Granulometry, chemistry and physical interactions of non-colloidal particulate matter transported by urban storm water

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GRANULOMETRY, CHEMISTRY AND PHYSICAL INTERACTIONS OF NON-COLLOIDAL PARTICULATE MATTER TRANSPORTED BY URBAN STORM WATER

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Civil and Environmental Engineering

by

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B.S., Xian University of Architecture and Technology, 1996
M.S., Xian University of Architecture and Technology, 1999
May, 2003
ACKNOWLEDGMENTS

I am grateful for the chance to be here, Louisiana State University, to pursue my Ph.D degree. I would like to thank Dr. John J. Sansalone, my advisor for his guidance and support throughout my three and half years’ doctorate program. His family embraced me as a friend since I landed on this continent and I feel being taken good care. Dr. Sansalone’s great character as a scholar and his consistent encouragement as an advisor guide me through the journey to reach my academic goals. I also thank Dr. Vijay Singh, Dr. Vadake Srinivasan, Dr. Linbing Wang and Dr. Chang for serving on my graduate committee. Their advices and assistance in my research are invaluable.

I am grateful to all of my colleagues in the engineering annex building – Ping Zhou, Zheng Teng, Chad Cristina, Erin Krielow, Christopher Dean, Aimee Blazier, Tianpeng Guo, Gaoxiang Ying, Yuhong Sheng and Jonathan Kolich – for their assistance and fellowship.

I am further indebted to Luke Wall and Craig Brown who provided great assistance in the laboratory during this research.

Finally, I would like to thank my family and friends back in China and here in United States, especially my husband Gang Feng. Without their love and unwearying support, this work would not have been possible.
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ABSTRACT

Urban rainfall-runoff is a major source of anthropogenic pollutions to the natural water bodies. Particulate matter generated from anthropogenic environments and activities is a constituent of environmental concern as well as a carrier substrate for reactive contaminants such as heavy metals. The discharge of these particulate materials may adversely affect the beneficial use of the receiving waters, flora or fauna. Partitioning, transport and transformation of particulate-bound contaminants are determined by their granulometry, physical and geochemical properties of particulate carriers. Previous research emphasized in the transport of colloidal and suspended particles in urban rainfall-runoff from an environmental perspective. The settleable and sediment material transported by urban rainfall-runoff were ignored though they are a major granulometric fraction which may contain most of the sorbed or transported constituents such as heavy metals, organics or inorganics. In this dissertation research, the entire flow section of rainfall-runoff was captured in a sedimentation tank from an elevated section of Interstate 10 in Baton Rouge, Louisiana. Particulate matters in the catchment were analyzed for solid fractions, metal partitioning and distribution, fractal nature, morphology, chemical composition, and settling characteristics. Coagulation and flocculation is a dynamic mechanism in urban rainfall-runoff because of the unsteady hydrodynamic conditions and short residence time. Natural coagulation/flocculation (C/F) as well as coagulants/flocculants assisted C/F were studied for particles in urban rainfall-runoff. A coagulation and flocculation model incorporating fractal geometry and sedimentation mechanism was applied to simulate the evolution of particle size distribution in a 2-m settling column test. The overarching objective of this research is to facilitate decision-making with respect to urban runoff management, regulations, treatment and potential disposal of runoff sediment residuals.
CHAPTER 1. INTRODUCTION

According to national water quality inventory report (USEPA 1996), urban rainfall-runoff is the leading source of impairments to surveyed estuaries and the third largest source of water quality impairments to surveyed lakes. Unlike natural landscapes such as forests, wetlands, and grasslands, impervious surfaces like pavement, bridges and parking lots do not allow precipitation slowly percolate into the ground. Rainwater remains above the surface, accumulates, and forms runoff in large volume. Urbanization increases the variety and amount of pollutants transported to receiving waters. Contaminants from vehicles and activities associated with road and highway construction and maintenance are washed off roads and roadsides when it rains or snow melts. A large amount of runoff pollution is carried directly to natural water bodies. Increased pollutant loads can cause damage to the biota, foul drinking water supplies, and make recreational areas unsafe.

Contaminants in urban rainfall-runoff pollution include sediments, oil and grease, metals, debris, road salts, fertilizers, pesticides, and herbicides (USEPA 1995).

With the development of urbanization, land is deforested or cleared to build roads or bridges. The rate of erosion increases due to the removal of the original vegetation cover and the exposure of the soil thereafter. Soil particles are easily washed away by rainfall-runoff. These particles settle out of the water in a lake, stream or bay onto aquatic plants, rock and the bottom as sediments, which prevent sunlight from reaching aquatic plants, clog fish gills, choke other organisms, and can smother fish spawning and nursery areas. Other pollutants such as heavy metals and pesticides adhere to sediments and are transported with them. Those pollutants degrade water quality and can harm aquatic life by interfering with photosynthesis, respiration, growth and reproduction.
Metal elements from natural sources such as minerals in rocks, vegetation, sand, and salt are insignificant. Major metal pollutions originate from different parts of vehicle such as worn tires, brake linings, weathered paint and its exhaust. Heavy metals are toxic to aquatic life and can potentially contaminate ground water.

Debris is another contaminant source in urban rainfall-runoff. Grass and shrub clippings, pet waste, food containers, and other household wastes and litter can lead to unsightly and polluted waters. Pet waste from urban areas can add enough nutrients to estuaries to cause eutrophication.

New developments should attempt to maintain the runoff volume at predevelopment levels by using structural controls and pollution prevention strategies (USEPA 1995). Management plans and practices are designed to protect sensitive ecological areas, minimize land disturbances, and retain natural drainage and vegetation. Controlling runoff from existing urban areas tends to be relatively expensive compared to managing runoff from new developments. Best management practices (BMPs) such as storm water retention/detention ponds, grass strips, temporary sediment traps, silt fences, and diversion trenches are means to reduce runoff pollution.

The stochastic nature and variability of both flow volume and duration are fundamental constraints when considering storm runoff treatment design. Hydrologic factors play an important role in the selection of treatment alternatives. In order to understand the unique characteristics of urban rainfall-runoff, the granulometric phases in natural waters and wastewater were discussed as well.

In natural waters under most hydrodynamic (steady, dry weather flows) and residence time conditions (days to weeks or longer) (Alexander et al. 1989), the colloidal and suspended fractions predominate in the water column since the settleable and sediment fractions have
separated from the water column at much shorter residence time and the stream power (the stream’s ability to move sediment or sediment-transport capacity, a function of specific weight of water, flow rate and water surface slope, FISRWG 1998) is not sufficient to entrain these coarser fractions. However, in flowing natural waters such as streams and rivers, the coarser settleable and sediment material can be transported along the channel bed as bed load (FISRWG 1998). Much research has focused on both the transport of colloidal and suspended material in the water column from an environmental perspective as well as the settleable and sediment material as bed load from a sediment transport and hydraulic perspective (Roth et al. 2001; Alber 2000, Michelbach and Wohrlie 1993a, b). Long residence time and equilibrium conditions have allowed coagulation and flocculation to occur and a steady-state granulometry to result.

In wastewater flows, residence time varies from several hours to days. Under most hydrodynamic condition which either as turbulent gravity or pressure flows in conveyance pipes, the colloidal and suspended fractions are well mixed with a separate bed load of settleable and grit material forming under low gradient conditions (Tchobanoglous and Burton 1991). The flow depths vary from centimeter (cm) to meter (m) depending on conveyance infrastructure. Under highly turbulent and entraining conditions at the entrance to most publicly owned treatment works (POTWs) the colloidal and suspended material is mixed with the settleable bed load material. One of the first preliminary unit operations in a POTW is separation of the settleable and grit material, conventionally in a grit chamber. Smaller material and larger organic material pass through the grit chamber and into the primary clarifier. The primary clarifier is typically designed using conventional overflow rate theory to remove organic settleable material and organic/inorganic suspended material. Basin loading is typically ranging from 24.42 to 32.56 (m³/m²·d), and settling efficiency for suspended solids is in the range of 50
to 70% (Tchobanoglous and Burton 1991). After primary clarification in the POTW, biological or oxidative treatment follows and finally secondary clarification provides particle separation for remaining suspended materials. The secondary clarifier is also typically designed using conventional overflow rate theory to remove biological flocs and remaining mainly-inorganic suspended material. POTWs with tertiary treatment or coagulation/flocculation may separate the colloidal fraction. The long residence time in conveyance pipe, mixing conditions and equilibrium established have allowed coagulation/flocculation to occur and a steady-state granulometry to result.

In urban rainfall-runoff at the upper end of the urban watershed under most hydrodynamic (unsteady, turbulent wet weather flows and shallow depth flows) and residence time conditions (minutes to hours), the colloidal and suspended fractions are mixed with the settleable and sediment fractions in a relatively shallow water column (mm to cm). With residence time of these particles in rainfall-runoff generally less than several hours and with unsteady flow, equilibrium and steady-state floc development has not occurred by the time such flows are treated in-situ or regionally for an urban catchment. This makes urban rainfall-runoff unique from natural waters and wastewater. Coagulation/flocculation and floc-breakup are still active processes at the location of many in-situ treatments at the upper end of the urban watershed. While the settleable and sediment fractions may be carried as a type of bed load, the shallow flow depths result in a much greater interaction between the various fractions and there is not as great of a vertical separation between the fractions because sufficient time or depth is not available.

The historical argument has been that the fraction of stormwater particles predominates in the fine size category (< 100-µm) (Randall et al. 1982; Kobriger, 1984; Ball and Abustan 1995;
Donovan and Pfender 1997; Jacopin et al. 1999; Drapper et al. 2000), therefore, the focus has been towards the suspended fraction. Much of this is due to conventional automated sampler development and widespread usage over the last two decades for stormwater runoff and combined sewage overflows (CSOs). The problem with automated sampling is multiple. First, the technical limitations of automatic samplers prevent them from providing data representative of particle size distributions particularly when sand-size material is in transport (Edwards and Glysson 1999). For example, automatic sampler with a typical sample hose of ¼ inch ID (Discrete stormwater sampler SS101, Global water instrumentation Inc.; 3700C Compact Portable Sampler, ISCO) can not uptake particles greater than ¼ inches. Increased intake diameter may be necessary to capture larger grain sizes but will lead to reduced intake velocity at the same pumping rate, which can compromise measured suspended sediment concentration. Secondly, automatic sampler is not capable of collecting isokinetic sample, which is defined as the velocity in the sample’s nozzle being approximately equal to that of the stream velocity (USGS 2001). The intake tube inlet end is rarely orientated towards the flow patterns to be sampled. The intake tube cross-sectional area is many times smaller than the total cross-section of flow yet not much larger than the \( d_{50} \) of the sediment particles. There is no assurance that the location that the tube is placed is representative, that the location has the representative gradation of particles with respect to the entire cross-section and that the tube can intake a representative gradation from the settleable and sediment fractions.

As a result of the above problems, past research has inadvertently missed the granulometric and environmentally important fraction whose capture is critical to the success of urban rainfall-runoff treatment in the future and therefore receiving water quality. Much research has focused on the transport of colloidal and suspended material in storm runoff from an environmental
perspective (Rostad et al. 1995; Gromaire-Mertz 1999; Furumai et al. 2002) but ignored the settleable and sediment material as a major granulometric fraction and as an environmental fraction that may contain most of the sorbed or transported constituents such as heavy metals, organics or inorganics.

The goal of this dissertation research is to study granulometry, chemistry and physical interactions of non-colloidal particulate matter transported by urban rainfall-runoff through the collection of the entire gradation of particulates in the rainfall-runoff. There are six major chapters of this research. Chapter 2 characterized the granulometry of non-colloidal particulate matter transported by urban rainfall-runoff. Chapter 3 studied granulometric-based distribution of metal elements for non-colloidal particulate matter transported by urban rainfall-runoff. Chapter 4 investigated the morphology, composition and fractal characteristics of these non-colloidal particulate matters. Chapter 5 evaluated the sedimentation of non-colloidal particulate matter through experimental settling column tests. Chapter 6 studied the coagulation and flocculation of the particulate matter transported by urban rainfall-runoff. In chapter 7, a coagulation and flocculation model incorporating fractal theories was applied to simulate the particle size distribution in a settling column test. The research aims to provide guidance for treatability, regulation and control of non-colloidal particulate matter.

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USEPA. (1996). Managing urban runoff, EPA841-F-96-004G.


CHAPTER 2. GRANULOMETRY OF NON-COLLOIDAL PARTICULATE MATTER TRANSPORTED BY URBAN RAINFALL-RUNOFF

SUMMARY

Urban rainfall-runoff is a significant source of anthropogenic particulate matter, colloids and solutes. While constitutes such as metals or organics are potentially a concern in any phase, the particulate matter itself represents an environmental and ecological concern. The physical granulometric characteristics of the particulate matter play an important role with respect to hydrodynamic transport, particulate-solute interaction, and eventual fate of both the particulate matter and solute. This study examines the physical granulometry of non-colloidal particulate matter from a series of urban transportation sites in three Southern USA cities. While size gradations were nominally separated into dissolved, suspended, settleable and sediment designations, gradation at all sites ranged in size from 1 to 10,000 µm. Results indicate that the suspended fraction \(d_{50v}\) [mean (\(\bar{x}\)), standard deviation (s)] was \([10.36, 4.69]\ \mu\text{m}, \ \rho_s\) was \([2.40, 0.19]\ \text{g/cm}^3\) from all twelve rainfall-runoff events. In contrast, the number based \(d_{50n}\) was \([1.62, 0.04]\ \mu\text{m}\) for the suspended fraction. Results indicate that the \(d_{50}\) for the sediment fraction was \([172, 63.35]\) for all twelve rainfall-runoff events, and \([421, 219.43]\) for the sediment fraction for all four sites. Over 50% of SA was associated with the particulate gradation >250-µm. Results suggest that a solute mass can preferentially partition to the gradation of particles with predominant SA.

INTRODUCTION

Issues related to the quality of storm water generated from urban areas of the USA have received increasing attention over the last decades. Stormwater runoff from urban
areas is a leading cause of impairment to U.S. water bodies which did not meet water quality standards (National Water Quality Inventory 1998). Water quality impacts from urban runoff can be significant particularly in environmentally or ecologically sensitive areas such as wetlands, ground-water recharge zones, and drinking water supply watersheds. Anthropogenic activities, pavement, tire interaction, and vehicular part abrasion are sources of the solids in urban storm runoff, ranging from rapidly soluble, submicron particles to insoluble gravel-size aggregates abraded from the paved urban surface (Muschack 1990). During storm events, this heterogeneous particulate matter is transported by urban storm water into the receiving environment. As a consequence of the large expanses of pavement in developed urban areas, hydrology and hydraulics have been altered, resulting in a more effective conveyance of anthropogenic particulate matter. These surface and drainage alterations in our constructed environments generate increased peak flow, increased flow volume and decreased lag time (Bedient and Huber 1992). As a result, stormwater in constructed urban environment has greater capacity to mobilize and transport dissolved, colloidal and particulate constituents in a heterogeneous mixture, which includes metal and organic constituents. Particulate matter is a potential reservoir for both chemical constituents and toxicity (Gjessing et al. 1984).

High concentrations of dissolved solids can contribute to a decrease in photosynthesis and water clarity. The dissolved ions may also combine with toxic compounds and heavy metals leading to an increase in water temperature. The settleable portion of total suspended solids (TSS) can cause imbalance in the biota, depletion of dissolved oxygen and reduction of the pH in the water body. Settleable solids may also reduce conveyance capacities and increase dredging frequencies and cost (James 1999).
Particulate matter in storm water ranges from nanometer-sized colloidal organic material to millimeter-sized sand, silt and gravel, more than six-order of magnitude (Makepeace 1995). Suspended solids in urban storm runoff are reported to have a range of 1.0 – 2,582 mg/L. Dissolved solids in urban stormwater have been found at a range of 27 – 2,792 mg/L. Among those contaminants that are of greatest concern, Pb is reported associating predominantly with suspended solids (Morrison, Revitt and Ellis 1990); while Cd and Cu are considered primarily associating with dissolved solids in storm runoff. Zn is mostly related to dissolved solids, although it will adsorb to suspended sediment and especially colloidal particles (Makepeace 1995). Many of the organic contaminants are also associated with suspended solids.

Best management practices (BMPs) are primarily designed to remove TSS and contaminants adsorbed to particles (James 1999). Gravitational settling is the predominant process for pollutant removal in storm runoff treatment. Studies report TSS reductions for wet detention basins range from 20-98%, generally greater than 50% (Schueler 1992). Measured field data indicated that 60-70% of settable particulate urban sediments can be settled out within the first 6 hours of retention with the remaining settling out over the next 2 days (Sansalone 1998).

The physical granulometric characteristics of particulate matter play an important role with respect to hydrodynamic transport, particulate-solute interaction, and eventual fate of both the particulate matter and solute. Knowledge of such granulometry is critical for effective treatability, control and regulatory frameworks for storm water discharges and the receiving environment.
PREVIOUS STUDIES

The focus on measurement of suspended solids has led to misleading conclusions that mass-based gradations in urban rainfall-runoff are primarily suspended. In many cases, settleable-sediment fractions are separated upstream, poorly sampled or not considered. A study in a stormwater sewage detention basin found that solids from the upper layer (0-10 cm) contained 62% fine materials smaller than 100-µm with a median diameter $d_{50}$ of 78-µm (Jacopin et al. 1999). Ball and Abustan (1995) carried out the study on particle size distribution in a residential catchment in Sydney. An automatic water sampler was connected to a trigger device to sample storm events. Particle size distribution for particles less than 600-µm showed particles less than 100-µm represented 70% to 92% of the total mass. In a study conducted by the Federal Highway Administration (Kobriger 1984), the particle size distribution (PSD) of the highway storm runoff indicated that 80% of the particles were less than 88-µm. PSD analysis of road runoff in southeast Queensland showed a significant proportion of the sediment found in the runoff was less than 100-µm (Drapper et al. 2000). The median diameters by volume for 21 sites studied were mostly less than 100-µm.

In contrast, studies that capture the entire cross-section of flow or sample close to the location of solids entrainment have shown that the majority of the original particle mass in urban rainfall-runoff and snowmelt are in settleable-sediment range (>250-400 µm). Sartor and Boyd (1972) investigated street surface runoff contaminants in storm water runoff and found that the total solids were composed of 6% of materials less than 43-µm, 37% ranged from 43 to 246-µm and 57% greater than 246-µm. Shaheen (1975) in a similar study found that in particles deposited on highways about 10% was less than 75-
μm, 32% between 75 and 250-μm, 24% between 250 and 420-μm, 19% between 420 and 850-μm and 15% between 850 and 3350-μm. Study by Sansalone (1997) investigated rainfall-runoff from a freeway and found 10% of the mass was less than 100-μm, 25% was from 100 to 400-μm, 15% was from 400 to 600-μm, 20% was from 600 to 1,000-μm and 30% was from 1000 to 10,000-μm. These studies suggest that the majority of the total suspended solid is transported as material larger than approximately 250-400 μm. Solids recovery in these studies did not employ automated samplers.

Automatic samplers are only capable of entraining and representatively sampling the suspended and finer settleable fraction. They usually cannot sample the entire gradation of particles, especially large grain size particles which settle quickly. By definition, the upper limit of sand-size material has the median diameter of 2-mm (Gray et al. 2000). Commonly used sampling procedures that employ automatic peristaltic pumps to draw samples would underestimate the total solids load because of their inability to sample the larger material carried in storm water. Suspended solids concentration (SSC) method instead of total suspended solid (TSS) analysis was recommended for the analytical procedure of sand-rich storm water. SSC data were produced by measuring the dry weight of all the sediment from a known volume of a water-sediment mixture.

Suspended particulate containing high concentrations of organic matter and certain clay minerals has the ability to adsorb significant quantities of chemical components. Clays and organic floccules tend to concentrate in the smaller size fractions and adsorb more contaminants per unit volume or mass due to their relatively large specific surface area (Horowitz et al. 1990). Because of the large surface areas of silts, clays and organic matter and the scavenging nature of oxides, these suspended particulate is also the major
transport medium for heavy metals (Louma 1989, Sinclair et al. 1989). Study on suspended particulate matter characteristics in the Lower Cape Fear River System (Roberts et al. 1999) showed that although organic suspended solids increased with rainfall, approximately 90% of suspended materials consisted of inorganic material following periods of excessive rain. Therefore, efforts to control urban rainfall-runoff contributions to the Cape Fear River focused on retaining the inorganic fraction.

**OBJECTIVES**

There were three objectives in this study. The first objective was to differentiate and examine the various solid fractions in urban rainfall-runoff through capturing the entire runoff flow from an elevated urban transportation section. The second objective was to examine the fundamental granulometry of non-colloidal particulate matter in sediment fraction transported by urban rainfall-runoff. The final objective was to investigate the difference and similarity between granulometric and physical parameters for different sites.

**METHODOLOGY**

**Experimental Site Characteristics**

The experimental site is located at the Interstate-10 city park lake overpass (Figure 2.1) at Baton Rouge, Louisiana. The total span over water of this elevated stretch is 270-m and the eastbound carries an average daily traffic load of 70,400 vehicles. The bridge pavement was constructed from a Portland cement concrete. Mean annual precipitation at the site is 1460 mm/year. This site was designed as a National Pollutant Discharge Elimination System (NPDES) Phase II region. Figure 2.2 showed a profile view of the site and the runoff collection system. Rainfall-runoff from the eastbound highway surface
was collected through the collection trough and transported by the collection pipe. Runoff traveled through the grit chamber where a small solid fraction was separated from the main flow and the rest of solids were carried into the 2130-L sedimentation tank.

Besides Baton Rouge site, sediments from three other urban transportation sites from two Southern USA cities (Little Rock and New Orleans) were also studied. There are two sites located in Little Rock. One of the site is located at the intersection of I-30, I-440 and I-530 (referred as Little Rock site 1), and the other site is located at I-40 and I-30 west (referred as Little Rock site 2). Figure 2.3 and Figure 2.4 showed the location of the two sites. Sampling site at New Orleans is located on the east of I-10 and Bonnabel Lane (Figure 2.5).

Figure 2.1  Location of Baton Rouge experimental site – I-10 City Park Lake Overpass
Figure 2.2  Profile view of sampling system at Baton Rouge experimental site

(a) Location of Little Rock site 1  
(b) Storm water collection ditch

Figure 2.3  Location and view of Little Rock site 1 – I-30 at I-440 at I-530
Twelve discrete rainfall events occurring between January 19 and June 27, 2002 were monitored and runoff was collected at Baton Rouge I-10 site. Two recycling pumps resuspended the sediments and kept the tank well mixed when sampling. Collection of samples for laboratory analysis was carried out by two approaches. First approach was to
collect thirty 1-L and 500-mL aqueous samples from the well-mixed tank. Thirty samples are required in terms of a valid statistical analysis. The second approach was to obtain sediments in the rainfall-runoff collection system. The sedimentation tank was allowed to settle for two days after sampling aqueous portion. The tank was then siphoned and the concentrated runoff was collected from the draining pipe at the bottom and brought back to the lab. Sediments in the grit chamber were also collected.

For the other three sites, sediments were collected from the storm catch basin along the road. Samples from Little Rock were collected on August 4, 2001, and sample from New Orleans was collected on August 25, 2001. Since the above samples were sediments deposited accumulatively by the urban rainfall-runoff, cumulative sediments from Baton Rouge site were also collected for comparison. The sediment samples were accumulated through nine storm events between January 1, 2001 and April 24, 2001.

**Analytical Methods**

**Solid fractionation**

Gustafsson and Gschwend (1997) proposed a classification scheme that separates particulate matter in aquatic systems into three categories: dissolved, colloidal and gravitoidal. Gravitoids are particles that are significantly affected by gravitational settling. Size 0.45 µm is considered to be the cutoff between dissolved and particulate. The critical size separating colloids and gravitoids is determined by the dynamic transference of smaller particles by coagulation and gravitational sedimentation (Grant et al. 2001). The distinction between gravitoids and colloids is a function of total solids concentration (Gustafsson and Gschwend 1997). In present study, solids were categorized
into four pools: dissolved, suspended, settleable and sediment. Settleable fraction is an indication of treatability through gravitational separation.

The entire runoff flow was collected at Baton Rouge site for the solid fraction analysis. The operational cut-off size to separate dissolved fraction is still 0.45-µm. Settleable solid is determined using Imhoff cone according to the Standard Method 2540 F. In this study, those particulate matters settled out in 1-hour Imhoff cone settling test are considered as “settleable” solids. Those particles remaining in Imhoff suspension after 1-hr are defined as suspended fraction. Mass of settleable solids in the entire flow stream therefore can be calculated according to the settleable fraction (mL/L), total runoff volume (L), water content (%) and density (g/cm³). Since the entire rainfall-runoff flow was captured, through siphoning the suspension, settleable solids and sediments are left behind (assuming settled suspended fraction after 1-hr is insignificant during siphoning). Sediment fraction can be obtained through mass balance, and it includes all settled solid excluding the fraction settled within 1-hour. An illustration of solid fraction in the sedimentation tank was shown in Figure 2.6.

The Imhoff cone procedure is as follows: Fill an Imhoff cone to the one-liter mark with a well-mixed sample. Allow sample to settle in the Imhoff cone for 45 minutes. Gently stir the sample with a glass rod to release the suspended matter clinging to the sides of the Imhoff cone. Allow sample settle for an additional 15 minutes. Record the volume of settleable solids (in mL) in the Imhoff cone. Settleable solids were retrieved and concentrated for density analysis. All aqueous samples were analyzed for suspended solid concentration (SSC), volatile suspended solid (VSS), and total dissolved solid (TDS) following the Standard Method 2540. Suspended solids were filtered and
concentrated for density analysis. A laser diffraction type of particle analyzer LISST-Portable (Sequoia Tech Inc.) was used to analyze the particle size distribution for the suspension of Imhoff cone settling test. Measurable size is ranging from 1.25 to 250 µm. Ultrasonic dispersion of samples before particle analysis was needed to prevent them from coagulation.

Figure 2.6 Illustration of solids fractions in urban rainfall-runoff

Solids collected from the entire runoff-flow went through a series of analysis. After air-dried under a constant temperature of 40°C, solids obtained were disaggregated and sieved through a set of graded mechanic sieves ranging from 9.5 mm (#3/8) through 25 µm (#500). Sieve analysis follows the standard procedure ASTM D422 (ASTM 1993). Particle size is defined by sieve diameter, which is the width of the minimum square aperture through which the particle passes (Allen 1990). Dry solids separated on each of the stainless steel sieves were weighed and stored separately in round clear sample bottles.
Particle size analysis

Particle size can either be quoted in metric (millimeters, microns) or logarithmic (Phi) units (Krumbein 1934). Inman (1952) recommended using the geometric mean of the particle diameters corresponding to the 16th and 84th percentiles for non-symmetrical or lognormal distributions. The rationale is one standard deviation of normal distribution on either side of the mean diameter is approximately $d_{16}$ and $d_{84}$ respectively. The geometric mean diameter obtained from $d_{16}$ and $d_{84}$ is used even if the distribution deviates from lognormal. This has become a standard procedure (Vanoni 1975). The geometric mean diameter $d_g$ is defined in Equation 1.

$$d_g = \sqrt{d_{16} \cdot d_{84}} \quad (1)$$

An estimate of the standard deviation $\sigma_g$ is obtained by Equation 2:

$$\sigma_g = \sqrt{d_{84} / d_{16}} \quad (2)$$

The median particle size ($d_{50}$) is linearly interpolated from the cumulative distribution curve to represent the particle diameter for which 50 percent dry weight of the sediment is coarser or finer. If the distribution is lognormal, $d_{50}$ is equal to the geometric mean of the distribution.

Sediment defined by their size class can be described based on the Wentworth classification system (Wentworth 1922). In most research on sediments, grain-size data is given in phi (Φ) size rather than in microns or millimeters. Phi (Φ) size relates to particle size in terms of the sieve size $d$ in the expression of

$$\Phi = -\log_2(d) \quad (3)$$

where $d$ is the particle size from sieve analysis in mm. It is built on the assumption that natural distributions of sediments are log-normal. Increase Φ values correspond to the
decreasing particle size. Particle size distribution was analyzed based on the cumulative curve and Φ size. Several important phi sizes are summarized as follows.

(1) Central tendency Φ₅₀
The median Φ value (Φ₅₀) is the value of Φ corresponding to 50% of the cumulative frequency. Φ₅₀ can be obtained through Equation 4.

\[
Φ_{50} = -\log_{2}(d_{50})
\]  

(4)

Table 2.1 showed the interpretation for Φ₅₀ in different ranges (Nybakken 1998).

(2) Degree of uniformity
The uniformity or homogeneity of the sediment can be obtained from the inclusive graphic standard deviation \( Iσ \).

\[
Iσ = \left( \Phi_{84} - \Phi_{16} + \Phi_{95} - \Phi_{5} \right) / 6.6
\]  

(5)

The value can be interpreted using Table 2.2, in which “well sorted” means homogenous.

(3) Degree of symmetry
Skewness is a unitless measurement of the distortion from a symmetrical distribution (Lee 1998). Inclusive graphic skewness assesses the predominance of particular sediment fractions.

\[
S_k = \frac{\Phi_{16} + \Phi_{84} - 2\Phi_{50}}{2(\Phi_{84} - \Phi_{16})} + \frac{\Phi_{5} + \Phi_{95} - 2\Phi_{50}}{2(\Phi_{95} - \Phi_{5})}
\]  

(6)

(4) Kurtosis
In the normal probability curve, defined by the Gaussian formula, the interval between Φ₅ and Φ₉₅ should be exactly 2.44 times the interval between Φ₂₅ and Φ₇₅. Kurtosis is the quantitative measure of the departure from normality. For normal curves, kurtosis equals
1. A distribution that is excessively peaked is said to be leptokurtic. A distribution that is squashed or flattened is called platykurtic. This parameter is an indication of the range of particle sizes in the sample.

\[ K_G = \frac{\Phi_{90} - \Phi_5}{2.44(\Phi_{75} - \Phi_{25})} \]  \hspace{1cm} (7)

The interpretation of \( S_k \) and \( K_G \) can be found in Table 2.3.

**Table 2.1** Central tendency analysis for particle size distribution based on \( \Phi_{50} \)

<table>
<thead>
<tr>
<th>( \Phi_{50} )</th>
<th>(-1&lt;\Phi_{50}&lt;-0)</th>
<th>(0&lt;\Phi_{50}&lt;1)</th>
<th>(1&lt;\Phi_{50}&lt;2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediment type</td>
<td>gravel</td>
<td>very coarse sand</td>
<td>coarse sand</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( \Phi_{50} )</th>
<th>(2&lt;\Phi_{50}&lt;3)</th>
<th>(3&lt;\Phi_{50}&lt;4)</th>
<th>(4&lt;\Phi_{50}&lt;8)</th>
<th>(8&lt;\Phi_{50})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediment type</td>
<td>fine sand</td>
<td>very fine sand</td>
<td>silt</td>
<td>clay</td>
</tr>
</tbody>
</table>

**Table 2.2** Uniformity analysis of particle size distribution based on \( \sigma_I \)

<table>
<thead>
<tr>
<th>( \sigma_i )</th>
<th>(\sigma_i &lt; 0.35)</th>
<th>(0.35 &lt; \sigma_i &lt; 0.5)</th>
<th>(0.5 &lt; \sigma_i &lt; 0.71)</th>
<th>(0.71 &lt; \sigma_i &lt; 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degree of sorting</td>
<td>very well sorted</td>
<td>well sorted</td>
<td>moderately well sorted</td>
<td>moderately sorted</td>
</tr>
<tr>
<td>( \sigma_i )</td>
<td>(1 &lt; \sigma_i &lt; 2)</td>
<td>(2 &lt; \sigma_i &lt; 4)</td>
<td>(4 &lt; \sigma_i)</td>
<td></td>
</tr>
<tr>
<td>Degree of sorting</td>
<td>poorly sorted</td>
<td>very poorly sorted</td>
<td>extremely poorly sorted</td>
<td></td>
</tr>
</tbody>
</table>

**Table 2.3** Symmetry \( (S_k) \) and Kurtosis \( (K_G) \) of particle size distribution

<table>
<thead>
<tr>
<th>( S_k )</th>
<th>Skewness</th>
<th>( K_G )</th>
<th>Kurtosis</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.30 to 1.00</td>
<td>strongly skewed towards fine</td>
<td>&lt; 0.67</td>
<td>very platykurtic</td>
</tr>
<tr>
<td>0.10 to 0.30</td>
<td>fine skewed</td>
<td>0.67 – 0.90</td>
<td>platykurtic</td>
</tr>
<tr>
<td>-0.10 to 0.10</td>
<td>symmetrical</td>
<td>0.90 – 1.11</td>
<td>mesokurtic</td>
</tr>
<tr>
<td>-0.10 to -0.30</td>
<td>coarse skewed</td>
<td>1.11 – 1.50</td>
<td>leptokurtic</td>
</tr>
<tr>
<td>-0.30 to -1.00</td>
<td>strongly skewed towards coarse</td>
<td>&gt; 1.50</td>
<td>very leptokurtic</td>
</tr>
</tbody>
</table>
Density determination

Density of dry solids is determined using an inert gas pycnometer according to Standard Method D5550-94 (ASTM 1994). The multi-pycnometer (Quantachrome Corp.) measures the true volume of solid materials by employing Archimedes’ principle of fluid (gas) displacement and the technique of gas expansion. True volume is measured using helium gas since it penetrates every surface flaw down to about one Angstrom, thereby enabling the measurement of powder volumes with great accuracy. By measuring the pressure difference when a known quantity of helium under pressure is allowed to flow from a precisely known reference volume \( V_R \) into a sample cell \( V_C \) containing the solid material, true solid volume \( V_S \) can be determined.

\[
V_S = V_C - V_R [ (P_1 / P_2) - 1 ]
\]  

(8)

Density of the sample then can be calculated using Equation 7:

\[
\rho_s = M_S / V_S
\]

(9)

Particle density is typically reported to the nearest 0.01.

Surface area measurement

Modified EGME (ethylene glycol monoethyl ether) method (Sansalone et al. 1998) was utilized for experimental determination of surface area. A representative sample of approximately 1.0 g (except for the coarse materials in which a few representative materials were selected regardless of the weight limit) dry weight was selected for each discrete size range. Once a constant dry weight was obtained, each solid sample was saturated with EGME, completely wetting all particle surfaces, and placed in an evacuated glass dessicator over 600 grams of an EGME-CaCl_2 solvate (The EGME to CaCl_2 ratio was 1 to 2.3). A constant vapor pressure was produced from this solvate.
Samples were held in an evacuated dessicator and weighted in 4-hour interval after 24 hours until a constant weight for each sample was obtained as determined by a weight differential of less than 1-mg across an interval of four hours. Granular activated carbon (GAC) was served as the control. Reported SSA for a Filtersorb F400 is 1100 m$^2$/g by the N$_2$-BET method (Calgon 1995).

Based on monolayer surface coverage and molecular weight of the EGME molecule, specific surface area (SSA) was calculated according to Equation 10:

\[
SSA = \frac{W_a}{0.000286W_s}
\]

(10)

SSA results were summed over each size gradation to yield a total surface area (SA) distribution. Equation 11 is employed in the surface area calculation.

\[
SA_i = (m_i)(SSA_i)
\]

(11)

SSA and SA are as a function of particle size gradation.

**Surface charge determination**

In combination with surface area, surface charge is a critical parameter for heavy metal adsorption or filtration (Liu et al. 2001). Surface charge of particulate can be developed in three principle ways: chemical reactions at the surface, lattice imperfections at the surface, or adsorption of a hydrophobic species or a surface ion (Stumm 1992). Potentiometric titration (Van Raij and Peech 1972) was modified and used to determine the surface charge of sediments across size gradation. A representative 0.5 to 1-g of dry sample was suspended in 50-mL of 0.01-M KCl. pH was adjusted to a range between 6 and 9 with HCl or KOH. A blank solution of 0.01-M KCl was set as control. The suspensions of sample and control were set on a reciprocating table at 22 – 23 °C in
airtight sealed 50-ml centrifuge tube for 24 hours. The pH values of the supernatant were then recorded. The amount of H⁺ and OH⁻ adsorbed on the surface of the sediment samples were estimated from the amount of acid or base added to bring the sample to the original pH, minus the amount necessary to bring 50-ml blank solution to the same pH.

