# Particle Destabilization in Highway Runoff to Optimize Pollutant Removal

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**Abstract:** Sedimentation column studies and simulations using particle size distribution suggest that low removal efficiencies of smaller particles in highway runoff would be obtained using sedimentation if coagulation-flocculation is not performed. Coagulation-flocculation studies, using metal salts (alum and ferric chloride) and one organic polymer in three molecular weights, were evaluated over the 2004–2005 storm seasons. Only the first flush or approximately the first hour of runoff was coagulated. Efficiencies were quantified with particle size distribution measurements and turbidity. Results with low dosages of metal salts were ineffective and did not improve water quality. High dosages of metal salts using a sweep floc mechanism were effective in dramatically lowering runoff turbidity, but resulted in large quantities of sludge production and required pH control. A cationic organic polymer at low dosages ($<$10 mg/L) was effective in coagulating highway runoff and reducing particle charge. Extended mixing time was required to achieve low turbidities ($\sim$5 NTU). A combination of organic polymer, followed by small doses of alum ($<$10 mg/L), reduced mixing time and produced high quality effluent.

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**CE Database subject headings:** Stormwater management; Particle size distribution; Coagulation; Runoff; Optimization; Pollutants.

## Introduction

A great proportion of pollutants in highway runoff, such as heavy metals and polynuclear aromatic hydrocarbons are bound to particles (Oliver et al. 1974; Herrmann 1981; Ongley et al. 1981; Hoffman et al. 1985; Hewitt and Rashed 1992; Legret and Pagotto 1999; Lau and Stenstrom 2005). The large surface-to-volume ratios of particles in highway runoff provide reactive locations for partitioning and transport of pollutants and may serve as reservoirs of these pollutants in downstream locations (Thomson et al. 1997; Cristina et al. 2002). In addition, pollutants sorbed to particles generally have less mobility and bioavailability than in their dissolved form (DePinto et al. 1994). Consequently, understanding characteristics of particles in highway runoff is crucial for future runoff management and best management practice (BMP) selection, which are often selected based upon total suspended solids (TSS) removal.

In an effort to understand and mitigate the impacts of highway runoff, the California Department of Transportation (Caltrans) sponsored a five year highway runoff characterization study at three monitoring sites in west Los Angeles from 1999 to 2004 (Han et al. 2006a,b). Table 1 summarizes the description of the three monitoring sites. The catchment areas range from 0.39 to 1.69 ha and annual average daily traffic ranges from 269,000 to 328,000 vehicles per day. The average annual rainfall is approximately 330 mm. The sites were instrumented with flow meters, tipping bucket rain gauges, and flow-weighted composite samplers (Model 950, American Sigma, Loveland, Colo.). Additional information on the sites can be obtained from previous publications (Kim et al. 2004; Han et al. 2006a).

This paper reports on methods to optimize the removal of particles as well as their associated pollutants in highway runoff. It is our first attempt to increase particle size through coagulation in order to enhance removal rates. Specific objectives of the study were to investigate: (1) effect of mechanical mixing without coagulants and effect of mixing time with a cationic polymer on the particle destabilization of highway runoff; (2) particle destabilization and associated pollutant removal using different methods of particle destabilization with alum, ferric chloride and a cationic polymer; and (3) optimum dosage of alum, ferric chloride and polymers as a function of initial characteristics of highway runoff. Our understanding and approach to this research is built upon previous work by Stumm and O'Melia (1968) and others.

## Background

### *Particle Settling*

Particle settling velocity is one of the most important factors for BMP performance. It depends on the particle size, shape, density,

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**Table 1.** Summary Description of Sampling Sites

| Site number | Freeway | Location | Area (ha) | AADT[a] (×1,000) | Imperviousness (%) |
|---|---|---|---|---|---|
| 1 (7-201) | US-101 | Intersection of US-101 and I-405 | 1.28 | 328 | 100 |
| 2 (7-202) | I-405 | Near Getty Center | 1.69 | 269 | 95 |
| 3 (7-203) | I-405 | Northbound exit to Santa Monica Blvd. | 0.39 | 322 | 100 |

[a]Average annual daily traffic (vehicles per day).

and is influenced by the liquid characteristics, such as temperature and viscosity. Particle size distribution (PSD) monitored in the three highway sites showed that 97% of particles (by number) were less than 30 μm in diameter (Li et al. 2005), which emphasizes the importance of small particle removal in BMP design. Additionally, the highest pollutant concentrations were associated with the smallest particle size. Fig. 1 shows the typical PSD of a series of grab samples collected through a storm event along with the associated turbidity, TSS, specific conductivity. Additional information about measuring techniques and more events are available elsewhere (Li et al. 2005).

