Laboratory Experiments on Mud Flocculation Dynamics in the Fluvial and Estuarine Environments

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ABSTRACT

Due to the flocculation process, suspended mud aggregates carried by rivers and streams can undergo changes in their size, shape, and settling velocity in response to environmental drivers such as turbulence, sediment concentration, organic matter (OM), and salinity. Some have assumed that salt is necessary for floc formation, and that mud, therefore, reaches the estuary unflocculated. Yet mud flocs exist in freshwater systems long before the estuarine zone, likely due to the presence of OM and ions in the water that facilitate binding and aggregation of mud particles. This research aimed to examine the flocculation state of mud over the fluvial as well as fluvial to marine transition (FtMT) zones of the Mississippi River basin and how salinity, or the ion concentration of water, and organic matter independently and together affect flocculation. Suspended mud was found to be mostly flocculated in the headwaters of the Mississippi River in southwest Virginia, USA. However, increasing the ion concentration of water samples to levels measured following winter storms changed the size distribution of suspended particles, led to more of the mud existing in large flocs, and resulted in an overall increase in average size by about 40%, thereby increasing the settling rate of the mud relative to the suspensions without salt. These results suggested that potential negative effects of road salts on mud deposition should be investigated further. Additional experiments were used to examine the flocculation of a natural mud sample with and without OM showed that the rate of floc growth and equilibrium size both increase with salinity regardless of the presence or absence of OM. However, the response of both to salinity was stronger when OM was present. In deionized water, natural sediment with OM was seen to produce large flocs. However, the size distribution of the suspension tended to be bimodal. With the addition of

salt, increasing amounts of unflocculated material became bound within flocs, producing a more unimodal size distribution. Here, the enhancing effects of salt were noticeable at even 0.5 ppt, and increases in salinity past 3 to 5 ppt only marginally increased the floc growth rate and final size. A salinity-dependent model to account for changes in floc growth rate and equilibrium size was presented. Laboratory experiments on the sediment suspended in the lower reaches of the Mississippi River were used to provide further insight on the mud flocs behavior in the FtMT. Turbulence shear rate, a proxy for the river hydrodynamics, was found to be the most influential factor in mud floc size. While artificial increase in salinity by adding of salts did not lead to considerable increase in floc size, addition of water collected from the Gulf of Mexico enhanced the flocculation. These effects were speculated to originate from the biomatter composition of the Gulf water, particularly where the nutrient-rich Mississippi River water reaches the marine water.

Laboratory Experiments on Mud Flocculation Dynamics in the Fluvial and Estuarine Environments

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GENERAL AUDIENCE ABSTRACT

Rivers bring a substantial amount of mud to coastal regions. Where this mud deposits is important in shaping the coastal land and nutrient dynamics. Mud particles are different from sand and gravel in that they can form aggregates known as flocs that constantly change shape and size under different conditions. As they change size, they change how fast they sink, and this influences where they deposit. Due to their small size, mud particles are also considered a pollutant as they can clog up fish gills and destroy freshwater habitats. Findings of this dissertation showed that the roadway deicing salts that make their way to streams can enhance the aggregation of mud particles, causing them to sink faster. This can be harmful to the species that live on streambeds. While salts are known to enhance flocculation, there is ample evidence that flocs exist in rivers before reaching the sea. It is possible, therefore, that flocs in estuaries are due to biological matter acting as a glue to bind mud particles together and may not be influenced by salt. This dissertation looked at the effects of saltwater on mud flocculation when biological matter is present and when it is absent. Findings showed that salinity increased the size of mud flocs, even more so than when organic matter was absent. However, organic matter was needed for flocs to reach sizes often found in nature. An equation was also provided to aid in the prediction of floc size under different salinities. Observations on the lower Mississippi River flocs showed that the turbulence of water was the most influential factor in determining the size of flocs.

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This journey would not have been possible without the support of my labmates in Baker Environmental Hydraulics Laboratory.

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List of Symbols and Abbreviations

ϵ Dissipation rate of turbulent kinetic energy

η Kolmogorov microscale

μ Dynamic viscosity of water

ν Kinematic viscosity of water

A_{adv} Advective length scale

C Concentration

d_f Floc diameter

d_p Primary particle size

d_{50} Median floc size by volume

F_y Yield strength of the flocs

G Turbulent shear rate

g Gravitational acceleration

h Flow depth

k'_A Dimensionless aggregation efficiency coefficient

k'_B Dimensionless breakup efficiency coefficient

n_f Fractal dimension

R_s Submerged specific gravity of the sediment

S Salinity

U Average stream velocity

w_s Settling velocity

Chapter 1

Introduction

1.1 Mud flocculation and its importance

Coastal regions are home to a growing percentage of the global population and are undergoing rapid changes (e.g., Creel, 2003; Neumann et al., 2015). Understanding past changes and monitoring the current state of coastal environments is essential to predicting the future trajectories of these regions, promoting healthy and resilient coastal ecosystems, and fostering the welfare of coastal communities (e.g., Arkema et al., 2017). Some of the environmental factors that are shaping the future of coastal systems include ocean acidification, global warming and sea level rise, increased violent storm activity, and eutrophication (e.g., Turner and Rabalais, 1994; González and Tornqvist, 2006; Guinotte and Fabry, 2008). A major component that greatly impacts coastal dynamics is the sediment carried by rivers to the coasts. Sediment can affect coastal morphology by building subaerial land in deltaic zones (e.g., Kenyon and Turcotte, 1985). The nutrients and pollutants bound to sediment particles can also influence the oceanic food web and ecosystem health. In the face of land loss and sea level rise, the deposition of sediment in coastal zones can be thought of as a benefit. However, within-channel sedimentation can be viewed as a negative factor, such as when it shoals the navigation channels and leads to significant dredging costs to keep the navigation ways open (McAnally et al., 2007). Therefore, gaining knowledge on the transport behavior and fate of sediment in deltaic and estuarine regions is essential in devising efficient environmental protection, preservation, and restoration plans.

One of the most important sediment parameters or properties for accurately modeling the transport and fate of suspended sediment is the settling velocity, (w_s) (e.g., Geyer et al., 2004; Harris et al., 2005; Shi, 2010). The settling velocity is the rate at which a particle is pulled by gravity through the water column. As such, it strongly influences the time that a particle stays in suspension and how the sediment is distributed over the water column. The settling velocity can also affect the re-suspension and re-entrainment potential of the particles (McAnally et al., 2007). The size, shape, and density of sediment set its settling velocity. For sediments with grain size greater than 62.5 µm, such as sand- and gravel-sized particles (i.e., non-cohesive sediment), settling velocity is fixed and can be readily estimated using available formulas (e.g., Rijn, 1984; Cheng, 1997; Ahrens, 2000; Jiménez and Madsen, 2003; Ferguson and Church, 2004). However, about 80% of the suspended sediments carried by large low-land rivers to coastal regions have grain sizes smaller than 62.5 µm (Milliman and Syvitski, 1992). This finer fraction of clay- and silt-sized sediment is often referred to as cohesive sediment or mud. Unlike non-cohesive sediment, cohesive sediment particles can change size and shape as an outcome of the aggregation and breakup they experience while being transported by the water (e.g., Gibbs, 1985; Mehta, 1986). This phenomenon is known as flocculation (e.g., Kranck, 1973; Dyer, 1989; Partheniades, 2009). Additionally, the relatively high surface area to mass of the clay particles causes them to be a suitable location for nutrient attachment and sticky biomatter, ultimately leading to further aggregation of mineral-organic matter mixture (e.g., Shen et al., 2019). Flocculation can significantly affect the transport of mud because it alters the size and density of the flocculated particles and increases their settling velocity by orders of magnitude compared to the disaggregated particles that make up the flocs (e.g., Winterwerp, 2002).

The continuously-evolving nature of mud flocs, as well as their significant role in the transport and distribution of fine-grained sediment in estuarine and deltaic areas, has directed efforts to identify the main parameters driving flocculation. As these drivers are identified and better understood, the dynamic nature of mud settling velocity can be better accounted for in models to more accurately predict mud transport and accumulation. The goal of this dissertation was to investigate how variations in two drivers that are relatively less understood and accounted for in mud flocculation models, namely salinity and organic matter, affect the flocculation rate, size, and settling rate of mud flocs in upstream freshwater reaches and through the fluvial to marine transition (FtMT) zone.