RESULTS AND ANALYSIS

Differentiation of Solid Fractions

The entire flow stream was captured for the solid fraction analysis at Baton Rouge I-10 site. Influent pipe was diverted from the sedimentation tank immediately after the tank was filled. Total runoff volume and the elapsed time were recorded. A summary of analyses of solid fractions for twelve observed rainfall-runoffs was shown in Table 2.4. For the twelve storms observed, no significant correlation had been found between previous dry hours, elapsed time of the event and the loading of transported sediments to the system. Table 2.5 showed the statistic summary for solid fractions.

Total dissolved solids (TDS) serve as the indicator for the water quality criteria and for assessment of use support. TDS ranged from 53 to 222 mg/L in the studied rainfall-runoff. For water bodies not specifically listed in the Numerical Criteria and Designated Table, increases over background levels of TDS may be permitted. Such increases shall not cause in-stream concentrations to exceed 500 mg/L (USEPA 2000). To protect the propagation of fish and wildlife, Louisiana’s water quality standard for TDS is 100 mg/L (USEPA 2000). In five out of twelve investigated runoffs, TDS exceeded this limit.

Turbidity is primarily influenced by suspended matter such as clay, silt, plankton, or microscopic organisms (APHA 1995).
Table 2.4  Summary of solid fractions and rainfall characteristics for 12 storm events occurred at Baton Rouge, Louisiana

<table>
<thead>
<tr>
<th>Storm Date</th>
<th>1/19/02</th>
<th>1/24/02</th>
<th>1/31/02</th>
<th>2/5/02</th>
<th>2/20/02</th>
<th>3/1/02</th>
<th>3/9/02</th>
<th>3/11/02</th>
<th>3/20/02</th>
<th>5/13/02</th>
<th>6/19/02</th>
<th>6/27/02</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1PDR (hr)</strong></td>
<td>15.75</td>
<td>77.50</td>
<td>42.25</td>
<td>102.50</td>
<td>164.00</td>
<td>213.75</td>
<td>172.25</td>
<td>54.50</td>
<td>149.50</td>
<td>469.75</td>
<td>74.75</td>
<td>20.50</td>
</tr>
<tr>
<td><strong>Volume (L)</strong></td>
<td>2129</td>
<td>532</td>
<td>2129</td>
<td>1703</td>
<td>426</td>
<td>2129</td>
<td>2129</td>
<td>469.75</td>
<td>74.75</td>
<td>20.50</td>
<td>788</td>
<td>920</td>
</tr>
<tr>
<td><strong>3Elapsed T (min)</strong></td>
<td>45</td>
<td>20</td>
<td>25</td>
<td>640**</td>
<td>20</td>
<td>135</td>
<td>23</td>
<td>720**</td>
<td>20</td>
<td>27</td>
<td>35</td>
<td>50</td>
</tr>
</tbody>
</table>

**Dissolved fraction (TDS)**

<table>
<thead>
<tr>
<th>Dissolved</th>
<th>(\bar{x})</th>
<th>53</th>
<th>138</th>
<th>53</th>
<th>53</th>
<th>156</th>
<th>75</th>
<th>42</th>
<th>67</th>
<th>222</th>
<th>176</th>
<th>120</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>[mg/L]</td>
<td>s</td>
<td>0.37</td>
<td>1.04</td>
<td>0.92</td>
<td>4.19</td>
<td>1.67</td>
<td>2.42</td>
<td>0.47</td>
<td>0.52</td>
<td>1.87</td>
<td>0.83</td>
<td>0.73</td>
<td>0.25</td>
</tr>
</tbody>
</table>

**Particulate – Suspended fraction**

<table>
<thead>
<tr>
<th>SSC</th>
<th>(\bar{x})</th>
<th>57.04</th>
<th>74.86</th>
<th>32.30</th>
<th>188.00</th>
<th>90.80</th>
<th>127.12</th>
<th>21.35</th>
<th>52.18</th>
<th>96.27</th>
<th>70.47</th>
<th>71.37</th>
<th>60.77</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\rho_p)</td>
<td>2.58</td>
<td>2.22</td>
<td>2.68</td>
<td>2.09</td>
<td>2.12</td>
<td>2.35</td>
<td>2.62</td>
<td>2.42</td>
<td>2.33</td>
<td>2.29</td>
<td>2.53</td>
<td>2.51</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>VSS</th>
<th>(\bar{x})</th>
<th>12.84</th>
<th>20.04</th>
<th>10.1</th>
<th>52.68</th>
<th>34.84</th>
<th>33.52</th>
<th>5.86</th>
<th>15.55</th>
<th>35.87</th>
<th>33.83</th>
<th>26.40</th>
<th>17.40</th>
</tr>
</thead>
<tbody>
<tr>
<td>[mg/L]</td>
<td>s</td>
<td>2.83</td>
<td>7.70</td>
<td>1.96</td>
<td>4.19</td>
<td>4.63</td>
<td>4.36</td>
<td>1.95</td>
<td>2.89</td>
<td>5.13</td>
<td>3.86</td>
<td>3.71</td>
<td></td>
</tr>
</tbody>
</table>

**Turbidity (NTU)**

<table>
<thead>
<tr>
<th>Turbidity</th>
<th>(\bar{x})</th>
<th>65.7</th>
<th>112.3</th>
<th>45.7</th>
<th>241.9</th>
<th>152.8</th>
<th>194.0</th>
<th>24.2</th>
<th>88.4</th>
<th>128.6</th>
<th>100.9</th>
<th>79.5</th>
<th>93.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NTU)</td>
<td>s</td>
<td>11.27</td>
<td>11.81</td>
<td>1.70</td>
<td>11.08</td>
<td>31.21</td>
<td>23.17</td>
<td>2.87</td>
<td>8.01</td>
<td>22.84</td>
<td>10.35</td>
<td>11.03</td>
<td>5.16</td>
</tr>
</tbody>
</table>

**TVC [\mu L/L]**

<table>
<thead>
<tr>
<th>TVC</th>
<th>(\bar{x})</th>
<th>54.11</th>
<th>72.00</th>
<th>40.43</th>
<th>132.05</th>
<th>196.37</th>
<th>141.5</th>
<th>36.85</th>
<th>98.57</th>
<th>113.01</th>
<th>211.09</th>
<th>97.65</th>
<th>53.03</th>
</tr>
</thead>
<tbody>
<tr>
<td>[\mu L/L]</td>
<td>s</td>
<td>15.82</td>
<td>34.67</td>
<td>10.65</td>
<td>47.14</td>
<td>38.61</td>
<td>26.00</td>
<td>13.60</td>
<td>19.81</td>
<td>25.37</td>
<td>15.20</td>
<td>16.45</td>
<td>4.25</td>
</tr>
</tbody>
</table>

**Particulate – Sediment fraction**

<table>
<thead>
<tr>
<th>Settetable solids</th>
<th>(\bar{x})</th>
<th>0.29</th>
<th>0.21</th>
<th>0.14</th>
<th>1.16</th>
<th>0.68</th>
<th>0.30</th>
<th>0.15</th>
<th>0.21</th>
<th>0.19</th>
<th>0.55</th>
<th>0.86</th>
<th>0.24</th>
</tr>
</thead>
<tbody>
<tr>
<td>[mL/L]</td>
<td>s</td>
<td>0.05</td>
<td>0.08</td>
<td>0.05</td>
<td>0.17</td>
<td>0.12</td>
<td>0.06</td>
<td>0.04</td>
<td>0.08</td>
<td>0.19</td>
<td>0.09</td>
<td>0.09</td>
<td>0.04</td>
</tr>
<tr>
<td>(\rho_p)</td>
<td>2.35</td>
<td>2.13</td>
<td>2.29</td>
<td>2.19</td>
<td>2.15</td>
<td>2.43</td>
<td>2.38</td>
<td>2.25</td>
<td>2.08</td>
<td>2.27</td>
<td>2.15</td>
<td>2.18</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Settleable solids (g)</th>
<th>290.20</th>
<th>47.62</th>
<th>140.42</th>
<th>865.39</th>
<th>123.78</th>
<th>310.43</th>
<th>152.02</th>
<th>201.20</th>
<th>168.29</th>
<th>531.65</th>
<th>291.23</th>
<th>96.22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediments (g)</td>
<td>348.51</td>
<td>138.08</td>
<td>149.49</td>
<td>1879.00</td>
<td>228.25</td>
<td>894.31</td>
<td>646.54</td>
<td>603.38</td>
<td>352.1</td>
<td>1536.1</td>
<td>345.68</td>
<td>318.30</td>
</tr>
<tr>
<td>Grit (g)</td>
<td>*627.29</td>
<td>*1705.90</td>
<td>1284.04</td>
<td>3060.76</td>
<td>2014.64</td>
<td>112.66</td>
<td>69.48</td>
<td>1134.10</td>
<td>2483.65</td>
<td>1415.82</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note:  
1PDR – previous dry hours  
2 Runoff volume  
3 Elapsed time – time consumed to fill up the sedimentation tank or till the runoff pipe was diverted  
\(\rho_p\) – Density of dry solids (g/cm³)  
SSC – Suspended solid concentration  
VSS – Volatile suspended solid  
TVC – Total volume concentration  
Average \(\bar{x}\) and standard deviation s based on 30 samples  
TDS – total dissolved solids  
Grit – sediments collected from grit chamber  
*Grit from two storm events  
**Non-continuous rainfall-runoff
Table 2.5 Statistic summary of different solid fractions in rainfall-runoff at Baton Rouge I-10 site

<table>
<thead>
<tr>
<th>Solid</th>
<th>Analysis</th>
<th>Mean</th>
<th>Std.Dev</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dissolved fraction</strong></td>
<td>TDS (mg/L)</td>
<td>100.42</td>
<td>60.18</td>
</tr>
<tr>
<td><strong>Suspended fraction</strong></td>
<td>SSC (mg/L)</td>
<td>78.54</td>
<td>44.54</td>
</tr>
<tr>
<td></td>
<td>VSS (mg/L)</td>
<td>24.91</td>
<td>13.62</td>
</tr>
<tr>
<td></td>
<td>VSS/SSC</td>
<td>31.79</td>
<td>7.08</td>
</tr>
<tr>
<td></td>
<td>Turbidity (NTU)</td>
<td>110.61</td>
<td>61.68</td>
</tr>
<tr>
<td></td>
<td>TVC (µL/L)</td>
<td>103.89</td>
<td>58.00</td>
</tr>
<tr>
<td></td>
<td>Density (g/cm³)</td>
<td>2.40</td>
<td>0.19</td>
</tr>
<tr>
<td><strong>Sediment and settleable fraction</strong></td>
<td>Settleable (mL/L)</td>
<td>0.42</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>Density (g/cm³)</td>
<td>2.24</td>
<td>0.11</td>
</tr>
</tbody>
</table>

TDS – total dissolved solids  SSC – suspended solids concentration  VSS – volatile suspended solids

As can be seen in Figure 2.7, the plotted data points of turbidity and SSC follow a discernable linear pattern in which turbidity increases as SSC increases. The strength of this relationship is measured using the correlation coefficient r. As the value of r approaches 1, there is a high correlation between two parameters. The correlation coefficient can be calculated by taking the square root of the coefficient of determination (r²) from the regression analysis. The correlation coefficient r for turbidity and SSC was determined as 0.97 indicating there was a strong relationship between turbidity and SSC. Numeric criterion for turbidity in the Louisiana Water Quality Standards (USEPA 2001) requires that for rivers such as Red, Atachafalya, Mississippi Rivers, turbidity shall not exceed 150 NTU; for estuarine lakes, bays, bayous, and canals, maximum turbidity can not exceed 50 NTU. The average turbidity for investigated runoff was 110.6 NTU with a few above 150 NTU. Control of suspended solids in urban rainfall-runoff is necessary to protect the receiving water streams.
Solid fractions in the sedimentation tank were calculated based on mass and results were shown in Figure 2.8. As seen in Figure 2.8, suspended solid fraction ranged from 6.6 to 36.8 % with an average value of 19.7%. Settleable solids made up of 40% in average of the sediments deposited in the system. There was approximately 60% of the material in the sediments remaining in suspension subsequent to 1-hour sedimentation though they might be settled afterwards. Experimental results showed there was no significant difference in total volume concentration for the suspension after 1-hour and 4-hour gravitational settling. Therefore, in general, approximately 68% of the materials remained in suspension after the first few hours in the stormwater treatment system.

**Granulometry of Suspended Fraction**

Figure 2.9 showed the number distribution and volume distribution for the suspended particulate matter in the urban rainfall-runoff. Number distribution of aquatic suspensions is found to follow a two-parameter power law distribution function given by the expression (Kavanaugh et al 1980):
If $\beta = 3$, the concentration of surface area is uniformly distributed in each logarithmic size interval. The volume or the mass of solids is predominated in the large sizes while the number concentration is dominant in the smaller sizes. If $\beta = 4$, the volume of solids is distributed equally in each logarithmic size interval while the surface area and number concentrations are primarily in the small sizes. Measured particle number distributions were modeled using the two-parameter power law functions as shown in Figure 2.9. The coefficient of determination ($r^2$) was 0.98 or greater. Majority of particles (greater than 100-\(\mu m\)) were removed in 1-hour settling.

Figure 2.8 Solid fractions in storm water runoff for twelve observed storm events at Baton Rouge site (settleable is a fraction of sediment)
Figure 2.9  Total volume concentration and power law fit for the number distribution
Median diameter by number $d_{50n}$ and median diameter by volume $d_{50v}$ were calculated for all twelve events and summarized in Table 2.6. The median $d_{50n}$ for all 12 storms were less than 2-$\mu$m with the average $\Phi_{50n}$ size of 9.27, while the median $d_{50v}$ for all the sites were less than 20-$\mu$m with the average $\Phi_{50v}$ size of 6.72, indicating that the particles in the suspension are very similar in size to silt and clay particles. These particles are of colloidal size and would theoretically require extended periods of detention (Draper et al. 2000). Though interactions with dissolved fractions may assist in the flocculation and sedimentation of particulates in urban rainfall-runoff (Draper et al. 2000), chemical coagulation and flocculation is still required for the advanced treatment of these suspended particles or produce an acceptable settling time.

Table 2.6 Median diameter and $\Phi$ size of suspended fraction

<table>
<thead>
<tr>
<th>Storm Date</th>
<th>$d_{50n}$</th>
<th>$d_{50v}$</th>
<th>$\Phi_{50n}$</th>
<th>$\Phi_{50v}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/19/02</td>
<td>1.60</td>
<td>7.47</td>
<td>9.28</td>
<td>7.06</td>
</tr>
<tr>
<td>1/24/02</td>
<td>1.59</td>
<td>6.69</td>
<td>9.30</td>
<td>7.22</td>
</tr>
<tr>
<td>1/31/02</td>
<td>1.61</td>
<td>7.47</td>
<td>9.28</td>
<td>7.06</td>
</tr>
<tr>
<td>2/05/02</td>
<td>1.60</td>
<td>5.89</td>
<td>9.29</td>
<td>7.41</td>
</tr>
<tr>
<td>2/20/02</td>
<td>1.71</td>
<td>18.27</td>
<td>9.19</td>
<td>5.77</td>
</tr>
<tr>
<td>3/01/02</td>
<td>1.65</td>
<td>8.32</td>
<td>9.24</td>
<td>6.91</td>
</tr>
<tr>
<td>3/09/02</td>
<td>1.61</td>
<td>17.53</td>
<td>9.28</td>
<td>5.83</td>
</tr>
<tr>
<td>3/11/02</td>
<td>1.64</td>
<td>13.67</td>
<td>9.25</td>
<td>6.19</td>
</tr>
<tr>
<td>3/20/02</td>
<td>1.61</td>
<td>6.50</td>
<td>9.28</td>
<td>7.26</td>
</tr>
<tr>
<td>5/13/02</td>
<td>1.56</td>
<td>11.92</td>
<td>9.33</td>
<td>6.39</td>
</tr>
<tr>
<td>6/19/02</td>
<td>1.66</td>
<td>15.00</td>
<td>9.24</td>
<td>6.06</td>
</tr>
<tr>
<td>6/27/02</td>
<td>1.57</td>
<td>5.53</td>
<td>9.31</td>
<td>7.50</td>
</tr>
<tr>
<td>Mean</td>
<td>1.62</td>
<td>10.36</td>
<td>9.27</td>
<td>6.72</td>
</tr>
<tr>
<td>Std.dev</td>
<td>0.042</td>
<td>4.686</td>
<td>0.037</td>
<td>0.633</td>
</tr>
</tbody>
</table>

According to the calculation by Newton’s Law assuming spherical particles, particles greater than 75-$\mu$m (settling velocity 0.514-cm/s) can be separated in the storm water treatment system. However, the existence of particles up to 100-$\mu$m in the suspension suggested that the settling behavior of the real particles differ from particles settled under
ideal circumstances. Besides gravitational and frictional drag force, short-range forces such as electrostatic forces, Van De Waals and hydrodynamic forces affect particle interaction and settling as well. The other factors affecting settling velocity include fractal structure of particles, flow regime, coagulation and flocculation.

**Granulometry of Sediment Fraction**

**Particle size distribution**

Sediments in the runoff originate primarily from particulate matter deposited on impervious areas (Sharpin 1995). If the sediments are from the same type of impervious area, similar particle size distributions is expected. Cumulative distribution curve is constructed by plotting the percent of sediment by weight that is finer than a given sieve size against the sieve diameter or particle diameter. Figure 2.10 showed the cumulative particle size distribution for the sediments collected out of 12 rainfall-runoff events at Baton Rouge site. Although the distributions illustrated variability between storm events, they were similar in shape. Characteristics of particle size distribution were summarized in Table 2.7 and Table 2.8. The average median diameter based on mass for the twelve events was 172-µm corresponding to a $\Phi$ size of 2.63, indicating that particulates in the sedimentation tank are similar in size to fine sand. Gravel size particulates were intercepted in the grit chamber and did not account for the sediment loads in the sedimentation tank. Solids in grit chamber are mainly coarse sand ($\Phi_{50} = 0.66$, Table 2.9), and this portion can be easily separated from the runoff stream through gravitational settling. Sediments from three other sites were analyzed similarly. Figure 2.11 showed the cumulative particle size distribution. The characteristics of particle size distribution were summarized in Table 2.10 and Table 2.11. If combining sediments from grit chamber and sedimentation tank for Baton Rouge site, a median size of
682-μm (Φ_{50} = 0.57) was obtained. This Φ size indicated that based on mass particulates in the urban storm runoff tend to be coarser sand at Baton Rouge site. Little Rock site 2 showed similar trend. However, sediment analysis for New Orleans site and Little Rock site 1 showed the majority mass resides in medium sand size range.

Figure 2.10 Cumulative size distribution for the sediments collected at Baton Rouge I-10 site from twelve storm events

Figure 2.11 Cumulative size distribution for the sediments collected at four different sites. Sediments from Baton Rouge sites combined sediments from storage tank and grit chamber.
Table 2.7  Summary of statistical characteristics of particle size distribution for the sediments at Baton Rouge site

<table>
<thead>
<tr>
<th>Storm Date</th>
<th>$d_{50}$ ($\mu$m)</th>
<th>$\Phi_{50}$</th>
<th>$d_g$ ($\mu$m)</th>
<th>$\sigma_g$</th>
<th>$\sigma_I$</th>
<th>$S_k$</th>
<th>$K_G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/19/02</td>
<td>169</td>
<td>2.56</td>
<td>248</td>
<td>3.42</td>
<td>1.72</td>
<td>0.36</td>
<td>0.77</td>
</tr>
<tr>
<td>1/24/02</td>
<td>164</td>
<td>2.61</td>
<td>174</td>
<td>3.45</td>
<td>1.73</td>
<td>0.16</td>
<td>0.75</td>
</tr>
<tr>
<td>1/31/02</td>
<td>95</td>
<td>3.40</td>
<td>158</td>
<td>3.21</td>
<td>1.61</td>
<td>0.51</td>
<td>0.63</td>
</tr>
<tr>
<td>2/05/02</td>
<td>270</td>
<td>1.89</td>
<td>227</td>
<td>3.50</td>
<td>1.72</td>
<td>-0.04</td>
<td>0.76</td>
</tr>
<tr>
<td>2/20/02</td>
<td>110</td>
<td>3.18</td>
<td>184</td>
<td>2.84</td>
<td>1.48</td>
<td>0.55</td>
<td>0.65</td>
</tr>
<tr>
<td>3/01/02</td>
<td>158</td>
<td>2.66</td>
<td>180</td>
<td>3.29</td>
<td>1.67</td>
<td>0.22</td>
<td>0.64</td>
</tr>
<tr>
<td>3/09/02</td>
<td>99</td>
<td>3.33</td>
<td>139</td>
<td>3.61</td>
<td>1.84</td>
<td>0.33</td>
<td>0.89</td>
</tr>
<tr>
<td>3/11/02</td>
<td>209</td>
<td>2.26</td>
<td>200</td>
<td>2.90</td>
<td>1.52</td>
<td>0.05</td>
<td>0.92</td>
</tr>
<tr>
<td>3/20/02</td>
<td>244</td>
<td>2.04</td>
<td>248</td>
<td>2.46</td>
<td>1.36</td>
<td>0.13</td>
<td>0.77</td>
</tr>
<tr>
<td>5/13/02</td>
<td>262</td>
<td>1.93</td>
<td>265</td>
<td>3.93</td>
<td>1.94</td>
<td>0.10</td>
<td>0.86</td>
</tr>
<tr>
<td>6/19/02</td>
<td>177</td>
<td>2.50</td>
<td>197</td>
<td>2.32</td>
<td>1.36</td>
<td>0.27</td>
<td>1.02</td>
</tr>
<tr>
<td>6/27/02</td>
<td>105</td>
<td>3.25</td>
<td>151</td>
<td>2.34</td>
<td>1.30</td>
<td>0.49</td>
<td>0.70</td>
</tr>
<tr>
<td>Mean</td>
<td>172</td>
<td>2.63</td>
<td>198</td>
<td>3.11</td>
<td>1.60</td>
<td>0.26</td>
<td>0.78</td>
</tr>
<tr>
<td>Std.dev.</td>
<td>63.35</td>
<td>0.55</td>
<td>41.25</td>
<td>0.53</td>
<td>0.20</td>
<td>0.19</td>
<td>0.12</td>
</tr>
</tbody>
</table>
Table 2.8  Summary of particle size distribution characteristics for the sediments at Baton Rouge site

<table>
<thead>
<tr>
<th>Storm Date</th>
<th>Central tendency</th>
<th>Uniformity</th>
<th>Skewness</th>
<th>Kurtosis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/19/02</td>
<td>fine sand</td>
<td></td>
<td>strongly skewed towards fine particles</td>
<td>platykurtic</td>
</tr>
<tr>
<td>1/24/02</td>
<td>fine sand</td>
<td></td>
<td>fine skewed</td>
<td>platykurtic</td>
</tr>
<tr>
<td>1/31/02</td>
<td>very fine sand</td>
<td></td>
<td>strongly skewed towards fine particles</td>
<td>very platykurtic</td>
</tr>
<tr>
<td>2/05/02</td>
<td>medium sand</td>
<td></td>
<td>symmetrical</td>
<td>platykurtic</td>
</tr>
<tr>
<td>2/20/02</td>
<td>very fine sand</td>
<td></td>
<td>strongly skewed towards fine particles</td>
<td>platykurtic</td>
</tr>
<tr>
<td>3/01/02</td>
<td>fine sand</td>
<td></td>
<td>fine skewed</td>
<td>very platykurtic</td>
</tr>
<tr>
<td>3/09/02</td>
<td>very fine sand</td>
<td></td>
<td>strongly skewed towards fine particles</td>
<td>platykurtic</td>
</tr>
<tr>
<td>3/11/02</td>
<td>fine sand</td>
<td></td>
<td>symmetrical</td>
<td>platykurtic</td>
</tr>
<tr>
<td>3/20/02</td>
<td>fine sand</td>
<td></td>
<td>fine skewed</td>
<td>platykurtic</td>
</tr>
<tr>
<td>5/13/02</td>
<td>medium sand</td>
<td></td>
<td>symmetrical</td>
<td>platykurtic</td>
</tr>
<tr>
<td>6/19/02</td>
<td>fine sand</td>
<td></td>
<td>fine skewed</td>
<td>mesokurtic</td>
</tr>
<tr>
<td>6/27/02</td>
<td>very fine sand</td>
<td></td>
<td>strongly skewed towards fine particles</td>
<td>platykurtic</td>
</tr>
</tbody>
</table>

Table 2.9  Statistical characteristics of particle size distribution for grit at Baton Rouge site

<table>
<thead>
<tr>
<th>Storm Date</th>
<th>d₅₀ (µm)</th>
<th>Φ₅₀</th>
<th>d₉₅ (µm)</th>
<th>σ₉₅</th>
<th>σₛ</th>
<th>S_k</th>
<th>K_G</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/05/2001</td>
<td>668</td>
<td>0.60</td>
<td>945</td>
<td>4.02</td>
<td>1.91</td>
<td>0.17</td>
<td>0.81</td>
</tr>
<tr>
<td>4/24/2001</td>
<td>735</td>
<td>0.47</td>
<td>969</td>
<td>3.90</td>
<td>1.87</td>
<td>0.14</td>
<td>0.80</td>
</tr>
<tr>
<td>2/05/2002</td>
<td>682</td>
<td>0.57</td>
<td>1066</td>
<td>4.19</td>
<td>1.97</td>
<td>0.24</td>
<td>0.76</td>
</tr>
<tr>
<td>3/01/2002</td>
<td>510</td>
<td>0.99</td>
<td>773</td>
<td>4.30</td>
<td>2.02</td>
<td>0.19</td>
<td>0.89</td>
</tr>
<tr>
<td>Mean</td>
<td>649</td>
<td>0.66</td>
<td>938</td>
<td>4.10</td>
<td>1.94</td>
<td>0.18</td>
<td>0.81</td>
</tr>
<tr>
<td>Std.dev.</td>
<td>96.64</td>
<td>0.23</td>
<td>121.89</td>
<td>0.18</td>
<td>0.07</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>Grit property</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>coarse sand</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>poorly sorted</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>fine skewed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>platykurtic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2.10  Summary of statistical characteristics of particle size distribution for the settleable solids and sediments collected from four different sites

<table>
<thead>
<tr>
<th>Sample Site</th>
<th>$d_{50}$ ($\mu$m)</th>
<th>$\Phi_{50}$</th>
<th>$d_g$ ($\mu$m)</th>
<th>$\sigma_g$</th>
<th>$\sigma_i$</th>
<th>$S_k$</th>
<th>$K_G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Little Rock 1</td>
<td>248</td>
<td>2.01</td>
<td>265</td>
<td>2.19</td>
<td>1.26</td>
<td>0.13</td>
<td>0.95</td>
</tr>
<tr>
<td>Little Rock 2</td>
<td>587</td>
<td>0.77</td>
<td>807</td>
<td>4.04</td>
<td>1.98</td>
<td>0.13</td>
<td>0.93</td>
</tr>
<tr>
<td>New Orleans</td>
<td>216</td>
<td>2.23</td>
<td>296</td>
<td>2.10</td>
<td>1.46</td>
<td>0.47</td>
<td>1.31</td>
</tr>
<tr>
<td>Baton Rouge*</td>
<td>633</td>
<td>0.67</td>
<td>844</td>
<td>5.20</td>
<td>2.23</td>
<td>0.13</td>
<td>0.78</td>
</tr>
<tr>
<td>Mean</td>
<td>421</td>
<td>1.42</td>
<td>553</td>
<td>3.38</td>
<td>1.73</td>
<td>0.22</td>
<td>0.99</td>
</tr>
<tr>
<td>Std.dev.</td>
<td>219</td>
<td>0.81</td>
<td>315</td>
<td>1.51</td>
<td>0.45</td>
<td>0.17</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Table 2.11  Summary of particle size distribution characteristics for the sediments at Baton Rouge site

<table>
<thead>
<tr>
<th>Sample Site</th>
<th>Central tendency</th>
<th>Uniformity</th>
<th>Skewness</th>
<th>Kurtosis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Little Rock 1</td>
<td>fine sand</td>
<td></td>
<td>fine skewed</td>
<td>mesokurtic</td>
</tr>
<tr>
<td>Little Rock 2</td>
<td>coarse sand</td>
<td>poorly sorted</td>
<td>fine skewed</td>
<td>mesokurtic</td>
</tr>
<tr>
<td>New Orleans</td>
<td>fine sand</td>
<td></td>
<td>strongly skewed towards fine particles</td>
<td>leptokurtic</td>
</tr>
<tr>
<td>Baton Rouge*</td>
<td>coarse sand</td>
<td>very poorly sorted</td>
<td>fine skewed</td>
<td>platykurtic</td>
</tr>
</tbody>
</table>

* Sediments from Baton Rouge are cumulative sediments from both grit chamber and sedimentation tank.

Physical properties of sediments

Particulate materials transported by the urban runoff are heterogeneous. Organic matter such as leaves and other plant materials, wood pieces, straw and tire debris have a higher percentage in the large size range. Majority of these materials were intercepted by 425-µm sieve or above. Density of such materials is relatively low compared to the inorganic sand particles. Measured density for the oak leaves is 1.94-g/cm$^3$. Results of experimental determination of density for materials collected at Baton Rouge site was illustrated in Figure 2.12. The measured results showed that density of sediments was relatively consistent for the materials less than 425-µm and within the range of 2.2 – 2.6 g/cm$^3$. Density of solids in the
grit chamber was consistently higher than density of the sediments in the storage tank. Such variation in density affects sediment transport by gravitational separation.

Figure 2.12 Mean and standard deviation trends for granulometric-based density of particulate materials captured from 12 individual rainfall-runoff events at the Baton Rouge site. The grit fraction was captured in a pre-screening grit chamber and the sediment fraction captured in a sedimentation basin. The entire mass of grit and sediment were recovered and analyzed for each event.

Density of sediments accumulated in storm water runoff catchments showed similar trend for the sites of Baton Rouge, New Orleans and Little Rock site 2. As shown in Figure 2.13, the densities are within the range of 2.2 – 2.6 g/cm³ which is close to the results measured for street surface sediments (Butler et al. 1992) and solids transported in suspension in stormwater sewers (Jacopin et al. 1999). Density of sediments from Little Rock site-1 showed a similar pattern as that of sediments collected from individual storm event at Baton Rouge site.

Measured specific surface area (SSA) across size gradation was shown as vertical error bars and calculated total surface area (SA) based on 1000-g mass was plotted as vertical bars on the same graph. Figure 2.14 showed SSA, SA and cumulative SA% for the sediments at Baton Rouge site. SSA was extraordinary high for particles greater than 425-µm due to the
large percent of organic materials in them. SSA leveled at approximate 40-m²/g for particles less than 425-µm. Total surface area is as a function of specific surface area and the mass distribution. Variability in mass distribution for the different storm events contributes to the variability of total surface area.

Figure 2.15 showed the results of surface area for the accumulative sediments from four urban transportation sites. A general trend of increasing SSA with decreasing size for the particles less than 425-µm was observed. Corresponding to the low-density organic materials, particles within large size end still possessed an unstable high SSA as seen in the results for sediments from Little Rock site 1. Complicated particle surfaces such as folds, pores, notches, pits and roughness contribute to the additional surface area especially for fine particles (Sansalone 1998). As a consequence, SSA is a function of not only particle size, but also particle shape, density and composition. It has been found that sediments from Baton Rouge and New Orleans have higher SSA than the sediments from Little Rock.

Surface chemistry

The potentiometric titration curves for storm runoff sediments across size gradation are shown in Figure 2.16. PZC was determined according to surface charge and was shown in the same plot. Surface charge of particles decreases with increase of pH. PZC was ranging from 7 to 9. For the four sites studied, smaller particle at Baton Rouge and Little Rock site 1 had lower PZC compared to New Orleans and Little Rock site 2.
Figure 2.13  Mean and standard deviation trends for granulometric-based density of accumulated (multiple rainfall-runoff events) sediments collected from Baton Rouge, Little Rock and New Orleans sites.

Figure 2.14  Specific surface area (SSA) and surface area (SA) (based on 1000-g dry mass) for sediments from twelve observed individual storms at Baton Rouge site. Range bars on incremental values represent standard deviations of all twelve events while the shaded bars represent the mean value for the site. Cumulative curve is based on the mean value.
Figure 2.15  Specific surface area and total surface area (based on 1000-g of sediments) for the sediments from four urban transportation sites in three USA cities
Figure 2.16  Surface charge and PZC for the particles across size gradation
CONCLUSIONS

Urban storm water is a significant source of anthropogenic particulate matter, colloids and solutes, with solutes partitioning between particulate, colloidal and solution phases. Through sampling the entire urban runoff flow from an elevated urban transportation site, solid fractions were studied and their granulometric properties were characterized. The study aims to provide guidance for treatability, regulation and control of non-colloidal particulate matter. Several conclusions were summarized as follows:

1. Analyses of solid fractions for sediments in a sedimentation tank showed that approximately 68% of the materials remained in suspended status after the first few hours’ retention. Results of particle analysis indicate that the suspended fraction $d_{50V}$ based on volume distribution was $[10.36, 4.69]$ µm, $\rho_s$ was $[2.40, 0.19]$ g/cm³ from all twelve rainfall-runoff events. The number based $d_{50n}$ was $[1.62, 0.04]$ µm for the suspended fraction, indicating that the particles in the suspended fractions are similar in size to silt and clay.

2. Sediments from Baton Rouge site showed similar granulometric characteristics. $d_{50}$ for the sediment fraction was $[172, 63.35]$ for all 12 rainfall-runoff events, indicating that particles in the sedimentation tank are similar in size to fine sand. Coarser sands were intercepted by the grit chamber prior to sedimentation tank. This portion could be easily separated from the runoff stream by gravitation settling. The particle size distributions for the accumulative sediments at four sites showed a great variability.

3. Density of sediments is consistent for the materials less than 425-µm and within the range of 2.2 – 2.6 g/cm³. Density of solids in the grit chamber is consistently higher than density of the sediments in the storage tank.
4. Over 50% of SA was associated with the particulate gradation >250-µm. Sediments from Baton Rouge and New Orleans have higher SSA than the sediments from Little Rock. Results suggest that a solute mass can preferentially partition to the gradation of particles with predominant SA.

IMPLICATIONS FOR BEST MANAGEMENT PRACTICES

A central conundrum in storm water treatment is the bioavailability, toxicity, mobility of contaminants, all associating with granulometry of particles in urban storm runoff. The ability of best management practices (BMPs) to remove particulate-bound particles from runoff stream increase with particle size, however, bioavailability and mobility of pollutants decrease with particle size. Development and design of treatment methods are based on the granulometry characteristics. For example, the granulometric distribution of a specific-site shows dominance of median to coarse materials. Sedimentation would be an effective treatment. BMP efficiency can be determined through the granulometry of particles. The degree to which contaminants partition to each solid fraction depends on several key physical characteristics of the particle such as surface area and surface charge potential. A predicative granulometric-metal model is expected to be developed to optimize the current BMPs and guild future design.

REFERENCES


USEPA. (2001). TOTAL MAXIMUM DAILY LOAD (TMDL) for TSS, Turbidity, and Siltation, for the 15 Subsegments in the Vermilion River Basin, 303(d) listed subsegments, USEPA Region 6.


