words | advanced stormwater treatment, coagulation, metals, particles, road runoff, suspended solids

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INTRODUCTION

Efficient stormwater treatment methods have been highlighted as an area in need of further research in terms of both performance and cost–benefit perspective (Meland 2016). Traditional stormwater control measures, such as retention basins, primarily aim at retaining stormwater flows, but treatment also occurs through sedimentation. An inherent weakness of retention basins is the physical inability of finer (<20 μm) particles to readily sediment during the retention period (Li *et al.* 2006). Thus, these particles are at risk of being discharged into the receiving waters. This particle fraction is important to include as a treatment target due to the particles' large surface area to volume ratio, onto which a large portion of the pollutants can adsorb (Langmuir 1997).

Chemical treatment or coagulation/flocculation (C/F) is a well-studied unit process used in water treatment applications, with ability to destabilize the colloidal fraction and cause it to sediment due to flocculation (Bratby 2016). However, only in a few studies has chemical treatment for stormwater been investigated.

Heinzmann (1994) constructed a pilot plant to investigate the treatment effect of C/F in conjunction with a filtration step to treat stormwater from a separate sewer system, and concluded that a C/F system with filtration compared to a sedimentation tank has higher average removal efficiencies of filterable solids (85% vs 10%) and phosphorus (70% vs 10%), with an estimated 10–40% higher financial cost.

Harper *et al.* (1999) describes the implementation of C/F instead of a conventional system such as a retention basin due to available land area restraint and too high property costs. They reported 90% reduction of total phosphorus, 50–70% reduction of total nitrogen and 50–90% reduction of heavy metals. They also report favourable economic costs compared to conventional treatment methods, and stress that the construction cost for a C/F system is largely independent of the catchment area.

Trejo-Gaytan *et al.* (2006) describe a screening of iron and aluminium coagulants for treating the phosphorus-ridden (up to 9,900% exceedance values of phosphorus and up to 13,100% exceedance of turbidity) stormwater discharged to Lake Tahoe to meet discharge limits set by the California state. The authors evaluated the coagulants on both synthetic stormwater and real stormwater and report successful reduction of the phosphorus concentration and turbidity to under the discharge limit (<100 μg/L of total phosphorus and maximum turbidity of 20 NTU) using a streaming current detector for dosage adjustment.

Kang *et al.* (2007) collected the first flush from highways in Los Angeles, treated it with alum and ferric chloride and measured the reduction of turbidity and metals. Their results indicate that low dose coagulation is not effective, but a high coagulant dosing is sufficient (sweep floc mechanisms) for removal of turbidity (<5 NTU) and metals (50% for As,

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Cu, Cr, Cd, Pb and Zn), but may require additional pH control.

Sansalone & Kim (2008) collected samples of retained stormwater from a bridge in Baton Rouge and treated it with alum and ferric chloride. They looked at the relationship between pH and zeta potential as well as redox potential in relation to the coagulant dose and reduction of turbidity and total suspended solids together with changes in particle size distribution. They report on details of the coagulation mechanism in their study and conclude that C/F can be used for an increased treatment effect of retained stormwater but system complexity will increase due to operation and maintenance aspects.

These few studies show promising results, yet little scientific work has been conducted on C/F in the context of stormwater treatment. This underscores the need for further research of C/F and its performance as a unit process in stormwater treatment.

This laboratory study aims at investigating C/F for treatment of polluted road runoff, and assessing process performance and capabilities (solids and metal removal). These results, taken together, provide essential information about C/F in the context of treatment of urban runoff.