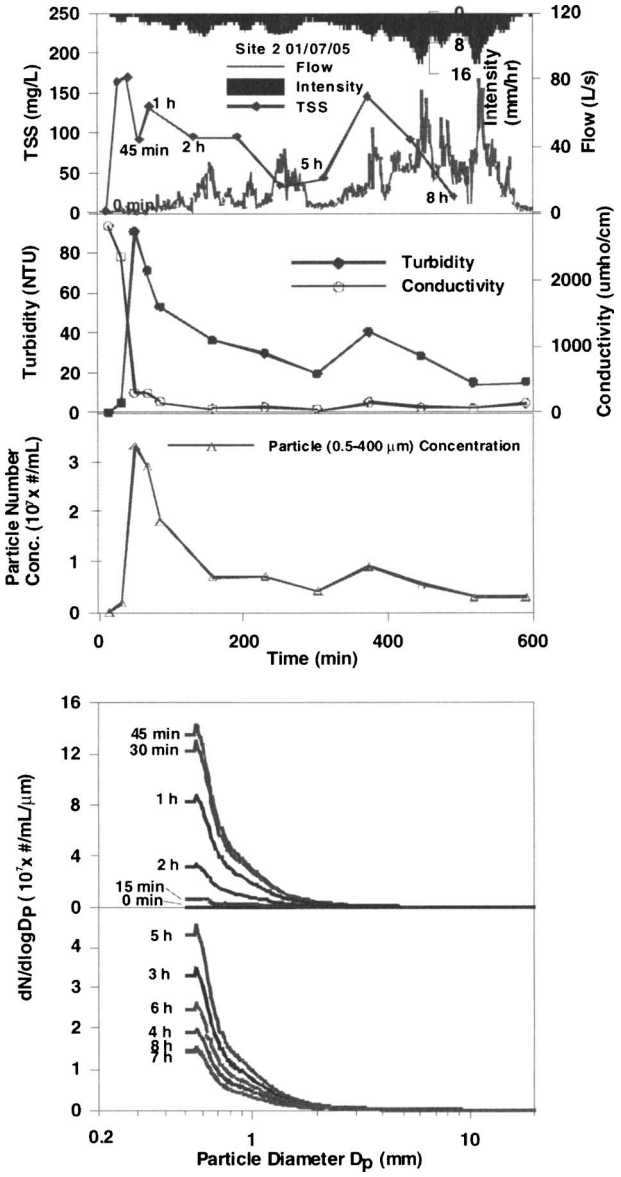


**Fig. 1.** Hydrograph with TSS, turbidity, conductivity, and PSD for Site 2, January 7, 2005. Sample times shown in the top panels correspond to times for PSD analysis shown in the lower two panels.

Li et al. (2006) simulated particle and pollutant removal efficiencies for 16 events for the entire 2002–2003 wet season, using particle settling velocities calculated using the law of Newton and Stokes for PSD measured during each storm event. Spherical particles corresponding to the measured PSD and having a uniform density 2.6 g/cm$^3$ were assumed. Continuous flow clarifiers with volumes sized to contain 1.6–26 mm of rainfall were simulated and were able to remove 75–92% of the particles between 2 and 1,000 μm, respectively. The simulations showed that only 3–29% of particles between 2 and 10 μm could be removed. The removal rate increases to 13–72% of particles between 2 and 25 μm. A series of settling column tests with fresh storm water samples showed much less removal than predicted, which suggests that settling velocities of smaller particles are much lower than calculated by the law of Newton and Stokes with the stated assumptions. The difference is probably due to a distribution of densities, and deviation from spherical shape. These results support anecdotal observations of poor performance of BMPs using only sedimentation for removing smaller particles (Greb and Bannerman 1997).

It is unfortunate that the smaller particles are not removed as they routinely have higher concentrations of heavy metals and total PAHs than the larger particles (Sansalone and Buchberger 1997; Roger et al. 1998; German and Svensson 2002; Morquecho and Pitt 2003; Lau and Stenstrom 2005). It is clear that achieving high efficiency using sedimentation for smaller particle removal will require some type of particle destabilization in order to increase particle size and improve settling velocity. This is challenging because it is desirable to operate stormwater BMPs unattended and without instrumentation, and stoichiometric methods for particle destabilization often requires operator assistance. In addition, remote management of many small-scale coagulation/flocculation systems could be difficult.

### *Particle Destabilization*

Particles in the aqueous system naturally aggregate due to the collision between particles resulting from Brownian diffusion, fluid shear, and differential settling (Svarovsky 1985). Colloidal particles are often highly charged which retards their natural aggregation. It is thus necessary to destabilize particles and thereby accelerate particle aggregation rate to separate fine particles from the solution easily.

Destabilization of dispersed particles in aqueous systems can be achieved by several different mechanisms: double layer compression, charge neutralization, bridging, and sweep floc. The formation of deltas in estuaries is a common example of the double layer compression mechanism. Engineered systems, however, typically use coagulants and coagulant aids for colloid destabilization involving either charge neutralization, bridging,

**Table 2.** Characteristics of 1 h Composite Runoff Samples

| Parameters | Range of values for untreated composite samples |
|---|---|
| pH | 6.3–7.1 |
| Temperature (°C) | 13.2–19.8 |
| Turbidity (NTU) | 51–197 |
| TSS (mg/L) | 76–612 |
| Chemical oxygen demand (mg/L) | 193–1,037 |
| Conductivity (μS/cm) | 141–1,014 |
| Zeta potential (mV) | From −46.5 to −26.5 |

sweep floc, or a combination of those mechanisms. Among the metal ions, $Al^{3+}$ and $Fe^{3+}$ are commonly used in the water and wastewater treatment. Depending on their dosage and water characteristics, $Al^{3+}$, $Fe^{3+}$, and their hydrolysis products neutralize charge on the negatively charged particles (stoichiometric destabilization) or precipitate as amorphous forms to enmesh colloidal particles (sweep floc coagulation) (Stumm and O'Melia 1968). Natural and synthetic polymers have been used as primary coagulants or flocculation aids in water and wastewater treatment systems for many years. Polymers bridge two or more particles by attaching themselves to the adjacent particles. Cationic polymers are used to reduce the repulsive force between particles, both by neutralization and bridging mechanisms. Anionic polymers are commonly used to flocculate negatively charged particles via bridging. Both bridging and neutralization mechanisms can fail with excessive concentrations of polymer because restabilization resulting from charge reversal can occur.