NOMENCLATURE

\[ d_g \] = geometric mean diameter

\[ d_{50} \] = median particle size based on particle mass

\[ d_{50s} \] = median particle size based on particle distribution

\[ d_{50v} \] = median particle size based on particle volume

\[ \Phi \] = Phi size, index of grain size distribution in sediment

\[ \sigma_I \] = inclusive graphic standard deviation

\[ S_k \] = skewness

\[ K_G \] = kurtosis

\[ \rho_s \] = density of particle (g/cm\(^3\))

\[ V_S \] = true sample volume (cm\(^3\))

\[ V_C \] = cell volume of pycnometer (cm\(^3\))

\[ V_R \] = reference volume of pycnometer (cm\(^3\))

\[ P_1 \] = initial pressure (psi)

\[ P_2 \] = final pressure (psi)

\[ M_s \] = mass of the sample determined prior to placement in the pycnometer (g)

\[ V_s \] = volume of specimen (cm\(^3\))

\[ \text{SSA} \] = specific surface area (m\(^2\)/g)

\[ W_a \] = measured weight of EGME retained by sample (g)

\[ W_s \] = measured weight of dried sample (g)

\[ \text{SA}_i \] = surface area of solids having particle diameter \( i \) (m\(^2\))

\[ m_i \] = mass of solids having particle diameter \( i \) (g)

\[ \text{SSA}_i \] = specific surface area of solids having particle diameter \( i \) (m\(^2\)/g)

\[ N \] = particle number density

\[ l \] = characteristic particle size

\[ \alpha, \beta \] = empirical constants

\[ r^2 \] = coefficient of determination

\[ \text{PSD} \] = particle size distribution

\[ \text{NPDES} \] = national pollutant discharge elimination system

\[ \text{EGME} \] = ethylene glycol monoethyl ether
CHAPTER 3. GRANULOMETRIC-BASED DISTRIBUTION OF METALS FOR NON-COLLOIDAL PARTICULATE MATTER TRANSPORTED BY URBAN RAINFALL-RUNOFF

SUMMARY

Metal element is partitioning between dissolved, colloidal and particulate phases and transported by urban rainfall-runoff. Partition of metal elements between dissolved and particulate phase was studied through experimental phase fractionation of urban rainfall-runoff. Particulate matters deposited from eight discrete storm events at Baton Rouge, Louisiana were examined for metal contamination. Results indicated that a significant reduction was achieved in total metal concentration for Cr, Cu, Zn and Pb by settling out the settable fraction. However, removal of settleable fraction does not translate to large overall reduction in total concentration for As and Cd because of their relative high dissolved fraction. As indicated by mass distribution, metal mass was dominant in medium to coarse ($75 < d < 2000 \mu m$) materials although fine particles ($< 75-\mu m$) were associated with a high level of metal concentration. The cumulative seasonal sediments collected from four storm catch basins at different urban transportation sites were characterized as well. No significant accumulative effect was found on metal concentration in the sediments. A cumulative power law model was utilized to predict metal mass from the granulometric indices in lieu of metal analyses. The utilization of this model is to assist the development of particle separation operations in stormwater best management practices to target the portion of mass gradation where the predominant metal mass is associated.

INTRODUCTION

Rainfall-runoff from urban land uses transports a wide gradation of particulate matter associated with a significant load of metal elements. Direct pollution is upon the aquatic
life in the receiving water system. This pollution may result in the destruction of fish, wildlife, and aquatic life habitats and threats to public health due to contaminated food, drinking water supplies and recreational waterways. Studies on 541 streambed-sediment samples collected across United States showed that 49 percent of the sites sampled in urban settlings had concentrations of one or more trace metal elements that exceeded levels at which adverse effects could occur in aquatic biota (Rice 1999). Metals Cr, Cu, Zn, As, Cd and Pb are among the most critical stormwater contaminants affecting aquatic life (Makepeace 1995).

Routine traffic and highway maintenance regimes are significant contributory sources of both particulates and metals. The abrasion of metal containing vehicular parts and the vigorous abrasion of vehicular tires against the pavement surface are primary sources of metals (Sansalone and Glenn 2002). Abraded pavement and abraded tire were reported to constitute 40-50% and 20-30% of the total particulate matter generated (Kobriger and Geinopolos 1984). Infrastructure is also an important source of anthropogenically generated constituents. For instance, zinc-galvanized guardrails contain zinc coating concentrations ranging from 4.5 up to 10.5 g/m² (Sansalone 2001).

PREVIOUS STUDIES

Metal loadings in urban rainfall-runoff have been studies extensively. On heavily traveled highways Cu, Zn, Cd and Pb often exceed surface water discharge criteria of USEPA and State EPA on an event basis (Sansalone et al 1997). Previous work emphasized on individual pollution investigations of four metals Cr, Cu, Pb and Zn because the hazardous or toxic effects of these metals are among the most serious. Pb, for instance, is carcinogenic chemical and may cause kidney tumors. Non-carcinogenic effects
of lead include anemia, high blood pressure, IQ impairment and decreased learning (LaGrega et al. 1994). There existed a large variability of individual metal loadings within each road category, typically ranging over several orders of magnitude (Ellis and Revitt 1982). A concrete surface was reported to yield high levels of Zn and Pb compared to an asphalt surface (Hird 2001). The concentrations of constituents varied widely during the history of each storm and appeared to be highest in the first flush (Shinya et al. 2000). From both a hydrological and geochemical viewpoint, gravel-size sediments ($\geq 2000 \mu m$) are generally considered to be less important in the transport of adsorbed metals from urban areas (Sartor and Boyd 1972). Several studies (Ellis and Revitt 1982, Xanthopoulos and Augustin 1992, Sansalone and Buchberger 1996, Milligan and Loring 1997) have found that most metals have a greater affinity for smaller particle sizes. Benthic organisms may be directly exposed to fine-grained (< 63 $\mu m$) fraction (Davis and Atkins 2001), therefore removal of fine particulates is critical for the protection of biota. Although the highest metal concentration typically occur in the fine size fraction (<17 $\mu m$), the medium sand fraction (75-300 $\mu m$) was reported to have the largest percentage contribution to the total metal mass (Murray 1999). In the study by Shinya (Shinya et al. 2000) a correlation was found between the metal concentrations and particulate diameter for Cu, Zn and Pb during a certain range. However, study on street sediments for Sault Ste Marie (Stone and Marsalek 1996) indicated that correlations between metal content and size fractions are either very weak or non-existent.

A sequential selective extraction of metals was carried out on sediments of various origins (Chartier et al. 2001). Zn, Cd and Pb were found mainly in the acid-soluble phase (carbonate fractions) and the fraction related to Fe-Mn oxides. Cu was found associated
with organic matter and sulfide fraction primarily. Cr was mostly found in the residue fraction.

Metals are subject to changing conditions in the stormwater system. Removal efficiency of metals in a stormwater basin is therefore related to the chemistry of the runoff such as the chemical nature of the particulates, pH and the redox condition of the basin (Whipple and Hunter 1981). Processes involved in the removal of metal elements include adsorption, precipitation, dissolution, deposition, dissociation, complexation, transformation and biochemical reactions (Makepeace 1995).

**OBJECTIVES**

There were three objectives in this study. The first objective was to examine the equilibrium of metal partitioning between the operationally dissolved (< 0.45 µm) and particulate phase of urban rainfall-runoff. The second objective was to quantify and characterize the granulometric-based metal distribution in incremental and cumulative sediment transported by urban rainfall-runoff. The final objective was to apply a cumulative power law model to predict metal mass from the granulometric indices in lieu of metal analyses. The prediction of the model was evaluated by comparing the predicted metal mass to the measured data.

**METHODOLOGY**

**Phase Fractionation for Equilibrium Analysis**

In order to examine the equilibrium of metal partitioning between dissolved and particulate phase in urban rainfall-runoff, phase fractionation was conducted for the raw storm water and the suspension after 1-hour Imhoff settling. Thirty 1-L samples were collected from the completely mixed sedimentation basin at Baton Rouge I-10
experimental site on March 20, 2002 immediately after the rainfall. 60-mL of fully homogenized sample was filtered through a 0.45 µm GFC cellulose acetate filter using a pressure filtration device according to Standard Methods 3030-B. Pressure of the compressor was set no greater than 60-psi to prevent rupturing of the filter membrane. After filtration, the filtrate was preserved in a clean 100-mL polypropylene sample jar with addition of 5-mL of trace metal nitric acid using a Brinkman dispenser. Samples were labeled as dissolved phase for metal digestion and analysis. Filtered solids along with the filter paper were carefully removed from the filtration base and folded inwards to encase the filtered solids. Folded filters were placed into a clean aluminum pan folded over the edges to prevent the filter paper from unfolding. The folded aluminum pan with filter solid paper was placed in a labeled petri dish as particulate phase for metal digestion and analysis.

**Sediment Collection**

Sediments analyzed in this study include: Sediments collected from 8 discrete storm events during February 5 to October 27, 2002 at Baton Rouge I-10 site; seasonal cumulative sediments transported by urban rainfall-runoff (January 1 to April 24, 2001) collected at the same site; and sediments collected from storm catchments at New Orleans and two Little Rock sites (Little Rock site 1 and Little Rock site 2). Site characteristics have been addressed in previous paper (Lin and Sansalone 2003).

Sediment samples were transported back to the lab and air-dried in 40°C hot room. Granulometric distribution of sediments was determined by sieving through mechanically shaken sieves according to ASTM D422-63 (ASTM 1990). Samples from each size gradations were stored in separate round-clear sample bottles for future analyses.
**Metal Digestion**

Filtered solids from phase fractionation and sediments were digested using hot plate according to Standard Method 3030 F prior to metal analysis. For the particulate phase, the filter was carefully unwrapped from the aluminum pan and placed into its respective flask. For the sediment, a representative portion (approximately 0.5 to 1-g) of dry particulate matter from each size gradation was weighted to ± 0.1-mg and placed in a 250-mL labeled flask. 3-mL of concentrated HCl and 9-mL of trace metal nitric acid were added to each flask. A blank (3-mL HCl + 9-mL HNO₃) and a standard (PriorityPollutn™/CLP inorganic solids, Environmental resource associates) were included. Flasks were covered with watch glasses and placed on the hot plate. Hot plate was preheated and adjusted to 150 °C. Samples were allowed to be heated for 1.5 hour and temperature of hot plate was increased to 175 °C for continuous heating of another 0.5 hour. After digestion, 10-mL D.I. was added to sample for quick cooling. Digested samples were then filtered to 100-mL volumetric flask by rinsing with 2% nitric acid. Each flask was filled up to the rim with 2% nitric acid and completely mixed. Diluted digestion solution was finally transferred to labeled polypropylene sample jars for metal analysis.

**Metal Analysis – ICP/MS**

Metal analysis was conducted with an inductive coupled plasma mass spectrometer (ICP-MS) (Elan 6000, Perkin-Elmer Science. The operation employed a four-point standard calibration (10, 20, 100, 500) and a blank (2% nitric acid) prior to analysis of samples. The instrument was operated under 100ms and 50 sweeps/reading for measurements. Three replicates were included for each measurement. The internal standards include Scandium (Sc 45), Germanium (Ge 74), Rhodium (Rh 103) and
Lutetium (Lu 175). Analytical controls were maintained throughout the process, which included analysis of control (QC50), blank samples, mass balance checks, and standard solution quantity checks for every 9 samples. Digested samples were transferred to 15-mL centrifuge tube for ICP-MS analysis. Analyzed metals in this study include Cr (52), Cu (63), Zn (64), As (75), Cd (114) and Pb (208). For sediments, ICP concentration result was converted from ppb (µg/L) to µg/g based on acid-digested volume dilutions and the measured dry mass. Results from metal concentration in terms of µg/g were converted to total metal mass using Equation 1.

\[ M_{ei} = (m_i) (c_i) \]  

(1)

where: \( M_{ei} \) = metal mass associated with particulate matter having particle diameter \( i \) (g); \( m_i \) = dry mass of particulate matter solids having particle diameter \( i \) (g); and \( c_i \) = concentration of particulate-bound metal for particle diameter \( i \) (µg/g). In this study, total metal mass calculation was based on 1000-g (\( \Sigma m_i = 1000 \) g). A cumulative metal mass can be obtained from summation of the incremental results across the gradation.

**Statistical Estimation of the Difference**

The difference of metals between sites or between events was estimated statistically. Null hypothesis is \( H_0 : \mu_1 - \mu_2 = 0 \). Under null hypothesis there is no difference between two populations. Alternative hypothesis is \( H_a : \mu_1 > \mu_2 \) or \( \mu_1 < \mu_2 \). This hypothesis is tested at a significance level of 0.05, indicating the 5% chances that null hypothesis \( H_0 \) were incorrectly reject.

\[ z = \frac{(\bar{x}_1 - \bar{x}_2)}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}} \]  

(2)
In the test statistic, \( n \) is the sample size, \( \bar{x} \) is the sample average, and \( s \) is the standard deviation of population which can be estimated by standard deviation of the samples. Critical \( p \)-value can be found from Statistical Table of Normal Curve Area. If \( p \)-value < 0.05, the null hypothesis is rejected while the alternative hypothesis is accepted.

**Pearson's Correlation Analysis**

The correlation between two variables reflects the degree to which the variables are related. The most common measure of correlation is Pearson's correlation designated by \( r \).

\[
 r = \frac{\sum xy - \frac{\sum x \sum y}{n}}{\sqrt{\left(\frac{\sum x^2 - \frac{(\sum x)^2}{n}\right)\left(\frac{\sum y^2 - \frac{(\sum y)^2}{n}\right)}}}
\]

In equation (3), \( x \) and \( y \) are two variables. \( n \) is the population size. \( r \) is in the range of -1 to +1. A positive value of \( r \) means a positive linear relationship, a negative value of \( r \) means a negative linear relationship. A correlation of 0 means there is no linear relationship between the two variables.

**Power Law Model**

Power law has been applied extensively in environmental and hydraulic engineering. The basic form of power law is \( y = ax^b \). The cumulative particle density (PND) can be modeled with a power law expression as described in Equation 4 (Bader 1970, Sansalone and Cristina 2002).

\[
N = \alpha_d (d_p)^{-\beta_d}
\]

\( N \) is the cumulative PND in counts/L\(^3\); \( \alpha_d \) is the best fit cumulative PND in counts/L\(^3\); \( d_p \) is the particle diameter in \( \mu \)m; and \( \beta_d \) is an exponent which is an indication of the location where the propensity of surface area (SA) lies.
Cumulative PND of a particle gradation can be expressed as a function of individual particle SA as shown in Equation 5.

\[ N = \alpha_A (A)^{-\beta_A} \]  

\( A \) is the surface area of an individual particle with diameter \( d_p \) in \( \mu m^2 \) and \( \beta_A \) is a dimensionless power law exponent based on particle surface area.

A least squares method was applied to select equation parameters to fit an equation to data. The source data is assumed to be normally distributed around the regression. Therefore, normality test is needed to test if the assumption is valid. Failure of the normality test indicates the presence of outlying influential points or an incorrect regression model. Kolmogorov-Smirnov (K-S) was used for normality test. Coefficient of determination (\( r^2 \)) is an indication of goodness of fit.

Power law model was utilized to predict metal mass. Pearson’s correlation showed a significant correlation (\( p \)-value > 0.05) between metal mass and dry solid particle mass for the sediments. A suggested power law model was expressed as

\[ Me_{cf} = \alpha M_{cf}^{\beta} \]  

Normalized cumulative metal mass (\( Me_{cf} \)) was plotted as a function of normalized cumulative particle mass (\( M_{cf} \)) in a log-log scale graph. The data appeared to be linearly related.

RESULTS AND ANALYSIS

Metal Partitioning in Dissolved and Particulate Phase

Metal analyses (Cr, Cu, Zn, As, Cd and Pb) were carried out for the dissolved and particulate phase for both untreated rainfall-runoff and the suspension subsequent to 1-hour quiescent settling for the storm on March 20, 2002. Analysis of solid fraction showed that
36% of the total suspended solids remained in suspension after 1-hour settling (Lin and Sansalone 2003). Phase fractionation was carried out for the aqueous part. Metals in dissolved and particulate phase were analyzed accordingly. Results of metal analysis were shown in Figure 3.1. It was found that all analyzed metals were dominant in the particulate phase. Cd also showed a strong affinity to the dissolved phase. Total metal concentrations were significantly reduced after 1-hour gravitational settling during which majority of particles was settled out. In dissolved phase, there was no significant change of metal concentration before and after 1-hour quiescent settling. A slight increase of Cu and Zn concentration ($p >0.05$) in the dissolved phase was observed after 1-hour settling. This may due to the change in redox conditions which affects metal sorption and desorption. Particulate-bound metals will be released into the solution when the redox decreases which explains the slight increase in the dissolved fraction for Cu and Zn. Table 3.1 summarized the results of metal partitioning in dissolved and particulate phase for the analyzed metals. It was found that total metal concentration in untreated rainfall-runoff exceeded EPA’s water quality criteria (USEPA 1999) for freshwater for all analyzed metals except for Cr(III) and As. By settling out the settleable fraction, a large reduction (>75%) in total metal concentration was achieved for Cu, Zn and Pb. However, for Cr, As and Cd removal of settleable fraction does not contribute to a large overall reduction in total metal concentration because of their relatively high dissolved concentration. In addition, metal concentrations of Cu, Zn and Cd in the suspension after 1-hour settling were still above the criteria, indicating the inability of removing dissolved metals and inefficiency of removing particulate-bound metal by gravitational sedimentation with a short retention time.
Table 3.1  Partitioning and distribution of metals – dissolved and particulate fractions in urban rainfall-runoff

<table>
<thead>
<tr>
<th>Metal Conc. (µg/L)</th>
<th>Cr</th>
<th>Cu</th>
<th>Zn</th>
<th>As</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMC</td>
<td>570(Cr³⁺)/16(Cr⁶⁺)</td>
<td>13</td>
<td>120</td>
<td>340</td>
<td>4.3</td>
<td>65</td>
</tr>
</tbody>
</table>

**Unsettled storm water**

<table>
<thead>
<tr>
<th></th>
<th>Dissolved</th>
<th>Particulate-bound</th>
<th>Total SMC (n=30)</th>
<th>f₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>11.1</td>
<td>61.1</td>
<td>72.2</td>
<td>0.15</td>
</tr>
<tr>
<td>Cu</td>
<td>23.0</td>
<td>195.3</td>
<td>218.3</td>
<td>0.11</td>
</tr>
<tr>
<td>Zn</td>
<td>46.1</td>
<td>1857</td>
<td>1903</td>
<td>0.02</td>
</tr>
<tr>
<td>As</td>
<td>1.9</td>
<td>34.4</td>
<td>36.3</td>
<td>0.05</td>
</tr>
<tr>
<td>Cd</td>
<td>19.3</td>
<td>52.5</td>
<td>71.8</td>
<td>0.27</td>
</tr>
<tr>
<td>Pb</td>
<td>17.7</td>
<td>117.7</td>
<td>135.3</td>
<td>0.13</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Dissolved</th>
<th>Particulate-bound</th>
<th>Total SMC (n=30)</th>
<th>f₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>11.0</td>
<td>32.7</td>
<td>43.7</td>
<td>0.25</td>
</tr>
<tr>
<td>Cu</td>
<td>23.9</td>
<td>47.0</td>
<td>70.9</td>
<td>0.34</td>
</tr>
<tr>
<td>Zn</td>
<td>48.0</td>
<td>398.0</td>
<td>446.0</td>
<td>0.11</td>
</tr>
<tr>
<td>As</td>
<td>1.4</td>
<td>31.4</td>
<td>32.8</td>
<td>0.04</td>
</tr>
<tr>
<td>Cd</td>
<td>18.2</td>
<td>41.2</td>
<td>59.4</td>
<td>0.31</td>
</tr>
<tr>
<td>Pb</td>
<td>16.2</td>
<td>23.7</td>
<td>39.8</td>
<td>0.41</td>
</tr>
</tbody>
</table>

**Separation efficiency by settling (R%)**

<table>
<thead>
<tr>
<th></th>
<th>Particulate-R%</th>
<th>Total SMC-R%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>46.52</td>
<td>39.48</td>
</tr>
<tr>
<td>Cu</td>
<td>75.95</td>
<td>67.54</td>
</tr>
<tr>
<td>Zn</td>
<td>78.57</td>
<td>76.56</td>
</tr>
<tr>
<td>As</td>
<td>8.63</td>
<td>9.56</td>
</tr>
<tr>
<td>Cd</td>
<td>21.46</td>
<td>17.31</td>
</tr>
<tr>
<td>Pb</td>
<td>79.89</td>
<td>70.57</td>
</tr>
</tbody>
</table>

CMC – Criteria Maximum Concentration (National recommended water quality criteria for priority toxic pollutants EPA 822-Z-99-001, April 1999)
SMC – solid matter concentration, Total SMC = (Dissolved + Particulate-bound)
f₃ – dissolved fraction (f₃ = Dissolved fraction/Total SMC)
Figure 3.1  Equilibrium of metal partitioning in dissolved and particulate phase before and after settling

U –untreated stormwater, S – supernatant after 1-hour quiescent settling,
P – Particulate phase, D – Dissolved phase.
Granulometric-based Metal Distributions in Sediments

Gradation for the sediments collected out of eight individual storm events at Baton Rouge site were characterized by sieve analyses and the granulometric gradations were shown in Figure 3.2. Granulometric-based metal concentrations were measured with ICP-MS for the particles across size gradation. Figure 3.3 illustrated the averaged metal concentrations for Cr, Cu, As, Cd, Pb and Zn as a function of particle diameter for the sediments from eight individual storms. As seen in Figure 3.3, it appeared that particles ranging from 106-µm to 600-µm had an increasing concentration with decreasing size. The metal concentration leveled from 106-µm and below for all analyzed metals. Particles above 600-µm were composed of significant heterogeneous materials. It has been observed that the collected sediments contained a significant amount of organic materials between gradation of 600-µm and 850-µm. Particulate mass was primarily associated with particulate matter greater than 75-µm (Figure 3.2). Granulometric-based total metal mass distribution showed approximately 80% of metal mass resides in the medium to coarse materials (75 < d < 2000 µm) as shown in Figure 3.4.

Long term seasonal cumulative sediments collected from four different urban rainfall-runoff catchments were analyzed for metal contamination as well. Granulometric mass distributions for these sediments were shown in Figure 3.5. Figure 3.6 (a) through (f) showed the incremental metal concentration, incremental metal mass and cumulative metal mass based on 1000-g dry solid mass for six metals (Cr, Cu, As, Cd, Pb and Zn). Except for Cr, all other metals analyzed exhibited a trend of increasing concentration with decreasing size. Figure 3.7 summarized the total metal mass and metal fraction associated with fine particulates (< 75 µm).
Figure 3.2 Incremental and cumulative particle mass distribution for the sediments from eight discrete storm events at Baton Rouge site
Figure 3.3  The incremental and cumulative particulate-bound metal concentration gradations for Baton Route site. (Range bars on incremental values represent standard deviations of all eight events while the shaded bars represent mean values for all eight events.)
Figure 3.4    Total metal mass (based on 1000-g dry solid mass) and cumulative metal mass for Cr, Cu, As, Cd, Pb and Zn – incremental sediments collected at Baton Rouge site (Range bars indicate the variation of eight individual storm events) Cumulative curves are based on the mean values.
Metal loadings in the sediments varied for four urban transportation sites. A high Zn and Pb level was observed for New Orleans site and it was thought to be related to the heavy traffic relevant to its downtown location. Except for total Pb in New Orleans, all other metal loadings were below the criteria of metal limit for soil (USEPA 1994), suggesting that these sediments were safe for land disposal. Metals associated with small size particulates (< 75 µm) were found consisting of less than 30% of total metal load (mg/based on 1000g) in seasonal cumulative sediments as seen in Figure 3.8 (except for Cu in New Orleans).

The power-law model was applied to fit the data for both the event-based sediments and the seasonal cumulative sediments. Figure 3.9 and Figure 3.10 showed the measured data for each metal in all eight rainfall events. A power law model was applied for each metal in all eight events. The power law parameters $\alpha$ and $\beta$ were listed in Table 3.2 and Table 3.3 for the event-based sediments and cumulative sediments respectively. $\alpha$ is thought to be an index for the amount of metal mass and related to a specific metal. $\beta$ is considered an index for metal association with a particle size gradation.

For Baton Rouge site, mean adjusted factors $\alpha$ and $\beta$ developed from power law model were applied to predict metal mass from granulometric mass gradation. The predicted results were compared with measured results. The residual errors of power law model for each metal in each storm event were summarized in Table 3.4. The model application to the experimental data suggested prediction of metal mass using the developed model in lieu of expensive and tedious metal analyses in the future for the characterized site. Granulometric-based particle gradation can be obtained from a simple and economical sieve analyses.
Figure 3.5  Granulometric mass distribution for the long-term seasonal cumulative sediments from four different urban transportation sites – Baton Rouge, New Orleans, Little Rock site 1 and Little Rock site 2.
Figure 3.6 (a) Metal concentration (µg/g), total incremental metal mass (mg) and cumulative metal mass fraction as a function of particle gradation for the long term sediments deposited at four urban transportation sites – New Orleans, Little Rock site 1, site 2 and Baton Rouge. (a) Cr (b) Cu (c) As (d) Cd (e) Pb (f) Zn (Metal mass based on 1000-g dry solid mass).
Figure 3.6 (b)
Figure 3.6 (c)
Figure 3.6 (d)
Figure 3.6 (e)
Figure 3.6 (f)
Figure 3.7  Total metal and finer fraction (<75 µm) metal mass (based on 1000-g dry solid mass) in the cumulative sediments from four transportation sites. Criteria (mg/kg) is based on EPA’s metal limit for soil (EPA-831-B-93-002b Part 503).
Figure 3.8 Finer metal fraction (< 75\mu m) in the cumulative seasonal sediments collected from four urban transportation sites.
Figure 3.9  Power law model $Me_{cf} = \alpha M_{cf}^\beta$

Application for the sediments collected from eight individual storm events occurred at Baton Rouge site. Total metal mass $Me_{T}$ for each investigated metal elements was summarized in the graph (based on 1000-g dry solid mass). $M_T$ is the total granulometric solid mass.
Figure 3.10  Power law model $M_{e_f} = \alpha M_{cf}^{\beta}$

Application for the long term sediments collected from four urban transportation sites. Total metal mass $M_{e_f}$ for each investigated metal was summarized in the graph (based on 1000-g dry solid mass).
Table 3.2  Adjusted factors for the predicative metal mass model $Me_{cf} = \alpha M_{cf}^\beta$ for non-colloidal sediments collected out of eight individual storm events in Baton Rouge, Louisiana. (SS – residual error; $r^2$ – coefficient of determinant)

<table>
<thead>
<tr>
<th>Storm Date</th>
<th>Cr</th>
<th></th>
<th>Cu</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$</td>
<td>$\beta$</td>
<td>$r^2$</td>
<td>SS</td>
</tr>
<tr>
<td>02/05/2002</td>
<td>1.000</td>
<td>0.940</td>
<td>0.991</td>
<td>0.016</td>
</tr>
<tr>
<td>03/01/2002</td>
<td>1.003</td>
<td>1.154</td>
<td>0.999</td>
<td>0.002</td>
</tr>
<tr>
<td>03/09/2002</td>
<td>1.125</td>
<td>0.944</td>
<td>0.982</td>
<td>0.033</td>
</tr>
<tr>
<td>03/11/2002</td>
<td>1.007</td>
<td>1.060</td>
<td>0.999</td>
<td>0.002</td>
</tr>
<tr>
<td>03/20/2002</td>
<td>1.004</td>
<td>1.094</td>
<td>0.999</td>
<td>0.002</td>
</tr>
<tr>
<td>05/13/2002</td>
<td>1.027</td>
<td>1.286</td>
<td>0.997</td>
<td>0.006</td>
</tr>
<tr>
<td>06/19/2002</td>
<td>1.013</td>
<td>1.165</td>
<td>0.998</td>
<td>0.005</td>
</tr>
<tr>
<td>10/27/2002</td>
<td>1.014</td>
<td>1.435</td>
<td>0.992</td>
<td>0.016</td>
</tr>
<tr>
<td>Mean</td>
<td>1.024</td>
<td>1.135</td>
<td>0.995</td>
<td>0.010</td>
</tr>
<tr>
<td>Std.Dev</td>
<td>0.042</td>
<td>0.167</td>
<td>0.006</td>
<td>0.011</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Storm Date</th>
<th>As</th>
<th></th>
<th>Cd</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$</td>
<td>$\beta$</td>
<td>$r^2$</td>
<td>SS</td>
</tr>
<tr>
<td>02/05/2002</td>
<td>0.991</td>
<td>1.025</td>
<td>0.994</td>
<td>0.010</td>
</tr>
<tr>
<td>03/01/2002</td>
<td>1.001</td>
<td>1.138</td>
<td>0.999</td>
<td>0.002</td>
</tr>
<tr>
<td>03/09/2002</td>
<td>1.118</td>
<td>0.841</td>
<td>0.983</td>
<td>0.030</td>
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<td>03/11/2002</td>
<td>1.001</td>
<td>1.107</td>
<td>0.998</td>
<td>0.003</td>
</tr>
<tr>
<td>03/20/2002</td>
<td>0.998</td>
<td>1.109</td>
<td>0.999</td>
<td>0.003</td>
</tr>
<tr>
<td>05/13/2002</td>
<td>1.004</td>
<td>1.140</td>
<td>0.998</td>
<td>0.004</td>
</tr>
<tr>
<td>06/19/2002</td>
<td>1.007</td>
<td>1.017</td>
<td>0.998</td>
<td>0.005</td>
</tr>
<tr>
<td>10/27/2002</td>
<td>0.993</td>
<td>1.592</td>
<td>0.995</td>
<td>0.010</td>
</tr>
<tr>
<td>Mean</td>
<td>1.014</td>
<td>1.121</td>
<td>0.995</td>
<td>0.008</td>
</tr>
<tr>
<td>Std.Dev</td>
<td>0.042</td>
<td>0.214</td>
<td>0.005</td>
<td>0.009</td>
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</table>

<table>
<thead>
<tr>
<th>Storm Date</th>
<th>Pb</th>
<th></th>
<th>Zn</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$</td>
<td>$\beta$</td>
<td>$r^2$</td>
<td>SS</td>
</tr>
<tr>
<td>02/05/2002</td>
<td>1.002</td>
<td>1.475</td>
<td>0.994</td>
<td>0.011</td>
</tr>
<tr>
<td>03/01/2002</td>
<td>1.005</td>
<td>1.373</td>
<td>0.999</td>
<td>0.003</td>
</tr>
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<td>1.142</td>
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</tr>
<tr>
<td>03/11/2002</td>
<td>1.001</td>
<td>1.441</td>
<td>0.998</td>
<td>0.005</td>
</tr>
<tr>
<td>03/20/2002</td>
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<td>1.654</td>
<td>1.000</td>
<td>0.001</td>
</tr>
<tr>
<td>05/13/2002</td>
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<td>2.138</td>
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<td>0.009</td>
</tr>
<tr>
<td>06/19/2002</td>
<td>1.012</td>
<td>1.245</td>
<td>0.998</td>
<td>0.006</td>
</tr>
<tr>
<td>10/27/2002</td>
<td>1.021</td>
<td>1.495</td>
<td>0.987</td>
<td>0.026</td>
</tr>
<tr>
<td>Mean</td>
<td>1.027</td>
<td>1.495</td>
<td>0.994</td>
<td>0.013</td>
</tr>
<tr>
<td>Std.Dev</td>
<td>0.045</td>
<td>0.303</td>
<td>0.007</td>
<td>0.014</td>
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</table>
Table 3.3  Adjusted factors for the predicative metal mass model $M_{ef} = \alpha M_{cf}^\beta$ for long-term (seasonal length) accumulated non-colloidal sediments from four urban stormwater catchments

<table>
<thead>
<tr>
<th>Site</th>
<th>Cr</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$</td>
<td>$\beta$</td>
</tr>
<tr>
<td>N.O.</td>
<td>0.963</td>
<td>0.792</td>
</tr>
<tr>
<td>B.R.</td>
<td>1.012</td>
<td>0.905</td>
</tr>
<tr>
<td>L.R.-1</td>
<td>1.004</td>
<td>1.153</td>
</tr>
<tr>
<td>L.R.-2</td>
<td>1.007</td>
<td>0.606</td>
</tr>
</tbody>
</table>

Table 3.4 Residual errors of power law model $M_{ef} = \alpha M_{cf}^\beta$ in the prediction of metal mass for incremental sediments collected out of eight individual storm events, the average $\alpha$ and $\beta$ value from eight storm events were employed in the model application.

<table>
<thead>
<tr>
<th>Storm Date</th>
<th>Cr</th>
<th>Cu</th>
<th>As</th>
<th>Cd</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>02/05/2002</td>
<td>0.038</td>
<td>0.038</td>
<td>0.015</td>
<td>0.027</td>
<td>0.014</td>
<td>0.018</td>
</tr>
<tr>
<td>03/01/2002</td>
<td>0.005</td>
<td>0.011</td>
<td>0.004</td>
<td>0.004</td>
<td>0.008</td>
<td>0.003</td>
</tr>
<tr>
<td>03/09/2002</td>
<td>0.187</td>
<td>0.397</td>
<td>0.301</td>
<td>0.275</td>
<td>0.273</td>
<td>0.344</td>
</tr>
<tr>
<td>03/11/2002</td>
<td>0.005</td>
<td>0.022</td>
<td>0.004</td>
<td>0.011</td>
<td>0.007</td>
<td>0.005</td>
</tr>
<tr>
<td>03/20/2002</td>
<td>0.004</td>
<td>0.016</td>
<td>0.004</td>
<td>0.021</td>
<td>0.016</td>
<td>0.070</td>
</tr>
<tr>
<td>05/13/2002</td>
<td>0.020</td>
<td>0.004</td>
<td>0.005</td>
<td>0.020</td>
<td>0.130</td>
<td>0.004</td>
</tr>
<tr>
<td>06/19/2002</td>
<td>0.007</td>
<td>0.007</td>
<td>0.012</td>
<td>0.018</td>
<td>0.027</td>
<td>0.013</td>
</tr>
<tr>
<td>10/27/2002</td>
<td>0.068</td>
<td>0.101</td>
<td>0.135</td>
<td>0.040</td>
<td>0.025</td>
<td>0.038</td>
</tr>
<tr>
<td>Mean</td>
<td>0.042</td>
<td>0.075</td>
<td>0.060</td>
<td>0.052</td>
<td>0.062</td>
<td>0.062</td>
</tr>
<tr>
<td>Std.Dev</td>
<td>0.06</td>
<td>0.13</td>
<td>0.11</td>
<td>0.09</td>
<td>0.09</td>
<td>0.12</td>
</tr>
</tbody>
</table>
Cumulative Effects in Sediments Transported by Urban Rainfall-runoff

In Figure 3.11, metal concentrations between event-based and cumulative sediment as a function of particle gradation were compared. No significant difference was found for the metal concentration in the sediments with gradation less than 2000-µm. Table 3.5 and Table 3.6 compared total metal mass and fine fraction between event-based sediment and cumulative seasonal sediments. Total metals associated with fine fraction (<75-µm) was less in cumulative sediments than those in event-based sediments. A decrease in total metal mass was observed in the cumulative sediment for all analyzed metals except for Cr. This decrease may due to the release to the dissolved phase and natural attenuation.