Laboratory experiments were used in this dissertation to fill a part of the knowledge gap on the effects of salinity and organic matter on mud flocculation. These experiments permitted control of the factors that are not controllable and often co-vary in natural settings, such as ion concentration of water, sediment type, and concentration, organic matter content of water, and turbulence. The designed experiments aimed to study the role of an individual parameter while mimicking the natural environments (by using natural mud or salts that are as similar as possible to sea salt) and provide data detailed enough to capture the dynamics of flocs' responses to variations in the studied parameters. Data were collected on size distribution, settling velocity, and visual appearance of flocs, turbidity of the suspension, and organic matter content of the suspension and the mud over an array of turbulent shear stresses, salt types and concentrations, and sediment types. These organized and deliberate data were used both to improve the existing models on floc size evolution and to provide a foundation for the future development of new models based on the captured flocculation dynamics. The subsections below describe in more detail the fundamentals and drivers of flocculation and how they vary in FtMT zones.

1.2 Fundamentals of flocculation

Floc growth and break-up both influence the floc size distribution. Flocs grow in size when particles in close proximity aggregate together due to the close-range attractional inter-particle forces overcoming any resisting forces. These attractional forces are only strong enough to result in aggregation when the particles are nearly touching. Therefore the collision, or near collision, of individual particles is critical to floc growth. There are three major drivers for these collisions, i.e., Brownian motion, differential settling, and turbulent mixing. Differential settling-induced collisions occur as a result of differences in the settling velocity of particles in the water column (e.g., Lick et al., 1993). It is the dominant driver of collisions in low-energy environments (e.g., Fugate and Friedrichs, 2003). Random Brownian motion can also cause the particles to collide (e.g., Melik and Fogler, 1984). Additionally, particles can be brought together by the turbulent motion of water (e.g., Eisma, 1986). This phenomenon is dominant in high-energy environments such as river and estuaries (e.g., Eisma et al., 1991). The number of collisions in all of these mechanisms is directly affected by the number of particles present in a unit volume, i.e., suspended sediment concentration.

Particle collisions provide the potential for aggregation. However, not all collisions lead to the aggregation of particles. Whether or not a particle in close proximity to another particle aggregates is influenced by how close the particles can get to each, the inherent charges on the particles, the ion concentration in the water, and the exact nature of other water and/or sediment agents present such as coagulants or organic binding agents (e.g., Lai et al., 2018). The charges on particles can affect whether or not the particles will aggregate. The ions present in the water, quantified using salinity or specific conductance of water, can cause the layers of water molecules that surround the particles to shrink, facilitating particle aggregation (e.g., Gregory and O'Melia, 1989). Depending on their size and structure, biomatter can have various effects on the process of flocculation. Lower molecular weight biomatter can alter the charges on the particles while the later biopolymers can act as bridges that connect several mineral and organic particles (e.g., Labille et al., 2005; Theng, 2012; Deng et al., 2022). Flocculation efficiency is a measure of how many of the statistical collisions result in flocculation as an outcome of the specific physical and biochemical state of sediment and water column.

Breakup of flocs can be due to viscous and turbulent shear (Argaman and Kaufman, 1970; Parker et al., 1972) that provide the energy to break the internal bonds between the component of the flocs beyond their tensile and shear strength (van de Ven and Hunter, 1977; Jarvis et al., 2005a). Flocs can also break up due to collision with other aggregates in suspension (Serra and Casamitjana, 1998). Floc breakup due to collision is a function of collision frequency and probability of disaggregation by collision and tends to be a more prominent disaggregation mechanism at high concentrations (Maggi, 2005).

1.3 Drivers of mud flocculation

Several parameters have been proposed as key drivers of flocculation based on the consideration that flocculation is the outcome of both aggregation and breakup processes (Figure 1.1). Historically, these primary drivers are considered to be suspended sediment concentration (SSC, which influences the number of particles and the collision frequency), particle size (smaller particles aggregate easier and increase the number concentration of particles for a given mass concentration of the suspension), turbulence (driver of both collisions or aggregation and breakup), salinity (a potential influencer of the aggregation efficiency and floc strength), and organic matter (also a potential influencer of the aggregation efficiency and floc strength). These drivers all change within a river or estuary as flows go up and down, sediment erodes and deposits, and seasons and inputs to the system change. Furthermore, even under steady-state conditions within a river, these parameters all systematically change in space as the river transits the fluvial to marine transition (Figure 1.1).

Higher SSC leads to greater numbers of particles in a given volume of water, which increases the likelihood of sediment particle collision that can potentially lead to aggregation and flocculation of the suspended particles. Although the settling velocity of flocs increases

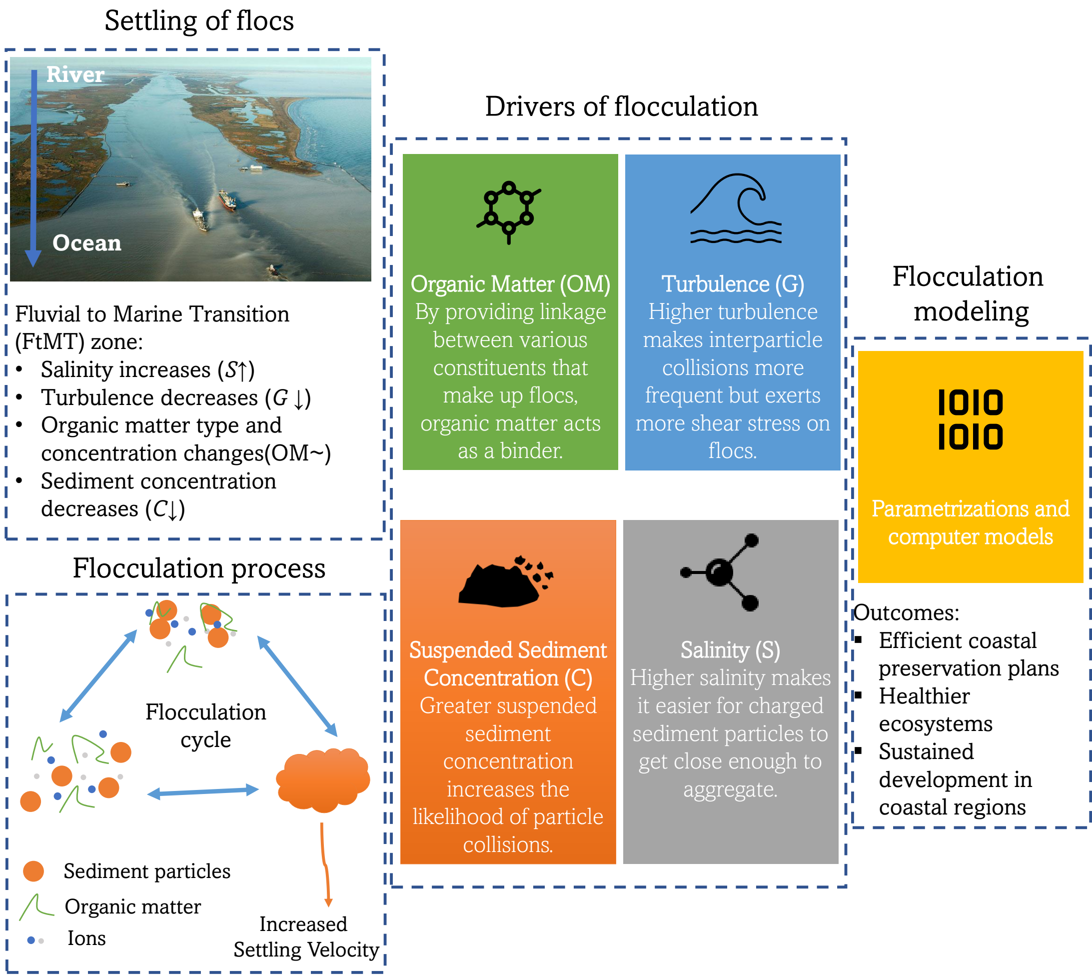

Figure 1.1: Fluvial to marine transition zones exemplify regions of rapid spatiotemporal variations in the parameters that drive mud flocculation.

with increasing SSC in a stagnant condition in settling columns (e.g., Mehta, 1986; Huang, 1994), floc size and settling velocity have not been found to be strongly affected by variations in SSC in natural environments (e.g., Winterwerp et al., 2006; Mikeš and Manning, 2010). In a laboratory setting, a, 8-fold increase in SSC was found to increase d_{50} of kaolinite-bentonite flocs by only ∼20% under turbulent conditions (Tran et al., 2018). The weakened contribution of sediment concentration on floc size and settling velocity in turbulent environments is due to the fact that the two collision mechanisms that are dominant in settling columns, i.e., differential settling and Brownian motion, are overshadowed by the turbulent mixing that is dominant in turbulent natural environments.