In storm-water treatment, coagulation and flocculation have also been proposed as methods for enhancing colloid destabilization. Polyaluminum chloride (PACl) has frequently been employed because its low acidity is advantageous for weakly buffered storm waters. Heinzmann (1994) has shown that the mixture of PACl and cationic polymer (polyacrilamide) was effective in the filtration system of urban storm water. Annadurai et al. (2003) investigated the efficiency of PACl to treat high turbidity storm water (1,650 NTU), and found that a high dose of PACl (>100 mg/L) is preferable to generate large flocs for easy solid-liquid separation. Caltrans also has recently conducted comprehensive coagulation studies using PACls to remove the turbidity and phosphorus from simulated storm water and actual storm water entering Lake Tahoe (Caltrans 2003, 2006; Trejo-Gaytan et al. 2006). Our study focused on treating first flush volume of 100% highway runoff that contains high concentrations of suspended solids, metals, and other pollutants, using different particle destabilization mechanisms. Highway runoff in the study area has 2–5 times higher metal concentrations compared to statewide values (Lau et al. 2006) and efficient particle destabilization strategies are most needed in this area, especially for treating the first flush, which may contain up to 50% of the total metal masses.

## Methodology

### *Preparation of Highway Runoff Samples*

Multiple composite samples were collected during the first hour of runoff from Site 2 (7–202) during the 2004–2005 wet season. One-hour composites were selected because an hour is generally equal to the time where the runoff volume of the first flush (~10–30% of the total runoff) contains the highest particle concentrations, and our objective was to simulate a BMP that would capture and treat the first flush. Samples were returned to the laboratory within one hour and a series of jar tests were performed using different coagulants and mixing strategies. Table 2 summarizes the range of sample characteristics. Standard Methods (APHA 1998) or USEPA approved methods (USEPA 1983, 1999) were used for all water quality analyses.

### *Mixing and Jar Tests*

Throughout the course of the experimental program, small changes in runoff samples were noted as storage time increased. By measuring the PSD, Li et al. (2005) were able to quantify the differences and develop a sampling protocol that avoided PSD change during storage. The natural aggregation of particles during sample storage is a problem for quantifying storm-water quality, but can be an advantage for BMP development since increases in particle size generally improve settling and filtration performance.

To investigate natural aggregation of the particles in the runoff sample, a series of mixing test was performed. Two 4 L bottles of runoff sample were prepared and labeled "no mixing" and "mixing," respectively. The bottle labeled no mixing was kept quiescent and the other labeled mixing was stirred to promote collisions between particles to accelerate aggregation. Slow mixing was provided by a magnetic stirring bar (2.5 cm) operating at 100 rpm, which corresponds to a $G$ factor of 9.3/s, calculated using the stir dimension and drag coefficient ($C_D$=1.8) for paddles. The experiment was performed over 300 h at ambient temperature (20°C). Samples were taken from each bottle (mixing and no mixing) and TSS and total dissolved solids (TDS) were analyzed at each measurement time. The experiment was repeated for four different storms (December 7, 2004, December 27, 2004, January 28, 2005, and February 6, 2005).

**Table 3.** Protocols for Coagulation/Flocculation Tests

| | Rapid mixing | Slow mixing | Settling | | |
|---|---|---|---|---|---|
| Experiment regime | Time/speed | Time/speed | Time | Coagulant | Remarks |
| Low dose coagulation | 1 min/100 rpm | 4–8 h/5–10 rpm | 16–20 h | Alum or ferric chloride | pH adjusted to 7 |
| Sweep floc coagulation | 1 min/100 rpm | 10 min/5–10 rpm | 40 min | Alum or ferric chloride | pH adjusted to 7 |
| Flocculation with polymer | 1 min/100 rpm | 4–8 h/5–10 rpm | 16–20 h | PolyDADMAC<br>HMW: 400,000–500,000<br>MMW: 200,000–350,000<br>LMW: 100,000–200,000 | |
| Flocculation with polymer followed low dose alum | 1 min/100 rpm | 10 min–4 h/5–10 rpm | 10 min–12 h | PolyDADMAC<br>HMW: 400,000–500,000 and alum. | pH adjusted to 7 |

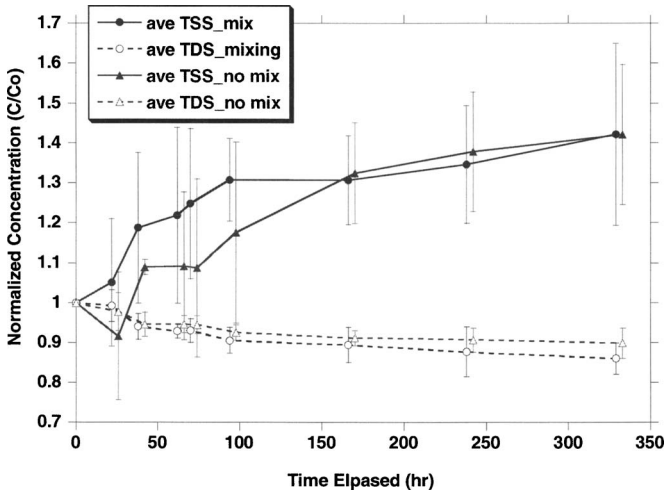


**Fig. 2.** TSS and TDS changes over time from the observation of natural aggregation. Mean values with 95% confidence levels (four replicate experiments).

The jar tests were divided into four different experimental regimes: (1) low dose coagulation; (2) sweep floc coagulation; (3) flocculation using organic polymers to neutralize charge; and (4) flocculation using organic polymer followed by alum. In the low dose coagulation, relatively small doses of alum or ferric chloride [less than 40 mg/L as $Al_2(SO_4)_3$ or $FeCl_3$] were applied followed by gentle mixing for 4–8 h. These procedures were intended to investigate the effect of metal coagulants on neutralizing and aggregating negatively charged particles. The second regime used higher doses to produce sweep floc coagulation. The high alum or ferric chloride dosage formed a sweep floc, enmeshing the colloidal particles. Optimum dose for each coagulant was estimated based on turbidity removal. pHs were always adjusted to 7 for both low dose and sweep floc coagulation tests. Next, flocculation tests were performed using polydiallyldimethylammonuim chlorides (polyDADMACs), a neutral pH, cationic organic polymer with different molecular weights (Table 3). Long periods of slow mixing were provided after 1 min of rapid mixing to allow sufficient contacting time for particle aggregation. The final series of testes used polyDADMAC with small concentrations of alum or ferric chloride to reduce mixing times. The general procedures of each coagulation/flocculation test are shown in Table 3.