Table 3.5  Comparison of metal mass between event-based and cumulative seasonal solids (entire gradation) for Baton Rouge site

<table>
<thead>
<tr>
<th>Metal mass (mg/kg)</th>
<th>Cr</th>
<th>Cu</th>
<th>As</th>
<th>Cd</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPA limit for soil* (mg/kg)</td>
<td>1200</td>
<td>1500</td>
<td>41</td>
<td>39</td>
<td>300</td>
<td>2800</td>
</tr>
<tr>
<td>Mean Event based solids</td>
<td>25.53</td>
<td>99.84</td>
<td>8.75</td>
<td>2.63</td>
<td>125.77</td>
<td>717.95</td>
</tr>
<tr>
<td>Std. Dev Event based solids</td>
<td>8.09</td>
<td>35.77</td>
<td>2.55</td>
<td>0.70</td>
<td>36.01</td>
<td>222.81</td>
</tr>
<tr>
<td>Cumulative solids</td>
<td>53.34</td>
<td>66.54</td>
<td>8.09</td>
<td>1.50</td>
<td>104.71</td>
<td>543.47</td>
</tr>
</tbody>
</table>

Table 3.6  Comparison of metal fraction for fine gradation (< 75-µm) between event-based and cumulative sediment from Baton Rouge site

<table>
<thead>
<tr>
<th>Fine gradation metal fraction %</th>
<th>Cr</th>
<th>Cu</th>
<th>Zn</th>
<th>As</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Event-based</td>
<td>18.17</td>
<td>25.79</td>
<td>20.31</td>
<td>25.70</td>
<td>24.90</td>
<td>22.28</td>
</tr>
<tr>
<td>Cumulative</td>
<td>3.96</td>
<td>12.77</td>
<td>6.81</td>
<td>13.65</td>
<td>7.61</td>
<td>9.26</td>
</tr>
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</table>
Figure 3.11  Comparison of metal concentration in event-based and cumulative sediments from Baton Rouge site
CONCLUSIONS

Metal elements Cr, Cu, Zn, As, Cd and Pb in urban rainfall-runoff are primarily associated with particulates though As and Cd also have a strong affinity with the dissolved fraction. By settling out the settleable fraction, a large reduction in total metal concentration can be achieved for Cr, Cu, Zn, and Pb. However, removal of settleable fraction does not translate to large overall reduction in total concentration for As and Cd because of their relative high dissolved fraction. An increasing metal concentration was found with decreasing size in the cumulative seasonal sediments. However, majority of metal mass was associated with medium to coarse (75 – 2000 µm) materials. Metal contaminants and pollution can be controlled through separation of majority mass of particulate matter from the stormwater suspension. A predicative methodology to estimate metal mass was proved to be effective. Metal mass for a characterized site can be predicted using a power law model through granulometric-based particle gradation.

A decrease in total metal mass was observed for the cumulative sediments compared to event-based sediments, which may due to the release of metals to the dissolved phase and natural attenuation.

IMPLICATIONS FOR BEST MANAGEMENT PRACTICES

The predicative granulometric-metal model developed was based on the statistic measurements between particle granulometric characteristics and metal mass. Assuming this relationship is site-specific or region-specific, the application of model in predicting metal mass in lieu of expensive metal analyses will be possible. For a given amount of materials recovered from an urban pavement area or industry watershed by sweeping, instead of going through the tedious metal analyses again, a simple and quick mechanical
sieve analysis is applied to determine the granulometric mass distribution. From the predicative model, the metal fraction which can be removed corresponding to a certain mass removal can be estimated. Any further best management practices will be carried out based on the predicted removal. If the particle mass is dominant in finer materials, traditional treatment through gravity sedimentation may not be effective. In addition, metals associated with dissolved and colloidal fraction can not be removed through sedimentation of non-colloidal particles. Alternative technologies such as coagulation and flocculation need to be evaluated.

REFERENCES


**NOMENCLATURE**

\( Me \) total metal mass (g)

\( m_i \) dry mass of particulate matter solids having particle diameter \( i \) (g)

\( c_i \) concentration of particulate-bound heavy metal for particle diameter \( i \) (µg/g).

\( N \) cumulative PND (counts/L³)

\( \alpha_d \) best fit parameter for cumulative particle number density (counts/L³)

\( d_p \) particle diameter (µm)

\( \beta_d \) power law exponent based on particle number density (dimensionless)

\( A \) surface area of an individual particle with diameter \( d_p \) (µm²)

\( \beta_A \) power law exponent based on particle surface area (dimensionless)

\( Me_{cf} \) normalized cumulative metal mass

\( M_{cf} \) normalized cumulative solid particle mass

\( a, b \) adjusted factors for the cumulative surface area predicative model

\( \alpha, \beta \) parameters for the power law predicative model
CHAPTER 4. MORPHOLOGY, COMPOSITION AND FRACTAL CHARACTERISTICS OF NON-COLLOIDAL PARTICULATE SUBSTRATES TRANSPORTED BY URBAN RAINFALL-RUNOFF

SUMMARY

While traditional indices such as suspended and settleable solids developed from wastewater practices have value for storm water, such indices cannot characterize the heterogeneous nature of storm water particulates. Particulate matter generated from anthropogenic environments and activities is a constituent of environmental concern as well as a carrier substrate for reactive constituents. Partitioning, transport and transformation of particulate-bound contaminants are determined by the physical and geochemical properties of particulate carriers. In this study, the image-based instrumental analyses, including scanning electron microscopy (SEM), light microscopy and X-ray microanalyses were employed to study the morphology and composition of particulates in urban runoff. Fractal geometry was introduced to describe the irregularity of the particles. One, two and three dimensional fractal dimensions were used to quantify the morphology of a particulate population. The amphoteric behavior of particulates was examined through granulometric-based surface charge measurement. Point of zero charge (PZC) shifted to lower pH with decreasing particle size, suggesting the affinity of clay minerals with smaller particulate substrate. Energy dispersive spectroscopy (EDS) identified the clay-covered outer layer of aggregates in urban rainfall-runoff, indicating a greater fractal nature and an increased capacity as a substrate for reactive constituents.

INTRODUCTION

Increased urbanization has altered natural landscape dramatically. With the original vegetative cover of land surface removed, soil particles are exposed to anthropogenic
activities and easily carried away by the rainfall-runoff. These particulate substrate and associated inorganic and organic contaminants are mobilized by urban rainfall-runoff and are potentially a source of impairment to receiving waters. Partitioning, transport and transformation of particulate-bound contaminants are determined by their physical and geochemical properties. For instance, particle settling is related not only to particle size but also to the geometry of the particulates. Morphology is important to frequency and efficiency of particle collision. In addition, mineral content and chemical composition of these particulates is useful to examine behaviors such as partitioning and repartitioning of reactive constituents such as aqueous metals.

Scanning electron microscopy (SEM) has been broadly used to characterize the mineralogy, chemical composition and particle concentration of environmental colloids (Seaman 1997; 2000) and particles (Ryan 1998). In present study, a combination of scanning electron microscopy (SEM) and X-ray microanalysis was introduced to study the morphology and geochemical composition of particulate matter transported in urban rainfall-runoff.

Previous research has demonstrated that particle aggregates generated in the processes of water and wastewater treatment possess fractal structures (Li and Ganczarczyk 1989). The fractal geometry has been used to describe the morphology of the highly irregular objects (Logan and Kilps 1995). In Euclidean geometry, points are in zero dimension; lines and curves are described in one dimension; plane figures like squares and circles relate to two dimensions, and solids such as cubes and spheres can be characterized three dimensionally. Unlike the classical Euclidean geometry which works with objects of integer dimensions, fractal geometry describes objects in non-integer
dimensions. If the linear size of an object in Euclidean dimension is reduced by 1/r in each spatial direction, its measure (length, area, or volume) would increase to N times the original (\( N = r^D \)). Fractal dimension \( D \) is mathematically defined as,

\[
D = \log(N) / \log(r)
\]

\( D \) can be a fraction. This geometry is illustrated in Figure 4.1 coupled with Euclidean geometry. Fractal object is self-similar (Mandelbrot 1975), which means the subsets of the fractal object are geometrically similar to the whole object. The Euclidean object has one-dimensional fractal dimension \( D_1 \) of 1, two-dimensional \( D_2 \) fractal of 2, and three-dimensional fractal dimension \( D_3 \) of 3. The deviation of calculated \( D_1, D_2 \) and \( D_3 \) from the Euclidean dimension indicates the fractal nature of the object. \( D_1 > 1 \) indicates that with increase of object size, the perimeter increases more rapidly than for Euclidean objects (De Boer and Stone 1999). \( D_2 \) is less than 2 for the particles in natural system. As \( D_2 \) decreases, the aggregate become less compact and more amorphous.

There is no general applicable empirical method of determining fractal dimensions for the natural fractals. Due to the limited accuracy of measurement and rounding errors at small scales, results do not always behave as for mathematical fractals (Stoyan 1994). The structures investigated under the high accuracy of measurement are digitized and thus simplified for small inter-pixel distances through approximation. It is significant to define the boundary of the object in terms of the digital raster and to measure its length with sufficient precision.

Fractal structure can be created when small compact particles coagulate into large porous aggregates (Li and Logan 1997). The particulates formed have a heterogeneous mass distribution. Particle properties such as density and settling velocity are a function
of the fractal dimension (Logan and Kilps 1995). In engineering application, a nonlinear relationship is used to characterize heterogeneously packed objects with irregular boundaries, where the property of the object scale with a characteristic length dimension raised to a power is defined as fractal dimension (Chakraborti et al. 2000).

<table>
<thead>
<tr>
<th>$r = 3$</th>
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<tbody>
<tr>
<td>$P = Np_0 = 3p_0$</td>
<td>$P = Np_0 = 4p_0$</td>
</tr>
<tr>
<td>$D_1 = \log(3)/\log(3) = 1$</td>
<td>$D_1 = \log(4)/\log(3) = 1.26$</td>
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<tr>
<td>$A = N^2A_0 = 3^2A_0$</td>
<td>$A = 3A_0$</td>
</tr>
<tr>
<td>$D_2 = \log(3)^2/\log(3) = 2$</td>
<td>$D_2 = \log(3)/\log(2) = 1.585$</td>
</tr>
<tr>
<td>$V = NV_0 = 3^3V_0$</td>
<td>$V_0$</td>
</tr>
<tr>
<td>$D_3 = \log(3)^3/\log(3) = 3$</td>
<td></td>
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</table>

Figure 4.1 Illustration of Euclidean geometry and fractal geometry
The linear size of an object in Euclidean dimension is reduced by $1/r$ in each spatial direction, its measure (length, area, or volume) will increase to $N$ times the original. $N = r^D$ ($D = \log N / \log r$). In fractal geometry, $D$ could be a fraction.

When fractal dimension being used to describe the fractal nature of the aggregate, it corresponds to the degree of irregularity and complexity or the space-filling capacity of an aggregate (Li and Logan 1997). Fractal dimension has been studied for qualifying aggregate morphology (Meakin 1989) and examining the mechanism of composite particle formation and deposition (Wiesner 1999). While an extensive study has addressed the fractal dimension of particles in nature water systems (Li, Passow, and Logan 1998; Risovic and Martinis 1996; Jackson and Burd 1998; De Boer, Stone and Lévesque 2000; Woodfield and Bickert 2001), such studies are relatively scarce in wastewater and have never been reported for particles in storm water.
Mineralogy and geochemical composition of the particulate substrates is critical to study their hydrological transport and chemical transformation of associated contaminants. With oxygen and silicon two most abundant elements in the earth’s crust, the abundance of silicates is not surprising, even in the anthropogenic environment. The structures of these silicate tetrahedrons form single units, double units, chains, sheets, rings and framework. Phyllosilicate is one of the subclass of silicate with a sheet-like structure. The clay minerals are a part of a general but important group within the phyllosilicates that contain large percentages of water trapped between the silicate sheets. Individual clay minerals are rarely found separately and are usually mixed not only with other clays but also with crystals of carbonates, feldspars, micas and quartz. Clay minerals are divided into four major groups including kaolinite, montmorillonite, illite and chlorite. They have a great potential to interact with various contaminants such as heavy metals and pesticides due to their large surface area and high cationic exchange capacity (Garcia 1995). The abundance of clay minerals in a variety of geochemical environments and their influence on adsorption of contaminants suggests a need for the experimental work to characterize the adsorption, desorption, and oxidation of contaminants on clay minerals (Lin and Puls 2000).

Point of zero charge (PZC) reflects surface mineralogy and surface organic content of particles. By definition, PZC is the pH value of the solution at which there is no net charge on the particles (Sposito 1981). Positive charge is balanced with negative charge at point of zero charge. PZC can be determined through experimental measurement of surface charge. The presence of clay minerals will shift the PZC to lower pH value. In
urban rainfall-runoff, PZC is useful in coagulation, surface complexation and sorption studies.

**BACKGROUND ON SCANNING ELECTRON MICROSCOPY**

In scanning electron microscopy, an electron beam is scanned across a specimen’s surface. A variety of signals are generated and detection of specific signals produces an image or a specimen’s elemental composition (Goldstein et al. 1992). Electron-specimen interaction volume can be determined through calculation of the theoretical electron range \( r (\mu m) \) using Equation 2 (Goldstein et al. 1992). \( r \) is interpreted as the half sphere centered on the beam impact site.

\[
r = \frac{0.0276A_m \times E^{1.67}}{\rho \times Z^{0.89}}
\]

\( A_m \) is atomic mass in g/mole, \( E \) is accelerating voltage in keV, \( \rho \) is density in g/cm\(^3\), \( Z \) is atomic number. For instance, at the accelerating voltage of 20-keV, the electron range for calcite (\( \rho = 2.7 \text{ g/cm}^3 \)) is 6.595-\( \mu \text{m} \).

Three signals that provide the greatest amount of information in SEM are the secondary electrons, backscattered electrons, and X-rays. Secondary electrons are detected from a near-surface region of the interaction volume with low energy and are used to characterize particle morphology and surface topography. Backscattered electrons are produced when primary electrons are reflected from atoms in the specimen. They can be detected from the interaction volume and much deeper parts of the specimen. The images give the information on the distribution of different chemical phases in the specimen. Higher atomic number elements appear brighter than lower atomic number elements. Therefore, backscattered electron images (BEI) can be considered to reflect variations in density between the specimen components. The sampling volume for X-rays
is similar in size to the interaction volume because X-rays are less easily absorbed by the material. X-rays result from the incoming electrons knocking inner shell electrons out of atoms in the specimen. As outer electrons drop into the vacancy, they are obliged to dispose of excess energy, often as an X-ray photon. Since each element has its own unique set of energy levels, the emitted photons are indicative of the element that produced them. Analyzers are then used to characterize the X-ray photons for their energy or wavelength and abundance to determine the chemistry of specimen (Goldstein et al. 1992). In energy dispersive X-ray spectroscopy (EDS), the X-ray emissions are sorted electronically. The EDS coupled with a computer based multi-channel analyzer (MCA) provides the analytical facility. The spectrometer plots energies of X-rays against specific count for each specific energy, giving a compositional spectrum of the specimen. Characteristics of X-rays are denoted by K, L, M and N etc., indicating the destination of the electron that gave rise to X-ray photon. EDS provides rapid qualitative or quantitative (with adequate standards) analysis of elemental composition with a sampling depth of 1-2 µm.

OBJECTIVES

There were three objectives in this research. The first objective was to study the morphology of particulate matter in urban rainfall-runoff. The fractal nature of individual particles and particulate population would be qualified through an image-based fractal analysis. The second objective was to identify the primary mineral content and geochemical composition of the particulate substrate through their optical properties and energy X-ray dispersive spectrum. The final objective was to study the amphoteric nature of the particulates through experimental surface charge measurement.
MATERIALS AND METHODS

Sample Collection

Particulate matters transported by urban rainfall-runoff were collected from the sedimentation tank at an experimental transportation site located in Baton Rouge, Louisiana. The materials were recovered from the slurry of the bottom sediments. Concentrated sediments were brought back to the lab where the particulate matters were air-dried at 40 °C in a constant temperature and constant humidity room.

Sample Preparation

Completely air-dried samples were disaggregated and sieved (ASTM 1993). The set of sieves encompassed the range of 9.5-mm (No. 3/8) through 25-µm (No. 500). Particulate matters were separated into 18 size gradations. Dry materials separated on each stainless steel sieve were weighed and stored separately in glass sample bottles. A small amount of representative specimen from each size gradation was glued on 46 x 26 mm petrographic slides using a colloidal graphite isopropanol base for SEM analysis.

A thin section of sediment mixture was prepared for optical mineral identification, backscattered image analysis and EDS. To prepare thin section, sediments were embedded in epoxy resin. The block was allowed to harden and sectioned into 1-cm chips. Representative specimen chips were selected, polished and placed on a petrographic slide. The slide and the chip were placed in the thin section machine and trimmed down to 50-µm thick on the slide. The slide was finally placed on a wheel that finely abrades to 30-µm thick at which point light can successfully transmit through.

SEM analyses require materials to be electrically conductive. Non-conductive specimens of dry particulates need to be coated with conductive material gold (Au) or
carbon (C) before analyzing. A sputter coater coats the specimen with Au atoms and a carbon coater coats a thin film of carbon on the specimen. The entire coating process was conducted in a glass vacuum vessel. Carbon coated particulate is transparent to X-ray and was used for compositional EDS analysis.

**SEM Analyses**

Coated samples were analyzed using scanning electron microscope (SEM-JEOL 840A) at accelerating voltage 20-keV for a lifetime of 100s. Gold-coated samples were used for secondary electron image acquisition. Carbon-coated samples were used to analyze the chemical composition. Backscattered electron image were acquired only for specimens prepared in thin section and carbon-coated.

**Image Processing and Analyses**

Quantitative analyses were conducted for the images obtained from SEM (Image-Pro Plus). In order to identify and measure individual particles in the images, the first step is to distinguish them from the surrounding background. This includes segmentation of edges and adjustment of brightness and contrast. After calibration of units, the selected measurements (area, diameters and perimeter etc.) were conducted for the particles in each image. The particles attached on the border were excluded from the analysis. In backscattered electron image of thin section (as seen in Figure 4.2), a sharp boundary was defined in the original image. No processing was needed and measurements were carried out on the original images. For secondary electron images, individual particles were traced manually and all measurements were processed for the traced objects. An illustration of the original SEI image of storm water particulate and the traced object was seen in Figure 4.3. The selected measurements include maximum, mean and minimum
diameter, perimeter, area, roundness, and fractal dimension of the object outline. Maximum diameter measured the longest length of the two outline points and passing through the centroid. Mean diameter measured the average length of the diameters measured at two degree intervals joining two outline points and passing through the centroid. Minimum diameter was the shortest length of the two outline points and passing through the centroid. Area comprised of all pixels within the object perimeter. Roundness was determined by Equation 3.

\[ R = \frac{P^2}{4\pi A} \]  

where \( P \) is the perimeter of the particle, \( A \) is the area of the particle. The circular object has roundness of 1 and other shapes have roundness greater than 1.

**Determination of Fractal Dimensions**

The divider stepping method is a precise method for manual determination of fractal dimensions of planar curves (Stoyan 1994). In the Image pro software, the fractal dimension is defined as the slope of the linear part of the function that relates the log of the outline length to the log of the stride (or step) length, where the stride length is how long a ruler we attempt to lay along the perimeter of the object. Perimeters change with different size rulers, as the rulers bridge various small wriggles in the outline. For each stride length \( r_i \), \( l(r_i) = r_i N(r_i) \). For a fractal, it is expected that

\[ \log l(r) = \log c + (1 - D) \log r \]  

Fractal dimension \( D \) can be calculated as 1 minus the slope of the regression line obtained by plotting the log of the perimeter (using a particular stride) against the log of the stride length.
Figure 4.2  BEI (Backscattered electron image) of storm water particulates prepared in thin section. Degree of grayness indicates the density. Lighter objects have higher density. Calibration bar 100-µm (right) and 20-µm (left)

Figure 4.3  An example of traced individual particles based on their SEM image

Fractal dimensions for an aggregate can be experimentally determined using image analysis. One-, two- and three-dimensional fractal dimensions are expressed in Equation 5 through 7 (Logan and Kilps 1995).

\[ P \propto l^{D_1} \]  \hspace{1cm} (5)

\[ A \propto l^{D_2} \]  \hspace{1cm} (6)

\[ N \propto l^{D_3} \]  \hspace{1cm} (7)

\( l \) is the characteristic length which can be taken as the shortest, longest, geometric mean or equivalent radius based on area (Chakraborti et al. 2000). \( P \) is perimeter of the particle;
$A$ is the projected area; and $N$ is the number of particles. When three-dimension fractal dimension is less than 2, $D_3$ is equal to $D_2$ (Johnson, Li and Logan 1996).

One or two-dimensional fractal dimension ($D_1$ and $D_2$) for an aggregate can be obtained from the slopes of log-log plots of characteristic particle diameter against perimeter or projected area. By plotting measured particle characteristic diameter against perimeter or projected area on the logarithms scale, the slopes of the regression line correspond to $D_1$ and $D_2$ respectively. Similarly, $D_3$ can be developed from the log-log plot of particle number as a function of characteristic particulate diameter. The same method was applied to urban rainfall-runoff system and the derived fractal dimensions represent a statistical value for the population of particles in the system.

**Mineral Identification for Particulate Matter in Sediment**

Absolute identification of minerals requires X-ray analysis or a series of chemical tests. The mineral can also be identified reliably through their physical properties such as color, cleavage, fracture and twinning. Uncoated thin section samples were studied using microscopy (Olympus BH-2) under plane-polarized light to identify minerals in the particulates. Plane polarized light vibrates in a single plane. Most of the optical properties of minerals observed in thin-section depend on a plane polarized light source.

**Surface Charge Determination**

Surface charge can be determined through potentiometric titration, ion adsorption and zeta potential analysis (Marcomo-Martinez and McBride 1989). In current study, potentiometric titration (Van Raj and Peech 1972) was modified and used to determine the surface charge of particulate matter in the sediment across size gradations. A representative 0.5 to 1-g of dry sample was suspended in 50-ml of 0.01-M KCl, and the
pH was adjusted to a range between 6 and 9 with HCl or KOH. The suspensions and control (blank solution of 0.01-M KCl) were set on a reciprocating table at 22 - 23 °C in sealed airtight 50-ml centrifuge tube for 24 hours. The pH values of the supernatant were then recorded. The amount of H\(^+\) and OH\(^-\) adsorbed by the sediment samples were estimated from the amount of acid or base used to titrate the samples to their original pH, subtracted by the amount necessary to bring 50-ml blank solution to the same pH.

**RESULTS**

**Morphology of Particulate Matter in Urban Rainfall-Runoff**

Secondary electron images (SEI) were acquired for particulate samples from the storm catch basin at Baton Rouge site. Figure 4.4 showed the SEI images for various gradations of particulates. Closer views for several individual particles were showed in Figure 4.5. As seen in these SEI images, particles in urban rainfall-runoff possess fractal structure. Clay-size particles are seen attached on the surface of large aggregates. Some particle displayed a plate-like morphology, and some particle exhibited shape of a bar. The high specific surface of fractal aggregates facilitates their active participation in chemical reactions (Emets et al 1994).

A fractal dimension (D\(_f\)) was obtained using divider stepping method for each traced particles from SEI and particles in BEI. Figure 4.6 showed the fractal dimension distributions for analyzing two sources of images for the same group of particles. The range of fractal dimension developed from SEI image analyses is from 1.0188 to 1.1299. Meanwhile, the fractal dimensions obtained from BEI image analyses range from 1.0309 to 1.1298. Distributions indicate similar results from SEI and BEI image analyses. The fractal dimensions indicated a slight fractal nature of these particulates.
The empirical slope method was applied to characterize the fractal particles in the system. A total of 1732 particles in the BEI ranging from 4-μm to 600-μm were used to calculate fractal dimensions of $D_1 = 1.031$ and $D_2 = 1.999$. Fractal dimensions $D_1 = 1.015$ and $D_2 = 1.926$ were calculated for a subset of 1261 particulates with diameter less than 75-μm. The values of $D_2$ are in good agreement with $D_2$ values (1.92) reported for inorganic aggregates clay-iron (Jiang and Logan 1991). For particles ranging from 75 to 600-μm, $D_1 = 1.022$ and $D_2 = 1.967$ were developed from 471 particles. Figure 4.7 showed the fractal dimensions developed from BEI. 95% predicted interval was shown as the dashed line in each plot.

![Secondary electron images (SEI) of the particulates from various gradations in urban rainfall-runoff (calibration bar 10, 20, 50 and 100-μm)](image-url)

Figure 4.4  Secondary electron images (SEI) of the particulates from various gradations in urban rainfall-runoff (calibration bar 10, 20, 50 and 100-μm)
Figure 4.5  Typical particulate morphology from SEI (calibration bar 20-µm)
Figure 4.6 Fractal dimension distribution (D1) obtained from SEI image and BEI image respectively for particles in urban rainfall-runoff

From SEI images of a subtotal 407 particulates less than 75-µm, fractal dimensions were calculated as $D_1 = 0.997$ and $D_2 = 1.943$. The fractal dimensions of 1.029(D1) and 1.961(D2) were obtained from the analyses of a subset of 396 particles ranging from 75-µm to 500-µm. Based on the image analyses for a total of 803 particulates in the urban rainfall-runoff, $D_1 = 0.983$ and $D_2 = 1.970$ were obtained from log-log plots of diameter against perimeter or projected area. The fractal dimensions, regression coefficients and predicted region from SEI image analyses were presented in Figure 4.8.

Though the developed fractal dimensions from neither BEI nor SEI showed a significant deviation from the values in Euclidean geometry, the two-dimensional fractal dimensions obtained from both sediment mixture and particles across gradations showed that fine particulate matter (less than 75-µm) population had a lower $D_2$ value than that of medium to coarse particles (greater than 75-µm), suggesting more fractal of smaller size particles in general. Reorganization of deposits due to breakage, re-deposition or deformation tends to make sediment particulate more compact (Wiesner 1999).
Aggregates formed from ballistic (straight-line) deposition of small particles tend to be more compact, fractal dimensions of which equal to Euclidean dimension (Wiesner 1999). Aggregates formed from diffusive deposition lead to more porous structure with smaller fractal dimensions and lower aggregate densities (Meakin 1988).

Figure 4.7 Fractal dimensions ($D_1$ and $D_2$) developed from BEI
Figure 4.8 Fractal dimension developed by SEI (fine particles) and optical images (larger particles)

N is the number of particles analyzed; $r^2$ is the regression coefficient; $D_1$ is one dimensional fractal dimension and $D_2$ is two-dimensional fractal dimension. $D_1$ and $D_2$ obtained from the slope of the regression line represent the statistical fractal dimension for the entire population. 95% predicted region was shown as the blue dashed line.

(a) and (b) are for fine particulates (<75-µm); (c) and (d) are for medium to coarse particles (75-µm to 600-µm); (e) and (f) are for the entire gradation analyzed.
**Mineral Identification**

Figure 4.9 showed a few typical minerals in the particulates transported by urban rainfall-runoff. They are identified as quartz, calcite, feldspar and biotite. One of the phenomena observed in the images was that the color of the minerals presented varied from the pure substance because of the impurities associated with them.

![Mineral Identification Images]

Figure 4.9 Mineral identification for the particulate matter in urban storm runoff
(a) quartz (b) feldspar (c) calcite (d) biotite

**Chemical Composition of Particulate Matter**

Figure 4.10 showed a wide view of backscattered electron image (BEI) for thin section sample. Brighter objects have higher density. Spot and scanning X-ray analysis of samples provides information about chemical composition in the specific area on the sample. A few typical energy dispersive spectrums (EDS) representing the chemical
composition in the specified area on BEI were included in Figure 4.11. EDS was displayed as a histogram, with the horizontal axis labeled in energy units and the vertical axis in numbers of counts.

A large amount of characteristic peaks were identified for element O, Al, Si and Ca. Some other frequently seen elements included Na, Mg, K and Fe. Unless specified, all the peaks were $K\alpha$ peak. The roughness of the overall spectrum represents channel-to-channel statistical fluctuations. EDS provides information to identify the class of these particulates in the sediments qualitatively. Some of the identified mineral classes were also listed in Figure 4.11.

Figure 4.10  Backscattered electron image for the thin section of the sediment mixture. Numbers in the plot indicate the identified object using EDS. The corresponding energy dispersive spectrums were shown in Figure 4.11
Figure 4.11 Energy dispersive spectrum for the specific particles in BEI corresponding to particles labeled in Figure 4. 10
Surface Charge and PZC

Surface charge is the most important factor either for dissolved or particulate matter adsorption. Potentiometric titration curves describe net adsorption and desorption of $\text{H}^+$ as a function of pH. The potentiometric titration curves for particulate in storm runoff sediments across size gradation were shown in Figure 4.12. Surface charge of particulates decreases with the increase of pH value across all size gradations. Point of zero charge (PZC) of the particles was determined and plotted in Figure 4.13. PZC ranged from 7 to 9. Storm water pH values are typically in the range of 6 to 8, which is above the point of zero charge (PZC). Therefore, particulates in the system are generally negatively charged. PZC is also a function of particle size. As shown in Figure 4.13, PZC of particles shifted to lower pH value with decrease of particle diameter suggesting the affinity of clay minerals with smaller particles. The fine fraction particulate matter therefore has a great potential to entrain heavy metal pollutions. This observation agrees with the study that high concentration of heavy metal associated with fine particulate matter in urban storm runoff.

CONCLUSIONS

Images obtained from scanning electron microscope illustrated the fractal nature of the particles in urban rainfall-runoff. The characteristic morphology includes layered-structure, clay-size particulate aggregation and relative smooth grain surface. Results from image based fractal analyses showed fine particle populations were slightly fractal than the medium to coarse materials though neither fractal dimensions showed a significant difference from Euclidean structure. $D_2$ developed from SEI images was 1.943 for fine particles (less than 75-$\mu$m) and 1.961 for medium to coarse particles (75-$\mu$m to
600-µm). Similarly in the analysis of BEI, D₂ for fine particulates was 1.926 and 1.967 for medium to coarse particles. The fractal characteristic facilitates the entrainment of contaminants. Removal of fine fractions is important because their high potential as a reservoir for contaminants. Although Euclidean geometry is still applicable to the primary particles in urban rainfall-runoff, aggregates formed during sedimentation or coagulation/flocculation are expected to be more fractal and the effect of the fractal characteristics are to be more significant in urban rainfall-runoff system. Fractal characteristics of these aggregates need to be studied further to provide information in designing unit operation.

Several common minerals identified in the particulate matter include quartz, calcite, feldspar and biotite. Particles in urban rainfall-runoff have negative surface charges. PZC of particles shifted to lower pH value with decreasing particle size, suggesting the affinity of clay minerals to smaller size particulates.

Two issues arisen from this study are to seek alternative technology to improve removal efficiency of fine particulates in storm water treatment system and study on the stabilization of residual sediments from treatment system.

REFERENCES


Figure 4.12  Surface charge for different gradations of particulate matter in urban rainfall-runoff

Figure 4.13  Point of zero charge as a function of particle size for the storm water particulates


NOMENCLATURE

\[ A_m \] Atomic mass (g/mole)

\[ E \] Accelerating voltage (keV)

\[ \rho \] Density (g/cm³)

\[ Z \] Atomic number

\[ l \] Characteristic length (µm)

\[ P \] Perimeter of the particle (µm)

\[ A \] Projected area (µm²)

\[ N \] Number of particles in the aggregate

\[ D_1 \] One-dimensional fractal dimension
<table>
<thead>
<tr>
<th>$D_2$</th>
<th>Two-dimensional fractal dimension</th>
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<tr>
<td>$D_3$</td>
<td>Three-dimensional fractal dimension</td>
</tr>
</tbody>
</table>
CHAPTER 5. SEDIMENTATION OF NON-COLLOIDAL PARTICULATE MATTER TRANSPORTED BY URBAN RAINFALL-RUNOFF

SUMMARY

Settling velocity is a fundamental parameter of non-colloidal storm water particulates. Determination of settling velocity is critical when designing or analyzing unit operations, in-situ controls or watershed controls for urban rainfall-runoff. A synthesis of settling velocity methodologies with applicability to characteristics of urban storm water particulate matter is presented. Utilizing two common settling devices, a settling column and an Imhoff cone, settling velocities of discrete non-colloidal particles in storm water were quantified. Theoretical settling velocity calculations are compared to measured results across the gradation of particles from 1 up to 2,000 µm. Results indicate Newton’s Law can be used to model the discrete settling of non-colloidal granular particles between 10 and 850-µm reasonably well. The difference between measured velocities using Imhoff cone and the results from settling column is less than 15%. In settling column tests for particles in the range of 1.25 to 200-µm, a linear decrease in particle mean size was observed with time during the settling process. Smaller particles (<10-µm) settle faster than predicted using Newton’s Law assuming Euclidean object. Results showed over 90% of non-colloidal particles in grit chamber and approximately 50% of the non-colloidal particles in sedimentation basin can be removed by gravitational settling in terms of volume concentration.

SETTLING VELOCITY – A REVIEW OF THE LITERATURE

The settling velocity of non-colloidal particles is one of the most important parameters in the description of the transport of particulate matter in storm water control systems. Determination of settling velocity is critical when designing or analyzing unit operations, in-situ controls or
watershed controls for storm water. The importance of particle settling velocities in the calculation of sediment fluxes, particle residence times, and aggregation rates has led to numerous attempts to predict settling velocity as a function of particle size, shape, and density (Hawley 1982).

Non-colloidal particles in storm water could be non-cohesive or cohesive. Non-cohesive materials are described as coarse-grained materials composed of particles greater than 62-µm (Simon, in press). Particle interaction between non-cohesive particles is solely mechanical and is restricted to momentum exchanges occurring from fluid drag, random collisions, and the interlocking support from adjacent grains. Cohesive materials are those particles finer than 2-µm in the fine silt and clay size range related to the existence of electro-chemical bonds between individual particles. The small mass of particles relative to the large specific surface area provides a net negative electrical-surface charge on the particle that is responsible for the electro-chemical forces and bonding between particles (Simon, in press).

The settling velocity of non-cohesive particles in a low concentration suspension can be calculated using Newton’s Law, in which only forces of gravitational and flow resistance of the particles are considered. When the particle concentration is high, particles interact with each other and the settling velocity becomes a function of the volumetric concentration of the particles in suspension (Burt 1986). Cohesive properties of the suspended particles result in the formation of flocs whose settling behavior cannot be predicted using Stokes’ Law (Kranck 1986). Brownian motion, local shear and differential settling are as significant as gravitational forces for such cohesive flocs. Brownian motion for cohesive particles becomes important when concentration exceed approximately 10 g/L (Kranck 1986). The cohesive particles collide with each other and form aggregates or flocs. The macroflocs demonstrate a size range of 20-µm up to
640-µm (Manning 1999). The size of a floc depends on the particle collision frequency and the strength of the cohesive forces. The floc forms are complex function of particle mineralogy and the electro-chemical nature of the suspending medium. For example, in suspension with a very low ionic strength, the double layer around these small cohesive particles is large and repulsive forces dominate, keeping the particles too far apart for attractive force to come into effect. As the ionic strength increases, the double layer is reduced in size smaller than about 1/3 of the particle radius size and the particles are brought close enough to overcome the repulsive forces and the attractive forces prevail. Particles aggregate on a time scale (Tawari and Koch 2002).

**Settling Velocity Fundamentals**

In Type-I sedimentation, each particle accelerates downward under the force of gravity until the opposing drag force rises to the same value, at which point the particle travels at a constant (terminal) velocity. The classic laws of sedimentation formed by Newton and Stokes can be used to analyze terminal settling velocity of discrete spherical particles (Tchobanoglous and Burton 1991).