Turbulence is another strong factor in the flocculation of sediment. While it contributes to the aggregation of mud particles and smaller flocs by increasing the probability of particle collision, turbulence can induce floc break-up due to increased shear stress exerted on them (e.g., Manning and Dyer, 1999). The role of turbulence in flocculation has already been implemented in the aggregation and breakup kernels of single-size class models (e.g., Winterwerp, 1998) and more complicated multi-size class models (e.g., Lee et al., 2011; Verney et al., 2011). In these models, turbulence is often represented by turbulent shear rate, G, which is a measure of the dissipation rate of turbulent kinetic energy, ϵ, and is defined as $G = \sqrt{\epsilon/\nu}$, where ν is the kinematic viscosity of water. The Kolmogorov length scale (λ_0), which is a quantity derived from the dissipation rate of turbulent kinetic energy, sets the maximum size flocs can grow to (Glasgow and Luecke, 1980; Dyer, 1989), as the eddies smaller in size than λ_0 bring particle together that may lead to aggregation.

Salinity (S) refers to the concentration of salt in water. An increase in salinity can promote flocculation because of the electric charges that exist on cohesive sediment particles. These charges can be the results of imperfections in the crystalline structure of the sediment particles, isomorphous substitution of ions with lesser negative charges with those with greater negative charges, or absorption of negatively charged low molecular weight biomolecules to the sediment particles (Tipping and Higgins, 1982; Tipping and Cooke, 1982; Partheniades, 2009). As salinity increases, the electric double layer (EDL) that forms around the charged particles and keeps them apart shrinks, making it easier for them to get close enough to aggregate. Additionally, divalent and polyvalent cations can promote bonding between the negatively-charged sediment particles (Gregory and O'Melia, 1989), further enhancing flocculation. Laboratory experiments using various types of salt representatives and clay materials have generally reported flocculation-enhancing effects of ions in water (e.g., Edzwald et al., 1974; Mietta et al., 2009a; Mikeš and Manning, 2010; Portela et al., 2013; Guo et al., 2021). Despite having the difficult task of isolating salinity effects on mud flocculation in an environment where many of the drivers of flocculation such as turbulent shear and suspended sediment concentration co-vary, *in-situ* field studies have highlighted the positive effects of an increase in salinity on mud flocculation (e.g., van Leussen, 2011; Guo et al., 2017; Zhang et al., 2021). Therefore, increased salinity due to mixing of fresh river water with sea water has been historically considered a major driver of flocculation and, as a result, mud deposition in estuarine and deltaic systems (Odd, 1988).

Although limited, there have been efforts to include salinity effects in mud flocculation using simple models as well. For instance, Delft3D assumes settling velocity, w_s, approaches $w_{s,max}$ as salinity approaches S_{max} (Deltras, 2021). In a model by Horemans et al. (2020) that used three data points from Edzwald et al. (1974), aggregation efficiency of flocs was set to reach a maximum as S approaches a prescribed maximum. However, the data similar to that used by Horemans et al. (2020) are often not resolved enough (particularly at $S<$ 5 ppt) to be able to capture the salinity variations that flocs experience in the FtMT zones or have used salts or sediments that are not suitable representatives of their natural counterparts.

Organic matter is another factor that can influence mud flocculation. Long twisted biopolymers are byproducts of macro- and microorganisms' metabolism, growth, and degradation. They host numerous functional charged and polar groups in their complex structures that can provide linkage between inorganic silt and clay as well as other biocompounds present in water (Labille et al., 2005; Gerbersdorf and Wieprecht, 2015; Lai et al., 2018; Deng et al., 2022). An example of organic matter is extracellular polymeric substances (EPS). EPS pools can contain various components such as polysaccharides, proteins, and DNA. They can significantly modify the mechanisms of interaction between the macro- and microscale organic and inorganic particles suspended in the water column and deposited in the bed through a myriad of mechanisms including adhesion, cohesion, sorption, and providing a nutrient source for living organisms (Flemming, 2016). Microorganisms themselves can attach to the assemblage of organic and inorganic material and live and metabolize there, contributing to the active production of biofilms on sediment particle surfaces and further enhancement of flocculation by increasing the aggregation efficiency of the particles that collide while being suspended in water (Liss et al., 1996; Droppo et al., 1997; Shang et al., 2014; Tang and Maggi, 2016; Shen et al., 2018). Laboratory experiments using materials such as xanthan gum and guar gum, which are assumed to mimic the binding effects of organic matter found in natural systems, have pointed to the positive effects of gums on flocculation of cohesive sediment (e.g., Tan et al., 2012; Zhang et al., 2013; Tan et al., 2014; Furukawa et al., 2014; Zeichner et al., 2021). However, there remain questions as to whether the gums can suitably represent the diverse components of the organic matter present in the natural environment, each with a different effect on sediment flocculation (Lee et al., 2019).

Efforts on modeling the roles of biomatter on mud flocculation are fairly recent. Maggi (2009) developed a model for the representative size of organic-inorganic flocs in nutrient-rich aqueous ecosystems using the data by Fettweis et al. (2006). Shen et al. (2018) developed and incorporated a model for biofilm growth in a multi-size class population balance model for flocculation. Using a two-size class flocculation model, Ho et al. (2022) examined the flocculation of microalgae-clay suspensions. Zhu et al. (2022) investigated the biomineral aggregation using a quasi-Monte-Carlo-based bivariate population balance model.

1.4 Research motivation and objectives

Mud flocculation studies have covered a wide range of topics over the years. Nevertheless, systematic data on how salinity, or the ion concentration of water, and organic matter independently and together affect the flocculation of mud in both freshwater and FtMT zones are still lacking. Furthermore, the absence of models suitable for accounting for the flocculation of mud on sediment transport dynamics in these two zones has hindered efforts to quantify the subaerial and subaqueous land-building potential of the sediment carried by rivers.

Historically, it has been assumed that mud is transported in an unflocculated state in freshwater systems (Wright and Parker, 2004), and that it is the increase in salinity in the FtMT that induces flocculation (e.g., Odd, 1988). However, there is an increasing body of analytical (e.g., Lamb et al., 2020), laboratory (e.g., Abolfazli and Strom, 2022), and observational (e.g., Droppo et al., 1997; Osborn et al., 2021) evidence on the presence of freshwater mud flocs and their significance in the transport of mud in freshwater. This can lead to two conclusions: 1. Water salinity may not be the most important factor in flocculation, and there are other factors such as organic matter that enhance mud flocculation in freshwater; or 2. The ions already present in rivers and streams with terrigenous origin can enhance flocculation enough such that freshwater flocs can in fact form and account for a significant fraction of cohesive sediment transported by rivers. The fact that organic matter has long been considered to enhance mud flocculation in freshwater environments has caused some researchers to come to the conclusion that it is not the ions, but the organic matter that is the main driver of mud flocculation in rivers and the resulting changes in the morphology of the land surrounding rivers (e.g., Zeichner et al., 2021).