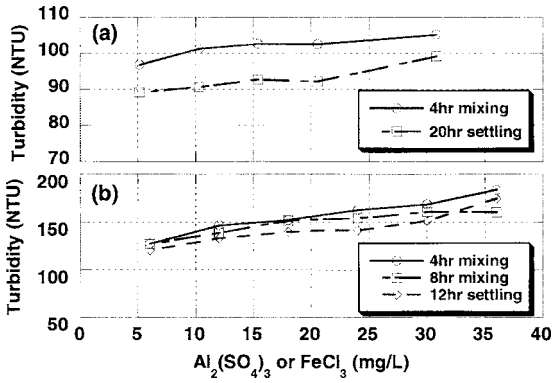


**Fig. 3.** Turbidity changes in the samples in low dose coagulation: (a) ferric chloride (November 27, 2004); (b) alum (November 7, 2004)

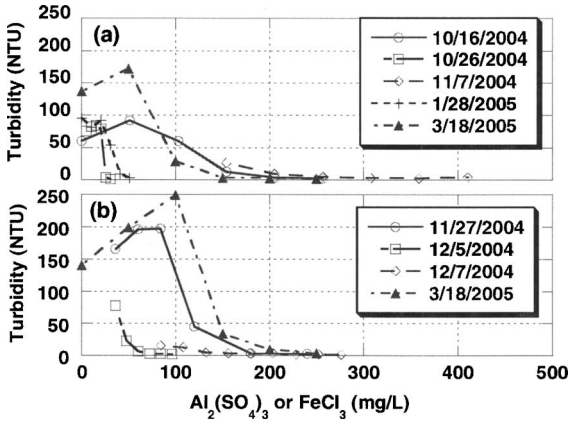


**Fig. 4.** Turbidity removal from sweep floc coagulation: (a) alum; (b) ferric chloride

### *Zeta Potential and PSD Measurements*

Particle zeta potential (ZP) was measured with a ZetaPALS instrument (Brookhaven Instruments Corp., Holtsville, N.Y.). When the sample turbidity was too high to measure ZP, they were diluted with de-ionized (DI) water before measurement. DI water was used after confirming that there was no difference in ZP or other coagulation properties when diluting with DI or storm water from the same event filtered through a 0.1 μm membrane.

PSD was measured with an AccuSizer 780 Optical Particle Sizer module (Nicomp Particle sizing Systems, Santa Barbra, Calif.). The light scattering/extinction sensor attached to the AccuSizer can measure the particle number in the solution in different size range from 0.5 to 400 μm. Detail procedures for the PSD measurement are described by Li et al. (2005).

## Results and Discussion

### *Particle Aggregation over Time*

Fig. 2 compares relative changes of TSS and TDS concentrations in runoff samples with and without mixing. TSS and TDS concentrations for each measurement were normalized using the initial concentrations, and the mean of the normalized concentrations (C/Co) from all four storms were plotted with 95% confidence levels. TSS concentration increased by about 30% and TDS concentrations decreased by about 10% of initial values during the first 160 h for both mixed and unmixed samples. No significant changes in the concentration of TSS and TDS were observed after 160 h. Mixing increase the rate of TSS increase, which increased rapidly over the initial 90 h and stabilized thereafter. The unmixed sample showed similar trends but required longer time to reach steady state. The decrease of TDS in the mixed and unmixed samples suggests that a portion of the dissolved solid precipitates, or particles less than 0.45 μm aggregate and are then captured on filters used for TSS analysis.

This experiment demonstrates that the particles in highway runoff naturally aggregate over time and mixing can increase aggregation rate. This supports the PSD measurement protocol of Li et al. (2005) that requires samples to be analyzed in less than 6 h when accurate measurements of PSD and associated pollutants are desired. The time required for naturally occurring particle aggregation may be too long for practical application. As a result, additional efforts for destabilizing particles are needed.