MATERIAL AND METHODS

Coagulation experiments and water analyses

Runoff from rain events was treated with two commercially available coagulant products, PAX-215 and PIX-111. PAX-215 is a polyaluminium product (relative basicity of 30%), a pre-hydrolyzed aluminium product containing several highly charged aluminium species. PIX-111 is an iron (ferric) chloride product. Both are frequently used products in coagulation treatment processes. Working solutions were prepared by diluting the coagulants by a factor of 10; concentrations were calculated based on the active substance (Fe/Al) using mass percentage and density according to manufacturer's product data sheet. Coagulation experiments were carried out in jar tests with six 1 L beakers, using one as a control and five for addition of varying coagulant concentrations, without pH adjustments. The jar test procedure consisted of an initial 60 second rapid mixing phase in which coagulant was added, followed by 15 minutes of slow mixing and lastly sedimentation for 30 min. The supernatant was decanted and water quality analyses performed, see below. The control beaker and the beaker with the highest turbidity reduction were further analysed for total suspended solids (TSS), total and dissolved organic carbon (TOC/DOC), and total and dissolved metals.

Before and after the treatment experiments, several analyses for water quality were performed in order to assess treatment efficiency. Turbidity was measured using a Hach Turbidimeter 2100N (Hach, Loveland, CO, USA), with the settings for signal average and ratio calculation. TSS analyses were done by glass fibre filtration (European Committee for Standardization 2005). Electrical conductivity (EC) was measured with a CDM210 device (Radiometer, Copenhagen, Denmark). A WTW pH 330 device (WTW, Weilheim, Germany) was used to record the pH values. End-point titration (International Organization for Standardization 1994) was used to determine alkalinity, calculated as mg/L as $CaCO_3$. TOC/DOC was determined by infrared spectrometry, with a reporting limit (RL) of 0.5 mg/L (Czech Office for Standards, Metrology and Testing 1997). Total (with acid digestion) and dissolved (without acid digestion) metal concentrations were determined. Samples for analysis of dissolved metals were filtered through 0.45 μm polyethersulfone filters. Concentrations of 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) were determined using ICP-SFMS (inductively coupled plasma sector field mass spectrometry) (International Organization for Standardization 2016), Zn (RL of 4/2 μg/L for total/dissolved) concentration was determined with ICP-AES (inductively coupled plasma atomic emission spectroscopy) (International Organization for Standardization 2007). All TOC/DOC and metal analyses were carried out by an accredited laboratory (ALS Scandinavia, Swedac Accreditation no. 2030), with extended uncertainty bounds (Joint Committee for Guides in Metrology 2008). Metal concentrations below the reporting limit were set to half the reporting limit. Particle size distribution was obtained using laser diffraction on a HORIBA LA-960 (HORIBA, Kyoto, Japan).

Road runoff collection

Collection was done from four rain events in the autumn of 2017 in downtown Luleå, northern Sweden. The first 25 L of road runoff were collected in a gully pot equipped with a stainless steel collector funnel. The gully pot receives runoff via a gutter from a one-direction two-lane road with a catchment area of approximately 300 m^2 and a traffic frequency (both directions) of approximately 17,800 annual average daily traffic. Time since last runoff event was estimated using open meteorological data from the nearest weather station, 4.5 km away (SMHI 2018). After filling the container, the runoff was transported to the laboratory. A subsample was taken for water quality characterization of the road runoff before being subdivided into two volumes for treatment with PIX-111 and PAX-215 respectively. The subsamples were also subjected to water quality characterization prior to the treatment experiments. Coagulation experiments were carried out on the same day of the road runoff collection.

Statistics

Statistical differences between group means were tested using one-way analysis of variance (ANOVA) (no treatment vs treatment). A post-hoc pairwise *t*-test (with Bonferroni correction) was used to compare means within groups (treatment method). All tests were performed using a significance level of 0.05.

RESULTS AND DISCUSSION

Road runoff

General road runoff data and corresponding water quality parameters are outlined in Table 1 for the four events. No street sweeping occurred between rain events. Measured alkalinity and pH were within sufficient operating range for coagulation reactions to occur.