Equating the gravitational force (gravity minus buoyancy) with the frictional drag force yield Newton’s law for terminal settling velocity, \( v_t \):

\[
v_t = \left[ \frac{4 \rho_s (\rho_s - \rho)d}{3 C_D \rho} \right]^{1/2}
\]

(1)

The drag coefficient \( C_D \) takes on different values depending on the flow regime surrounding the particle and the shape of particles. Fair, Geyer and Okun (1968) have developed \( C_D \) as a function of Reynold’s number (\( Re_d \)) using the following regression expression.

\[
C_D = \frac{24}{Re_d} + \frac{3}{\sqrt{Re_d}} + 0.34
\]

(2)

Expressions for \( v_t \) are depended on the flow regimes (Weber 1972).
Under laminar flow \((Re_d < 1)\), settling velocity can be described by Stokes’ Law.

\[
v_t = \frac{g}{18\mu} (\rho_s - \rho_L)d^2
\]

(3)

In transitional zone \((1 < Re_d < 1000)\),

\[
v_t = \left[2.32(\rho_s - \rho_L)d^{1.6} \rho_L^{-0.4} \mu^{-0.6}\right]^{0.714}
\]

(4)

Under turbulent flow \((Re_d > 1000)\),

\[
v_t = 1.82 \sqrt{\frac{(\rho_s - \rho_L)d\gamma}{\rho_L}}
\]

(5)

For the transitional regime an iterative procedure must be adopted to obtain the settling velocity. From Equation 1, an initial \(v_t\) needs to be assumed, \(Re_d\) is calculated and \(C_D\) determined. This \(C_D\) is substituted back in Equation 1 and \(v_t\) is recalculated. Iterations continue until \(v_t\) values converge.

Table 5.1 summarized a series of expressions of \(v_t\) for discrete natural non-cohesive particles in simplified formulations.

**Modified Settling Velocity Formulas**

**Cohesive settling model:** Lau and Krishnappan (1992)

Experiments on settling of cohesive sediments were carried out in turbulent flow in an annular flume using two sediments. One was a kaolinite clay with a mean diameter of about 6.8-\(\mu m\). The other was natural river sediment containing a combination of kaolinite and mortmorillonite with a mean diameter of approximately 12-\(\mu m\). Data on concentration and size distribution of dispersed samples were used to calculate the effective settling velocities for different size fractions.
Table 5.1 Summary a series of expressions for $v_t$ of discrete natural non-cohesive particles

<table>
<thead>
<tr>
<th>Expressions for Settling Velocity</th>
<th>Notes</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_t = \left[ \frac{4 g (\rho - \rho_s) d}{3 C_D \rho} \right]^{1/2}$</td>
<td>$C_D = \frac{24}{Re_d} + \frac{3}{\sqrt{Re_d}} + 0.34$</td>
<td>Newton’s Law</td>
</tr>
<tr>
<td>$\ln(v_t) = -54.6322 + 40.4532 \ln(-\ln d) - 0.3367 \ln(\ln S_g) + 8.2637 \ln(-\ln v) - 12.5788 \ln(-\ln d)^2 + 0.6165 \ln(-\ln d) \ln(\ln S_g)$</td>
<td>$S_g = 1.001 \sim 2.65$</td>
<td>Bhargava and Pajagopal (1992)</td>
</tr>
<tr>
<td>$v_t = \frac{1}{24} \frac{(S_g - 1) g d^2}{v}$</td>
<td>(a) $v_t = 1.4 \sqrt{(S_g - 1) g d}$</td>
<td>(b) $d &lt; 0.01 \text{ cm}$</td>
</tr>
<tr>
<td>(c) $d &gt; 0.2 \text{ cm}$</td>
<td>(c) $0.01 &lt; d &lt; 0.2 \text{ cm}$</td>
<td></td>
</tr>
<tr>
<td>$v_t = 67.6 (S_g - 1) d + 0.52 (S_g - 1)(\frac{T}{26} - 1)$</td>
<td>(b) $v_t = 1.068 \sqrt{(S_g - 1) g d}$</td>
<td>(c) $d &lt; 0.15 \text{ cm}$</td>
</tr>
<tr>
<td>$v_t = \frac{10 \nu}{d} (\sqrt{1 + 0.01 (d^*)^3} - 1)$</td>
<td>(c) $0.01 &lt; d &lt; 0.1 \text{ cm}$</td>
<td></td>
</tr>
<tr>
<td>$v_t = \sqrt{\frac{-24 \cos^3 \alpha + \sqrt{576 \cos^6 \alpha + (18 \cos^3 \alpha + 3.6 \sin^2 \alpha) (d^*)^3}}{9 \cos^3 \alpha + 1.8 \sin^2 \alpha}}$</td>
<td>$\alpha = 0$ for $d^* \leq 1$</td>
<td>Zhu and Cheng (1993)</td>
</tr>
<tr>
<td>$\alpha = \frac{\pi}{2 + 2.5 (\log d^<em>)^3}$ for $d^</em> &gt; 1$.</td>
<td>$D_n = \left( \frac{6 \nu}{\pi} \right)^{1/3}$</td>
<td>Swamee and Ojha (1989)</td>
</tr>
<tr>
<td>$v_t = a \left[ \left(18 \nu^* \right)^{0.54} \right]^3 + \left[ \left(10^6 \nu^* \right)^{0.7} + 1.43 \times 10^6 \right]^{0.346} \right]^{-0.1}$</td>
<td>$Re_d \leq 1.5 \times 10^5$</td>
<td></td>
</tr>
</tbody>
</table>

$v_t$ = Terminal settling velocity of particle (m/s)
$\nu$ = Kinematic viscosity of the liquid (m$^2$/s)
$\mu$ = Dynamic viscosity of the liquid (N s/m$^2$)
$\rho$ = Density of fluid (kg/m$^3$)
$\rho_s$ = Density of particle (kg/m$^3$)
$d$ = Particle diameter (m)
$D_n$ = Nominal diameter
$C_D$ = Drag coefficient
$S_g$ = Specific gravity
$d^*$ = Dimensionless particle diameter
$\nu^*$ = Nondimensional kinematic viscosity
Size distribution was modeled from a numerical model assuming discrete particle settling. Using the initial size distribution and total concentration, the initial concentration of each size class was calculated. The model was then applied to each size class to obtain the change in concentration, resulting in a change in size distribution with time. The time rate of concentration change in the suspension can be written as

$$\frac{dC_i}{dt} = -\frac{v_i C_i}{h}$$  \hspace{1cm} (6)

For cohesive sediment, the settling velocity is not consistent during the settling process. An average settling velocity $\bar{v}_i$ for any discrete period of time was defined as

$$\bar{v}_i = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} v_i dt$$  \hspace{1cm} (7)

By integrating Equation 7, the average settling velocity over a given time period can be calculated from the concentration data as:

$$\bar{v}_i = \frac{h}{t_2 - t_1} \ln \frac{C(t_1)}{C(t_2)}$$  \hspace{1cm} (8)

An average effective settling velocity over the period of time $t$ can be expressed as (Lau 1994):

$$v_{avg} = \frac{h}{t} \ln \left[ \frac{C_0}{C(t)} \right]$$  \hspace{1cm} (9)

Temperature has a significant influence on the settling of cohesive sediments. According to Stoke’s Law, settling velocities increase with temperature. However, experimental results for a kaolinite clay and natural river sediments demonstrated that the settling velocity increased as temperature was lowered (Lau 1994). There is an increased deposition with large settling
velocities when temperature is lowered. This increased deposition is likely due to the effect of electrochemical forces on the properties of the flocs.

**Multiple grain size model:** Teeter (2001)

Enhanced settling occurs over a concentration range from a lower concentration limit $C_{ll}$ to an upper concentration limit $C_{ul}$. Below $C_{ll}$, particle collisions are too infrequent to promote aggregation. $C_{ll}$ is typically 50-300 mg/L depending on particle characteristics. At $C_{ul}$, collisions are so numerous that particles interact completely, resulting in the settling rates of all flocs to converge to one value. At concentration greater than $C_{ul}$, particle interactions become hindered settling. $C_{ul}$ has been found to be 1-10 kg/m$^3$ for estuarine sediments. Camp (1946) found the onset of concentration-hindered settling to be 1-5 kg/m$^3$ for turbid river water.

In the multiple grain size model the general form for grain size class settling velocity $v_s(gs)$ is:

$$v_s(gs) = v_{\text{max}} \left( \frac{C}{C_{ul}} \right)^{n(gs)}$$

where $v_{\text{max}}$ is a mass-weighted average maximum floc settling velocity for a size class and it can be calculated using Equation 11.

$$v_{\text{max}} = \frac{1}{C} \sum_{gs=1}^{NS} v_{\text{max}}(gs) C(gs)$$

$C$ is the total concentration for all grain size classes; $(gs)$ is the size class index ranging from 1 to the number of size classes (NS); $C_{ll}$ and $C_{ul}$ are mass-weighted average lower and upper concentrations. At $C \geq C_{ul}$, $v_s(gs)$ equals $v_{\text{max}}$ for all size classes. At $C \leq C_{ll}$, settling velocities are independent of concentration and equal to $v_s(gs)$ evaluated at $C_{ll}$. 

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The exponent \( n(\text{gs}) \) can be determined empirically using information from settling tests conducted over a range of concentrations. \( n(\text{gs}) \) has been determined to range below a value of about 1.33. Two empirical relations between median settling velocity and concentration were developed as follows.

Teeter (1993) \( v_{s50} = 1.13C^{4/3} \) (12)

Kranck and Milligan (1992) \( v_{s50} = 30.9C^{0.99} \) (13)

The difference in the exponent is attributed to differences in turbulence conditions.

A settling velocity function including the effects of both concentration and fluid shear rate \((G)\) has been proposed by Malcherek and Zielke (1996) and Teisson (1997) as:

\[
v_s' = v_s \left( \frac{1 + a_2 G}{1 + a_3 G^2} \right)
\] (14)

Based on experimental results, the following functional relationship is proposed to reflect the effects of concentration and shear rate on settling velocity:

\[
v_s(\text{gs}) = v_{\text{max}} \left( \frac{C}{C_{ul}} \right)^{n(\text{gs})} \left[ \left( \frac{1 + a_2 G}{1 + a_3 G^2} \right) \exp \left( -a_4 \frac{C}{C_{ll}} \right) + 1 \right]
\] (15)

\[C_{ll} \leq C \leq C_{ul}\]

\(a_2, a_3\) and \(a_4\) are constants. \(G\) is in the range of 0 to 40 Hz.

**Settling Velocity of Particles of Various Shapes**

Storm water particles are not generally spherical while Newton’s Law is commonly applied based on the assumption of spherical particles. Therefore, shape factors, distortion factors and fractal dimension have been introduced to the settling model.

**Shape factor**

The shape factor of a non-spherical particle \(\beta\) is expressed as (Swamee and Ojha 1989):
\[ \beta = \frac{z}{\sqrt{xy}}. \]  

(16)

in which \( x, y \) and \( z \) are lengths of the three principle axes of the particle in decreasing order of magnitude. \( \beta = 0 \) for a two-dimensional plate; \( \beta = 1 \) for a sphere. The experimental data of Schulz et al. (1954) that pertains two groups of non-spherical particles, natural sediments and crushed rock fragment, were used to derive empirical relationships for the drag efficiency and settling velocity.

Drag coefficient for natural particles is expressed as:

\[
C_D = 0.84 \left[ \frac{33.78}{(1 + 4.5\beta^{0.35})^{0.7} \text{Re}_d^{0.56}} + \left( \frac{\text{Re}_d}{\text{Re}_d + 700 + 1000\beta} \right)^{0.28} \frac{1}{\left( \beta^4 + 20\beta^{20} \right)^{0.175}} \right]^{1.428} (17)
\]

Non-dimensional settling velocity for natural particles (valid for \( \nu^* \geq 1.8 \times 10^{-4} \sqrt{\beta} \):

\[
w^* = \left[ \frac{44.84(\nu^*)^{0.667}}{(1 + 4.5\beta^{0.35})^{0.833}} + \frac{0.794}{\beta^4 + 20\beta^{20} + (\nu^*)^{2.4} \exp(18.6\beta^{0.4})} \right]^{0.125} (18)
\]

Drag coefficient for crushed particles:

\[
C_D = \left[ \frac{48.5}{(1 + 4.5\beta^{0.35})^{0.8} \text{Re}_d^{0.64}} + \left( \frac{\text{Re}_d}{\text{Re}_d + 100 + 1000\beta} \right)^{0.32} \frac{1}{\left( \beta^{18} + 1.05\beta^{0.8} \right)} \right]^{1.25} (19)
\]

Non-dimensional settling velocity for crushed fragments (valid for \( \nu^* \geq \frac{1.8 \times 10^{-4}}{\beta} \):

\[
w^* = \left[ \frac{44.84(\nu^*)^{0.667}}{(1 + 4.5\beta^{0.35})^{0.833}} + \frac{0.866}{\beta^{18} + 1.05\beta^{0.8} + 34.0(\nu^*)^2} \right]^{0.625} (20)
\]

Distortion Factor

The volume of irregular shaped particles can be calculated using an equatorial radius \( R \) relating to an equal volume of a sphere with radius \( r \) (Lerman, Lal and Dacey 1974).
For a spheroid equal in volume to a sphere, the following relationship can be applied.

\[ R = r(1 - E)^{-1/3} \]  \hspace{1cm} (21)

In this expression, \( E \) is a measure of distortion of the sphere. \( E = 1 - c/a, \) \( c \) is the polar semi-axis and \( R \) is the equatorial radius. In a sphere, \( E = 0; \) in an oblate spheroid, \( 0 < E < 1. \) In a prolate spheroid, \( E < 0. \)

The settling velocity of a spheroid oriented with its polar axis \( c \) parallel to the direction of settling can be defined as:

\[ v_r = \frac{2g(\rho_s - \rho)(1 - E)R^2}{9\mu(1 - 0.2E)} \]  \hspace{1cm} (22)

The correction factor for Stoke’s Law in this case is \((1 - E)/(1 - 0.2E)\).

Substituting Equation 21 into Equation 22, the settling velocity of such a spheroid can be expressed as:

\[ v_r = \frac{2g(\rho_s - \rho)(1 - E)^{1/3}r^2}{9\mu(1 - 0.2E)} \]  \hspace{1cm} (23)

The settling rate of a spheroid oriented with its polar axis \( c \) perpendicular to the direction of settling is defined as:

\[ v_r = \frac{2g(\rho_s - \rho)(1 - E)R^2}{9\mu(1 - 0.4E)} \]  \hspace{1cm} (24)

In terms of the radius \( r \) of a sphere with equal volume, the settling velocity can be rewritten as:

\[ v_r = \frac{2g(\rho_s - \rho)(1 - E)^{1/3}r^2}{9\mu(1 - 0.4E)} \]  \hspace{1cm} (25)

As \( E \) tend to zero, the relationship between the drag force and the settling velocity of the spheroid tend to be the Stoke’s Law for a sphere.

Fractal dimension
Aggregates found in natural system or generated in water and wastewater treatment systems are fractals. Settling velocity of fractal aggregates had been developed by Jiang and Logan (1991).

\[
v_t = \left[ \frac{2gD}{a\rho_0} \left( \frac{\xi_0}{\xi} \right) \left( \frac{\xi}{\xi_0} \right)^{D/3} l_0^{1+D_2-D} \nu^{-b} l^{D+b-D_2} \right]^{1/(2-b)}
\]  

(26)

\(a\) and \(b\) are determined for different ranges of Reynold’s numbers as listed in Table 5.2. Scaling relationships between settling velocity and characteristic length \(l\) were summarized in Table 5.3 for different ranges of Reynold’s numbers and fractal dimensions.

### Table 5.2 Parameter determination for Equation (26) for different ranges of Reynold’s number

<table>
<thead>
<tr>
<th>Reynold’s number</th>
<th>(a)</th>
<th>(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Re}_d \leq 0.1)</td>
<td>24.0</td>
<td>1.0</td>
</tr>
<tr>
<td>(0.1 &lt; \text{Re}_d &lt; 10)</td>
<td>29.03</td>
<td>0.871</td>
</tr>
<tr>
<td>(10 &lt; \text{Re}_d &lt; 100)</td>
<td>14.15</td>
<td>0.547</td>
</tr>
</tbody>
</table>

### Table 5.3 Scaling relationships between settling velocity \(v_t\) and characteristic length \(l\) (Johnson 1996)

<table>
<thead>
<tr>
<th>Reynold’s Number</th>
<th>General expression</th>
<th>(D_2 &lt; 2)</th>
<th>(D_2 \geq 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Re}_d \ll 1)</td>
<td>(v \propto l^{D-1})</td>
<td>(v \propto l^{D-1})</td>
<td>(v \propto l^{D-1})</td>
</tr>
<tr>
<td>(\text{Re}_d \ll 1)</td>
<td>(v \propto l^{D-D_2+1})</td>
<td>(v \propto l)</td>
<td>(v \propto l^{D-1})</td>
</tr>
<tr>
<td>(\text{Re}_d \ll 1, \ b=1)</td>
<td>(v \propto l^{(D-D_2+b)/(2-b)})</td>
<td>(v \propto l)</td>
<td>(v \propto l^{D-1})</td>
</tr>
<tr>
<td>(0.1 &lt; \text{Re}_d &lt; 10, \ b=0.871)</td>
<td>(v \propto l^{(D-D_2+b)/(2-b)})</td>
<td>(v \propto l^{0.77})</td>
<td>(v \propto l^{0.89(D-1)})</td>
</tr>
</tbody>
</table>

The experimental results from previous study (Johnson 1996) demonstrated that fractal aggregates composed of inorganic microspheres can settle on average 4 to 8.3 times faster than predicted by calculations for impermeable or permeable spheres of identical mass, cross section area, and primary particle density.
Methods for Determining Settling Velocity

Several types of settling column have been developed for settling velocity measurement for both dry weather flows and wet weather flows (Pisano 1996). Two types of method, homogeneous suspension and floating layer, have been classified and developed for measuring the settling velocity of particles in liquid (Aiguier 1996).

The “homogeneous suspension” method (HS) is the analysis of a suspension with solids homogeneously divided throughout the depth of settling column at the start of measurement. The “floating layer” method (FL) consists of distributing the solids in a thin uniform layer at the surface of the fluid at the start of measurement, and plotting the mass fraction of particles decanted as a function of their settling velocities.

Stationary settling column (Figure 5.1)  Pisano (1996)

The most common settling column is a stationary settling column made of clear Plexiglas having peripherical withdraws along the column length. The typical stationary column is 1.8 to 3.7 m (6 to 12 ft) high with a diameter of 15 to 30 cm (6 to 12 inches). Column depth is usually equivalent to that of a clarifier or settling basin. Various methods have been used to pre-mix the sample before the column test begins. A variation of the stationary method involves various mechanical means to pre-mix the column contents by rotating the entire column against its axis.

UFT-type Settling column (Figure 5.2)  Michelbach and Weiß (1996)

Umwelt and Fluid Technik (UFT) developed a settling column to study the settling properties of solids in either an unmodified or a pre-settled sample. Particles which are not settled in an Imhoff cone within one hour are considered as unsettleable from an economic point of view. For those settled materials in Imhoff cone, UFT-type column were used to analyze effluents with particles with different settling behaviors and solids concentration.
The pre-settled solid samples were introduced into the top of the column. Samples were withdrawn from the bottom of the column at times $t_1$, $t_2$, $t_3$, $t_4$, ..., $t_n$. The sample withdrawn at $t_n$ represented the material that settled between time $t_{n-1}$ and $t_n$. Each sample was evaporated and drained to obtain the total solids in terms of mass. The sum of the mass of samples 1 through $n$ was taken to be the total amount of mass that settled within the time frame of the test. From these results, the cumulative settling curves were constructed. The settling velocity was calculated by determining how far the particles fell in a given time. The settling curve was constructed by plotting the settling velocity against cumulative mass fraction. Mass-based settling curves are developed using this method.

The effect of water level drop in the test column needs to be taken into account. The particles collected after the $n^{th}$ withdrawn from the column have experienced a drop in water level $n$ times. Correcting for the dropping water level involves obtaining the volumetric flow rate (cm$^3$/s) by measuring the amount of water and the time it takes to withdraw that water during each sampling event. The corrected settling velocity is:

$$v(n^{th}) = (H - v_i \cdot n \cdot t_p) / t$$  \hspace{1cm} (27)

where $v(n^{th})$ is the settling velocity at $n^{th}$ withdrawal (m/s); $v_i$ is the average velocity at which the water level drops (m/s), calculated by dividing the volumetric flow rate during each sampling event by the column cross section. $H$ represents column height in meter, and the elapsed time of sampling is described using $t_p$. $t$ is the entire experimental elapsed time.

ASTON- Settling column (Figure 5.3) Tyack (1996)

Settling velocity test method developed by Tyack (1996) at Aston University (U.K.) for combined sewage overflow (CSO) was used to determine the settling velocity across the entire gradations. The column had a central settlement length of 1.50 m, which was sufficient to allow
full development of the flocculation process based on the work carried out by Owen (1970). The diameter of the bottom withdrawal tube was 25-mm. Owen recommended a column diameter of 50-mm for solids concentrations between 50 and 200 mg/L. The walls of the column imposed definite boundaries that provided an effective resistance to the motions of the particles and the fluid that was displaced by their motion.

Figure 5.1 Stationary settling column      Figure 5.2 UFT-type Settling column

Figure 5.3 ASTON- Settling column (in mm)
CERGRENE Column  Aiguier and Chebbo (1996)

In the Cergrene method (Chebbo 1992), the settling velocity measurement was carried out in a 1.81-m settling column for particles greater than 50-µm, and an Andréasen pipette (length 0.2-m; diameter 50-mm) was used for settling velocity measurement for particles smaller than 50-µm. Particles were wet sieved prior to the measurement.

The settling velocities obtained from the ASTON-column and CERGRENE-column are significantly lower compared with the UFT method (Aiguier and Chebbo 1996). The reason for the lower settling velocity in these two devices is that UFT-method takes only the settleable solids from 1-hour Imhoff cone test into account, while the other two methods include the entire size range of particles.

Compared to the traditional settling column, the CERGRENE columns have a shorter time to fill (approximately 7 seconds) and may be more completely mixed at the initial sample time. It is thought that the CERGRENE column may account for a wider range of settling solids which may result in establishing better design parameters for wet weather flow. The CERGRENE column was designed for field as well as laboratory use. Settling velocities of samples measured in the field immediately after storm are different from samples transported back or stored in the lab because agglomeration may occur during transportation and storage.


The method consists of a column for measuring the settling velocity and density of constituent matter of aggregates, a microscope for size determination and a camera for recording images for shape information. The linear density gradient was constructed from the Metrizamine stock solution. The upper 110-cm of the column was filled with filtered (0.45 µm Millipore) sea
water, and sterilized with 0.2% sodium azide. The lower 40-cm of the column contained a sea water – Metrizamide mixture. The density gradient was developed as a linear expression.

$$\rho = -0.1936 + 0.01088 \times h$$  \hspace{1cm} (28)$$

The column temperature was kept at 15 ± 0.5 °C. Particles were introduced to the top of the column and settling velocity was measured in the sea water layer. Settling velocity is a function of the density difference between the aggregate and ambient fluid. The aggregate density was obtained from the ambient fluid density where the particle stops settling.

Newton’s second law applied to an aggregate of radius \( r \) yields:

$$\rho_s V \frac{dV}{dt} = (\rho_s - \rho_L) g V - \frac{1}{2} \rho_L V \frac{dv}{dt} - 6\pi \mu_1 r v$$ \hspace{1cm} (29)$$

Densities in Equation (29) are in g/cm\(^3\). From Equation (29), the settling velocity is obtained.

$$v = \frac{2(\rho_s - \rho_L) g_1 r^2}{9 \mu_1} (1 - e^{\beta' t})$$ \hspace{1cm} (30)$$

$$\beta' = -\frac{9\mu_1}{2(\rho_s + \rho_L)r^2}$$ \hspace{1cm} (31)$$

The distance \( X \) that a particle settles as a function of time can be determined.

\[
X = \int v dt = \frac{2(\rho_s - \rho_L) g_1 r^2}{9 \mu_1} \left[ t + \frac{2(\rho_s - \rho_L) g_1 r^2}{9 \mu_1} e^{\beta' t} - \frac{1}{\beta'} \right] \hspace{1cm} (32)
\]

Settling velocity and permeability of the biological aggregates generated in a lab-scale sequencing batch reactor were investigated using an apparatus of double columns vertically connected (Yuan 2000). The upper column was filled with water while the lower column was filled with a denser solution of NaCl or EDTA having a density of 1.005 g/cm\(^3\) at room
temperature. The settling velocity observed in water was in good agreement with the predictions of Stoke’s Law for the identical but impermeable porous particles, suggesting insignificant internal permeation of biological aggregates. The settling velocities decreased when the aggregates settled from water phase into the EDTA or NaCl solution. The reduction from water to EDTA was greater than that from water to NaCl, indicating that mass transport from the liquid phase into bio-aggregates was likely dominated by molecular diffusion rather than convection.

**The Effect of Turbulence**

A vertical recirculating settling column with an oscillating grid generating turbulence was built to study the effect of turbulence on settling velocity (Rasmussen and Larsen 1996). A continuous recirculating flow of suspended sediment has the advantage of keeping the sediment concentration constant. The settling column is 1.2-m high with a depth of 0.3-m. Turbulence is generated by 11 oscillating grids, spaced 0.1-m apart. Figure 5.4 showed schematic of the column with oscillating grid. Comprehensive experiments for the calibration of the relation between the movement of the grid and the generation of turbulent kinetic energy had been conducted by Rasmussen and Larsen (1996).

![Figure 5.4 Recirculating column (in cm)](image-url)
The settling velocity was determined from the continuity equation for the mass flux of sediment assuming steady state conditions. The flux in the inlet zone equals the flux in the uniform zone yielding:

\[ v_p C_{in} = (v_p + v_s) C_{uniform} \]  \hspace{1cm} (33)

\[ v_s = v_p \left( \frac{C_{in} - C_{uniform}}{C_{uniform}} \right) \]  \hspace{1cm} (34)

Concentration was measured indirectly via the turbidity with a turbidity sensor. A best fit relationship was developed from the analysis of the experimental results.

\[ v_s = 1.3 \times 10^{-5} \frac{C_0^{6.3}}{G^{1.19}} \exp \left[ -0.5 \left( \frac{C_s + 0.07}{1.73} \right)^2 \right] + 0.024 \]  \hspace{1cm} (35)

\( \bar{G} \) is the average turbulence velocity gradient and is calculated as \( \bar{G} = \sqrt{\epsilon / \mu} \), where \( \epsilon \) is the turbulent dissipation assumed equal to the generated turbulent kinetic energy by the grid.

**Wall Effect in Cylindrical Column**

The terminal settling velocity \( v_t \) of a particle decreases as the diameter of the sedimentation vessel decreases. This is known as wall effect (Kehlenbeck and Di Felice 1999).

The wall factor can be expressed as

\[ \frac{V_{IB}}{v_{t\infty}} = f(Re_{t\infty}, \lambda) \]  \hspace{1cm} (36)

The wall factor is a function of both the sphere Reynold’s number \( Re_{t\infty} \) and the diameter ratio \( \lambda \). Two physical boundary conditions have to be fulfilled: For \( \lambda = 0 \), the settling velocity \( v_{IB} \) must coincide with the terminal settling velocity in an infinite vessel \( v_{t\infty} \). For \( \lambda = 1 \), the settling velocity \( v_{IB} \) must be equal to zero.
On the basis of over 100 experiments in a Reynold’s number region of \(2 \leq \text{Re}_{\infty} \leq 185\) and a diameter ratio of \(\lambda \leq 0.9\), the relationship for the wall factor was developed as:

\[
\frac{v_B}{v_{\infty}} = \frac{1 - \lambda^p}{1 + \left(\frac{\lambda}{\lambda_0}\right)^p}
\]  

(37)

Two parameters \(\lambda_0\) and \(p\) were found to depend on the sphere Reynold’s number \(\text{Re}_{\infty}\). The relationship between \(\lambda_0\) and \(\text{Re}_{\infty}\) was described in Equation (39).

\[
\frac{\lambda_0 - 0.283}{1.2 - \lambda_0} = 0.041 \text{Re}_{\infty}^{0.524}
\]  

(38)

Parameter \(p\) correlated to \(\text{Re}_{\infty}\) under two different flow regimes.

For \(\text{Re}_{\infty} \leq 35\), the best approximation was

\[
p = 1.44 + 0.5466 \text{Re}_{\infty}^{0.434}
\]  

(39)

For \(\text{Re}_{\infty} \geq 35\), the best fitting was obtained with

\[
p = 2.3 + 37.3 \text{Re}_{\infty}^{-0.8686}
\]  

(40)

With \(p\) fixed at 2.2 fixed and \(\lambda_0\) expressed as a function of \(\text{Re}_{\infty}\), a simplified correlation was obtained as Equation 41.

\[
\frac{\lambda_0 - 0.27}{1.2 - \lambda_0} = 0.05 \text{Re}_{\infty}^{0.65}
\]  

(41)

The accuracy is lower but a good prediction of the measured wall factors can still be obtained.

**OBJECTIVES**

A review of the literature indicates that although settling curves have been developed through gravimetric analyses for combined sewage overflow (Aiguier and Chebbo 1996; Tyack and Naomi 1996; Hedges 1998; Wong 2000), settling velocity analysis of stormwater particles has
not been reported through laser diffraction analysis of particle size distribution (PSD). Therefore, to measure settling velocities through PSD, two common settling velocity measurement devices, stationary settling column and Imhoff cones, will be applied in the experiment. A review of literature indicates that an examination and comparison of results from these two settling velocity devices has not been reported in the previous studies. In addition, characteristics of sediments deposited by urban storm water are quite different from natural river sediments and wastewater solids. The settling behaviors of particulates in urban storm water are also influenced by the factors such as suspended solids (SS) concentration and residence time.

Four objectives were proposed for this study. First, a thorough compilation of literature on settling velocity was presented with purpose of providing a sound background. Second, a methodology was developed using a laser diffraction type of particle analyzer to determine PSD and settling velocity. Third, two settling velocity devices – settling column and Imhoff cone – were compared for the settling velocity measurement of storm water particles. Sampling and analytical procedures were developed and compared. The final objective was to estimate and analyze the settling velocity model through comparing the measured velocities to the modeled value.

METHODOLOGY

Materials – Urban Rainfall-Runoff Particles

Particulates were obtained from a paved urban site impacted by transportation. Materials analyzed include cohesive and non-cohesive sediments transported by urban runoff into a storm catch basin and storage tank. Experimental site was shown in Figure 5.5. Sediments were collected, brought back to lab and air-dried at 40°C. Dried solids were disaggregated and sieved into 18 size gradations. Table 5.4 illustrated the size gradations of mechanical sieve analysis.
Figure 5.5  Profile view of experimental site sampling system (Baton Rouge I-10 Site)

Table 5.4  Size gradations of mechanical sieve analysis

<table>
<thead>
<tr>
<th>ID</th>
<th>Sieve # Designation</th>
<th>Nominal Opening (µm)</th>
<th>Size Range (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3/8 inch</td>
<td>9500</td>
<td>&gt;9500</td>
</tr>
<tr>
<td>2</td>
<td>1/4 inch</td>
<td>4750</td>
<td>9500-4750</td>
</tr>
<tr>
<td>3</td>
<td>No. 10</td>
<td>2000</td>
<td>4750-2000</td>
</tr>
<tr>
<td>4</td>
<td>No. 20</td>
<td>850</td>
<td>2000-850</td>
</tr>
<tr>
<td>5</td>
<td>No. 30</td>
<td>600</td>
<td>850-600</td>
</tr>
<tr>
<td>6</td>
<td>No. 40</td>
<td>425</td>
<td>600-425</td>
</tr>
<tr>
<td>7</td>
<td>No. 50</td>
<td>300</td>
<td>425-300</td>
</tr>
<tr>
<td>8</td>
<td>No. 60</td>
<td>250</td>
<td>300-250</td>
</tr>
<tr>
<td>9</td>
<td>No. 80</td>
<td>180</td>
<td>250-180</td>
</tr>
<tr>
<td>10</td>
<td>No. 100</td>
<td>150</td>
<td>180-150</td>
</tr>
<tr>
<td>11</td>
<td>No. 140</td>
<td>106</td>
<td>150-106</td>
</tr>
<tr>
<td>12</td>
<td>No. 200</td>
<td>75</td>
<td>106-75</td>
</tr>
<tr>
<td>13</td>
<td>No. 230</td>
<td>63</td>
<td>75-63</td>
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<tr>
<td>14</td>
<td>No. 270</td>
<td>53</td>
<td>63-53</td>
</tr>
<tr>
<td>15</td>
<td>No. 325</td>
<td>45</td>
<td>53-45</td>
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<td>16</td>
<td>No. 400</td>
<td>38</td>
<td>45-38</td>
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<tr>
<td>17</td>
<td>No. 500</td>
<td>25</td>
<td>38-25</td>
</tr>
<tr>
<td>18</td>
<td></td>
<td></td>
<td>&lt;25</td>
</tr>
</tbody>
</table>
Methods

Specific gravity

Density or specific gravity of particles was determined by an inert gas (helium) pycnometer (Quantachrome Corp.) The method applied was ASTM protocol D5550-94 (ASTM 1994). The pycnometer determines the true volume of solid samples by measuring the pressure difference. A known quantity of helium under pressure was allowed to flow from the chamber with a precisely known reference volume \( V_R \) into a sample cell containing the solid or powder material. The pressures were recorded and the difference can be obtained. True solid volume can be calculated through Equation 42:

\[
V_s = V_c - V_R \left( \frac{P_1}{P_2} - 1 \right)
\]  

(42)

Density of the sample then could be calculated using Equation 43

\[
\rho_s = \frac{M_s}{V_s}
\]  

(43)

The density for the solid material is typically reported to the nearest 0.01. Specific gravity \( S_g \) was obtained through Equation 44.

\[
S_g = \frac{\rho_s}{\rho_L}
\]  

(44)

Settling velocity measurement

The aqueous phase utilized in the following experiments to evaluate settling velocity was the pre-settled stormwater supernatant, in which the total particle volume concentration was no greater than 5-\( \mu \)L/L. Below the concentration limit of 50 mg/L, particle collisions are too infrequent to promote aggregation (Teeter 2001). Assuming storm particle density of 2.5-g/cm\(^3\), the volume concentration limit for Brownian coagulation is 20-\( \mu \)L/L and the mass concentration limit is 50-mg/L. The rational for using pre-settled storm water as the suspended medium in the settling column and Imhoff cone test is that it would simulate the viscosity, density and
chemistry of the liquid phase in a real storm water treatment system. In order to reduce the interference of particles in the aqueous phase to the tested particles, a pre-settled time of three days was set to ensure that the impact of particles in the suspended medium is insignificant.

For particles greater than 180 µm (retained on No. 80 sieve), 100 individual particles from each size classes were randomly selected for settling velocity measurements. The floating layer method (Aiguier and Chebbo 1996) was used in these experiments. Individual particles were introduced into the column or the Imhoff cone just below the water surface. Before the settling test, particles were immersed in the pre-settled storm water and any attached bubbles removed. Sedimentation timing starts as soon as the particle was released from an at-rest position just below the water surface. Time for settling the predetermined distance ($H_{\text{Imhoff}} = 425$ mm, $H_{\text{column}} = 2466$ mm) for each individual particle was measured by a stopwatch manually. The average settling velocity of measured particles can be calculated using Equation 45.

$$\bar{v} = \frac{H}{t}$$  \hspace{1cm} (45)

Sediment samples and grit samples were tested separately in both settling column and Imhoff cones. The calculated settling velocities according to Newton’s Law are shown in Table 5.5 for the grit and Table 5.6 for the sediment.