In the FtMT zone, salinity can both increase longitudinally as the freshwater mixes with the seawater and vertically due to seawater intrusion in microtidal estuaries. The type and concentration of organic matter can also change as the habitat and nutrient availability undergo a transition. These two drivers can also interact as the salinity gradient has been shown to impact phytoplankton dynamics within the salt wedge haloclines (Kasai et al., 2010). These variations can affect the flocculation of suspended mud. However, it is unclear how the combined effects of these two drivers influence the flocculation process in the FtMT zone. Considering that the effects of organic matter and ions in cohesive sediment flocculation both arise from altering the surface charges of sediment particles and the interparticle interactions, it may be their simultaneous effects that enhance flocculation.

In this dissertation, the aim was to investigate how salinity and organic matter independently and together affect the size and settling velocity of mud flocs both in the freshwater environment and in the FtMT. The lack of systematic data on the influence that these two substances have on flocculation has hindered efforts to parameterize their effects and include them in computational flocculation models. While insightful laboratory studies have been conducted on salinity and organic matter effects in mud flocculation, there seem to be shortcomings that need to be addressed to further our knowledge of such effects. For instance, some studies have conducted experiments in stagnant settling columns that cannot be well justified as flocs rarely experience such conditions and are often under turbulent mixing. Additionally, some studies have used sediment, salts, or artificial organic matter that may not be suitable representatives for their counterparts in natural systems, which may reduce the applicability of the data to natural systems. The overarching goal of this dissertation was to address these shortcomings and provide systematic qualitative and quantitative data that can be used as a foundation for model development and calibration.

The specific objectives of this dissertation were to:

1. Investigate the state of mud flocs in streams in the Valley and Ridge province of southwestern Virginia that ultimately drain into the Mississippi River (Paper 1, Chapter 2).

2. Determine if road salt that makes its way into upland freshwater streams can influence the settling properties of the suspended mud by altering the flocculation state of the mud (Paper 1, Chapter 2).

3. Measure the flocculation response of natural mud containing organic matter from different zones of the Mississippi River basin to small increases in salinity in comparison

to mud without organic matter to answer the question, does salt matter if organic matter is present? (Paper 2, Chapter 3)

4. Provide a model for salinity effects on the aggregation efficiency of natural mud (Paper 2, Chapter 3).

5. Characterize the behavior of mud flocs in the lower Mississippi River and their response to variations in environmental drivers during summer and winter (Paper 3, Chapter 4).

Several new methods were developed and used in the course of this research to sample, identify, and produce flocs and to mimic the transient state of the FtMT zone. Findings on outcomes of these methods and how well laboratory-generated flocs can mimic natural flocs are presented in Appendices A-C.

The remainder of the dissertation is organized as follows. The presentation of each of the three journal papers mentioned above, in association with the research objectives, are given in order as complete papers in Chapters 2 (paper 1), 3 (paper 2), and 4 (paper 3); these chapters are then followed by discussion and conclusion chapters. The methods that were tested or developed as part of the work are then given in the appendices. At the time of submission of this dissertation, paper 1 has been published, revisions to paper 2 have been submitted, and paper three is in draft form. Appendix A has been published as a refereed conference paper and the remainder of the appendices are unpublished.

1.5 Attribution

- For Chapter 2, Ehsan Abolfazli designed the methodology of the research, performed the research, collected the data and performed the analysis, and drafted the manuscript. Dr. Kyle Strom conceptualized the research, provided guidance on research direction, and contributed to manuscript preparation. The paper has been published as: Abolfazli, E. & Strom, K. (2022). Deicing Road Salts May Contribute to Impairment of Streambeds through Alterations to Sedimentation Processes. ACS ES&T Water, 2(1), 148–155. `https://doi.org/10.1021/acsestwater.1c00300`.

- For Chapter 3, Ehsan Abolfazli designed the methodology of the research, performed the research, collected the data and performed the analysis, and drafted the manuscript. Dr. Kyle Strom conceptualized the research, provided guidance on research direction, and contributed to manuscript preparation. Chapter 3 has been submitted to Journal of Geophysical Research: Oceans. Revisions have been submitted to the journal.

- For Chapter 4, Ehsan Abolfazli designed the methodology of the research, performed the research, collected the data and performed the analysis, and drafted the manuscript. Dr. Kyle Strom conceptualized the research, provided guidance on research direction, and contributed to manuscript preparation. This chapter is a draft of a manuscript in preparation to be submitted to Frontiers in Earth Science.

- For Appendix A, Ehsan Abolfazli designed the methodology of the research, performed the research, collected the data and performed the analysis, and drafted the manuscript. Ryan Osborn contributed to running the experiments. Dr. Kyle Strom conceptualized the research, provided guidance on research direction, and contributed to manuscript preparation. Appendix A is a refereed conference paper published in the proceeding of River Flow 2020 (10th Conference on Fluvial Hydraulics, Delft, The Netherlands).

- For Appendix B, Ehsan Abolfazli designed the methodology of the research, performed the research, collected the data and performed the analysis, and drafted the manuscript. Ryan Osborn contributed to running the experiments. Dr. Kyle Strom conceptualized the research, provided guidance on research direction, and contributed to manuscript preparation.

- For Appendix C, Ehsan Abolfazli, Sunmin Lee, and Katherine Wardinski designed the methodology of the research. Ehsan Abolfazli conducted the flocculation experiments. Ehsan Abolfazli and Sunmin Lee prepared samples for excitation-emission matrix spectroscopy (EEMS) annalysis. Katherine Wardinski conducted the EEMS analysis. Ehsan Abolfazli drafted the manuscript. Dr. Kyle Strom conceptualized the research, provided guidance on research direction, and contributed to manuscript preparation.

Chapter 2

Deicing road salts may contribute to impairment of streambeds through alterations to sedimentation processes

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2.1 Abstract

Deicing road salts have been increasingly used in the United States over the past 80 years. Previous studies have shown that these salts can have deteriorating effects on freshwater organisms. Here we hypothesize that the introduction of road salts to stream water can also boost aggregation of mud particles suspended in the water column. Such aggregation, also known as flocculation, enhances deposition rates and may lead to increased accumulation of fine sediment on streambeds, thereby contributing to the degradation of benthic ecosystems. In this laboratory study, we specifically investigate how road salts impact (1) the size distribution of mud aggregates in a turbulent water column and (2) the overall settling rate of the mud. The results showed that adding road salts to water samples collected from a stream in southwest Virginia, USA changed the distribution of suspended particle sizes. The addition of salt led to more of the mud existing in large flocs and an overall increase in average size by about 40%. As a result, the settling rate of the mud increased relative to the suspensions without salt. Our results suggest that potential negative effects of road salts on mud deposition should be investigated further.

2.2 Introduction

Adding salts to roadways is a highly effective way of reducing the extent of ice buildup on roads in winter conditions, thereby increasing roadway safety. As a result, the use of deicing road salts in the United States (US) has increased drastically over time, from 164,000 tons in 1940 to more than 22 million tons in 2019 (USGS, 2009; Bagenstose, 2019). In fact, the use of salt in brines and deicing agents is so significant that highway deicing alone accounted for approximately 43% of all the salt (sodium chloride) used in the US in 2020 (USGS, 2020). Roadway deicing salts generally contain sodium chloride, calcium chloride, and magnesium chloride. There are also numerous types of ice melt products that are commercially available and used by the general public for deicing of residential spaces. The ions in the deicing materials such as sodium, calcium, magnesium, and chloride can eventually enter streams (Jackson and Jobbágy, 2005), leading to concentrations that can, at times, be of the order of magnitude of the ion concentration in sea water (Kaushal et al., 2005). Once mobilized in streams and rivers, the ions can ultimately enter groundwater (Williams et al., 2000) and lakes (Novotny et al., 2008). These ions are generally toxic to freshwater species with their degree of toxicity depending on ion type and concentration. The potential negative effects of increased ionic concentration have been well documented on zooplankton (Sarma et al., 2006), microinvertebrates (Kefford et al., 2007), macroinvertebrates (Shenton et al., 2021), and fish (Tollefsen et al., 2015; Hintz and Relyea, 2017). These effects can range from disrupted metabolism and reduced reproduction rate to increased mortality (Hintz and Relyea, 2019).