Several metals (Cr, Cu, Ni, Pb and Zn) found in the road runoff exceeded suggested discharge limits (Table 2) in a proposal for the city of Stockholm (Riktvärdesgruppen 2009), indicating a considerable pollution of the collected road runoff. The dissolved fraction of the total metal content, generally considered the more bioavailable and therefore more toxic (Chapman *et al.* 1998), constituted 1–12% of the total metal concentration (Table 2). The runoff was characterized by highly varying pollutant levels (Tables 1 and 2), and this high variance has been previously observed at the site (Westerlund *et al.* 2003) and could be due to numerous factors that were not investigated in this study. Runoff was only collected during rain events in the autumn period and included no melt events. A concern for possible treatment of runoff collected during melt events would be if de-icing salts were applied; then it is likely that the outcome would be different. The de-icing salts may then cause metal mobilization and increased ionic strength, leading to increased concentrations of dissolved metals and less coagulant needed respectively (Bäckström *et al.* 2004).

Table 1 | Water quality parameters for the road runoff used in the coagulation treatment experiments

Date	Time since last runoff event (hours)	Turbidity (NTU)	TSS (mg/L)	EC (µS/cm)	pH	Alkalinity (mg/L as $CaCO_3$)
2017-08-24	57	370	690	71.8	7.3	33.3
2017-09-19	81	330	390	73.4	8	38.1
2017-10-03	290	600	750	134	8.1	55.5
2017-10-10	73	1,000	820	96	8.3	65.1

Treatment efficiency

The coagulant doses, where optimal turbidity reduction was achieved, were determined through a series of jar tests (Table 3). Initial dose and the range for each jar test were based on initial turbidity and prior experience. The dose concentrations were calculated as active substance (mg/L) of Al or Fe in the coagulant product. Treatment efficiency was calculated as the percentage removal of pollutants from the road runoff in relation to treatment, either sedimentation control with no coagulation addition, or the coagulation treatment with optimal dose of coagulant.

Table 2 | Concentrations (mean ± SD, three significant digits) of total and dissolved metals in the road runoff in relation to a proposal for discharge limits for stormwater pollutants in Stockholm, Sweden

Metal	Total (µg/L)	Dissolved (<0.45 µm) (µg/L)	Dissolved as a fraction of total (%)	Suggested discharge limits* (µg/L)	Exceedance* (%)
Cd	0.377 ± 0.669	ND	–	0.4/0.5	–
Cr	61.6 ± 9.33	1.71 ± 1.7	3	10/25	516/146
Cu	182 ± 15.5	21.8 ± 4.71	12	18/40	900/355
Ni	30.3 ± 6.50	1.81 ± 2.16	6	15/30	102/1
Pb	36.6 ± 6.99	0.24 ± 0.71	1	8/15	358/144
Zn	802 ± 25.7	28.8 ± 5.21	4	75/125	969/542

*Discharge to: water body/separate sewer system; ND, not detected; –, not calculated.

Table 3 | Coagulant dose ranges tested and the optimal dose for each coagulant and event as determined by highest turbidity reduction

Coagulant	Runoff event	Dose range (mg/L)*	Optimal dose (mg/L)*	Initial turbidity (NTU)	Final turbidity (NTU)	Initial TSS (mg/L)	Final TSS (mg/L)
PIX-111							
	2017-08-24	5.4–14.2	12.0	500	11	1,200	<8
	2017-09-19	8.7–13.9	11.3	300	5.4	1,200	9
	2017-10-03	16.3–21.8	18.5	650	5.3	920	<8
	2017-10-10	16.3–25.0	16.3	1,000	14	820	21
PAX-215							
	2017-09-19	1.4–4.0	3.6	330	11	1,200	<8
	2017-10-03	4.1–8.1	7.9	600	11	750	11
	2017-10-10	5.4–9.8	6.6	1,000	9.5	1,900	9

*Expressed as active substance (mg Al/L or mg Fe/L).