For particles less than 180-µm (particles passing through the No. 80 sieve), settling velocities were determined through analyses of particle size distribution in the settling column test. The columns were filled up with tap water. In order to remove fine bubbles, the solution was allowed to sit in the columns for at least four hours before the experiment started. A sample from each column was taken from sampling port 2 (as shown in Figure 5.6) and analyzed to set the background particle concentration in the analyzer (Lisst Portable, Sequoia Tech.), which would be subtracted from the particle analysis for the real storm particles in the column runs.
Table 5.5  Modeled settling velocity using Newton’s law for the particles entrained in the grit chamber at Baton Rouge I-10 site (Assume T=20 °C)

<table>
<thead>
<tr>
<th>ID</th>
<th>Particle Diameter (µm)</th>
<th>Measured Density (g/cm³)</th>
<th>(v_t)(mm/s)</th>
<th>Reynold’s Number (Reₐ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4750</td>
<td>2.48</td>
<td>457</td>
<td>2428</td>
</tr>
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<td>3</td>
<td>2000</td>
<td>2.41</td>
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<tr>
<td>4</td>
<td>850</td>
<td>2.37</td>
<td>140</td>
<td>133</td>
</tr>
<tr>
<td>5</td>
<td>600</td>
<td>2.44</td>
<td>104</td>
<td>70.0</td>
</tr>
<tr>
<td>6</td>
<td>425</td>
<td>2.57</td>
<td>76.2</td>
<td>36.2</td>
</tr>
<tr>
<td>7</td>
<td>300</td>
<td>2.61</td>
<td>50.3</td>
<td>16.9</td>
</tr>
<tr>
<td>8</td>
<td>250</td>
<td>2.58</td>
<td>38.5</td>
<td>10.8</td>
</tr>
<tr>
<td>9</td>
<td>180</td>
<td>2.56</td>
<td>23.0</td>
<td>4.64</td>
</tr>
<tr>
<td>10</td>
<td>150</td>
<td>2.47</td>
<td>16.2</td>
<td>2.72</td>
</tr>
<tr>
<td>11</td>
<td>106</td>
<td>2.55</td>
<td>9.3</td>
<td>1.10</td>
</tr>
<tr>
<td>12</td>
<td>75</td>
<td>2.53</td>
<td>5.2</td>
<td>0.44</td>
</tr>
<tr>
<td>13</td>
<td>63</td>
<td>2.53</td>
<td>3.7</td>
<td>0.26</td>
</tr>
<tr>
<td>14</td>
<td>53</td>
<td>2.61</td>
<td>2.8</td>
<td>0.16</td>
</tr>
<tr>
<td>15</td>
<td>45</td>
<td>2.51</td>
<td>1.9</td>
<td>0.09</td>
</tr>
<tr>
<td>16</td>
<td>38</td>
<td>2.54</td>
<td>1.4</td>
<td>0.06</td>
</tr>
<tr>
<td>17</td>
<td>25</td>
<td>2.49</td>
<td>0.6</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Flow regime Re > 1000, Turbulent flow; 1 < Re < 1000, Transitional flow; Re < 1, Laminar flow.
Table 5.6  Modeled settling velocity using Newton’s law for particles in the sedimentation basin at Baton Rouge I-10 site (Assume T=20 °C)

<table>
<thead>
<tr>
<th>ID</th>
<th>Particle Diameter (µm)</th>
<th>Measured Density (g/cm³)</th>
<th>v_t (mm/s)</th>
<th>Reynold’s Number (Re_d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4750</td>
<td>1.34</td>
<td>219.00</td>
<td>1164</td>
</tr>
<tr>
<td>3</td>
<td>2000</td>
<td>1.52</td>
<td>154.27</td>
<td>345.3</td>
</tr>
<tr>
<td>4</td>
<td>850</td>
<td>1.61</td>
<td>83.10</td>
<td>79.0</td>
</tr>
<tr>
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<td>600</td>
<td>2.13</td>
<td>88.39</td>
<td>59.3</td>
</tr>
<tr>
<td>6</td>
<td>425</td>
<td>2.26</td>
<td>65.00</td>
<td>30.9</td>
</tr>
<tr>
<td>7</td>
<td>300</td>
<td>2.33</td>
<td>43.33</td>
<td>14.5</td>
</tr>
<tr>
<td>8</td>
<td>250</td>
<td>2.31</td>
<td>33.02</td>
<td>9.24</td>
</tr>
<tr>
<td>9</td>
<td>180</td>
<td>2.28</td>
<td>19.40</td>
<td>3.91</td>
</tr>
<tr>
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<td>150</td>
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<td>13.69</td>
<td>2.30</td>
</tr>
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<td>106</td>
<td>2.24</td>
<td>7.51</td>
<td>0.89</td>
</tr>
<tr>
<td>12</td>
<td>75</td>
<td>2.26</td>
<td>4.32</td>
<td>0.36</td>
</tr>
<tr>
<td>13</td>
<td>63</td>
<td>2.33</td>
<td>3.22</td>
<td>0.23</td>
</tr>
<tr>
<td>14</td>
<td>53</td>
<td>2.33</td>
<td>2.28</td>
<td>0.13</td>
</tr>
<tr>
<td>15</td>
<td>45</td>
<td>2.38</td>
<td>1.70</td>
<td>0.09</td>
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<td>0.05</td>
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<tr>
<td>17</td>
<td>25</td>
<td>2.50</td>
<td>0.57</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Solid particles were obtained from mechanical sieve analysis pass through No. 80 (180-µm).

To avoid the interaction among the particles, suspended solid concentration in the settling column was no greater than 100-mg/L, indicating the dry solid mass no greater than 3.78-g (Volume of the column = 37.8 L). A certain amount of particles (less than 3.78-g) was weighed and add into D.I. water to prepare the solid mixture. The mixture was then sonicated for over 20-min until all the clogs and aggregates break up. Experiments were designed in three settling columns with short-term, mid-term and long-term sampling time respectively. Table 5.7 illustrated the experimental matrix. Combining the results from three columns, settling velocity distributions for particles ranging from 1.36 to 180-µm can be acquired.
Determination of settling velocities for fine particles (less than 180-µm) was also carried out using particle size distribution. The procedure for adding solution of fine particles into the settling column or the Imhoff cone was as follows.

1. Immerse the petri-dish which holds the solution of particles at a known location near the liquid surface;
2. Carefully introduce the particle suspension into the aqueous phase of storm water ensuring quiescent conditions remain;
3. Start sedimentation time immediately;
4. For settling column, initial sample is withdrawn from sampling port 1 (Figure 5.6) and the time is recorded as $t_0$; For the Imhoff cone, the initial sample is analyzed before adding into the cone;
5. Approximately 120-mL sample is withdrawn each time from sampling port 2 as shown in Figure 5.6 in the settling column test;
6. Sampling at time $t_1$, $t_2$ …… $t_n$ as shown in Table 5.7 for different columns;
7. For the settling column, record the drop of water level for the correction of settling depth for each sampling time;
8. In Imhoff cone test, sample 30-mL each time using a wide-bore syringe with a rigid tubing connected to the end at the depth of 275-mm below the surface of the liquid every minute for 10 minutes. Figure 5.7 showed the Imhoff cone and the sampling schematic.

Total volume concentration for particles of each size gradation ranging from 1.25 to 200 µm was obtained from particle size analysis using LISST Portable particle analyzer at time $t_1$, $t_2$, … $t_n$. Volume concentration was converted to number concentration assuming spherical particles.
Table 5.7  Experimental design – sampling time for the column test

<table>
<thead>
<tr>
<th>Sampling time (sec)</th>
<th>Column I</th>
<th>Column II</th>
<th>Column III</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
<td>min</td>
<td>hr</td>
</tr>
<tr>
<td>1</td>
<td>20</td>
<td>0.33</td>
<td>10</td>
</tr>
<tr>
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<td>40</td>
<td>0.67</td>
<td>20</td>
</tr>
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<tr>
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<td>820</td>
<td>13.67</td>
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<td>42</td>
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<tr>
<td>48</td>
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</tbody>
</table>
Figure 5.6 Sampling schematic for the settling column

Figure 5.7 Imhoff cones (all units in mm) (left) and sampling schematic (right)
At each sampling time, an average of settling velocity can be obtained by Equation 45. Therefore, for a given size particle, settling velocity distribution is obtained and it is expected to be normal. The mean value of the normal distribution was considered measured settling velocity for the particle of this size. Theoretical settling velocity of this size can be calculated according to Newton’s Law. Table 5.8 listed the theoretical calculated settling velocities. Measured settling velocities were compared to the modeled settling velocities.

Table 5.8 Modeled settling velocity using Newton’s law for fine particles (1.25 ~ 250 µm) Assuming density = 2.50 g/cm$^3$, T=20 °C.

<table>
<thead>
<tr>
<th>Size (µm)</th>
<th>Settling Velocity (mm/s)</th>
<th>Size (µm)</th>
<th>Settling Velocity (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25</td>
<td>0.00</td>
<td>19.20</td>
<td>0.34</td>
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<tr>
<td>1.36</td>
<td>0.00</td>
<td>22.66</td>
<td>0.47</td>
</tr>
<tr>
<td>1.60</td>
<td>0.00</td>
<td>26.74</td>
<td>0.65</td>
</tr>
<tr>
<td>1.89</td>
<td>0.00</td>
<td>31.56</td>
<td>0.91</td>
</tr>
<tr>
<td>2.23</td>
<td>0.00</td>
<td>37.24</td>
<td>1.27</td>
</tr>
<tr>
<td>2.63</td>
<td>0.01</td>
<td>43.95</td>
<td>1.77</td>
</tr>
<tr>
<td>3.11</td>
<td>0.01</td>
<td>51.86</td>
<td>2.46</td>
</tr>
<tr>
<td>3.67</td>
<td>0.01</td>
<td>61.20</td>
<td>3.42</td>
</tr>
<tr>
<td>4.33</td>
<td>0.02</td>
<td>72.22</td>
<td>4.77</td>
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<tr>
<td>5.11</td>
<td>0.02</td>
<td>85.22</td>
<td>6.64</td>
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<tr>
<td>6.03</td>
<td>0.03</td>
<td>100.57</td>
<td>9.24</td>
</tr>
<tr>
<td>7.11</td>
<td>0.05</td>
<td>118.67</td>
<td>10.98</td>
</tr>
<tr>
<td>8.39</td>
<td>0.06</td>
<td>140.04</td>
<td>14.67</td>
</tr>
<tr>
<td>9.90</td>
<td>0.09</td>
<td>165.26</td>
<td>19.39</td>
</tr>
<tr>
<td>11.69</td>
<td>0.12</td>
<td>195.02</td>
<td>25.33</td>
</tr>
<tr>
<td>13.79</td>
<td>0.17</td>
<td>230.14</td>
<td>32.67</td>
</tr>
<tr>
<td>16.27</td>
<td>0.24</td>
<td>250.00</td>
<td>36.90</td>
</tr>
</tbody>
</table>

**RESULTS AND ANALYSIS**

As shown in Figure 5.8, density of solids collected from grit material is significantly higher than that of clarified sediments collected from the sedimentation tank. The difference is significant for the particles greater than 600-µm. By observation, samples in the clarified
sediments for large particle size contain more organic matter such as shredded tire, bark and straw pieces, which contribute to the low density of the sample.

![Particle Diameter vs. Density](image)

**Figure 5.8** Density of solids deposited by urban storm runoff

Settling velocity measurement for visible non-colloidal individual particles (greater than 180-μm) was carried out using Imhoff cone and settling column. Measured settling velocities and modeled values were showed in Figure 5.9. Experimental measured data were presented as box plots representing statistical results. The boundary of the box closest to zero indicates the 25th percentile and the line within the box marks the median. The boundary of the box farthest from zero indicates the 75th percentile. Whiskers above and below the box indicate the 90th and 10th percentiles. Individual circles showed in the plot represent the 5th and 95th percentile. Modeled settling velocities using Newton’s law assuming Euclidean structure were shown in the same plot as triangles.

Table 5.9 summarized the measured and modeled velocities of visible individual particles from the grit chamber and sedimentation tank. Table 5.10 compared the measured results using two different devices.
Figure 5.9  Settling velocity measurement for individual particles (180-2000 µm) from grit chamber and sedimentation tank at Baton Rouge I-10 site, compared with modeled value assuming Euclidean structure using Newton’s Law.
Table 5.9  Comparison of measured and modeled settling velocity for visible individual non-colloidal particles

<table>
<thead>
<tr>
<th>Particle size (µm)</th>
<th>180</th>
<th>250</th>
<th>300</th>
<th>425</th>
<th>600</th>
<th>850</th>
<th>2000</th>
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</thead>
<tbody>
<tr>
<td>Imhoff cone (Settling distance = 425 mm)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Grit</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Median</td>
<td>27.3</td>
<td>39.5</td>
<td>53.7</td>
<td>69.7</td>
<td>106.3</td>
<td>135.6</td>
<td>177.5</td>
</tr>
<tr>
<td>Model</td>
<td>23.0</td>
<td>38.5</td>
<td>50.3</td>
<td>76.2</td>
<td>104.3</td>
<td>139.5</td>
<td>289.6</td>
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<td>Diff(%)</td>
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<td>2.55</td>
<td>6.80</td>
<td>8.53</td>
<td>1.94</td>
<td>2.86</td>
<td>38.73</td>
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</tr>
<tr>
<td>Median</td>
<td>17.6</td>
<td>18.2</td>
<td>42.4</td>
<td>38.3</td>
<td>46.9</td>
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<tr>
<td>Model</td>
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<td>33.0</td>
<td>43.3</td>
<td>65.0</td>
<td>83.1</td>
<td>88.4</td>
<td>154.3</td>
</tr>
<tr>
<td>Diff(%)</td>
<td>9.28</td>
<td>44.88</td>
<td>2.27</td>
<td>41.16</td>
<td>43.56</td>
<td>71.27</td>
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<td></td>
</tr>
<tr>
<td>Settling column (Settling distance = 2466 mm)</td>
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</tr>
<tr>
<td>Median</td>
<td>25.7</td>
<td>34.6</td>
<td>49.0</td>
<td>65.6</td>
<td>100.8</td>
<td>140.2</td>
<td>199.1</td>
</tr>
<tr>
<td>Model</td>
<td>23.0</td>
<td>38.5</td>
<td>50.3</td>
<td>76.2</td>
<td>104.3</td>
<td>139.5</td>
<td>289.6</td>
</tr>
<tr>
<td>Diff(%)</td>
<td>11.74</td>
<td>10.06</td>
<td>2.55</td>
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<td>3.33</td>
<td>0.44</td>
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<tr>
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<td>21.0</td>
<td>38.8</td>
<td>40.8</td>
<td>47.4</td>
<td>27.9</td>
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<tr>
<td>Model</td>
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<td>33.0</td>
<td>43.3</td>
<td>65.0</td>
<td>83.1</td>
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<td>154.3</td>
</tr>
<tr>
<td>Diff(%)</td>
<td>9.28</td>
<td>36.55</td>
<td>10.58</td>
<td>37.31</td>
<td>43.02</td>
<td>68.49</td>
<td>71.97</td>
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Table 5.10  Comparison of measurement of Imhoff cone and settling column for visible individual non-colloidal particles

<table>
<thead>
<tr>
<th>Effective Size (µm)</th>
<th>180</th>
<th>250</th>
<th>300</th>
<th>425</th>
<th>600</th>
<th>850</th>
<th>2000</th>
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<tr>
<td>Imhoff cone</td>
<td>27.3</td>
<td>39.5</td>
<td>53.7</td>
<td>69.7</td>
<td>106.3</td>
<td>135.6</td>
<td>177.5</td>
</tr>
<tr>
<td>Settling column</td>
<td>25.7</td>
<td>34.6</td>
<td>49.0</td>
<td>65.6</td>
<td>100.8</td>
<td>140.2</td>
<td>199.1</td>
</tr>
<tr>
<td>Diff %</td>
<td>6.23</td>
<td>14.02</td>
<td>9.59</td>
<td>6.25</td>
<td>5.46</td>
<td>3.28</td>
<td>10.85</td>
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<tr>
<td>Imhoff cone</td>
<td>17.6</td>
<td>18.2</td>
<td>42.4</td>
<td>38.3</td>
<td>46.9</td>
<td>25.4</td>
<td>38.9</td>
</tr>
<tr>
<td>Settling column</td>
<td>21.2</td>
<td>21.0</td>
<td>38.8</td>
<td>40.8</td>
<td>47.4</td>
<td>27.9</td>
<td>43.3</td>
</tr>
<tr>
<td>Diff %</td>
<td>16.98</td>
<td>13.13</td>
<td>9.29</td>
<td>6.13</td>
<td>0.95</td>
<td>8.80</td>
<td>10.06</td>
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</table>

For the particles ranging from 180 to 850-µm collected from the grit chamber, measured velocities using Imhoff cone demonstrate good agreement with modeled velocities with a difference of less than 15%. However, measured velocity for grit over 850-µm showed a deviation nearly 40% from the modeled velocity assuming Euclidean structure in the Imhoff cone test. For the particles in the clarified sediments, modeled velocities were within the range of the 25th and 75th percentile for particles in the gradation of 180 to 425-µm. However, measured
velocities for the particles above 425-µm were significantly lower than the median velocity calculated from the model. The difference between the median of the measured velocities and the modeled velocity increases with larger sizes. There is a large percent of organic materials in the upper size range of the particles from sedimentation tank. Their settling behavior is different from the granular particles due to their complicated structure. Measured settling velocities for dispersed individual particles can hardly represent their settling in the real system because these particles usually agglomerate with clay or other materials and settle as aggregate.

Comparing the measured velocities in the two devices, it has been found that for grit material less than 600-µm (pass through No. 4 sieve), measured settling velocities using Imhoff cone are consistently higher than the velocities obtained from settling column test. For particles in the sedimentation tank, measured velocities from settling column test are higher than those obtained from Imhoff cone test except for the particle with the gradation of 300-µm. But the difference between two devices was no greater than 15% (one exception). Sediments collected from the sedimentation tank consist of more organic matter with low density. A longer settling distance is supposed to provide more accurate average velocity.

For particles less than 180-µm, monitoring of individual particle settling through visual observation becomes extremely difficult and particle analyzer was used to measure PSD and to estimate the settling velocity. Figure 5.10 showed the initial particle size distribution of the grit and sediments. Particles in the grit chamber had a peak volume distribution around 60-µm. Particles smaller than 10-µm consist of less than 12% of the total volume concentration. While approximately 40% of the particles in the sediments from the sedimentation tank are within the size range of 10 to 40 μm. Settling column and Imhoff cone tests were carried out for the solids collected from grit chamber and sedimentation tank respectively.
Figure 5.10 Initial particle number distribution and volumetric concentration fraction (vertical bars) for the suspended particles in grit chamber and sedimentation tank in settling column test.

Figure 5.11 illustrated the evolution of particle size distribution during the settling process in the settling column for the particles from the grit chamber. It has been found that the peak of the distribution moved towards the smaller size range with time, and the volume concentration reached the maximum at approximately 14-min quiescent settling. The majority of the particles in the grits were having the settling velocity of 2 to 4 mm/s. As shown in Figure 5.11(b), the mean size of the particle distribution linearly decreased with the logarithm of the settling time. The linear regression coefficient was determined as 0.93 for 40 samples. As shown in Figure 5.11(a), over 90% of the particulate matter in terms of volume concentration can be removed with one-hour sedimentation in the settling column. The particles left in the column have a mean size less than 40-µm as seen in Figure 5.11 (b). The results indicated sedimentation is an effective treatment for the removal of grit materials from urban rainfall-runoff.

Similar experiments were carried out for the non-colloidal particulate matter from the sedimentation tank. Results were shown in Figure 5.12.
Figure 5.11  Particle size distribution (PSD) in the settling column test for the materials from grit chamber as a function of time (min) (a) Total volume concentration and cumulative volume concentration as a function of settling time in the settling column test (b) Decrease of PSD mean size as a function of settling time
In Figure 5.12(a), total volume concentration showed a similar pattern during the settling process as that of the particles from grit chamber, except for the extended settling hours. Mean size of the particle distribution decreased with settling time which was shown in Figure 5.12(b). A linear regression was developed between the mean size of PSD and the logarithm of settling time in the range of 6 to 200-min. After 200-min settling, mean size remained stable around 10-\(\mu\)m. Approximate 50% removal in terms of volume concentration was obtained following 1-hour settling.

Figure 5.13 showed the settling velocity distribution in log-log scale determined by particle size analysis. The measured settling velocity can be modeled by a lognormal distribution reasonably well. The mean of the lognormal distribution was plotted against the theoretical modeled settling velocity as seen in Figure 5.14. It has been found that non-colloidal particles less than 10-\(\mu\)m settled significantly faster than predicted assuming Euclidean object, with the discrepancy being greater for the smaller particles. Deviation from the modeled velocity is attributed to the fractal characterization. The fractal property of particles has been observed in scanning electron microscope (SEM) images and the two-dimensional fractal dimension for fine particles (<75 \(\mu\)m) was found smaller than that of medium to coarse (75-850 \(\mu\)m) materials (Lin and Sansalone 2003). Further studies on the fractal model will be addressed in the following chapter.

Settling velocity experiments for fine particles (1.25 – 200 \(\mu\)m) through particle size analysis were also tried in the Imhoff cone with a settling distance of 275-mm. The amount of particles added to the Imhoff cone was pre-determined to keep the concentration of suspension around 200 mg/L. Samples were withdrawn at one-minute interval for 10 minutes. Results were shown in Figure 5.15 and Figure 5.16. Figure 5.15 illustrated the particle size distribution change during
the settling process for the particles from grit chamber. Figure 5.16 showed the particle size distribution change during the settling process for the particles from sedimentation tank. Regression between mean size and the settling time was very weak. A decrease of volume concentration with settling has been observed for both grits and sediments in Imhoff cone test. Because of the short settling distance, this approach is proved to be unsuccessful to estimate settling velocity using particle analysis.

CONCLUSIONS

The following conclusions have been drawn from the present study:

Measured settling velocities agree reasonably well with the modeled settling velocities according to Newton’s Law for non-colloidal granular particulate matter in size range of 10 to 850-µm. Measured settling velocities for particles in the clarified sediment were lower than the measured velocity of granular particulate matter from the grit chamber. Non-colloidal particles less than 10-µm settled much faster than predicted from Newton’s Law assuming spherical particles. Fractal structure attributes to this discrepancy.

In the settling tests for individual particles, measured velocities using Imhoff cone and settling column demonstrate good agreement with less than 15% difference. Results from settling column are closer to the modeled value. Imhoff cone is not suitable for the PSD determined settling velocity measurement for fine particles (< 200 µm).

For particles in the range of 1.25 to 250-µm, over 90% of non-colloidal particles in grit chamber and approximately 50% of the non-colloidal particles in sedimentation tank can be removed by gravitational settling in terms of volume concentration. Particles remaining in the suspension after 1-hour sedimentation was less than 40-µm.
Figure 5.12 Particle size distribution (PSD) in the settling column test for the materials from sedimentation tank as a function of time (min) (a) Total volume concentration and cumulative volume concentration as a function of settling time in the settling column test (b) Decrease of PSD mean size as a function of settling time.
Figure 5.13 Settling velocity distribution (log-normal) for fine size particles (d in µm)
Figure 5.14 Mean and standard deviation of measured settling velocities distributions under quiescent conditions for discrete stormwater particles in the size gradation from 1 to 200-µm compared to modeled settling velocities based on Newton's Law for this size range. For this size range (1 to 200 µm) a measured particle density of 2.50 g/cm³ was utilized for both measured and modeled results.
Figure 5.15  Particle size distribution in Imhoff cone test for the particles from the grit chamber (a) Mean size and total volume concentration as a function of settling time; Poor regression between mean size and settling time ($r^2 = 0.46$)

Figure 5.16  Particle size distribution in Imhoff cone test for the particles from the sedimentation tank (a) Mean size and total volume concentration as a function of settling time; Poor regression between mean size and settling time ($r^2 = 0.20$)
IMPLICATIONS FOR BEST MANAGEMENT PRACTICES

Settling velocity study showed that the current sedimentation design according to overflow theory based on Euclidean assumption was applicable to granular materials under individual quiescent settling. Imhoff settling test is a practical field testing for BMPs. Bench scale column test is very useful to determine the settling characteristics in the real system. In the best management facilities, particle settling is affected by many factors such as solid concentration, temperature, and hydrological conditions. With a short retention time, sedimentation is an effective treatment to remove coarse materials but not fine particulate matter. Alternative technology such as chemical coagulation and flocculation is proposed to enhance removal of those fine particles.

REFERENCES


NOMENCLATURE

\[ \text{Re}_d = \text{Reynold’s number based on diameter, } \text{Re}_d = \frac{v_d \rho}{\mu} \]
\( v_t \) = Terminal settling velocity of particle (m/s)

\( d \) = Particle diameter (m)

\( \rho \) = Fluid density (kg/m\(^3\))

\( \mu \) = Dynamic viscosity of the liquid (N \cdot s/m\(^2\))

\( \rho_p \) = Density of particle (kg/m\(^3\))

\( \rho_L \) = Density of liquid (kg/m\(^3\))

\( C_D \) = Drag coefficient, a function of \( \text{Re}_d \)

\( g \) = Acceleration due to gravity (9.8 m/s\(^2\))

\( S_g \) = Specific gravity, \( S_g = \rho_p / \rho_L \)

\( \nu \) = Kinematic viscosity of the liquid (m\(^2\)/s)

\( d^* \) = Dimensionless particle diameter, \( d^* = \left( \frac{(S_g - 1)g}{\nu^2} \right)^{1/3} d \)

\( T \) = Temperature (\(^\circ\)C)

\( \nu^* \) = Non-dimensional kinematic viscosity, \( \nu^* = \frac{1}{\text{Re}_d} \sqrt{\frac{4}{3C_D}} \)

\( w^* \) = Non-dimensional settling velocity, \( w^* = \frac{v_t}{\sqrt{(S_g - 1)gD_n}} \)

\( D_n \) = Nominal diameter, diameter of sphere having same surface area as particle, \( D_n = \left( \frac{6\nu}{\pi} \right)^{1/3} \)

\( C_i \) = Concentration of the \( i \)-th size class (mg/L)

\( v_i \) = Effective settling velocity for size class \( i \) (m/s)

\( h \) = Depth of the water (m)

\( t \) = Time (s)

\( \bar{v}_i \) = Average settling velocity (m/s)

\( v_{\text{max}} \) = A grain class mass-weighted average maximum floc settling velocity (m/s)

\( C \) = Total concentration for all size classes (kg/m\(^3\))

\( (gs) \) = Size class index ranging from 1 to the number of grain classes

\( C_{ll} \) = Mass-weighted average lower concentrations (kg/m\(^3\))

\( C_{ul} \) = Mass-weighted upper concentrations (kg/m\(^3\))

\( v_{S50} \) = Median settling velocity (mm/sec)
\( v_s \) = Concentration-dependent settling velocity
\( v_{s'} \) = Concentration and shear flow rate determined settling velocity
\( G \) = Fluid shear rate (Hz)
\( \beta \) = Non-spherical particle shape factor
\( x, y, z \) = Lengths of the three principle axes of the particle in decreasing order of magnitude
\( E \) = Distortion factor
\( c \) = Polar semi-axis
\( R \) = The equatorial radius
\( r \) = Radius of a sphere
\( \xi_0 \) = Shape factor of the primary particle
\( \xi \) = Shape factor of the aggregate (three-dimension)
\( \xi_2 \) = Two dimensional shape factor (relate aggregate size to projected area)
\( l \) = Characteristic length of a fractal aggregate
\( l_0 \) = Length of primary particle in the aggregate
\( D \) = Three dimensional fractal dimension
\( D_2 \) = Two dimensional fractal dimension
\( \rho_0 \) = Density of the primary particle
\( \zeta \) = Packing factor
\( v(n^{th}) \) = Settling velocity at \( n^{th} \) withdrawal (m/s)
\( H \) = Column height (m);
\( t_P \) = Elapsed time of sampling (s);
\( h' \) = The height from the top of the linear density column (cm), \( h' > 110 \) cm
\( \mu_1 \) = Dynamic viscosity [ \( g/(cm \cdot s) \)]
\( V \) = Volume of the particle (cm\(^3\))
\( v \) = Settling velocity (cm/s)
\( g_1 \) = Gravitational constant (980 cm/s\(^2\))
\( v_p \) = Flow velocity in the column
\( C_{in} \) = Inlet concentration
\( C_{uniform} \) = Concentration in the uniform zone
\( C_0 \) = Suspended concentration (kg/m\(^3\))
$C_S$ = Salinity concentration (ppb)

$v_S$ = Settling velocity (mm/sec)

$\overline{G}$ = Average turbulence velocity gradient $\overline{G} = \sqrt{\varepsilon / \mu}$

$\varepsilon$ = The turbulent dissipation

$v_{ib}$ = Terminal velocity in a bounded liquid;

$v_{\infty}$ = Terminal velocity in an infinite liquid;

$Re_{\infty} = $ Sphere Reynold’s number, $Re_{\infty} = \frac{\rho dv_{\infty}}{\eta}$;

$\lambda$ = Diameter ratio, $\lambda = d / D'$

$D'$ = Diameter of the column

$d_i$ = Diameter of $i$th sieve in the stack

$d_u$ = Diameter opening through which particles will pass (sieve proceeding $i$th)

$d_o$ = Diameter opening through which particles will not pass ($i$th sieve)

$V_S$ = True sample volume in pycnometer (cm$^3$)

$V_C$ = Cell volume in pycnometer (cm$^3$)

$V_R$ = Reference volume in pycnometer (cm$^3$)

$P_I$ = Initial pressure in pycnometer (psi)

$P_2$ = Final pressure in pycnometer (psi)

$M_s$ = Mass of the sample specimen determined prior to placement in the pycnometer (g)

$V_s$ = Volume of specimen (cm$^3$)

$\overline{v}$ = The mean measured settling velocity (cm/s)

$H$ = Settling distance (cm)

$t$ = Measured settling time (s)

$\overline{v}_k$ = Average settling velocity for size gradation $k$

$N$ = Total number of particles with size gradation $k$

$N_i$ = Number of particles in the sample taken at time $t_i$ with size $k$

$v_k$ = Measured settling velocity at time $t_i$ for particle with size $k$
CHAPTER 6.  COAGULATION AND FLOCCULATION OF PARTICULATE MATTER TRANSPORTED BY URBAN RAINFALL-RUNOFF

SUMMARY

Urban particulate matter transported by rainfall-runoff is a heterogeneous mixture, with particles range in size from submicron to gravel-size. While continuing a potential water quality concern as suspended, settleable or sediment matter, particulate matter in urban rainfall-runoff is unique compared to other particulate-loaded discharges because of the very large size gradation (<1 µm to > 10,000 µm) and destabilized nature of particles with relatively short exposure to the aqueous matrix (typically less than several hours). This study investigates coagulation and flocculation (C/F) in urban rainfall-runoff with and without the addition of coagulants or flocculants incorporating particle size distribution analyses. Results demonstrated that without coagulant/flocculant addition, particulate matter in rainfall-runoff remains stable in suspension for extended hours. While a significant particulate removal can be achieved in a short retention period with addition of alum or polymers. In terms of particle volume distribution, turbidity and total suspended solids removal, Alum with a dosage of 30-mg/L is suggested for rainfall-runoff treatment at the cost of $4.8x10^{-6}/L (rainfall-runoff). In contrast to the commonly accepted mechanism of double layer compression, alum is effective coagulant through adsorption, charge neutralization and sweep floc development. As a comparison, C/F in river water and wastewater were also studied. FeCl₃ was proved to be most effective in improving settleability of particles in primary wastewater influent. A high charge density anionic polyacrylamide worked best in the C/F test for river water.
INTRODUCTION

Rainfall-runoff related inputs of nutrients, suspended solids, metals and bacteria have the potential to impact water quality of the receiving water bodies. Survey by National Water Quality Inventory (1998) showed that urban rainfall-runoff (wet weather flows) was a leading cause of impairment to nearly 40 percent of water bodies in United States which did not meet water quality standards. Currently, most rainfall-runoff is discharged untreated directly into the water bodies. The anthropogenically-impacted rainfall-runoff will degrade and deteriorate the receiving water bodies, resulting in the destruction of fish, wildlife, and aquatic life habitats; a loss in aesthetic value; and potential impact to public health through contaminated food, drinking water supplies, and recreational waterways.

New land development projects in many states require rainfall-runoff management. Traditional best management practices (BMPs) such as retention or detention ponds are utilized to minimize post-development discharge of constitutes such as suspended solids to receiving water bodies. However, majority of existing land development occurred before implementation of current rainfall-runoff regulations and, therefore, contain no facilities for rainfall-runoff management. Many of these areas are highly urbanized and fully developed, with little space available for retrofitting activities using traditional rainfall-runoff management techniques.

On the other hand, gravitational settling is unable to remove the colloidal pollutants and insufficient in removing particles with low settling velocity (Gromaire-Mertz et al. 1999). Colloidal and fine particles (<75-µm) tend to stay in the suspension for extended periods of time. While the medium to coarse fraction of particles has been shown to
transport the predominance of adsorbed constitute mass, the fine fraction of particles has
the great potential bioavailability (Sansalone et al. 1998). If discharged without
clarification of these fine particles, rainfall-runoff will cause turbidity of the water body,
reduce levels of dissolved oxygen, and pose toxicity threat to aquatic life.

In view of the above issues, alternative technologies or enhanced sedimentation are
required to address urban rainfall-runoff treatment. Chemical treatment is seen as one
possible enhancement. Coagulation and flocculation (C/F) processes have generated
renewed interest in urban wastewater treatment for several reasons. First, C/F processes
removes phosphorous, suspended solids, organic matter as well as metals bounded to the
particulates. Secondly, C/F processes can accommodate daily and seasonal variations
both in flow and wastewater composition with demonstrated economic feasibility
(Passino and Ramadori 1999). In third, when sedimentation is followed by C/F process or
combined with a C/F process, particles down to 0.1-µm may be separated.

C/F is also a possible solution to reduce the impact of combined sewer overflows
(CSO) on surface water quality (De Cock et al. 1999). Anderson et al. (1992) proposed
application of C/F to rainfall-runoff overflow treatment, claiming that it could achieve
sedimentation rates up to 20-m/h (5.55-mm/s) and solids removal efficiencies of greater
than 90% on a mass basis. Camp Dresser & McKee Inc. developed an approach for the
wastewater plant in Fort Worth, Texas to deal with wet weather flows by incorporating
C/F and ballasted sedimentation (Crumb and West 2000).

A prototype rainfall-runoff alum treatment system was introduced in a lake
restoration project on Lake Ella in Tallahassee, Florida in 1986, based on the flow-
weighted injection of liquid aluminum sulfate (alum, Al₂(SO₄)₃·18 H₂O) into the rainfall-
runoff flows inside storm sewer lines before discharging to the lake (ERD 1999). Alum treatment of rainfall-runoff has been shown to consistently reduce concentrations of orthophosphorous and total phosphorus by 85%-95%, metals by 80%-90%, suspended solids by 95%, total nitrogen by 50%-80%, and coli form bacteria by more than 99%. Six more alum rainfall-runoff treatment systems have been constructed since Lake Ella. These systems typically require little acquisition or rainfall-runoff basin construction, thus greatly reducing the capital cost of rainfall-runoff retrofit projects.

**Unique Characteristics of Urban Rainfall-Runoff**

In storm runoff at the upper end of the urban watershed, the colloidal and suspended fractions are mixed with the settleable and sediment fractions in a relatively shallow water column (mm to cm). With residence times of these particles in rainfall-runoff generally less than several hours and with unsteady flow, equilibrium and steady-state floc development has not occurred in rainfall-runoff by the time such flows are treated in-situ or regionally for an urban catchment. This makes rainfall-runoff unique from natural waters and wastewaters. Coagulation/flocculation and floc-breakup are still active processes at the location of many in-situ treatments.

Particulates are important in understanding the impact of the pollution from urban rainfall-runoff and have been studied extensively (Yu et al. 1994; Characklis and Wiesner 1997; Sansalone et al. 1998; Drapper et al. 2000). While researchers have found that the greatest metal concentrations are associated with fine particles (<50-µm) (Xanthopoulos and Augustin 1992; Sansalone and Buchberger 1996), the greatest amount of metal mass has been found relating to the medium to coarse size particles (Sansalone 1998). Nature and size distribution of the particles play an important role in determining their transport.
and fate, as well as any associated contaminants. Large solids in runoff may settle into sewers and urban waterways, however, these particles and contaminants can be mobilized by subsequent storms or pose a chronic threat to aquatic life. Smaller, colloidal particles remain in suspension and can be transported much greater distances, while still pose a chronic threat to aquatic life. Therefore, granulometric-based distribution of particles in urban rainfall-runoff results in both spatial and temporal variations in particle transport and contaminant fate (Characklis 1997).