While the direct effects of road salts on freshwater organisms have received extensive attention (Hintz and Relyea, 2019), we suggest that road salts could have an additional adverse impact on stream ecosystems through an indirect path that has been overlooked. The indirect pathway is through increased deposition rates, and potentially accumulation rates, of muddy sediment (fine cohesive sediments in the clay and silt size ranges with diameters <63 µm) suspended in streams and rivers due to ion-enhanced aggregation or flocculation of the suspended particles. Flocculation is the process of aggregation and breakup of small mineral and organic suspended material that can result in the average size of the suspended mud being a function of local hydrodynamic, chemical, and biological conditions. Specifically, we hypothesize that the post-storm concentrations of road salts can be high enough to meaningfully enhance flocculation of mud particles and create larger and more abundant mud flocs, which can increase the settling velocity (and therefore deposition rate) of the mud fraction from its state in stream water without salinity from road salts.

Flocculated mud is conventionally associated with estuarine and marine settings. Yet, many studies have observed that suspended aggregates of mud, or flocs, also exist in freshwater streams and rivers. For example, Droppo and Ongley (1994) concluded that 90% of the fine sediment transported by six rivers in Canada was flocculated. Fox et al. (2014) found two distinct size classes of suspended aggregates (i.e., 11-20 μm, and 20-53 μm) in samples collected using a sediment trap in the Elkhorn Creek, Kentucky, USA. Furthermore, McLachlan et al. (2017) found that particles >40 μm in the Mekong River had effective densities that were half that of discrete quartz particles and therefore attributed it to presence of mud flocs. Using sediment concentration profiles, Lamb et al. (2020) also recently inferred that mud is likely to be flocculated in many freshwater systems and to have a significant effect on the overall settling velocity of the mud fraction. Droppo and Ongley (1994) and others typically attribute the ability of mud to flocculate in freshwater settings to the presence of organic binders.

While flocs do likely exist in most freshwater rivers, ion-mediated flocculation of muddy sediment has also been observed and studied within the context of estuarine and oceanic sediment transport dynamics and water and wastewater treatment both with and without the presence of organic material and coatings. In general, the addition of ions from salts has been linked to increased flocculation rates (Edzwald et al., 1974) and larger flocs (Mietta et al., 2009a). This phenomenon is thought to result from shrinkage of the electrical double layer (EDL) surrounding the particles due to increased ionic concentration (van Olphen, 1964). Shrinkage of the layer leads to aggregation because the thinner the layer becomes, the easier it is for particles to get close enough to overcome the inter-particle repulsion force and form aggregates. The resulting flocculation increases the size of mud flocs (Mietta et al., 2009b; van Leussen, 1999), leading to higher settling velocities (Portela et al., 2013).

We are proposing that the addition of deicing road salts to freshwater streams, whether they are naturally flocculated in their freshwater state or not, may alter the size distribution of suspended mud through ion-mediated enhanced flocculation with the net result being that deicing road salts produce an increase in the settling velocity of the mud. Increased settling velocity may in turn lead to greater accumulation of fine sediment on the streambed that ultimately degrades the health of benthic organisms. According to the United States Environmental Protection Agency (US EPA), more than 22% of streams (by length) in the US were impaired due to excess streambed sediments (EPA, 2019), which can degrade the benthic ecosystem health. One reason for this is that increased accumulation rate of fine sediment can lead to increased mortality rate of less mobile species due to burial (Conroy et al., 2018). Accumulation of fine sediment can also make the substrate unstable (i.e., easily erodible) and unsuitable for some benthic organisms (Richards and Bacon, 1994). Microbial activity, as well as reduced water percolation, within the accumulated mud layer can cause oxygen depletion (Pretty et al., 2006). Fine sediment accumulation can also negatively affect habitat (Burdon et al., 2013) and food (Suttle et al., 2004) availability for benthic organisms.

To test our hypothesis, we conducted a series of laboratory experiments to study how the size and settling rate of mud flocs respond to the presence of road salts in the suspension at concentrations typical of wintertime storm events in Stroubles Creek, which is a stream located in southwest Virginia, USA. For this purpose, we used a mixing tank as a controlled environment in which the mud aggregates that result from the flocculation process could be explored. We used Stroubles Creek because the specific conductance (SC) of the stream water is continuously monitored and the levels of wintertime SC were shown to be inversely related to the duration of time between brining the roads and storms (Lakoba et al., 2021). This outcome points to the direct influence of road salts on the chemical properties of the stream water during winter and therefore, potentially, the deposition of mud within the stream.

2.3 Materials and methods

2.3.1 Overview

This research aims to investigate: (i) the dependence of the size of suspended mud flocs on the presence and type of road salt in stream water, and (ii) the effect of flocculation on mud deposition rates. These aims were met using a laboratory mixing tank apparatus. The mixing tank provides an ideal environment to examine the size evolution of suspended mud floc populations through the use of a specialized camera system and a set of image processing routines. The laboratory experiments also help isolate the effects of road salt use from other phenomenon that also occurs in winter, e.g., the increase in sediment concentration driven by the freeze-thaw processes (Inamdar et al., 2018) due to soil erosion and bank instability (Couper and Maddock, 2001; Ferrick and Gatto, 2005). Combining the tank, imaging system, image processing routines, and a turbidity sensor allows for high-resolution measurements of floc size and concentration within the tank under a range of road salt types and turbulence levels. Below we first introduce Stroubles Creek, the creek used to set the salt level context for the study and to provide muddy sediment for the experiments. Following this, we outline the experimental apparatus and experimental conditions, procedures, and calculations. The key experimental parameters measured were floc sizes and water turbidity as a function of time under different turbulent mixing conditions (quantified by the shear rate, G, in s^{-1}) and water bio-geochemistry (deionized water, unimpaired stream water, stream water with added calcium chloride, magnesium chloride, and a commercial deicing mixture).

2.3.2 Stroubles Creek

Stroubles Creek is an example of a stream with multi-year high-frequency SC data that has been shown to be impacted by road salts and experience general sedimentation impairment (noa, 2020). It is approximately 19 km long and both starts and flows through the town of Blacksburg and campus of Virginia Tech (VT) in southwest Virginia, USA, before ultimately draining into the New River (a tributary of the Kanawha River, and ultimately, the Mississippi River). Due to the presence of the town of Blacksburg and VT campus, the watershed at the upper part of Stroubles Creek is highly developed. During winter, roadways in the Stroubles Creek watershed are brined by VT facility services and the town of Blacksburg, leading to post-storm SC values as high as 3921 µS cm^{-1} (Lakoba et al., 2021). Stroubles Creek was used to provide sediment for the experiments and to define target SC values.

2.3.3 The mixing tank apparatus

Experiments were conducted in a 13 L mixing tank equipped with an overhead paddle stirrer with adjustable rotation speed. The stirrer allowed for subjecting the suspended particles to variable turbulent shear rates, $G = \sqrt{\epsilon/\nu}$, where ϵ is the dissipation rate of turbulent kinetic energy, and ν is the kinematic viscosity of water. Turbulent shear rate is a major driver of floc size and is commonly used in modelling of the cohesive sediment flocculation process (Winterwerp, 1998) as it affects the frequency of collision of particles (leading to aggregation) as well as stress exerted on them (leading to break up). Floc size within the tank is measured using a specially designed imaging system. The imaging system consists of a digital camera fitted with a 2x microscope lens placed outside of the tank and focused on a plane just inside the tank and a waterproofed LED light source. The LED is placed inside the tank to (1) create a flow-through imaging plane between the tank wall and face of the LED housing, and (2) provide backlighting of the imaging plane within the tank. Further details on the camera setup can be found in Tran and Strom (2017). Collected images are processed in ImageJ to identify particles and measure their area. A Python script, based on the method of Keyvani and Strom (2013), is used to obtain particle size distributions based on the measured area of the identified particles. Turbidity within the mixing tank is continuously measured and recorded using an optical backscatter sensor (OBS).