Figure 1 shows the treatment effect in terms of particle reduction (turbidity and TSS) as well as organic carbon (TOC/DOC). Both coagulants, PIX-111 and PAX-215, were significantly better than the sedimentation control in reducing turbidity and TSS. There was a significantly higher residual turbidity compared to residual TSS between sedimentation and coagulation treatment due to non-settling colloids. In many cases TSS was reduced below reporting limit (<8 mg/L). There is no observable difference in reduction of TOC/DOC as compared to the sedimentation control, indicating that TOC is mostly associated with readily settleable particulates and DOC remains unaffected by the coagulation mechanism in this experiment.

Figure 2 shows the difference in metal treatment effect of coagulation and sedimentation on the road runoff as compared to only sedimentation. For the total metal fraction significant differences between treatment groups (PIX-111, PAX-215 and sedimentation) were observed, and coagulation treatments had a significantly higher reduction of total metal content. Reduction of the total fraction of Zn was significantly higher using PAX-215 compared to PIX-111. The reduction of metals did vary slightly depending

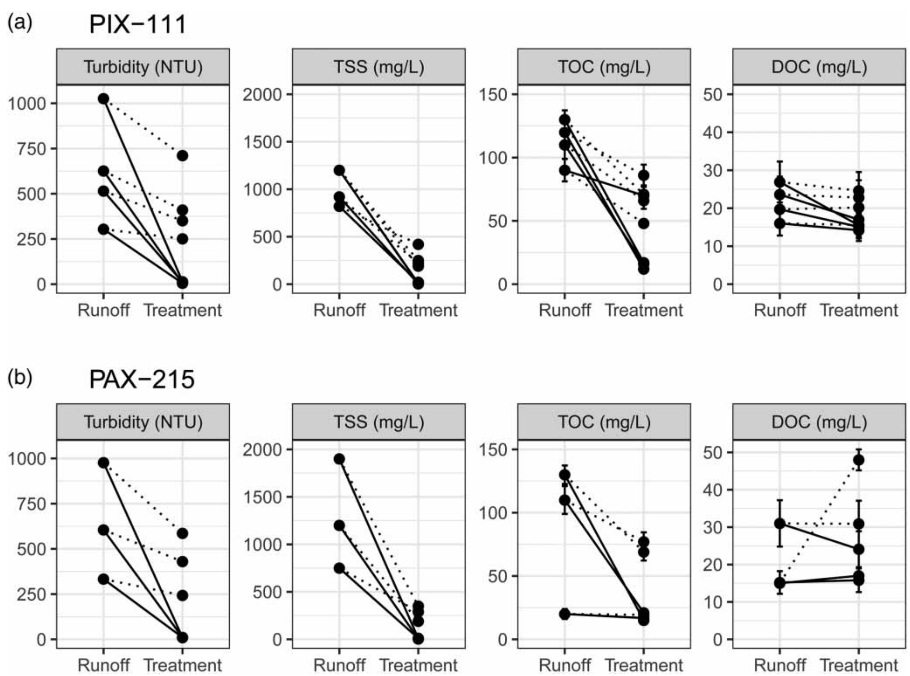

Figure 1 | Treatment effects for PIX-111 (a) and PAX-215 (b) with respect to particles (turbidity and TSS) and organic carbon (total and dissolved). Solid line (—) represents treatment with a coagulant plus sedimentation, dotted line (···) represents the control (only sedimentation) in the jar tests. Error bars cover two standard deviations from the mean as reported by the laboratory where applicable.