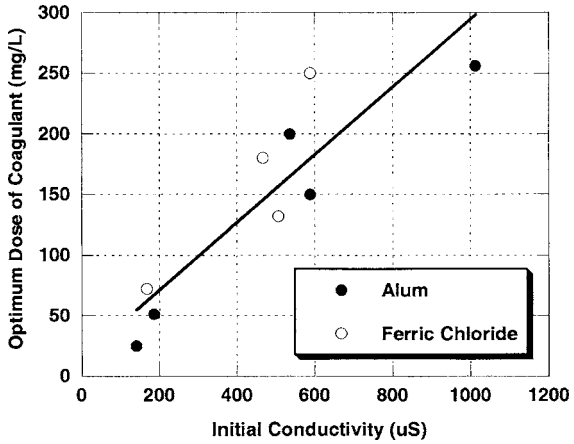


**Fig. 5.** Optimum dose of alum and ferric chloride as a function of the initial conductivity values of runoff samples

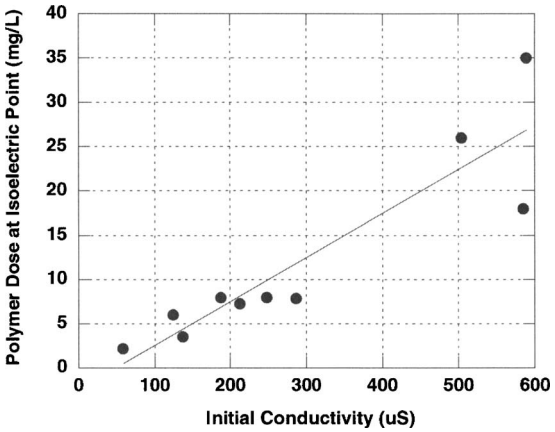


**Fig. 7.** Polymer dose at isoelectric point as a function of the initial conductivity values of runoff samples

### *Low Dose Coagulation*

The first series of experiments were performed with low dosages of coagulants to avoid significant pH changes that might occur with the low alkalinity runoff and to avoid the expense of high coagulant dose and resulting sludge production. Fig. 3 shows the turbidity changes during the low dose coagulation tests for two different storm events using alum and ferric chloride. In these tests, alum or ferric chloride was added in varying amounts up to 40 mg/L, which did not produce sweep floc. Fig. 3 shows that in low dosages, neither coagulant is able to produce settleable particles but instead forms pin flocs, increasing turbidity. Settleable particles were never produced even though extended periods of slow mixing were investigated. This is likely due to the high surface area and negative charge of the suspended solids, which requires too much coagulant to neutralize. This conditioning might have been useful for granular media filtration (Caltrans 2003), but was not investigated.

### *Sweep Floc Coagulation*

Fig. 4 shows the turbidity removals using sweep floc coagulation with alum and ferric chloride, respectively. Each storm event had a different optimum dose, ranging from approximately 40 to 500 mg/L. Optimum dose was defined as the minimum coagulant concentration required to produce 5 NTU or less in turbidity. For both alum and ferric chloride, the isoelectrical point of ZP could not be obtained, and sweep floc was routinely observed from −20 to −10 mV ZP.

The optimum dose was plotted as a function of specific conductivity in Fig. 5, showing that the optimum dose is proportional to the initial conductivity. This relationship is not thought to be due to changing electrochemical properties with conductivity, but from the higher concentrations of dissolved and colloidal material, which are positively correlated to conductivity, and consume more coagulants to achieve destabilization. Han et al. (2006b) showed that initial turbidity and other pollutant concentrations are proportional to the amount of contamination in the runoff, which is related to dilution of the storm water. Other parameters such as TSS might be better indicators of coagulant dose, but conductivity can be easily measured in real-time, and hence an automatic controller might be used to adjust coagulant dose. The large coagulant dose will more than double sludge production, and pH control chemicals will also increase costs, which will limit this application.

One test was performed to evaluate the impact of ionic strength on coagulation efficiency. Sodium chloride (NaCl) was added over the range of 10,000–50,000 mg/L in a series of jar tests. No significant drop in turbidity was observed over this range of salt concentration. However, at 30,000 mg/L NaCl,

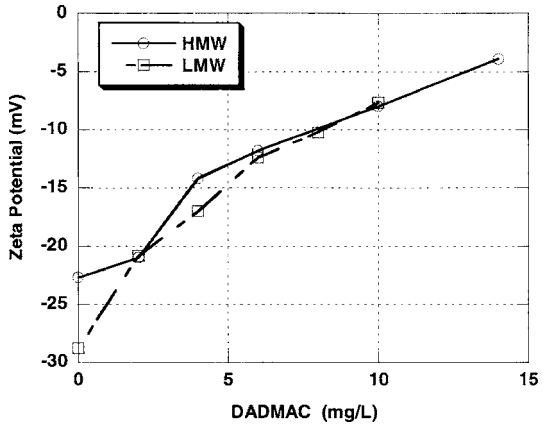


**Fig. 6.** ZP changes in the runoff sample after adding two different molecular weight polyDADMACs on February 6, 2005

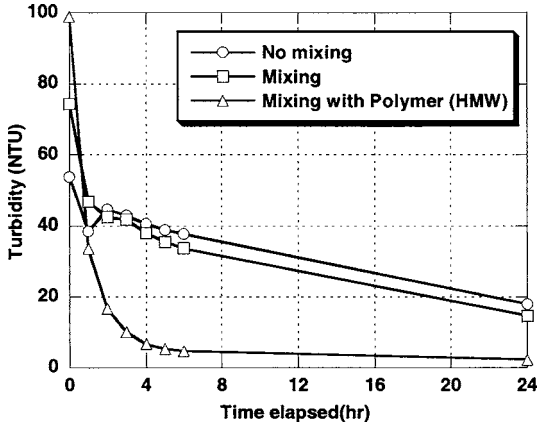


**Fig. 8.** Effect of mixing time on the turbidity removal with and without polymer on January 28, 2005

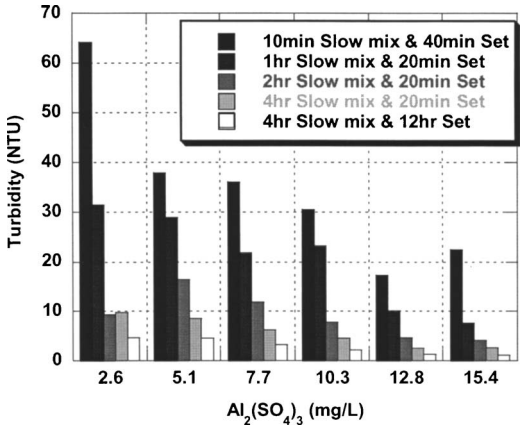


**Fig. 9.** Effect of alum addition on the mixing time using polymer coagulation on January 28, 2005 (polymer concentration was fixed at 8 mg/L)

the required alum or ferric chloride concentration to produce sweep floc was reduced to approximately 25% of the dose required without salt.

### *Flocculation with Cationic Polymer*

#### Charge Neutralization with Different Molecular Weight Polymers

Fig. 6 shows the ZPs as a function of polymer dose for two different molecular weight polyDADMACs. Both polymers were equally effective in reducing the ZP. Fig. 7 shows the polymer dose for isoelectric point as a function of initial conductivity, which is similar to the previous results showing optimum alum or ferric chloride dose (dose required to produce 5 NTU or the lowest supernatant turbidy) related to initial conductivity. Usually, 4–7 NTU could be obtained from −6 to +4 mV ZP with extended slow mixing time.