2.3.4 Experimental conditions and procedures

Five main experiments were conducted. In each experiment, either the specific conductance of water or the type of road salt used to arrive at the target SC was varied. Experiment 1 was conducted in deionized (DI) water to examine the potential of the mud to flocculate in extremely low SC water (0-1 $\mu S\ cm^{-1}$). Experiment 2 used unaltered stream water, which is stream water collected from a local unimpaired stream without the addition of salts. Experiments 3-5 used the same stream water from the unimpaired stream as the second experiment (Table 2.1), but with salt added to reach the median wintertime SC in Stroubles Creek (i.e., 947 $\mu S\ cm^{-1}$) (Lakoba et al., 2021).

Water from Toms Creek was used as the baseline unaltered or unimpaired stream water for experiments 2-5. Toms Creek sits in the same county as Stroubles Creek (Montgomery County, VA) and is comparable in stream order (2nd), habitat, and stream power to Stroubles Creek, yet it meets water quality standards that Stroubles does not (sedimentation, E. coli., and nitrates concentrations (Gronwald et al., 2008)). For this reason, Toms Creek has been used as a biological reference reach for Stroubles in restoration efforts (Committee et al., 2006). The initial background SC of the collected water ranged from 116 to 147 $\mu S\ cm^{-1}$ across experiments. The background SC level in the Toms Creek samples were all significantly lower than the SC levels in Stroubles Creek that has been impacted by the long-term effects of deicing salt use in its watershed (Hession et al., 2020).

In the US, deicing salts generally consist of one to three components: sodium chloride, calcium chloride, and magnesium chloride. Therefore, three different road salts were used in Experiments 3-5. The first one was a commercial road salt that is a mixture of sodium chloride, calcium chloride, and magnesium chloride (Road Runner ice melt, Scotwood Industries, KS, USA). The second and third road salts were calcium chloride and magnesium chloride, respectively.

The fine sediment used in the experiments was collected from the bed of Stroubles Creek. The same sediment sample was used for all the experiments to minimize the potential effects of temporal variability in sediment characteristics on the flocculation experiments. The sediment was kept in a laboratory refrigerator maintained at 4°C for the duration of the study. The sediment was wet-sieved through a number 200 sieve to remove any sand from the sample. The disaggregated median size of the sediment by volume was 7.6 µm, and the fraction of organics estimated from loss on ignition from a subset of the sample was 10.2%. The sediment leftover after the loss on ignition measurement was not used in any of the flocculation experiments. For those experiments, sub-samples were extracted from the large unaltered and well-mixed sample that had been wet sieved.

Each of the five flocculation experiments commenced with a suspended sediment concentration of 100 mg L^{-1}. This initial concentration was produced by sonicating 1300 mg of sediment in a small vessel for 15 min to break up any aggregates or flocs present and to ensure a consistent initial state for each experiment, and then adding the sonicated mixture to the mixing tank filled with the specified water mixing at a rate of $G = 35$ s^{-1}. Imaging of the suspension commenced once sediment was added to the tank, and flocs were allowed to grow at the mixing condition of $G = 35$ s^{-1} for 60 minutes. Following this period of floc growth from a sonicated state, the suspension was subjected to high shear rate of 550 s^{-1} for 15 minutes to break the flocs down to a more natural, turbulence-generated initial condition (Tran and Strom, 2017). The suspension was then subjected to five consecutive 150-min mixing conditions at shear rates of 95, 70, 50, 35, and 20 s^{-1}. Throughout this time the suspension was imaged with the camera. Time series data from the experiments showed that the overall floc size population statistics were approximately constant over the last 35 minutes of each step in G. Therefore, the last 35 minutes of each shear rate step was used to determine the population of floc sizes at equilibrium, and at least 1051 in-focus particles were included in each equilibrium measurement.

2.3.5 Settling velocity and advective length scale calculations

The relationship in Strom and Keyvani (2011) was used to estimate floc settling velocity based on the size of the flocs as,

$$w_s = \frac{gR_s d_f^{n_f-1}}{b_1 \nu d_p^{n_f-3} + b_2\sqrt{gR_s d_f^{n_f} d_p^{n_f-3}}} \tag{2.1}$$

where g is gravitational acceleration, R_s is the submerged specific gravity of the sediment, d_f is the floc diameter, d_p is the primary particle size (the size of smallest particles making up the flocs), n_f is the fractal dimension of the flocs, and b_1 and b_2 are shape coefficients. A typical fractal dimension of n_f=2.2 was considered (Winterwerp, 1998). We used b_1 and b_2 of 18 and 0.548, respectively (Strom and Keyvani, 2011).

The advective length scale, L_{adv},

$$L_{adv} = \frac{hU}{w_s} \tag{2.2}$$

was also calculated as a simple scale of a single hop length that a suspension of particles of a particular settling velocity might travel downstream under the action of vertical settling and horizontal advective transport. In Equation 2.2, h is the water column depth in the stream, U is average stream velocity, and w_s is calculated from Equation 2.1.

2.4 Results

2.4.1 Floc size

The first component of our hypothesis is that the addition of road salts will increase the size of suspended mud aggregates. Measures of floc size with time were obtained in the experiments using the images captured by the camera. At the beginning of each turbulent shear level (G), flocs grew until they reached an equilibrium size where the overall population statistics did not change with time until the mixing rate was again altered.

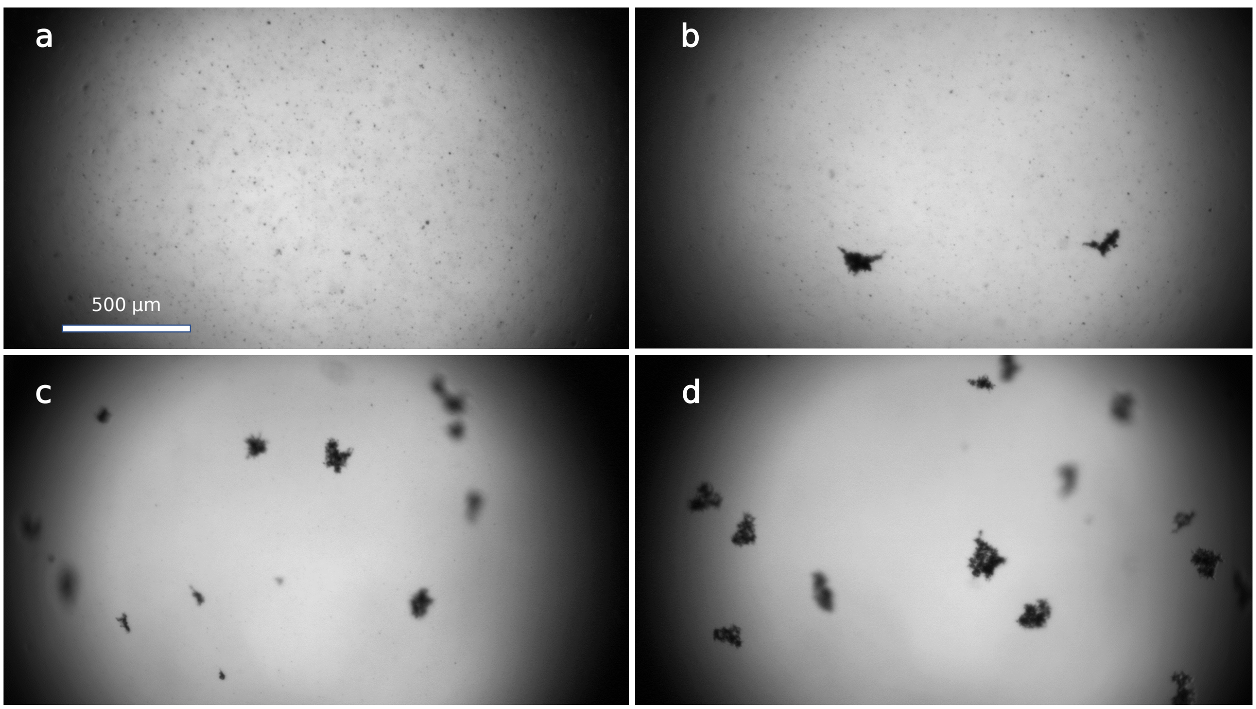

Figure 2.1: Sample images showing flocculated and unflocculated particles in a) DI water, b) unaltered stream water, and water with c) mixed road salt, and d) calcium chloride at the turbulent shear rate of 35 s^{-1}.