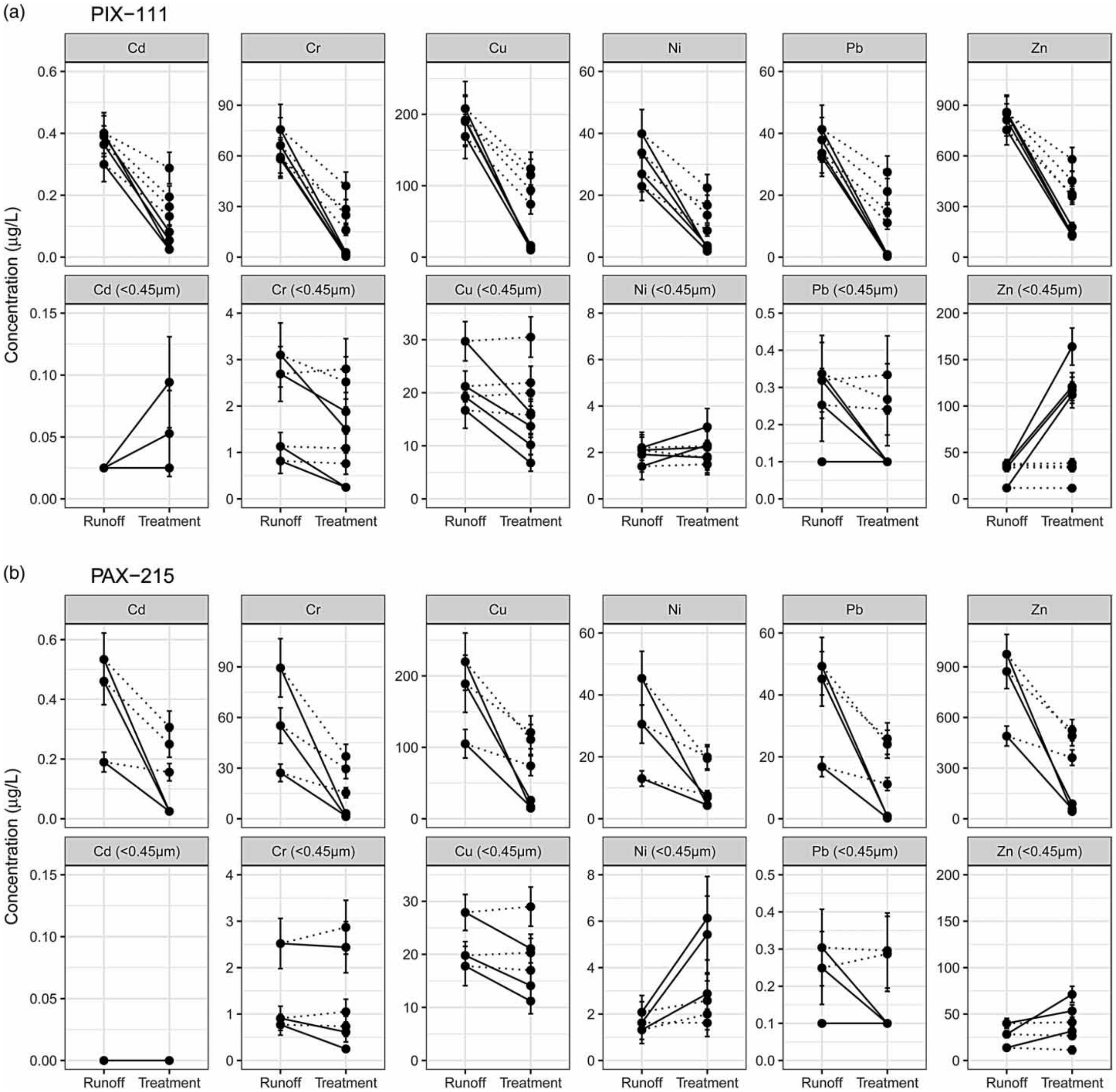

Figure 2 | Metal treatment effects for road runoff treated with PIX-111 (a) and PAX-215 (b). Solid line (—) represents treatment with a coagulant plus sedimentation, dotted line (···) represents the control (only sedimentation) in the jar tests. Error bars cover two standard deviations from the mean as reported by the laboratory.

on the coagulant used (Table 4); overall the mean reduction rate was 50% for sedimentation and 91% for coagulation. The high reduction of the total metal fraction is correlated with the high reduction of particles, which can be explained by the propensity of metals to adsorb onto particles (McKenzie *et al.* 2008).