Removal of only the gross solids (greater than 6-mm) from sewer overflows would do little to reduce the impact of sewer overflows on receiving waters, other than to remove some of the more visible pollution (Xanthopoulos et al. 1993). Separation of fine particulate and colloidal solids is necessary in order to reduce the pollutant load from sewer overflows to levels acceptable for discharge to receiving waters (Booker et al. 1996). In general, rainfall-runoff is of low hardness with a low acid combining capacity. While the colloids and the suspended particles have a negative charge in rainfall-runoff, the concentration of salt is generally low (Heinzmann 1994). In water of low hardness, colloids are very stable, because the operational range of the electrostatic repulsion is higher than in hard water. Odegaard et al. (1990) have shown that at equal colloid and particle concentrations, soft water contains more colloids and particles with a diameter of < 1-µm and less particles with a diameter of > 1-µm than hard water. Therefore, the coagulant dose for destabilization is lower in water of high hardness than in water of low hardness.

**Characteristics of Particles in Wastewater**

Particles in wastewater are generally negatively charged (van der 1990).
The negative surface charge of the particles is primarily developed in three principle ways: dissolving and acid/base reactions at the boundary layer; adsorbed ions or polymers and grid imperfections (Nieuwenhuijzen 2002). Zeta potential in wastewater was experimentally determined in the range of -15 to -40 mV (Henze et al. 1995, Elmitwalli 2000). A significant part of pollutants in municipal wastewater is associated with colloidal and suspended particles (Levine et al 1985, 1991). The particle-related pollutants can be removed by physical-chemical unit treatment procedures. One of the first preliminary unit operations in a public owned treatment works (POTW) is separation of the settleable and grit material, conventionally in a grit chamber (Metcalf and Eddy 1991). Smaller material and larger organic material pass through the grit chamber and into the primary clarifier. The primary clarifier is typically designed using conventional overflow rate theory to remove organic settleable material and organic/inorganic suspended material (Metcalf and Eddy 1991). The long residence time, mixing conditions and equilibrium established during the transportation have allowed coagulation/flocculation to occur and a steady-state granulometry to result.

**Characteristics of Particles in Natural River Water**

Natural river waters transport both cohesive (fine silts and clay-size particles) and non-cohesive particles (medium size silts and coarser particles) (Hayter and Gu 2001). In natural waters under most hydrodynamic (steady, dry weather flows) and residence time conditions (days to weeks or longer), the colloidal and suspended fractions predominate in the water column since the settleable and sediment fractions have separated from the water column at much shorter residence times and the stream power is not sufficient to entrain these coarser fractions. Fine particles cannot be settled by gravity and can be
easily re-suspended in response to fluctuating energy over a wide range of time scales (Nichols 1986). These fine particles in the natural rivers are mixture of inorganic minerals, organic materials and biochemicals (McAnally and Mehta 2001). Much research has focused on both the transport of colloidal/suspended material in the water column from an environmental perspective (Myrhaug et al 1993) as well as the settleable/sediment material as bed load from a sediment transport and hydraulic perspective (Krank 1986). Cohesion induced particle aggregation for clay-sized particles affects sediment behavior. The degree of cohesion displayed by fine particles is a function of particle cationic exchange capacity and fluid properties (McAnally and Mehta 2001).

**Coagulation and Flocculation Processes**

Coagulation and flocculation is a two-step serial process in which the destabilization of suspended particles is known as coagulation while aggregation of destabilized particles is known as flocculation. Mechanisms of destabilization include: double layer compression by different electrolytes; charge neutralization by specifically adsorbed charged species; enmeshment in a precipitate (formation of sweep floc); and adsorption and inter-particle bridging. There are three mechanisms for particle attachment (Flocculation). First mechanism is perikinetic (or Brownian) flocculation, which is due to particle diffusion and only significant for particles less than 1-μm. Second mechanism is orthokinetic flocculation under which particle contacts are caused by differences in fluid velocity. The third mechanism is differential settling under which particles with different settling velocities collide. This mechanism is significant for suspensions with larger particles (>50-μm).
**Coagulants and Flocculants**

Inorganic coagulants can be electrolytes or polyelectrolytes and are typically based on iron (ferric), aluminum, calcium, or magnesium. When these coagulants are dissolved in water, they generate highly charged cationic ions for destabilizing dispersed solid particles. When these cationic ions are introduced into a system with negative charged particles, they interfere with the repulsive stabilization by charge neutralization and allow the particles to come into close contact. This starts the coagulation process. Large aggregates formed from destabilized particles are separated from the stream through clarification. $\text{Al}^{3+}$ or $\text{Fe}^{3+}$ ions can also be hydrated to form aquo metal complexes of $[\text{Al(H}_2\text{O)}_6]^{3+}$ or $[\text{Fe(H}_2\text{O)}_6]^{3+}$. These positively charged species could cause destabilization of negatively charged colloids by adsorption and charge neutralization. Precipitation of amorphous metal hydroxide is necessary for sweep-floc coagulation. Inorganic coagulants usually offer a low unit price, therefore are widely available. They are quite effective in removing most suspended solids, and also capable of removing a portion of the organic precursors which may combine with chlorine to form disinfection by-products. The large volumes of floc they produced can entrap bacteria during the process of settling. Application of inorganic coagulants such as alum or ferric will consume alkalinity resulting in the alteration of pH in the water. For this reason, alum and iron salts generate demand for lime and soda ash. They also require corrosion-resistant storage and feed equipment. The large volumes of settled floc need to be disposed of in an environmentally acceptable manner.

Synthetic flocculants have been used in water treatment since 1960's. Linear and branched polymers are most frequently encountered types. Molecular weights for
polymers range from a few hundred thousand to tens of millions. A polymer is referred as a polyelectrolyte if its monomers contain ionizable groups. Nonionic polymers contain no charge-bearing groups and anionic polymers are usually copolymers of acrylamide and acrylic acid, sodium acrylate or another anionic monomer. Anionic polymers acquire a negative charge upon ionization. They are ineffective for negatively charged particles when used alone in coagulation. Cationic polymers can be copolymers of acrylamide with a cationic monomer, cationically modified acrylamide or a polyamine. The cationic charge in these polymers is derived from nitrogen in the form of a secondary, tertiary or quaternary amine group. Those containing secondary or tertiary amines are sensitive to pH. The charge on these polymers drops off quickly as the pH rises above 6. Cationic polymers become positively charged when dissolved. Cationic polymers are effective for negatively charged particles during coagulation process. Attachment of polymer to particle is via electrostatic attraction or ion exchange. Inter-particle bridges are formed during the process of flocculation.

Flocculation requires adsorption of polymer segment onto the particle surface. This adsorption is made possible through hydrogen bonding and hydrophobic interaction in which a polymer with significant hydrophobic character is “squeezed” out of the aqueous solvent to adsorb onto the particulate surface (Hecker 1998). Charged polyelectrolytes interact with a particle surface through ionic mechanisms: electrostatic interactions between oppositely charged polymer and particulate surface; or polyvalent ion bridging between similarly charged polymer and particle surface. Polymers are efficient flocculants at low concentrations.
The most common flocculants are polyacrylamide which is a non-ionic polymer and its derivatives. They bring about agglomeration of the particles by inter-particle bridging. Polyacrylamides can be given an anionic charge by co-polymerizing acrylamide with acrylic acid. Cationic polymers are prepared by co-polymerizing acrylamide with a cationic monomer. The polyacrylamides are usually less pH sensitive.

OBJECTIVES

This research was to study coagulation and flocculation of colloidal and non-colloidal particulate matter in urban rainfall-runoff and compared to C/F processes in wastewater and natural river water. There are three objectives included. The first objective was to examine coagulation-flocculation in urban rainfall-runoff through jar testing of specific coagulants and flocculants. The second objective was to evaluate the effect of C/F assisted removal of particulates through particle size distribution analyses in bench-scale settling column test. The third objective was to compare C/F processes in rainfall-runoff treatment with C/F in wastewater and natural river water. C/F mechanisms in each water scheme were to be discussed.

METHODOLOGY

Sample Collection

Wastewater samples were collected from the influent chamber of primary clarifiers from South Wastewater Treatment Plant at Baton Rouge, Louisiana. River water was sampled from Mississippi river. Urban rainfall-runoff was collected from the sedimentation basin at an elevated section of interstate highway bridge located in Baton Rouge, Louisiana immediately following rainfall event. All samples were brought back to the lab for tests and analyses.
Jar Test Design

Design effects include type of coagulant and dosage. Type of coagulant is fixed with six levels including alum (Al₂(SO₄)₃·18H₂O) – A, ferric chloride (FeCl₃) – B, cationic polyacrylamide flocculants (CP) 1 & 2 and anionic polyacrylamide flocculants (AP) 1 & 2. The difference between cationic or anionic polyacrylamide 1 and 2 is the charge density. The charge density of polymer indicates the amount of charge available to accomplish destabilization and flocculation. It is expressed as the weight percentage of charged monomers. CP₁ and AP₁ have the charge density of 20% and 30% respectively, while CP₂ and AP₂ have the charge density of 5% and 10%. There were 7 dosage levels for coagulant alum and ferric chloride, 6 dosage levels for flocculants CP and AP as listed in Table 6.1. Each dosage-coagulant/flocculant combination was randomly assigned to the jar and experiments were replicated. Turbidity, total suspended solids, particle size distribution, pH were measured for each sample.

Table 6.1 Experimental matrix for C/F with coagulants or flocculants

<table>
<thead>
<tr>
<th>Coagulant/flocculants</th>
<th>Dosages (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alum/FeCl₃</td>
<td>0 (control)</td>
</tr>
<tr>
<td></td>
<td>5</td>
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<td></td>
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<tr>
<td></td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>50</td>
</tr>
<tr>
<td>CP/AP</td>
<td>0 (control)</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
</tr>
<tr>
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<td>10</td>
</tr>
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<td>12.5</td>
</tr>
</tbody>
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The inorganic coagulants were prepared by dissolving the powders to make 10-g/L solution. A polymer solution was prepared by diluting the stock polymer emulsions just prior to the experiment. The working solution for the polymers is 0.1%. Under same experimental conditions (pH, temperature, mixing intensity and time, clarification time), best coagulant/flocculant and optimal dosages were determined according to the statistical analysis results.
Jar Test Procedure

The objective of jar test is to determine the most effective coagulant and the optimal dosage. The parameters in jar test include concentration of wastewater, river water or rainfall-runoff; type and dosage of coagulants and flocculants. Temperature, pH value, mixing intensity, mixing time and flocculation time are the controlling experimental parameters. Turbidity, total suspended solids (TSS) and particle size distribution (PSD) of samples were measured to evaluate the effectiveness of various C/F processes.

The jar tester employed in this study (Phipps & Bird PB-900) employs 2-L jar with designed settling distance of 100-mm. Agitator paddle speed is linearly related to the velocity gradient (G, s⁻¹). The samples for turbidity and PSD measurement were taken at the same depth, trying not to disturb the remainder of the jar. Prior to the sampling time, the siphon tube was drained and the tube volume about 5-ml was discarded. Jar test was following standard procedure ASTM D 2035-80. After recording the raw water pH, temperature, turbidity and particle size distribution, the lab-scale jar-test started from rapid mix at 120 rpm for 1 minute. The mixing speed was reduced to 20 rpm after that and the slow mixing remained 20 minutes. 15-min clarification settling was followed to allow the flocs to settle down.

Settling Column Test

An acrylic settling column was designed with a settling distance of 2466-mm and inside diameter of 139.7-mm. A view of settling column and sampling ports in the lab was shown in Figure 6.1. The optimal coagulant/flocculant and dosage determined from jar-test was applied in the settling column test. Column C/F test procedure was similar to that in jar-test. After addition of coagulant/flocculant to the mixing tank (50-gallon),
rapid mixing was initiated and lasted for one minute, followed by 20-min slow mixing. The water was then pumped into the column and started clarification. Samples were collected from two sampling ports along the column – top and bottom as indicated in Figure 6.1. Each sample was analyzed for particle size distribution immediately. Turbidity, pH, conductivity and TSS were also analyzed for each sample. The effectiveness of C/F, clarification process was determined by particle removal measured through turbidity, TSS and particle size distribution during the clarification process. Samples were taken every hour for six hours. Particle size distribution measurements were characterized by volume distribution and number distribution. A laser diffraction particle analyzer LISST-Portable (Sequoia Tech) was used to measure the particle volume distribution. Number distribution was calculated based on the assumption of spherical particles. Measurable size is ranging from 1.25 to 250 µm.

Figure 6.1 Illustration of settling column employed in the experiment
**Floc Characterization**

The retrieved flocs from C/F process were characterized using image analysis. Each floc was observed under optical microscope (BX-600) and scanning electron microscope.

**RESULTS AND ANALYSIS**

**Jar Test for Rainfall-runoff**

The experiments were conducted under constant lab temperature $23 \pm 0.5^\circ C$. pH of raw rainfall-runoff was $7.40 \pm 0.05$. Figure 6.2 through Figure 6.7 showed the particle volume distribution and cumulative particle number distribution for rainfall-runoff C/F with addition of alum, FeCl₃, CP (1&2) and AP (1&2) at different dosages.

Raw rainfall-runoff and control (zero dosages of any coagulants/flocculants) were also analyzed for comparison. Except for a small reduction of particles greater than 10-µm, majority of particles in rainfall-runoff remained their stable status without interference of coagulants or flocculants. With addition of alum at dosage of 20-mg/L and above, destabilized clay-size (<2-µm) particles began to coagulate; large aggregate was then removed from the suspension by clarification. In similar, with dose of FeCl₃ at 20mg/L and above, clay-size particles began to destabilize and formed large aggregates during C/F process. However, the FeCl₃ flocs did not settle as well as alum flocs. A significant amount of particle volume between 30 to 60-µm had been seen in Figure 6.3.

With addition of CP₁, a high charge density cationic polyacrylamide, particles less than 10-µm were efficiently removed at dosage 7.5-mg/L or higher. It has been observed that large aggregates were formed. The presence of these large flocs in the sample was attributed to the peak volume distribution in the larger size end. Similarly, AP₁ (anionic polyacrylamide, charge density 30%) showed a significant removal even at a very low
dosage. In addition, the aggregates settled quickly from the suspension. In contrast, low charge density anionic polyacrylamide AP₂ was not as effective as AP₁ though it also achieved a decent removal of particles. Low charge density cationic polyacrylamide CP₂, on the other hand, was not effective in removing fine colloidal size particles.

Jar-test results in terms of turbidity and TSS were illustrated in Figure 6.8 and removal efficiencies for turbidity and TSS with all types of coagulants and flocculants were summarized in Figure 6.9. In general, anionic polymer with a high charge density worked best in the C/F process for rainfall-runoff. However, because of the high viscosity of polymer, it was not easy to mix them well with a large volume of rainfall-runoff. Alum, instead, was chosen as the coagulant for the column test thereafter. According to jar test, at dosage of 30-mg/L alum, 80% of TSS removal was achieved. The pH value was reduced to 7.25, which was within the acceptable range. Based on dosage of 30-mg/L alum, the estimated chemical cost is $4.8x10⁻⁶/L ($160/dry ton, HSA 2001).

Zeta potential (ψ) measurement showed that there was no significant difference before and after C/F using alum (Before Ψ = −14.7 ± 1.3 mv; after Ψ = −15.3 ± 1.3 mv). It indicating that instead of the commonly accepted mechanism double-layer compression, alum is an effective coagulant in rainfall-runoff through adsorption, charge neutralization and sweep floc enmeshments.

**Jar Test for Wastewater**

Raw wastewater showed a skewed particle size distribution towards larger size. By gravitational settling, a significant amount of large particles can be removed. Figure 6.10 through Figure 6.15 showed the results of jar-test for wastewater with alum, FeCl₃, CP 1 & 2 and AP 1 &2. FeCl₃ was proved to be the most effective coagulant for enhanced
wastewater pretreatment. According to jar-test, at dosage of 30-mg/L, 86% removal was obtained and pH dropped to 7.14. Anionic polyacrylamide did not work at all because of the negative charge of wastewater. CP1 at a dosage of 5-mg/L or above improved the particle removal. Figure 6.16 summarized the turbidity and TSS results of jar-test for C/F in wastewater. Removal efficiencies were plotted in Figure 6.17. In all aspects, FeCl3 was chosen for the following column test.

**Jar Test for Natural River Water**

River water has the longest retention time among the three waters investigated. Jar-test results for river water were shown in Figure 6.18 through Figure 6.25. Quiescent settling can settle out particles greater than 100-µm. However, small size particles, especially clay-size colloidal particles cannot be removed by gravitational sedimentation. C/F experiments on river water showed that alum, at dosage of 20-mg/L or higher, enhanced the particle removal of small size range. AP1 in this case still worked best and therefore was chosen to be applied in the lab-scale column test thereafter.

**Settling Column Tests**

Alum, FeCl3 and AP1 were chosen respectively for rainfall-runoff, wastewater and river water coagulation/flocculation column test. Quiescent settling column tests without addition of any coagulants or flocculants were carried out for three types of waters and results were compared with C/F settling column tests. Particle volume distribution and number distribution were illustrated for each sample withdrawn from top and bottom sampling ports. Figure 6.26 through Figure 6.34 showed the settling column test results for rainfall-runoff, wastewater and river water.
Under quiescent settling of rainfall-runoff, there was no significant change in particle distribution throughout the column during the first three hours as seen in Figure 6.26. Particles in raw rainfall-runoff remained stable in suspension. Until the fourth hour of retention, a decrease of particle volume distribution was observed for particles in the range of 5 to 100-µm. In contrast, with addition of alum at dosage of 30-mg/L, small particles (<10-µm) were destabilized, coagulated and clarified from the suspension rapidly. Time zero in the C/F column test was starting from clarification, during which destabilized particles were settled out by gravitational force in the column. A higher volume distribution analyzed for the sample withdrawn from the bottom sampling port indicated the sedimentation of large aggregates formed from the C/F process. With increase of retention time, particle removal increased. Turbidity and suspended solid concentration (SSC) removal for C/F with alum was compared with quiescent settling of rainfall-runoff. Results were shown in Figure 6.28. An average of 74.2% removal of SSC, 66.0% removal of turbidity was obtained with addition of alum after 2-hour retention. In contrast, only 23.1% of SSC and 16.0% of turbidity removal was attained with same retention time under quiescent settling.

In the C/F column test for wastewater, gravitational sedimentation can remove particles in the large size range efficiently given retention time over 3 hours. The typical retention time for primary sedimentation tank is 1 to 2.5 hr (Tchobanoglous 1991) based on the wastewater flow. Application of FeCl₃ enhanced the particle removal by 37% in terms of turbidity and 10% in terms of SSC (Figure 6.31).

For the river water, quiescent settling cannot remove particles less than 5-µm (Figure 6.32). With a high charge density anionic polyacrylamide (AP₁), the fine size particles
were destabilized and coagulated. As shown in Figure 6.33, an increase in volume concentration was observed for the samples taken from the bottom ports in later time. This increase was attributed to descending particles intercepted at the point of sampling. As a result of quiescent settling, turbidity removal was 18% and SSC removal was 52%. In comparison, C/F with AP1 for natural river water achieved 80% of turbidity removal and SSC removal.

**Floc Characteristics**

Flocs obtained from jar-test for three types of waters were retrieved and analyzed under optical microscope. The transmitted light optical images and scanning electron images of these flocs were shown in Figure 6.35. As seen in Figure 6.35, flocs formed by flocculants are large flake-size aggregates, especially in wastewater C/F. Inter-particle bridging effect was apparent in Figure 6.35 (e) and (f). Flocs formed through inorganic coagulants are more densely packed.

**CONCLUSIONS**

Particles in rainfall-runoff remain stable and stay in the suspension for an extended period. Traditional gravitational settling can not remove small particles efficiently from rainfall-runoff suspension. The conducted jar test experiment and settling column test showed that with addition of alum or high charge density polyacrylamide, particles were destabilized, coagulated, flocculated and settled out of solution within a short retention time. The addition of metal salts alum resulted in a slight decrease of pH. No significant pH effect was found when dosing flocculants since polyacrylamide is less pH-sensitive. Aggregates formed through alum induced coagulation are smaller than those formed by flocculants. Considering the field application, alum was recommended for urban rainfall-
runoff treatment. Through adsorption, charge neutralization and sweep floc development alum is an effective coagulant in rainfall-runoff, in contrast to the more commonly accepted mechanisms of double-layer compression.

C/F was also applied to improve the particle removal in primary wastewater treatment. FeCl₃ was proved to be effective to remove negatively charged particles in primary wastewater stream. River water contains more particles with fine size (less than 5-µm), which cannot be removed by sedimentation. These particles are also easily resuspended by turbulent flow. They will be a concern for sensitive watershed. Removal of these particles can also be realized through C/F.

REFERENCES


Figure 6.2 Coagulation and flocculation jar-test of alum for rainfall-runoff (shaded bars are the measured incremental volume distribution as a function of particle diameter; scattered plots with error bars are cumulative particle number distribution calculated from particle volume distribution.)
Figure 6.3  Coagulation and flocculation jar-test of FeCl$_3$ for rainfall-runoff
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- **Turbidity (NTU)**
  - Control
  - FeCl₃
  - Alum

- **SSC [mg/L]**
  - Control
  - Alum
  - FeCl₃

Figure 6.25 Removal of turbidity and SSC for C/F jar-test of river water:

- **Turbidity removal %**
  - Alum
  - FeCl₃

- **SSC removal %**
  - Control
  - AP₁
  - AP₂
  - CP₁
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CHAPTER 7. COAGULATION AND AGGREGATION MODEL INCORPORATING FRACTAL THEORIES FOR PARTICULATES IN URBAN RAINFALL-RUNOFF

SUMMARY

Particulate matter plays an important role in transport and transformation of contaminant. Separation of particulate from urban rainfall-runoff is one of the major goals of best management practices in urban rainfall-runoff treatment. Sedimentation has been used generally in removing settleable particulates. Coagulation and flocculation was applied to removal colloidal and fine particles in order to improve the treatment efficiency. The fractal nature of particles in urban rainfall-runoff and heterogeneous distributions complicated the process. Theoretical settling model and coagulation and flocculation model cannot predict the behavior of real particles in the system. Design based on traditional model would be inappropriate. A thorough literature review on the contaminant removal mechanisms – sedimentation, coagulation and flocculation was summarized in this study. Based on the granulometry and fractal study, a modified fractal model was evaluated to simulate and predict the particle size distribution during the sedimentation and coagulation process in urban rainfall-runoff treatment system. The simulation applied to a 2-m settling column system with sediment particles from urban rainfall-runoff. Fractal dimension and collision efficiency $\alpha$ are considered important factors in determining particle size distribution.

INTRODUCTION

Pollution from suspended particles to natural water bodies is one of many consequences of the intensive utilization of the land. Urban rainfall-runoff is one of the major sources of these particles. Besides the fact that the particles themselves are
pollutants because of the displeasing effect esthetically and the decreasing rate of photosynthesis, particles are also of concern because toxic heavy metals and persistent organic compounds are predominantly transported within particles or adsorbed on the surfaces (Hunt 1980). Sedimentation and coagulation cause the removal or loss of a particle of a given size from a volume of fluid. Sedimentation removes particles from the volume of fluid, while coagulation and flocculation transports many smaller particles into fewer larger particles with the fluid volume.

In natural and polluted waters there exists a continuous distribution of particle sizes. The dynamics of a continuous size distribution is defined in Equation 1.

\[
dN = n(d_p)\Delta(d_p)
\]

where \(dN\) is the number of particles per fluid volume with diameters in the range of \(d_p\) to \(d_p + \Delta(d_p)\).

The sedimentation flux (\(F\)) of particles is the Stokes’ settling velocity of a spherical particle with diameter \(d_p\) times the number of particles in the size interval \(d_p\) to \(d_p + \Delta(d_p)\).

\[
F = \frac{g}{18\mu} \left(\frac{\rho_s - \rho_L}{\rho_L}\right) d_p^2 n(d_p) \Delta(d_p) \quad [L^2 t^{-1}]
\]

\(\rho_s\) and \(\rho_L\) are the particle and fluid density respectively. The dimensional unit of time is indicated by \([t]\) and \([L]\) represents a fluid length.

**Coagulation Processes**

Coagulation and flocculation traditionally is a two-step serial process in which the “destabilization” of suspended particles is known as coagulation while aggregation of destabilized particles and the rate of floc growth are known as flocculation. Mechanisms
of destabilization include: Double layer compression by different electrolytes (elevated ion concentration reduces double layer thickness); Charge neutralization by specifically adsorbed charged species; Enmeshment in a precipitate (formation of sweep floc); and adsorption and inter-particle bridging. There are three mechanisms for particles attachment. For particles significantly less than 1-µm, perikinetic flocculation (or Brownian motion) is dominant due to particle diffusion. Particle contacts caused by differences in fluid velocity are considered orthokinetic flocculation (shear driven transport and collision). For particles greater than 50-µm, differential settling is the significant mechanism for particle flocculation.

**Classical Flocculation Model**

The fundamental mathematical model of flocculation process was developed by Smoluchowski (Thomas 1999). The basic equation for the flocculation process is expressed as:

$$\frac{dn_k}{dt} = \frac{1}{2} \alpha \sum_{i+j=k} \beta(i, j)n_i n_j - \alpha \sum_{i=1}^{c} \beta(i, k)n_i n_k$$

Equation 3 defines the rate of change in the number concentration of particle size \( k \). \( \alpha \) is the collision efficiency, \( \beta(i, j) \) is the collision frequency between particles of size \( i \) and \( j \), and \( n_i, n_j \) are the particle concentrations for particle of size \( i \) and \( j \) respectively. Subscript \( i, j \) and \( k \) represent discrete particle sizes. \( c \) is the largest size considered. The basic concept for the above model is that the concentration of the particles of a given size \( k \) can be increased by the collision and attachment of two small particles whose total volume is that of a \( k \)-size particle (first term on the right side), and decreased by the collision and
attachment of a \( k \)-size particle with any size particle to form a larger particle (second term on the right side).

The assumptions made for simplifications include that collision efficiency \( \alpha \) is unity for all collisions; fluid motion undergoes laminar shear; the particles are mono-dispersed; no breakage of flocs occurs; all particles are spherical in shape and remain so after collision; and collision involves only two particles (Binary collisions). Base on these assumptions, the equations to describe the collision frequency for each flocculation are as follows.

For perikinetic flocculation,

\[
\beta_p = \frac{2kT}{3\mu} \left( \frac{1}{d_i} + \frac{1}{d_j} \right)(d_i + d_j)
\]

(4)

For orthokinetic flocculation,

\[
\beta_o = \frac{1}{6} \left( \frac{du}{dy} \right)(d_i + d_j)^3
\]

(5)

where \( k \) is Boltzmann’s constant, \( T \) is the absolute temperature of the fluid, \( \mu \) is the dynamic viscosity of the fluid, and \( du/\text{dy} \) is the velocity gradient of the fluid.

For differential sedimentation,

\[
\beta_D = \left( \frac{g\pi}{72\mu} \right)(\rho_s - \rho_l)(d_i + d_j)^3|d_i - d_j|
\]

(6)

where \( d_i \) and \( d_j \) are the diameters for the particle \( i \) and \( j \) respectively.

**Modified Flocculation Model**

The classical approach leads to analytical expressions to define the coagulation and flocculation process; however, their pertinence to real systems is constrained by the
assumptions. The validity of each of the assumptions leads to the modification of the fundamental model. In turn, each assumption is reviewed in terms of modeling.

Assumption 1: The collision efficiency factor $\alpha$ is unity for all collisions.

Not all collision leads to attachment. The effect of short-range forces such as electrostatic repulsion, van de Waals or hydrodynamic forces is non-negligible in the real system. The combined effect of electrostatic repulsion and van de Waals attraction between two particles is described by the DLVO theory (Deryaguin and Landau 1941; Verwey and Overbeek 1948). This theory assumes that the effect of two forces is additive, and the results can be displayed in the form of a potential energy diagram shown in Figure 7.1. The lower the energy barrier, the closer to unity $\alpha$ becomes.

Figure 7.1 DLVO theory-Potential energy diagram

The Smoluchowski model assumes that inter-particle interactions are negligible until the point of contact, whereupon adhesion takes place with 100% efficiency. The inter-particle interaction based on this assumption is described as rectilinear. However, in the real system the hydrodynamic forces have significant impact on the colloidal particles.
They cause the approaching particles to rotate slightly around one another, which are known as curvilinear. Rectilinear model and curvilinear model were discussed considering the hydrodynamic forces (Han and Lawler 1992). Three important conclusions arise from the developments of curvilinear models: First, orthokenetic flocculation is far less important in the curvilinear model than in the rectilinear model; Secondly, the curvilinear model predicts a much lower collision frequency than the rectilinear model, although the reduction is less when the particles are of similar size; Finally, orthokenetic flocculation is no longer seen as being directly proportional of velocity gradient $G$ (Camp and Stein 1943).

Current developments in the modeling of hydrodynamic forces between colloid particles are developing in two areas: non-uniform porosity (Veerapaneni and Wiesner 1996; Li and Logan 1997a, b; Wu and Lee 1998) and uniformly porous flocs (Adler 1981, Kusters et al. 1991). It was found that above a critical limit of the dimensionless radius (defined as the $R/\sqrt{k}$, where $R$ is the aggregate radius, and $k$ is aggregate permeability) the collision efficiency became zero.

**Assumption 2: Fluid motion undergoes laminar shear.**

Camp and Stein (1943) defined the term $G$, the local root-mean-square velocity gradient for a small local element of fluid undergoing strain, and linked $G$ with the local rate of energy dissipation $\varepsilon$:

$$G = (\varepsilon / \nu)^{1/2}$$  \hspace{1cm} (7)

where $\nu$ is the kinetic viscosity of the fluid.

The global scale was further defined as the global root-mean-square velocity gradient $G^*$ for a flocculating system.
\[ G^* = (\varepsilon^*/\nu)^{1/2} \]  

where \( \varepsilon^* \) is the average energy dissipation for the whole flocculating system. Camp and Stein assumed that Smoluchowski’s \( du/dy \) could be replaced by \( G \) for linear flow regimes and by \( G^* \) in turbulent flow regimes.

Kramer and Clark (1997) identified two errors in Camp and Stein’s work: incorrect association of \( G \) with \( \varepsilon \) due to the ignoring the contribution made by the pure-normal strain component of the rate-strain tensor; and inaccuracy of assuming that \( G^* \) was a representative measure of the fluid dynamics within a flocculating system.

In practice, few real-life flocculation units operate under laminar flow. In overall terms, turbulence is still poorly understood. However, isotropic model has been successfully adopted in flocculation modeling. Such models describe turbulence as a cascade of eddies of diminishing size. Based on the cascade model, Casson and Lawler (1990) put forward that collisions between particles are promoted by eddies of a size similar to those of the colloid particles in turbulent flow. Energy expended during mixing in the creation of large eddies could be ineffectual.

Through studying the effect of hydrodynamic retardation upon the collision constants in the Smoluchowski model, Han and Lawler (1992) came to the conclusion that the actual contribution of orthokinetic flocculation to the overall flocculation process was minimal because of the pronounced effect of hydrodynamic retardation. Therefore, mixing simply provided a means of suspending the particles to keep the particle number count high enough for collision to occur.

*Assumption 3: The particles are mono-dispersed; all have the same size.*
In real systems, particles are hetero-dispersed indicating a composition of particles with a great variety of gradations. Tambo (1965) and his various coworkers (Tambo and Ogasawara 1970; Tambo and Watanabe 1979; Tambo 1991) proposed that dimensionless product $Gt\phi$ be used to determine the flocculation process. $\phi$ is the volume fraction of the particles. Harris et al (1966) observed the extent of aggregation and floc formation to be a function of both $Gt\phi$ and particle size distribution. O’Melia (1972) has shown the dependence of flocculation process on particle size and size distribution and noted that flocculation is more rapid in heterogeneous suspensions. Harding (1972) also found that flocculation is primarily dependent on particle size distribution.

Particle size distribution is important because it controls many physical and chemical properties. It will be changed throughout the flocculation process. Particle size distribution can be modeled by a two-parameter power-law distribution function given by the following expression.

$$N_T = \alpha_1 \cdot l_{nv}^\beta$$  \hspace{1cm} (9)

$N_T$ is the particle number density; $l_{nv}$ is the number volume mean size; and $\alpha_1$ and $\beta$ are empirical constants (Kavanaugh et al. 1980). A rapid estimate of contaminant distribution can be made from the magnitude of the model parameter $\beta$, which describes the slope of the frequency distribution.

Treweek and Morgan (1977) found that turbidity measurements alone were inadequate to measure the effectiveness of treatment process, since large changes in the particle size distribution during the flocculation process do not produce corresponding changes in turbidity. It has been shown that flocculation test based on particle size and count is more reliable. Particle size distribution measurements were characterized by the
total volume concentration, the peak of the volume concentration, and the slope of the particle size distribution function $\beta$. These measurements are particularly appropriate for showing the differences in flocculation over time and between experiments. However, the volume distribution does not provide clear evidence of flocculation at greater concentrations as it does for lesser concentrations.

*Assumption 4: No breakage of flocs occurs.*

According to Spicer and Pratsinis (1996), the balance of aggregation and break-up determines the floc size and mass distributions. Computer simulation (Fair and Gemmel 1964; Costas *et al.* 1995) identified the importance of breakage in modeling flocculation. The break-up mechanisms can have significant effect on both initial rates of reaction and eventual steady-state concentration.

It is generally accepted (Mühle 1993) that the breakage mechanism in turbulent flow depends upon a floc’s size relative to the Kolmogorov microscale, which is defined as the transition between the domain where inertial forces dominate and that where viscous forces dominate (Peters and Marrasé 2000). For flocs smaller than the Kolmogorov microscale, viscous forces predominate and erode the surface of the floc. In contrast, for flocs larger than the Kolmogorov microscale, deformation or fracture may occur as a result of fluctuating dynamic pressure. These ideas imply that floc strength is proportional to floc size. However, Yeung and Pelton (1996) suggested that floc compactness rather than its size is related to the strength. The more compact flocs were more likely they undergo erosions whereas less compact flocs were more likely to undergo fracture.
A connection between break-up phenomenon and the value of $G$ was pointed out by Ritchie (1955). The empirical relationship between applied $G$ and maximum floc size indicated the existence of a critical value of $G$ for a particular system, above which flocculation performance would be reduced. A similar effect was observed by Tambo and Hozumi (1979), who proposed the following relationship between maximum floc size and mixing intensity:

$$\text{max(Flocsize)} = C(G)^{-x} \quad (10)$$

Parker et al (1972) calculated theoretical values for $C$ and $x$ for different break-up mechanism (erosion and fracture) for particle larger or smaller than the Kolmogorov microscale. It was proposed that particle erosion was proportional to $G^2$ for the viscous domain and $G^4$ for the inertial domain.

To model the rate of change for particles of a given size due to the process of aggregation and breakup, Lick and Lick (1988) proposed the following expression:

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{j=k}^\infty \alpha \beta j n_j n_j - n_k \sum_{i=1}^\infty \alpha \beta k n_i - B_i n_k + \sum_{j=k+1}^\infty \gamma j B_j n_j$$

$$- n_k \sum_{i=1}^\infty \alpha j \beta k n_j + \sum_{j=k+1}^\infty \gamma j n_j \sum_{i=1}^\infty \alpha j \beta j n_i \quad (11)$$

$\gamma j k$ is the breakage distribution function defining the volume fraction of the fragments of size class $k$ coming from the disaggregation of a particle of size class $j$. $\alpha j$ represents the probability of disaggregation after collision. $B$ is the breakage rate.