The vertical distribution of turbulent shear rate in a river with production and dissipation of turbulence in balance can be calculated as $G(\zeta) = [u_*^3((1-\zeta)/\zeta)/(\kappa\nu h)]^{1/2}$, where u_* is friction velocity, ζ is the vertical coordinate non-dimensionalized with depth, and κ is the von Karman constant. Considering an average channel slope of 0.0023 m m^{-1} in Stroubles

Creek (Azinheira et al., 2014), we expect the suspended flocs to experience shear rates of $15 < G < 150$ s^{-1} during a flood event. To explore most of this space, we ran each of the flocculation experiments at five different turbulent shear rates as described in the methods. For the presentation and discussion of results we have selected $G = 35$ s^{-1} as a representative moderate flow regime that can keep most of the flocs in suspension. Therefore, the results presented below are focused on $G = 35$ s^{-1}, but we found similar trends across all mixing conditions.

Increase in the SC of water due to the dissolution of deicing salts increased the flocculation of suspended mud, leading to larger aggregates, compared to that of deionized (DI) water and unaltered, or unimpaired, stream water (Fig. 2.1). When suspended in DI water, the mud particles formed few aggregates and instead tended to remain as discrete particles of diameter <30 µm (Fig. 2.1a). Mud particles in the unaltered, or unimpaired, stream water created a few relatively large flocs (some larger than 100 µm in diameter). However, these larger flocs were significantly outnumbered by smaller particles (Fig. 2.1b). In the experiments with higher SC due to the presence of road salts, a much larger fraction of the particles aggregated to form large flocs (as evident by comparing Fig. 2.1b and Fig. 2.1c). These effects were found to be stronger in the experiments with calcium chloride (Fig. 2.1d) and magnesium chloride (no image shown in the figure) compared to the mixed road salt (Fig. 2.1c) so that in the experiment with calcium chloride, discrete particles were rarely captured by the camera, and the majority of particles were larger than 100 µm.

The change in particle size distribution is evident from the normalized frequency of flocs by size class (Fig. 2.2). In the DI water experiment, the majority of the particles were smaller than 50 µm. The particle size distribution shifted slightly towards the larger sizes in unaltered stream water with some flocs with size of >150 µm forming in the mixing tank. However, a significant number of particles were still in the un-aggregated form. With increase in SC as a result of addition of road salt, the fraction of discrete and un-aggregated particles decreased

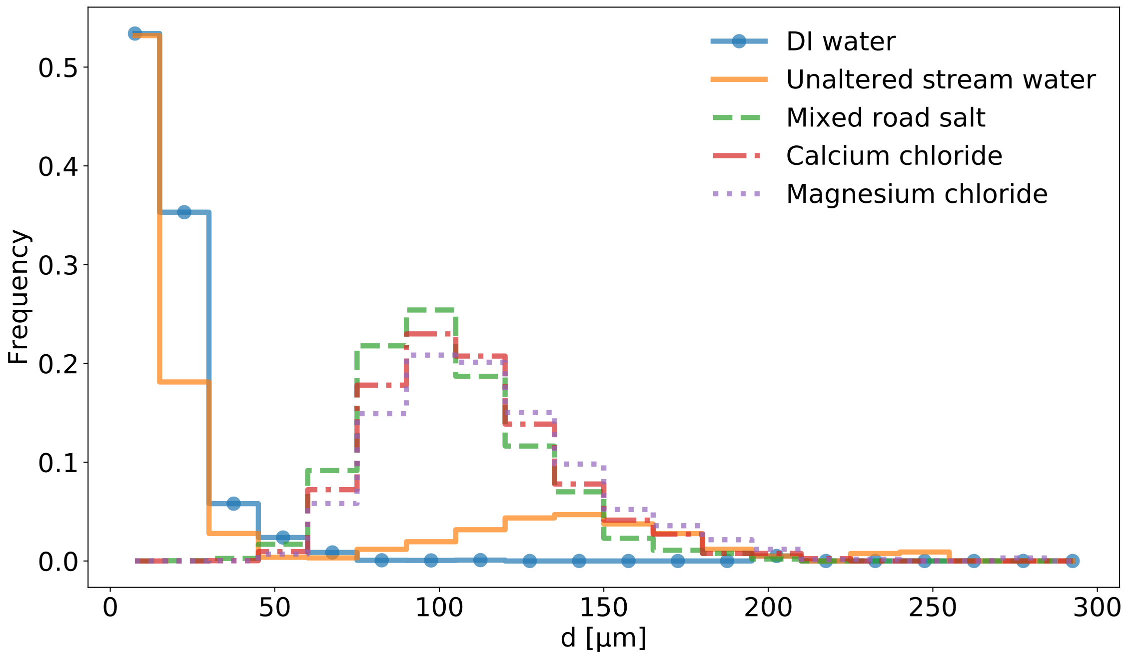

Figure 2.2: Volume-weighted normalized particle size distribution across different experiments at equilibrium at the turbulent shear rate of 35 s^{-1}.

substantially, shifting the particle size distribution towards the larger particles. This points to the enhanced and evident aggregation potential of the mud particles in the presence of road salt. The effects of magnesium chloride and calcium chloride were comparable and stronger than mixed road salt.

We also examined the particle and floc size distributions at shear rates of 20, 50, 70, and 95 s^{-1} to examine how changes in stream flow rate and turbulence might impact the floc sizes with different salt types. All findings were consistent with what can be seen in sample images (Fig. 2.1) and particle size distributions (Fig. 2.2) from the $G = 35$ s^{-1} case. The addition of road salts decreased the number of small un-aggregated particles and increased the overall size of the mud particles or flocs in suspension. Within this overall effect of salt, floc sizes generally decreased with increasing shear rate. For example, the equilibrium floc or particle size for which 50% of the material in suspension was finer than by volume, d_{50eq}, for the experiment with magnesium chloride was 146, 105, 81, 69, and 58 μm for shear rates of $G = 20$, 35, 50, 70, and 95 s^{-1}, respectively. A summary of d_{50eq} values for all shear rates and water types is given in Table 2.1.

Table 2.1: Equilibrium floc size (d_{50eq}) at different turbulent shear rates (G) for different experiments

		d_{50eq} [µm]				
		Turbulent shear rate [s^{-1}]				
Experiment	Water/salt type	20	35	50	70	95
1	DI water	11	12	13	15	15
2	Unaltered water	21	71	59	35	33
3	Mixed road salt	134	99	79	67	41
4	Calcium chloride	150	111	84	69	59
5	Magnesium chloride	146	105	81	69	58

2.4.2 Settling rate

The addition of road salts clearly increases the number and size of large muddy flocs. The second component of our hypothesis is that this increase in floc size will lead to higher settling rates of mud. To test this idea we examined the clearing rate of suspended sediment in the water column in the tank for each experiment at two different mixing rates or flow velocities. The first was when the suspension was experiencing a shear rate of 20 s^{-1}, i.e., during the last step of the floc growth experiments. The second was when the stirrer was turned off, leading to a turbulence level within the tank that decayed with time. The first roughly corresponds to flows within the core of the flow, perhaps on the waning limb of a flood hydrograph. The second would mimic a stream reach where the width expands and velocities drop and/or the channel margins or pockets of reduced velocity where deposition of mud can be significant. For example, fine-grained channel margins deposits have been shown to account for 17-43% of the suspended sediment load in the South River, Virginia, USA (Skalak and Pizzuto, 2010).

When flocs were experiencing a shear rate of 20 s^{-1}, a fraction of them grew sufficiently large that they were not able to remain in suspension. The strongest settling over a period of 3 hours occurred in the experiments with road salt. For these cases, 22%, 33%, and 42% of the suspended sediment deposited during this time of lower shear for the experiments with the mixed road salt, calcium chloride, and magnesium chloride experiments, respectively (Fig. 2.3a). Comparatively, the experiments with DI water and unaltered stream water lost only 8% and 12% of their initial turbidity during the same duration of time. This points to the enhanced sinking rate of mud particles and their accumulation on the bottom of the mixing tank in the presence of road salts even when they are experiencing a turbulent mixing condition comparable to when they are being advected by the stream flow (for example the lowermost Mississippi River (MacDonald et al., 2007).)