Treatment tests were not carried out on the entire runoff volume, but rather the first 25 L. Possibly, the pollutant concentrations would have been lower if the entire runoff volume had been retained and treated (Mangani *et al.* 2005). However, the four different events were characterized by varying levels of pollutants, and no difference in treatment magnitude based on initial pollutant levels was detected.

The reduction of the dissolved fraction was lower compared to the total fractions. In general the reduction of the dissolved metals was on average 40%. A significant reduction was observed for dissolved Cr, Cu and Pb with PIX-111 and likewise for dissolved Cu and Pb with PAX-215, although PIX-215 had a significantly higher treatment effect for Cu than PAX-215. This effect was presumably due

Table 4 | Treatment effect per pollutant in percent shown as mean reduction and one standard deviation

	Sedimentation	PIX-111	PAX-215
Turbidity	30 ± 10	98 ± 1	98 ± 1
TSS	74 ± 20	99 ± 1	99 ± 1
TOC	33 ± 23	71 ± 33	62 ± 40
DOC	−36 ± 126	26 ± 13	2 ± 18
Total metal			
Cd	41 ± 20	87 ± 7	92 ± 5
Cr	54 ± 15	98 ± 1	96 ± 2
Cu	43 ± 13	93 ± 2	88 ± 5
Ni	48 ± 17	90 ± 3	78 ± 12
Pb	46 ± 17	99 ± 1	98 ± 0
Zn	42 ± 16	83 ± 2	91 ± 4
Dissolved metal (<0.45 μm)			
Cd	–	–	–
Cr	0 ± 14	57 ± 21	34 ± 32
Cu	−1 ± 6	47 ± 10	30 ± 6
Ni	−11 ± 28	−26 ± 33	−182 ± 59
Pb	0 ± 15	50 ± 34	42 ± 37
Zn	4 ± 11	−417 ± 294	−105 ± 63

No treatment effect was calculated for dissolved Cd as data were at or below reporting limit (only two values for treatment with PIX-111 were above reporting limit).

to different metal hydroxide precipitations. In contrast, the dissolved fraction of Ni increased for PAX-215 and for PIX-111; this effect was stronger for PAX-215. A similar effect was observed with the dissolved fraction of Zn, but here the effect was stronger for PIX-111 and probably caused by the lower end pH for the runoff treated with PIX-111 (mean pH 5.9) compared to PAX-215 (mean pH 7), as Zn is known to have increased mobility at lower pH (<6) ranges (Houben *et al.* 2013). The observed increase in dissolved Zn is in contrast to previous coagulation studies with road runoff (Kang *et al.* 2007), where coagulation significantly decreased the concentrations of dissolved Zn. One possible explanation for this difference could be that Kang *et al.* (2007) adjusted the pH to 7, thus retaining Zn adsorbed onto particulates.

Overall, coagulation of road runoff exhibited a good treatment performance in terms of reduction of total metals. Both coagulants in this study reduced the metal concentrations below proposed discharge limits, which was not achieved by sedimentation alone. The observed conflicted effects regarding the dissolved metal fraction are noteworthy and warrant further studies, although the effects in this case can be considered small as the dissolved fraction corresponded to only 1–12% of the total metal concentration.

Changes in particle size distribution

The particle size distribution (Figure 3) of the road runoff is characterized by larger particles both in terms of area