Fig. 8 shows the effect of mixing time on the turbidity removal with and without polymer. As can be seen, at least six hours were needed to reduce turbidity to less than 5 NTU after particles were destabilized. An extended mixing period might be required for particle aggregation and sedimentation although the isoelectric point is reached soon after adding polymers. It is important to note that mixing alone may not produce 10 NTU or less in turbidity after 24 h.

Fig. 9 shows the effect of alum addition on the mixing time in the flocculation using the polymer on January 28, 2005. Turbidity removals are displayed with slow mixing and after settling for different alum doses from 2.6 to 15.4 mg/L with 8 mg/L polymer dose, which was the optimum dose for this storm event. As more alum was added, shorter mixing time was required to reduce the turbidity in the supernatant. For example, 5 NTU was achieved after 2 h of mixing at 15.4 mg/L of dry alum, where as at least 4 h of mixing was required at 7.7 mg/L of dry alum to obtain the same water quality. By adding alum or ferric chloride, the increased concentration of negatively charged species ($Al(OH)^{4-}$, $Fe(OH)^{4-}$) might provide greater chance of contact for the polymer to form neutralized cluster. As a result, mixing time required for flocculation by combining polymer and other coagulants such as alum or ferric chloride can be reduced.

#### Impact of Coagulation on PSD

Fig. 10 shows that particle sizes were dramatically increased after coagulation. The vertical axis shows the relative increase or decrease in the number of particles in a given size range, which is shown on the horizontal axis. Relative increase or decrease is calculated relative to the initial particle concentrations. The various lines show a time series from just after rapid mixing to 8 h and the final line shows the particle concentration after sedimentation. The graphs in Fig. 10 show that the relative number of smaller particles in the 2–3 to 20–30 μm ranges increases rapidly after chemical addition and initial mixing. This is direct evidence for particle aggregation. After settling the numbers of particles is much lower in all size ranges. Particles larger than 30 μm are almost immediately removed. The 12 h settling line should be similar to the removal efficiency that might be obtained in a clarifier or sedimentation basin after coagulation. The low, medium (not shown) and high molecular weight polymers produced similar results with 87, 90, and 91% of mass removal efficiencies for the particles less than 30 μm, assuming spherical particle shape.

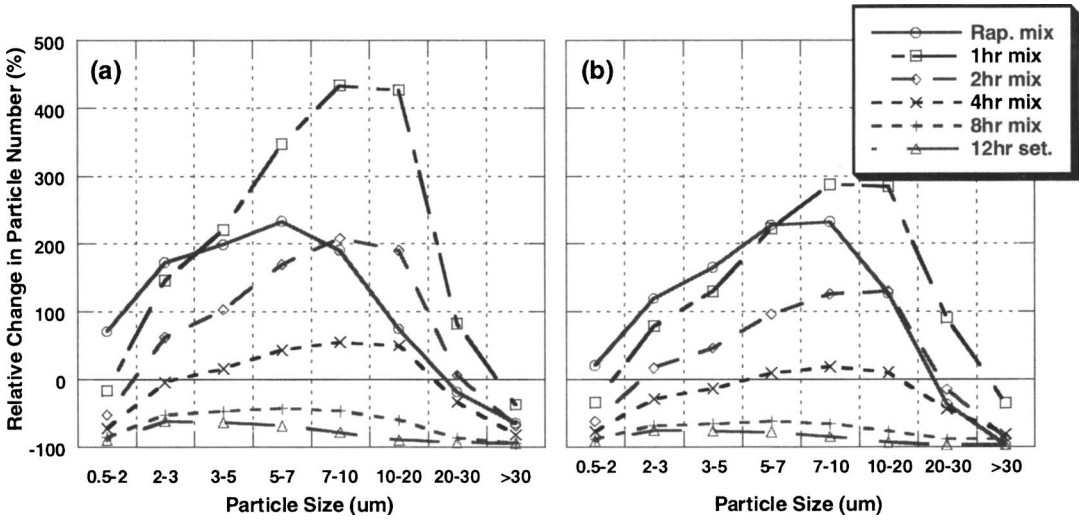


**Fig. 10.** Relative PSD changes after addition of 24 mg/L of polyDADMACs with different molecular weight on February 11, 2005: (a) low molecular weight; (b) high molecular weight