The first two terms on the right side of the above equation are used to model the aggregation processes which are identical to the classical model, given in Equation 3, while the others are added for the disaggregating processes. The third term represents the loss of size class $k$ particles, giving particles with smaller diameters due to the effect of
shear rate. The fourth term represents the rate of increase of size class \( k \) particles due to the disaggregation of larger particles caused by the shear rate. The fifth term represents the loss of size class \( k \) particles due to unsuccessful collisions with all the other particles. The last term represents the rate of increase of size class \( k \) particles after unsuccessful collisions between particles of size classes \( i \) and \( j \), where \( j \) is greater than \( k \).

A similar coagulation and fragmentation model was applied by Spice and Pratsinis (1996) where the rate terms were assumed to be functions of both floc size and \( G \). Over a range of \( G \) value (25-125 s\(^{-1}\)) experimental results revealed that the rate of breakage was proportional to \( G^{1.6} \). Fragmentation prevents further growth of flocs so the distributions were found steady after a certain time. Increasing \( G \) leads to a more pronounced increased fragmentation rate, thus shifting the steady-state floc-size distribution into smaller floc sizes.

In the research of Lawler, Izurieta and Kao (1983), the velocity gradient, chemical conditions and particle concentration were varied and the other variables were held constant in the experiment design. Sedimentation instead of break-up of flocs was found to be the reason for explaining the discrepancy of experimental results with predictions of the mathematical model. The model was modified by the addition of terms for sedimentation to the classical expression:

\[
\frac{dn_{k,m}}{dt} = \frac{1}{2} \sum_{i+j=k} \beta(i, j)n_{i,m}n_{j,m} - \alpha \sum_{i=1}^{\text{max}} \beta(i, k)n_{i,m}n_{k,m} + \gamma^{w_k} \frac{n_{k,m}}{z} - \gamma^{w_k} n_{k,m}
\]

The third term added in the classical model describes the addition of particles into the compartment \( m \) as a result of particles settling from the compartment above; \( w_k \) is the Stoke’s settling velocity of size \( k \) particle; \( z \) is the depth of the compartment, and \( \gamma \) is the
fraction of the total area in which the mixing intensity is smaller enough to allow sedimentation to occur. The fourth term on the right side reflects the loss of particles from the compartment under consideration to the compartment below.

More complete mass balance equations can be written by taking into account particle sedimentation and particle breakup (Thill et al. 2001).

\[
\frac{dn_k}{dt} = \frac{1}{2} \alpha \sum_{i+j=k} \beta(i,j)n_i n_j - \alpha n_k \sum_{i=1}^{\text{max}} \beta(i,k)n_i - F_i n_k + \sum_{i}^{\text{max}} \gamma(k,i)F_i n_i - \frac{v_k}{z} n_k \tag{13}
\]

\(F_i\) is the fragmentation rate of floc of size \(i\), \(\gamma(k,i)\) is the breakage distribution function defining the volume fraction of the fragments of size \(k\) coming from \(i\)-size particles. \(v_k\) is the settling velocity of aggregates of size \(k\), and \(z\) is the height of a horizontal subdivision of the water column in which particle concentration is to be considered.

**Assumption 5: All particles are spherical in shape and remain so after collision.**

In reality, particles in the majority of flocculating systems do not coalesce on contact. This is particular true for water and wastewater systems where flocs are difficult to characterize because of their highly irregular and disorder nature. Li and Ganczarczyk (1989) recognized the fractal structure of these particles and aggregates. Their porosity is a function of aggregate size and increases with increasing floc size. The mathematical equation is expressed in Equation 14.

\[
p = 1 - S * R^{D-3} \tag{14}
\]

\(p\) is the floc porosity; \(D\) is three-dimensional fractal dimension and takes values between 1 and 3; \(S\) is a system specific constant. Fractal dimensions correspond to the degree of irregularity and complexity or the space-filling capacity of an aggregate. Fractal aggregates have a heterogeneous mass distribution, a structure resulting from the
coagulation of small and more densely packed clusters into larger and overall less dense aggregates (Johnson, Li and Logan 1995). The lower the fractal dimension, more “open” the aggregate structure. A closely packed Euclidean structure has fractal dimension of 3. If $D$ equals 3 (Smoluchowski’s assumption), the porosity is constant and consequently density is independent of size. However, $D$ is less than 3 for the majority of the flocs in natural system.

When the fractal dimension is considered, volume is not conserved after two particles collide even though mass is conserved. When two particles of radius $r_i$ and $r_j$ collide, the radius of the resultant floc is defined as:

$$r_{ij}^D = r_i^D + r_j^D$$  \hspace{1cm} (15)

Flocs with a low fractal dimension allow fluid to flow through them, resulting in a faster settling velocity and much more suspended small particles flowing into the aggregate. This phenomenon is known as advection. The degree of advection is characterized by fluid collection efficiency $\eta$, defined as the ration of the volume of fluid flowing through a floc to the volume of fluid approaching a floc. $\eta$ takes values between 0 for a totally impermeable floc and 1 for a totally porous floc.

In effect, the rectilinear approach assumes flocs are totally porous whereas curvilinear approach assumes flocs are totally impermeable. Neither of the cases is true for fractal flocs. In practice, particles approach one another along semi-curved paths, a compromise between the straight paths assumed in rectilinear model and the curved paths assumed in curvilinear model. Chellam and Wiesner (1993) demonstrated theoretically that $\eta$ was correlated to the fractal dimension. The degree of advection became significant when $D$ is less than 2. Where advection is significant, the rectilinear approach overestimate the rate
of collision, while the curvilinear model underestimates the rate of collision. However, there is currently no theoretical basis to predict an accurate rate.

The effect of fractal structure of flocs has been demonstrated for differential sedimentation flocculation (Li and Logan 1997a) and orthokinetic flocculation in turbulent flow (Li and Logan 1997b). A correlation between fractal dimension and collision frequency in turbulent flow was identified as:

$$\beta(i, j) \sim G^{(1-D/3)}$$

(16)

**Assumption 6:** Collision involves only two particles (Binary collisions).

The validity of this assumption is questionable when systems become concentrated such that collisions between more than two particles are likely. In highly concentrated suspension, swamping effect of the previous flocculated particles is profound. An alternative approach is thermodynamic theory of coagulation, in which coagulation is seen as a “phase-separation” process: the stabilized colloid represents the dispersed phase and the destabilized/aggregated colloid represents the solid phase. Rajagopalan (1993) applied thermodynamic theory to a colloid dispersion represented by an idealized potential-separation graph. Analysis of the constructed phase diagrams allows one to calculate the required degree of destabilization to promote flocculation.

**Macroscopic Approach to the Flocculation Process**

Surface chemical effects such as precipitation, destabilization and surface adsorption are always ignored or dealt with in a simplistic manner in a flocculation model. So, experiment results based on idealized particle suspensions are unlikely to be representative of the behavior of the real system. Focusing on the microscopic behavior of real particles in an attempt to deduce correlations between process parameters (e.g.
mixing intensity, coagulation dosage) and flocculation kinetics (i.e. collision efficiencies) is still extremely difficult. Accordingly, macroscopic approach is required to make a successful attempt at modeling flocculation. Measurement of particle size distribution and fractal dimension of the floc aggregates are such macroscopic approaches.

**Fractal Coagulation Model**

Fractal theory has been applied to describe the irregularity of natural objects and quantify the morphology of aggregates (Li and Ganczarczyk 1989; Jiang and Logan 1991; Li and Logan 1997a, b). A coalesced fractal sphere (CFS) model was proposed for modeling fractal particle aggregation (Lee et al. 2000). The CFS model assumes that all aggregates consist of a single type of primary particles which are compact spheres; all aggregates formed in a particular system are coalesced fractal sphere with a constant fractal dimension, independent of aggregate size; when two aggregates collide and attach, fractal dimension of the newly formed aggregate is same as the colliding aggregates, the solid volume of which is the sum of the two colliding aggregates. The schematic of CFS model was illustrated in Figure 7.2.

![Figure 7.2 Illustration of coalesced fractal sphere model (CFS)]
The one-dimensional advective-dispersive transport model in an experimental settling column was described in Equation 17 (Ernest et al. 1991).

\[
\frac{\partial n_k}{\partial t} = D_z \frac{\partial^2 n_k}{\partial z^2} - v_z \frac{\partial n_k}{\partial z}
\]  

(17)

To consider particle coagulation and settling in a continuous particle size distribution, Equation 18 was proposed to simulate the changes in PSD in the settling column (Ernest et al 1995, Lee et al 2000).

\[
\frac{\partial n_k}{\partial t} = \frac{1}{2} \sum_{i+j=k} \beta_{ij}(i, j)n_i n_j - \sum_{i=1}^{\text{max}} \alpha \beta_{ij}(i, k)n_i n_k + D_z \frac{\partial^2 n_k}{\partial z^2} - v_k \frac{\partial n_k}{\partial z}
\]  

(18)

Collision frequency function \( \beta_{ij}(i, j) \) for the CFS model was summarized in Table 1. \( z \) is the vertical distance from the top of the settling column. \( D_z \) is the hydrodynamic dispersion coefficient, which may be viewed as the cumulative effect of Brownian diffusion, eddy diffusion, and mechanical dispersion (Ernest et al 1991). \( v_k \) is the settling velocity for the fractal aggregate with size \( k \).

In Equation 18 only binary collisions are considered in this model and particle fragmentation is neglected. Volume is conserved during the coagulation. Collision efficiency \( \alpha \) is assumed to be a constant. Particle collisions are modeled using CFS assumption based on the rectilinear motion.

The boundary condition for Equation 18 is described in terms of particle flux \( F_1 \), which is defined as

\[
F_1 = D_z \frac{\partial n_k}{\partial z} - w_k n_k
\]  

(19)
At the top of the column, \( F_1 = 0 \). Therefore \( D_z \frac{\partial n_k}{\partial z} = w_k n_k \) (top boundary condition). At the bottom of the column, \( F_1 = -w_k n_k, \ D_z \frac{\partial n_k}{\partial z} = 0 \) (bottom boundary condition). In this model, the column was divided into \( n \) sections vertically. The partial differential equation was converted to numerically solvable equations and these equations were then solved using the fourth order Runge-Kutta method with variable time step. Size distribution \( n_k(t) \) was calculated for particles in the size range of 2 to 200 \( \mu \text{m} \) as a function of time.

**OBJECTIVES**

Previous experimental work and models on coagulation and flocculation has been reviewed. In this study, a coagulation model incorporating sedimentation and fractal theory was applied to simulate the evolution of particle size distribution (PSD) of storm water particles in a settling column. Modeled PSD was compared to the experimental results. Various parameters of the fractal dimensions and the collision efficiency factors were selected for the model simulations to study the effects on the resulting PSD.

**MODEL AND METHODOLOGY**

By introducing fractal geometry, the classical approach for the coagulation and flocculation is designated as CFS-C/F model, which is described in Equation 20.

\[
\frac{dn_k}{dt} = \frac{1}{2} \alpha \sum_{i,j=k} \beta_{j}(i,j)n_i n_j - \alpha \sum_{i=1}^{\text{max}} \beta_{j}(i,k)n_i n_k
\]

(20)

The collision efficiency factor \( \alpha \) is one of the most important parameters in characterizing coagulation. It is believed to represent the chemical stability of particles (Lee et al. 2000). Collision efficiency \( \alpha \) is assumed to be a constant during the coagulation and flocculation process. Studies on the estuarial sediments showed a
collision efficiency of 0.2 (Gibbs 1983; Ernest et al. 1995). Concentration of particles in urban rainfall-runoff system varied. Collision efficiency was chosen as 0.02, 0.2 and 1, which covers an upper and lower range of the studied collision efficiency of estuarial sediments. Collision frequency \( \beta_j(i, j) \) was calculated based on the CFS model. Table 7.1 listed the collision frequency function under different flocculation mechanisms. Collision frequencies for each combination of \( i, j \) and \( i,k \) were calculated. Since particle number distribution is a function of time, Equation 20 was solved numerically. Assuming a constant distribution in a small time scale (1 minute), a rate of change can be calculated at any time. The initial measured distribution was used to initiate the model at time 0.

Table 7.1 Collision frequency functions for the coalesced fractal sphere (CFS) model

<table>
<thead>
<tr>
<th>Mechanisms</th>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Brownian motion</strong></td>
<td>( \beta_{br}(i, j) = \frac{2kT}{3\mu} (v_i^{1/D} + v_j^{1/D})(v_i^{-1/D} + v_j^{-1/D}) )</td>
</tr>
<tr>
<td><strong>Fluid shear</strong></td>
<td>( \beta_{sh}(i, j) = \frac{G}{\pi} v_0^{(1-3/D)} (v_i^{1/D} + v_j^{1/D})^3 )</td>
</tr>
<tr>
<td><strong>Differential sedimentation</strong></td>
<td>( \beta_{ds}(i, j) = \frac{g}{12\mu} \left( \frac{\pi}{6} \right)^{-1/3} (\rho_s - \rho) v_0^{(1/3)-(1/D)} (v_i^{1/D} + v_j^{1/D})^2 \left</td>
</tr>
<tr>
<td></td>
<td>( \beta_{ds}(i, j) = \frac{g}{12\mu} \left( \frac{\pi}{6} \right)^{-1/3} (\rho_s - \rho) v_0^{(4/3)-(3/D)} (v_i^{1/D} + v_j^{1/D})^2 \left</td>
</tr>
</tbody>
</table>

*Solid particle volume \( v_s = \frac{\pi}{6} d_0^{3-D} d^D \)
Sedimentation is another important mechanism in the settling column test. With the addition of terms for sedimentation, the Smoluchowski model was modified (Lawler et al. 1983). A CFS-C/F-Sedimentation model was defined as:

\[
\frac{dn_{k,m}}{dt} = \frac{1}{2} \alpha \sum_{i+j=k} \beta_j (i, j) n_{i,m} n_{j,m} - \alpha \sum_{i=1}^{\max} \beta_j (i, k) n_{i,m} n_{k,m} + \frac{v_k}{z} n_{k,m-1} - \frac{v_k}{z} n_{k,m} \tag{21}
\]

Equation 21 was employed to derive the modeled particle size distribution in the settling column tests in this study. Settling velocities \( v_k \) for particles of any given size were calculated according to Newton’s Law. Table 7.2 listed the settling velocities for particles ranging from 1.25 to 250-\( \mu \)m.

The column was divided into 6 compartments vertically as seen in Figure 7.3. Samples were withdrawn from sampling port S1, S2, S3, S4 and S5. The analyzed distribution for each sample was assumed to represent the PSD of the section above this port. \( dn_{k,m} / dt \) was calculated for each \( k \) size category in each compartment.

Assuming conserved volume after coagulation of particle \( d_i \) and \( d_j \), equivalent particle diameter \( d_k \) is calculated using the following equation:

\[
d_k^3 = d_i^3 + d_j^3 \tag{22}
\]

For each combination of \( d_i \) and \( d_j \), a value of \( d_k \) was obtained according to Equation 22. When a large particle collides with a small particle, the size of the formed aggregate is not significantly different from the size of the larger particle before aggregation. By selecting a geometric progression \( d_{i+1} = \sqrt{2} d_i \), the interval size ratio \( \Delta d / d_k \) is approximately constant to ensure statistical reliability. According to this constraint, the upper and lower range of \( d_k \) can be calculated for 32 given size \( k \) as listed in Table 7.3.
The calculated $d_k$ from Equation 22 was compared to each range in Table 7.3. If the calculated $d_k$ falls into a certain range of size $k$ in Table 7.3, the average of all $d_k$ in the same range is assumed to be the diameter for the aggregate $k$ within this range. All combination of $d_i$ and $d_j$ will be included in this size category.

Figure 7.3  Side view of settling column (all units in mm); Column was divided into six compartments for modeling purposes. Samples were taken from 5 sampling ports along the depth of the column S1, S2, S3, S4 and S5.
Table 7.2  Settling velocity for particles in urban rainfall-runoff (Density = 2.5 g/cm³, Temperature = 20°C)

<table>
<thead>
<tr>
<th>Size (μm)</th>
<th>V(mm/s) Newton’s Law D=3.0</th>
<th>Size (μm)</th>
<th>V(mm/s) Newton’s Law D=3.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.36</td>
<td>0.0015</td>
<td>1.79</td>
<td>0.0028</td>
</tr>
<tr>
<td>1.60</td>
<td>0.0021</td>
<td>1.98</td>
<td>0.0034</td>
</tr>
<tr>
<td>1.89</td>
<td>0.0029</td>
<td>2.26</td>
<td>0.0043</td>
</tr>
<tr>
<td>2.23</td>
<td>0.0041</td>
<td>2.65</td>
<td>0.0059</td>
</tr>
<tr>
<td>2.63</td>
<td>0.0056</td>
<td>3.10</td>
<td>0.0081</td>
</tr>
<tr>
<td>3.11</td>
<td>0.0079</td>
<td>3.63</td>
<td>0.0110</td>
</tr>
<tr>
<td>3.67</td>
<td>0.0110</td>
<td>4.25</td>
<td>0.0150</td>
</tr>
<tr>
<td>4.33</td>
<td>0.0153</td>
<td>4.99</td>
<td>0.0205</td>
</tr>
<tr>
<td>5.11</td>
<td>0.0213</td>
<td>5.81</td>
<td>0.0276</td>
</tr>
<tr>
<td>6.03</td>
<td>0.0296</td>
<td>6.88</td>
<td>0.0384</td>
</tr>
<tr>
<td>7.11</td>
<td>0.0412</td>
<td>8.09</td>
<td>0.0527</td>
</tr>
<tr>
<td>8.39</td>
<td>0.0574</td>
<td>9.52</td>
<td>0.0725</td>
</tr>
<tr>
<td>9.90</td>
<td>0.0799</td>
<td>11.20</td>
<td>0.0996</td>
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<tr>
<td>11.69</td>
<td>0.1114</td>
<td>13.17</td>
<td>0.1367</td>
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<tr>
<td>13.79</td>
<td>0.1550</td>
<td>15.54</td>
<td>0.1890</td>
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<tr>
<td>16.27</td>
<td>0.2157</td>
<td>18.34</td>
<td>0.2612</td>
</tr>
<tr>
<td>19.20</td>
<td>0.3005</td>
<td>21.64</td>
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<tr>
<td>22.66</td>
<td>0.4185</td>
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<td>140.04</td>
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<td>165.26</td>
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</tr>
<tr>
<td>195.02</td>
<td>23.2998</td>
<td></td>
<td></td>
</tr>
<tr>
<td>230.14</td>
<td>30.2348</td>
<td></td>
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</table>
Table 7.3  Upper and lower limit of particle size $k$

<table>
<thead>
<tr>
<th>$d_k$</th>
<th>$d_{kL}$</th>
<th>$d_{kU}$</th>
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</tr>
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<td>1.88</td>
</tr>
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<td>1.57</td>
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</tr>
<tr>
<td>2.23</td>
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<td>2.61</td>
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<tr>
<td>2.63</td>
<td>2.18</td>
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<td>3.64</td>
</tr>
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</tr>
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<td>4.23</td>
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</tr>
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<tr>
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<td>13.69</td>
</tr>
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<td>11.42</td>
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<td>13.48</td>
<td>19.07</td>
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<tr>
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<td>15.91</td>
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</tr>
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<td>18.77</td>
<td>26.55</td>
</tr>
<tr>
<td>26.74</td>
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<td>31.56</td>
<td>26.14</td>
<td>36.97</td>
</tr>
<tr>
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<td>30.85</td>
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</tr>
<tr>
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<td>36.41</td>
<td>51.49</td>
</tr>
<tr>
<td>51.86</td>
<td>42.96</td>
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<td>71.70</td>
</tr>
<tr>
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<td>84.61</td>
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</tr>
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<td>98.31</td>
<td>139.04</td>
</tr>
<tr>
<td>140.04</td>
<td>116.02</td>
<td>164.07</td>
</tr>
<tr>
<td>165.26</td>
<td>136.91</td>
<td>193.62</td>
</tr>
<tr>
<td>195.02</td>
<td>161.56</td>
<td>228.48</td>
</tr>
<tr>
<td>230.14</td>
<td>190.65</td>
<td>269.62</td>
</tr>
</tbody>
</table>

$d_k = \frac{1}{2}(d_{kU} + d_{kL}) \quad d_{kU} = \sqrt{2}d_{kL}$

The rate of change of particle numbers due to settling was corrected for each size gradations of particles in compartment 1 through compartment 5.

$$dn_{k,m} = \int_0^t \left( \frac{v_k}{z_m} n_{k,m-1} - \frac{v_k}{z_m} n_{k,m} \right) dt = \frac{v_k}{z_m} \int_0^t (n_{k,m-1} - n_{k,m}) dt$$
Equation 23 was used to calculate the particle number change due to the settling effect.

The resulting modeling method was applied to a 2-m settling column in the laboratory. Rainfall-runoff collected from the experimental field under an elevated Interstate bridge was used to carry out the settling column tests immediately after rainfall. The suspended particle concentration of the collected runoff in this experiment was approximately 100-mg/L. A laser type particle analyzer LISST Portable (Sequoia Tech) was employed to measure the particle size distribution for particles ranging from 1.25 to 250-µm. The raw data from the LISST Portable was recorded into 32 size categories, which were used as the given size category data. The fixed parameters used in the model are summarized in Table 7.4. The volume of the primary particle \( (v_0) \) was assumed the same as the volume of the lowest size category (1.36-µm), which was \( 1.3164 \times 10^{-12} \) cm\(^3\).

Initial particle size distributions at 5 sampling ports were analyzed, as well as samples taken after settling for 20 minutes. According to the calculated settling velocity based on Newton’s Law, particles greater than 57.29-µm would settle out in 20 minutes.

Table 7.4  Fixed parameter used in the model

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absolute temperature (T) K</td>
<td>293 K</td>
</tr>
<tr>
<td>Density of fluid ( (\rho_f) ) g/cm(^3)</td>
<td>1.0 g/cm(^3)</td>
</tr>
<tr>
<td>Density of particles ( (\rho_s) ) g/cm(^3)</td>
<td>2.5 g/cm(^3)</td>
</tr>
<tr>
<td>Average velocity gradient (G) s(^{-1})</td>
<td>10 s(^{-1})</td>
</tr>
<tr>
<td>Diameter of primary particle (µm)</td>
<td>1.36 µm</td>
</tr>
</tbody>
</table>
RESULTS

Figure 7.4 showed the measured and CFS-C/F modeled evolution of particle number distribution at five depths along the column for a simulation time of twenty minutes. Initial PSD at each depth was analyzed to initiate the numerical model simulation. Vertical transport of particles due to settling was not accounted for in this case. As seen in Figure 7.4, there is a noticeable discrepancy between measured data and modeled results with Euclidean assumption. This difference tends to increase towards the larger size end. The predicted PND increased with the increasing collision efficiency factor.

Fractal dimensions D = 2.2 and D = 2.5 were chosen and applied in the model to simulate the evolution of PSD in the settling column. Collision efficiency of 0.02, 0.2 and 1 were assumed for the model predication. Figure 7.5 showed the results for the fractal dimension of 2.2, and Figure 7.6 showed the results for fractal dimension of 2.5. Vertical transport due to settling was included in neither simulation. Similar to the model prediction for the Euclidean particles, there are also discrepancies between measured data and modeled results for particles in the larger size range (>50 µm). Significant differences were seen as a result of application of different collision efficiencies (0.02, 0.2 and 1).

Figure 7.7 showed the comparison of the prediction under Euclidean and fractal assumptions. Collision efficiency was taken as 0.2 in the modeling. It appears that model incorporating fractal geometry of particles predicts better than Euclidean prediction without consideration of sedimentation effect in the settling column. Though the particle size distribution for small size particles (< 20-µm) in the settling column could be
modeled using CFS-C/F model reasonably well, the model does not provide a good fit for particles in the larger size categories.

Sedimentation of large aggregates is accounted for in the CFS-C/F-Sedimentation model for each defined compartment. Settling velocities of Euclidean particles were calculated according to Newton’s Law. Figure 7.8 showed the results from CFS-C/F-Sedimentation model. At sampling depth of H₃, H₄, and H₅, there have seen an improvement of model prediction for larger particles.

Many other factors will also have influences on the evolution of PSD during the settling column test, such as temperature which affects viscosity of fluid, particle concentration, turbulence etc. As particle concentration increases, the impact of both coagulation/flocculation and sedimentation will be significant. The inclusion of sedimentation in the coagulation model appears to be an applicable approach to study particle size distribution in the treatment system of urban rainfall-runoff. As to the collision efficiency \( \alpha \) and fractal dimension of storm water particles, more experimental work is needed to provide an empirical parameter for the certain system.

**CONCLUSIONS**

Based on the assumption of coalesced sphere and the rectilinear motion, the coagulation/flocculation model in this research incorporated the fractal theory and sedimentation mechanism to simulate the evolution of particle size distribution in a 2-m settling column using particles from urban rainfall-runoff. Modeling results showed that coagulation played an important role in the vertical transport for small particles (less than 20-\( \mu \)m). The effect of sedimentation is evident for particles in the larger size end. In the modeling, both fractal dimension D and collision efficiency \( \alpha \) are important factors in
determining PSD. The effect of other factors such as temperature and particle concentration needs to be studied further.

Figure 7.4 Fractal CFS-C/F model simulation of PSD at different depth (t = 20min) for Euclidean particles (D=3.0) in the settling column under different collision efficiency (α=0.02, 0.2 and 1.0) compared to measured PSD at t = 0 and t = 20-min.
Figure 7.5 Fractal CFS-C/F model simulation of PSD at different depths (t = 20min) for fractal particles (D=2.5) in the settling column under different collision efficiency $\alpha=0.02$, 0.2 and 1.0) compared to measured PSD at $t = 0$ and $t = 20$-min.
Figure 7.6 Fractal CFS-C/F model simulation of PSD at different depths (t = 20min) for fractal particles (D=2.2) in the settling column under different collision efficiency ($\alpha$=0.02, 0.2 and 1.0) compared to measured PSD at t = 0 and t = 20-min.
Figure 7.7 Comparison of CFS-C/F model simulation of PSD at different depths (t = 20-min) for Euclidean and fractal particles in the settling column, assuming collision efficiency of 0.2.
Figure 7.8 CFS-C/F-Sedimentation model simulation of particle size distribution in the settling column after 20-min sedimentation; Modeled results under fractal dimensions of 2.2 and 2.5 were compared with that assuming Euclidean dimension and measured PSD ($\alpha = 0.2$).

REFERENCES


**NOMENCLATURE**

\( \alpha \) collision efficiency

\( \beta(i, j) \) collision frequency \( (L^3 T^{-1}) \)

\( \beta(f(i, j)) \) collision frequency in CFS model

D fractal dimension

\( d_i \) diameter of particle \( i \) \( (L) \)

\( d_p \) particle diameter \( (L) \)

\( d_0 \) diameter of primary particle \( (L) \)

k Boltzmann constant \( (M L^2 T^{-2} K^{-1}) \)

G local root-mean-square velocity gradient \( (T^{-1}) \)

\( G^{*} \) global root-mean-square velocity gradient \( (T^{-1}) \)

\( n_i \) concentration of particles of size \( i \) \( (L^{-3}) \)

\( N_i \) total concentration of particles at time \( t \) \( (L^{-3}) \)

\( n_i(t) \) concentration of particles of volume \( v \) at time \( t \) \( (L^{-3}) \)

T absolute temperature \( (K) \)

\( \nu \) kinetic viscosity of water

\( \varepsilon \) local rate of energy dissipation \( (L^2 T^{-3}) \)

\( \varepsilon^{*} \) global rate of energy dissipation \( (L^2 T^{-3}) \)

\( \phi \) volume fraction of particles

r radius of particles

\( \rho_0 \) density of primary particle \( (g/cm^3) \)

\( \rho_w \) density of water \( (g/cm^3) \)

\( \mu \) dynamic viscosity \( (g/cm^3 s) \)
\( \nu_0 \) volume of primary particle (cm^3)
\( \nu_i, \nu_j \) solid volume for particle \( i \) and \( j \) (cm^3)
\( du/dy \) velocity gradient
\( N_T \) particle number density
\( l_{nv} \) number volume mean size
\( \gamma_{ik} \) breakage distribution function
\( B \) breakage rate
\( \alpha' \) probability of disaggregation
\( z \) compartment depth
\( w_k \) Stoke’s settling velocity of size \( k \) particle
\( F \) sedimentation flux
\( F_i \) fragmentation rate of particle \( i \)
\( \gamma(i,k) \) breakage distribution function
\( v_k \) settling velocity of particle \( k \)
\( p \) floc porosity
\( \eta \) fluid collection efficiency
\( D_z \) hydrodynamic dispersion coefficient
\( g \) gravitational acceleration
CHAPTER 8. SUMMARY AND CONCLUSIONS

A central conundrum in urban rainfall-runoff treatment is the bioavailability, toxicity, mobility of contaminants, all associating with granulometry of particles. The ability of best management practices (BMPs) to remove particulate-bound contaminants from runoff stream increase with particle size, however, bioavailability and mobility of pollutants decrease with particle size. Development and design of treatment methods are based on the granulometry characteristics. In this research, rainfall-runoff generated from a 544-m² Portland cement concrete pavement surface was collected under an elevated Interstate (I-10) lane at Baton Rouge, Louisiana. The entire gradation of solids was obtained. The physical granulometry of non-colloidal particulate matter were studied. While size gradations were nominally separated into dissolved, suspended, settleable and sediment designations, particle gradation ranged in size from 1 to 10,000 µm. Results showed that $d_{50v}$ (volume based median particle diameter) of the suspended fraction was $10.36 \pm 4.69$ µm with density ($\rho_s$) of $2.40 \pm 0.19$ g/cm³ developed from twelve studied rainfall-runoff events at Baton Rouge site. Meanwhile, the number based median diameter $d_{50n}$ was $1.62 \pm 0.04$ µm for the suspended fraction, similar to the size of silt and clay. Since coarser sands were intercepted by the grit chamber prior to sedimentation tank, the average mass based median diameter $d_{50m}$ was $172 \pm 63.35$ µm for the sediment fraction in the sedimentation tank for twelve rainfall-runoff events. If combined sediments from grit chamber and sedimentation tank for Baton Rouge site, a median size of 682-µm was obtained, indicating a skewed particle size distribution to coarser sand. Granulometry studies demonstrated that solid phase gradation transported in rainfall-runoff is not primarily “suspended” as shown in previous literatures, but also composed
of settable and sediment fraction. Over 50% of surface area was associated with the particulate gradation greater than 250-µm.

Partition of metals between dissolved and particulate phase was studied through experimental phase fractionation of urban rainfall-runoff. Particulate matters deposited from eight discrete storm events at Baton Rouge, Louisiana were examined for metal contamination. Results indicated that a significant reduction was achieved in total metal concentration for Cr, Cu, Zn and Pb by settling out the settable fraction. However, removal of settleable fraction does not convert to large overall reduction in total concentration for As and Cd because of their relative high dissolved fraction. As indicated by mass distribution, metal mass was dominant in medium to coarse (75 < d < 2000 µm) materials although fine particles (< 75-µm) were associated with a high level of metal concentration. Accumulated sediments collected from four storm catch basins at different urban transportation sites were characterized as well. No significant accumulative effect was found on metal concentration in the sediments. A cumulative power law model was developed from measured data and utilized to predict metal mass from the granulometric indices in lieu of metal analyses. The model was proved to be successful in predicting metal mass. The application of this model is to assist the development of particle separation operations in stormwater BMPs to target the portion of mass gradation where the predominant metal mass is associated.

Particles in urban rainfall-runoff are fractals. Images obtained from scanning electron microscope illustrated the fractal nature of these particulates. The characteristic morphology includes layered-structure, clay-size particulate aggregation and relative smooth grain surface. Results from image based fractal analyses showed fine particle
populations were slightly fractal than the medium to coarse materials though neither fractal dimensions showed a significant difference from Euclidean structure ($D_2=2$). Two dimensional fractal dimension $D_2$ developed from secondary electron image (SEI) was 1.943 for fine particles (less than 75-$\mu$m) and 1.961 for medium to coarse particles (75-$\mu$m to 600-$\mu$m). Particles in urban rainfall-runoff have negative surface charges. Point of zero charge (PZC) of particles shifted to lower pH value with decreasing particle size, suggesting the affinity of clay minerals to smaller size particulates. The fractal characteristic facilitates the entrainment of contaminants. Removal of fine fractions is important because their high potential as a reservoir for contaminants. Although Euclidean geometry is still applicable to the primary particles in urban rainfall-runoff, aggregates formed during sedimentation or coagulation/flocculation are expected to be more fractal and the effect of the fractal characteristics are to be more significant in urban rainfall-runoff system. Fractal characteristics of these aggregates need to be studied further to provide information in designing unit operation.

Settling velocity is a fundamental parameter of non-colloidal rainfall-runoff particulates. Determination of settling velocity is critical when designing or analyzing unit operations, in-situ controls or watershed controls for storm water. This research presented a synthesis of settling velocity methodology with applicability to characteristics of particulate matter in urban rainfall-runoff. Settling velocities of discrete non-colloidal particles in rainfall-runoff were quantified utilizing a bench-scale settling column with designed settling distance. Measured settling velocities were compared to the theoretical settling velocities across the gradation of particles from 1 up to 2,000 $\mu$m. Results indicate Newton’s Law can be used to model the discrete settling of non-colloidal
granular particles between 10 and 850-µm reasonably well. In settling column tests for particles in the range of 1.25 to 200-µm, a linear decrease in particle mean size was observed as a function of time during the settling process. Smaller particles (<10-µm) settle faster than predicted using Newton’s Law assuming Euclidean object. Over 90% of non-colloidal particles in grit chamber and approximately 50% of the non-colloidal particles in sedimentation tank can be removed by gravitational settling in terms of particle volume. In addition, a significant amount of fine particles cannot be removed through traditional best management practices i.e. stormwater detention basin.

Particulate matter in urban rainfall-runoff is unique compared to other particulate-loaded discharges (natural river water or wastewater) because of the very large size gradation (<1 µm to > 10,000 µm) and destabilized nature of particles with relatively short exposure to the aqueous matrix (typically less than several hours). This research investigated coagulation and flocculation (C/F) in urban rainfall-runoff with and without the addition of coagulants or flocculants incorporating particle size distribution analyses. Results demonstrated that without coagulant/flocculant addition, particulate matter in urban rainfall-runoff remains stable in suspension for extended hours. However, a significant particulate removal can be achieved in a short retention period with addition of alum or polymers. In terms of particle volume distribution, turbidity and total suspended solids removal, Alum with a dosage of 30-mg/L is suggested for rainfall-runoff treatment at the cost of $4.8x10^{-6}$/L (storm water). In contrast to the more common accepted mechanism of double-layer compression, alum is an effective coagulant in rainfall-runoff through adsorption, charge neutralization and sweep floc enmeshments.
Separation of particulate from urban rainfall-runoff is one of the major goals of best management practices in urban rainfall-runoff treatment. Sedimentation has been used generally in removing settleable particulates. Coagulation and flocculation was applied to improve the treatment efficiency. The fractal nature of particles in urban rainfall-runoff and heterogeneous distributions complicated the process. Theoretical settling model and coagulation and flocculation model cannot predict the behavior of real particles in the system. Based on the literature review on the contaminant removal mechanisms – sedimentation, coagulation/flocculation (C/F), a modified C/F model incorporating fractal geometry and sedimentation mechanism was employed to simulate and predict the particle size distribution during the sedimentation and coagulation process in urban runoff treatment system. The simulation applied to a 2-m settling column system with sediment particles from urban rainfall-runoff. The results showed a reasonably goodness of fitting.
VITA

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