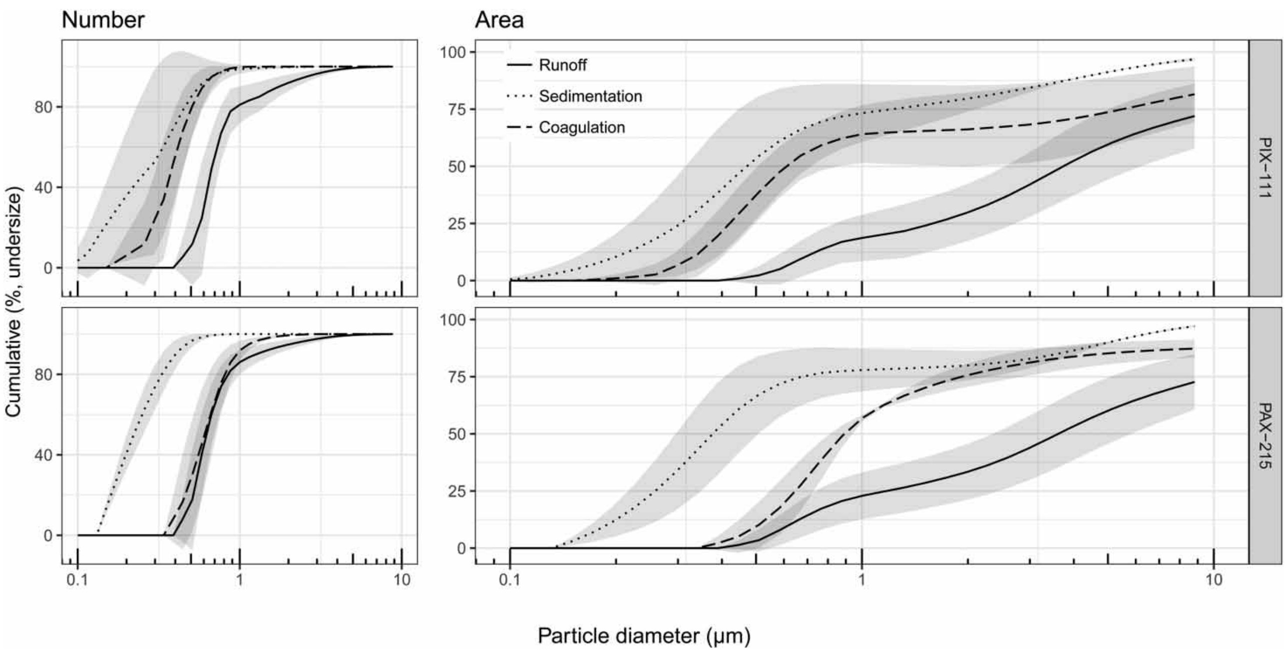

Figure 3 | Average particle size distribution for the road runoff, and after treatment (sedimentation and coagulation). Left column uses number as it transformation basis and right column uses area. The y-axis represents the cumulative percentage of undersize particles for the given basis. Shaded region includes one standard deviation around the mean.

(diameter >1 μm) and number (diameter >0.5 μm). The sedimentation treatment shifts this distribution towards smaller particles, as the settleable fraction is removed and the remaining particles are mostly suspended colloids. The coagulation treatment reduces this fraction and therefore the particle size distribution is shifted right towards larger particles compared to the sedimentation treatment. The particles dominating the size distribution for the coagulation treatment are mostly attributed to flocs that were disturbed and resuspended during decantation.

CONCLUSIONS

The first 25 litres of road runoff from four rain events were collected and subjected to a coagulation process, using the commercial coagulants PIX-111 and PAX-215. The treatment effect in terms of reduction of particle content and changes in size distribution as well as reduction of organic carbon and metal were investigated. Overall, the reduction of particles (turbidity and TSS) and total metal fraction was above 90%. The dissolved fraction of Cr, Cu and Pb was reduced by 40%. The difference between coagulants was most pronounced with regards to the treatment effects on the dissolved metal fractions. PIX-111 resulted in a higher reduction of dissolved Cr and Cu compared to PAX-215. Concentrations of dissolved Zn increased during coagulant treatment, probably due to the pH decrease, resulting in a higher Zn mobility. A pre-hydrolysed coagulant with a high basicity may have less effect on the pH and keep Zn bound to particles. A particle size distribution together with turbidity data indicate that road runoff subjected to sedimentation is dominated by small particles (<0.5 μm in diameter), and that this fraction can be reduced with a coagulation process.

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