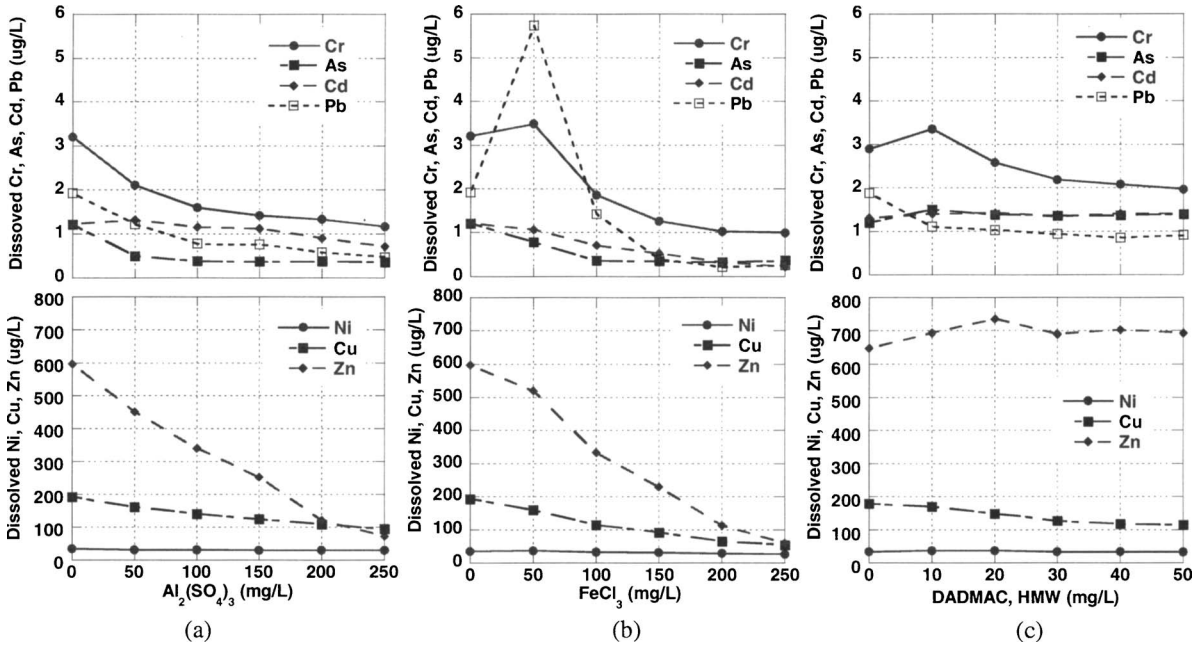


**Fig. 11.** Dissolved metal concentrations in the treated runoff from different coagulation/flocculation tests on March 18, 2005: (a) sweep floc coagulation with alum; (b) sweep floc coagulation with ferric chloride; and (c) flocculation with polymer

### *Removal of Dissolved Heavy Metals by Coagulation/Flocculation*

Fig. 11 displays the dissolved phase concentrations of seven species of heavy metals in the treated water from sweep floc coagulation with alum, ferric chloride, and flocculation with polymer on March 18, 2005. Particulate-phase metals are not shown because they are expected to be removed as the turbidity and TSS are removed. Figs. 11(a and b) show that dissolved heavy metals except Ni can be reduced in proportion to the amount of alum or ferric chloride added. The removal efficiencies of dissolved Cr, As, Cd, As, and Cu were over 50% at the sweep floc regimes of alum and ferric chloride. Dissolved Zn dramatically declined with the addition of alum or ferric chloride, and the maximum removal efficiency was over 85%. The spike of dissolved Pb at 50 mg/L of ferric chloride [Fig. 11(b)] was probably due to sample contamination. PolyDADMAC was not effective in removing dissolved heavy metals as revealed in Fig. 11(c) although dissolved Cr and Pb were selectively removed to some extent. Dissolved Ni could not be removed in both sweep floc coagulation and flocculation with polymer.

Fig. 12 shows turbidity, ZP, concentration and removal efficiency of dissolved metals in the treated runoff with combined polymer and alum dose at 16 mg/L. As can be seen, combinations of polymer and alum effectively remove turbidity with short mixing time (~10 min). Dissolved Pb was removed up to 60% with comparatively large amount of polymer (polyDADMAC >6 mg/L). Dissolved As was removed up to 40%. This removal may have been due to precipitation or it could be a result of aggregation of particles less than 0.45 μm. Metals adsorbed to particles less than 0.45 μm will be classified as dissolved by the analytical methods. In no cases did the combination of polymer and alum achieve high removals of dissolved heavy metals, as observed in the sweep floc experiments. The magnitude of dissolved metal removal may or may not be important, depending on the application.

### *Potential Practical Application of the Results*

Coagulation can greatly increase particle sizes in storm-water runoff, which will make sedimentation BMPs much more efficient, especially for small particle removal. Li et al. (2006) proposed a two-compartment sedimentation tank with a first compartment to hold the initial runoff volume (first flush) for an extended period of time and a second compartment to treat the rest as a continuous flow clarifier. By holding the first flush and treating the remaining volume in a continuous flow clarifier, the two-compartment settling tank will remove a higher fraction of the smaller particles in storm water runoff. This concept can be extended using coagulation and flocculation.

Based upon the results from particle settling experiments using highway runoff, only 27.1 and 27.5% particle mass reductions were possible in settling basins with 24 and 72 h retention times, respectively, using a storage tank designed to capture a 26 mm rainfall. In contrast, 90% of total particle mass could be removed by providing 8 h slow mixing and 4 h settling with polymer addition.

Removal efficiencies of heavy metals were also evaluated utilizing the particle removal efficiency and metal-particle mass ratio reported by Morquecho and Pitt (2003). The suspended solids reduction with polymer addition can reduce approximately 85% of particulate Cu and Zn, which correspond to the total removal efficiencies of 35 and 23% for Cu and Zn, respectively.

BMPs in the field need unattended operation, as well as robustness because pollutant concentration in the highway runoff always change as a function of rainfall characteristics, antecedent dry days, average daily traffic, and other factors. Therefore, runoff concentrations will be different for each storm event and BMPs must be able to cope with a range of influent concentrations and flow rates without special controls. A combination of cationic polymer with small amounts of alum and sufficient mixing time should enable effective colloid removal without close monitoring of dosages. Unattended polymer addition (automatic)

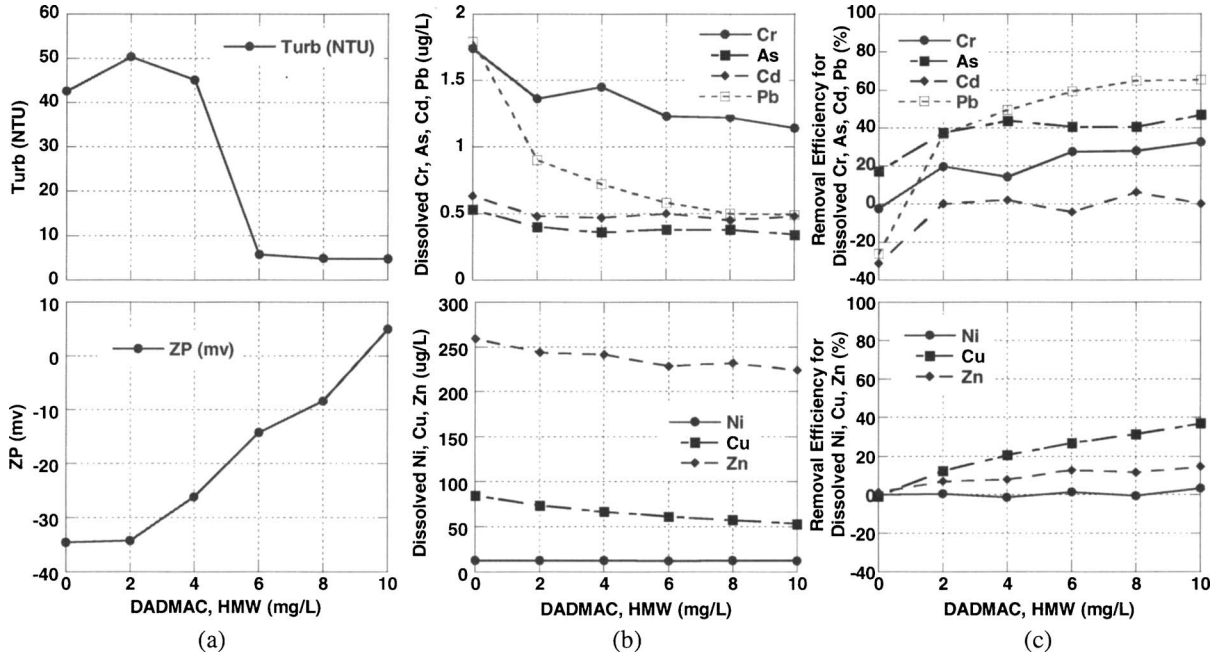


**Fig. 12.** Coagulation results with different polymer doses at alum=16 mg/L for April 28, 2005: (a) turbidity and zeta potential; (b) concentrations of dissolved metals; and (c) removal efficiencies of dissolved metals

to the first compartment can be also easily achieved by using the initial conductivity of the runoff and the fixed compartment volume. Unattended polymer addition to a continuous flow compartment will need further investigation due to the dynamic runoff retention time. Further studies on particle change with different mixing periods with polymer addition are on-going in our laboratory.

The buffering capacity of runoff will also present challenges to overcome. The pH for the storm waters collected from this site over a four-year period (Han et al. 2006a) ranged from 5.5 to 9.0 with mean of 6.7, and alkalinity ranged from 6 to 78 mg/L (as $CaCO_3$) with mean of 20 mg/L, respectively. This means that an acidic coagulant such as alum or ferric chloride is limited to approximately 20 mg/L as $Al_2(SO_4)_3$ or as $FeCl_3$ without the addition of pH control chemicals. Therefore the use of a polyelectrolyte such as polyDADMAC or a neutral pH coagulant such as polyaluminum chloride (Trejo-Gaytan et al. 2006) is more favorable. There will also be an issue of residual toxicity of cationic polymers. Cationic polymers such as DADMAC were reported toxic to aquatic organisms at low concentration less than 1 mg/L (de Rosemond and Liber 2004; Liber et al. 2005). Therefore, polymers should be optimally used to minimize residual polymer concentration, reducing toxicity in the treated water. Previous studies for runoff from this site have shown that the runoff, particularly the early runoff, is toxic (Kayhanian et al. 2006). The potential toxicity of residual coagulant must be evaluated in comparison to the toxicity reduction provided by improved coagulation.

## Conclusions

Particles in samples collected in the 2004–2005 wet season were subjected to a variety of coagulation and flocculation methods using both metal salts and organic polymers. In general, it was found that almost no removal of small particles (<30 μm) was possible in untreated samples. The results presented in this paper are supported by earlier studies, which analyzed for water quality data, first flush mass ratios, litter information, and other data (Han et al. 2006a; Kim et al. 2004, 2005; Lee et al. 2004). This research has shown that highway runoff can be effectively coagulated with a combination of metal salts (alum and ferric chloride) and organic cationic polymers. The following conclusions are made:

1. Alum or ferric chloride alone cannot effectively coagulate highway runoff at low concentrations (<40 mg/L), suggesting that bridging and charge neutralization are not effective mechanisms for this application.
2. Alum and ferric chloride at high doses produced sweep floc that removed turbidity and suspended solids to low concentrations (<5 NTU). Unfortunately the sludge production and the need for pH control limit this application. Alum appeared to be slightly more effective that ferric chloride. The dissolved concentrations of As, Cu, Cr, Cd, Pb, and Zn were reduced by as much as 50% during these experiments. Dissolved Ni concentration was unchanged.
3. Small dosages (<10 mg/L) of an organic polymer in three different molecular weights were useful in obtaining the isoelectric point. Gentle mixing ($G \sim 2.6$/s) over extended periods (~8 h) was effective in producing low effluent turbidity. Dissolved Pb concentration was reduced by 50% but other dissolved metal concentrations were unchanged. The addition of alum (~8 mg/L) after optimal polymer dosing reduced mixing time by 50%, but only slightly increased dissolved metals removal.
4. Optimal dosage of metal salts and polymer was correlated with the initial conductivity of the runoff, which is typically proportional to the amount of contamination in the runoff. This suggests that conductivity might be useful for controlling coagulant dosage.
5. The removal of dissolved metals, with the possible exception of Pb, occurred only with high concentrations of metal salts. This suggests that removal occurred because of precipitation

of truly dissolved metals, as opposed to removal of small particles ($<0.45$ μm) that are classified as dissolved due to the working definition of soluble and particulate phases.

Further research is necessary to validate this work at larger scale and over a range of conditions to provide a robust and unattended operation. Unattended operation will be challenging since optimum coagulant dosage varied with storm water quality. The mechanisms of particle destabilization is reversible, and over coagulant over dose will degrade particle removal, and may increase residual toxicity. Finally, pH control may be required, depending on the type and amounts of coagulants.

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