In the settling test with decaying turbulence (mixer turned off), the DI water lost about 1% of its initial turbidity over a 15-minute period (Fig. 2.3b), indicating the dispersed and small nature of the particles in the water column that makes them harder to settle out. The decrease in turbidity in the unaltered stream water experiment was approximately 15% over the same period of time. The rate of clearance was considerably higher in the road salt experiments, indicating that the majority of the mud was bound in larger flocs that were sufficient in size to settle out of the suspension quickly. The water containing mixed road salt lost 48% of its turbidity, slightly less than that of the magnesium chloride and calcium chloride experiments where turbidity decreased by 66% and 72%, respectively, over the same time period.

2.4.3 Advective length scale

As flocs grow larger, their settling velocity increases. Concentration-weighted settling velocities for the suspension were calculated from each experiment using the measured particle/floc sizes and Equation 2.1. These suspension average values of w_s for $G = 35$ s^{-1} are presented

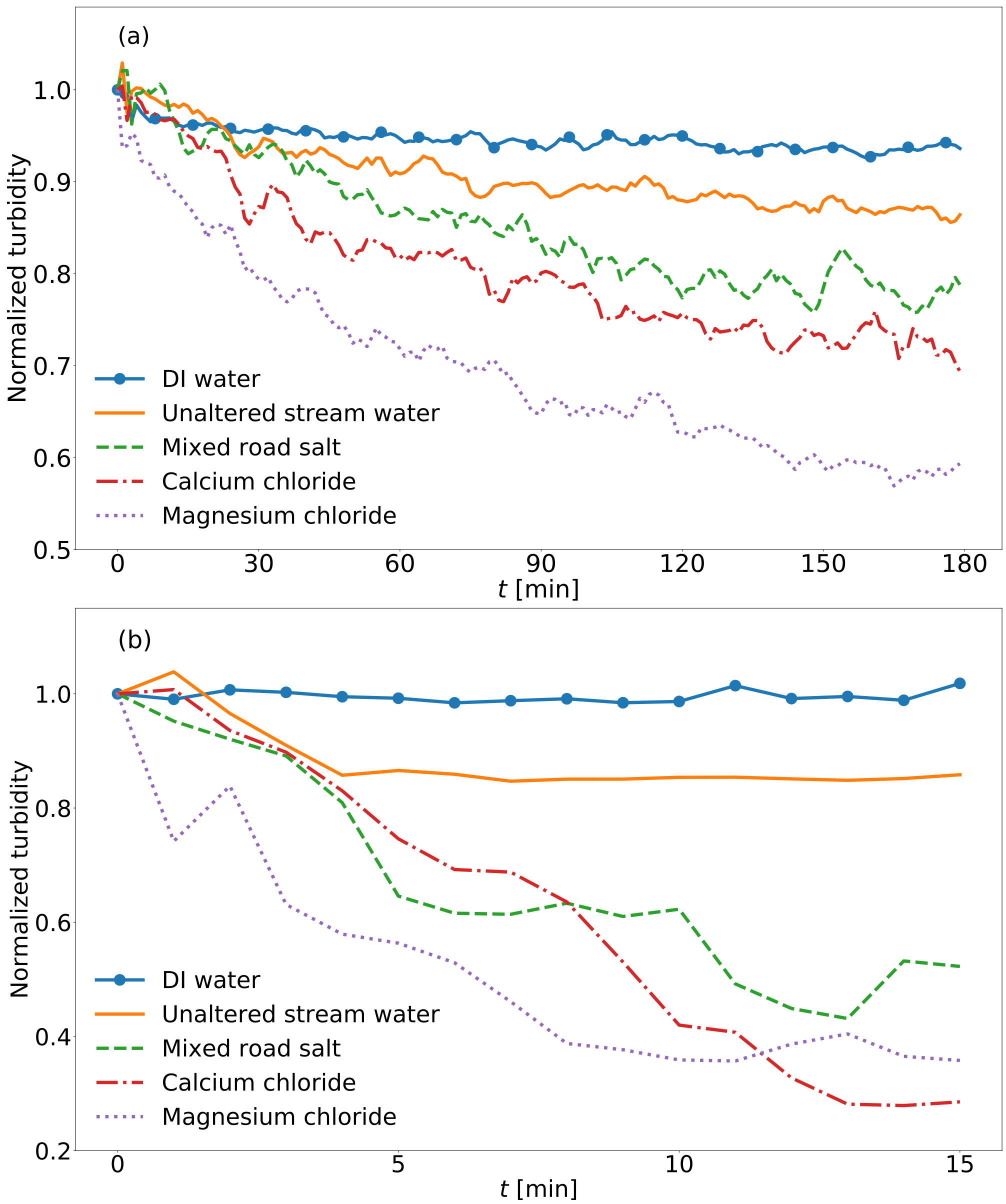

Figure 2.3: Time series of normalized turbidity at a) turbulent shear rate of 20 s^{-1} and b) stagnant water.

in Table 2.2. The highest settling velocities belonged to the experiment with magnesium chloride where calculated settling velocity was just above 1 mm s^{-1}. The settling velocity for the experiment with unaltered stream water was about 56% of that with calcium chloride and 60% of that with magnesium chloride.

Settling velocity affects the duration of time that mud stays in the water column before coming in contact, on average, with the bed while being advected downstream by the stream flow. The advective length scale, $L_{adv} = hU/w_s$, is a scale or measure of this time or length. Specifically, L_{adv} represents the distance downstream traveled by a particle with a settling velocity of w_s starting from the free surface traveling over a depth of h while being advected downstream at an average velocity of U. Another way to conceptualize L_{adv} is the distance downstream from a sediment source needed to clear the water column of sediment assuming that there is no further source of sediment input from re-suspension of deposited sediment or input from tributaries or the land surface. Here L_{adv} is calculated for a range of flow depths and velocities using the calculated settling velocities from the flocculation tests to further contextualize the significance of road-salt-mediated flocculation and potential deposition of mud to the streambed. Representative post-storm stream depths of 1 and 5 m and average stream velocities of 0.5 and 1.5 m s^{-1} were considered for the estimates. At $U = 1.5$ m s^{1} and $h = 5$ m, adding salt reduced the advective length scale from 12.7 km for the unaltered stream water to 7.1 km for magnesium chloride and 7.6 km for calcium chloride (Table 2.2). For the same flow conditions, advective length scale was 52.5 km for DI water. Similar reductions were found at other combinations of depth and velocity. These estimates are all within the range of 3-400 km that was calculated using a formulation similar to Equation 2.2 for sediment travel distance in rivers in Intermountain West at near bankfull discharge (Whiting et al., 2005).

Table 2.2: Advective length scale (L_{adv}) and settling velocity (w_s) at different flow depths (h) and average stream velocities (U) at a representative turbulent shear rate of 35 s^{-1}

Experiment	Water/salt type	w_s [mm s^{-1}]	U [m s^{-1}]	h [m]	L_{adv} [km]
1	DI water	0.12	0.5	1	4.2
			0.5	5	20.8
			1.5	1	12.5
			1.5	5	52.5
2	Unaltered water	0.59	0.5	1	0.8
			0.5	5	4.2
			1.5	1	2.5
			1.5	5	12.7
3	Mixed road salt	0.92	0.5	1	0.5
			0.5	5	2.7
			1.5	1	1.6
			1.5	5	8.1
4	Calcium chloride	0.99	0.5	1	0.5
			0.5	5	2.5
			1.5	1	1.5
			1.5	5	7.6
5	Magnesium chloride	1.05	0.5	1	0.5
			0.5	5	2.4
			1.5	1	1.4
			1.5	5	7.1

2.5 Discussion and conclusion

The presence of road salt in the stream water we used in our tests affected the flocculation potential of the suspended mud. In the presence of road salts, the vast majority of the fine sediment aggregated into floc structures (Fig. 2.1). Flocs did exist in the natural or unaltered stream water without the addition of salt. However, the distribution of particle sizes in the unaltered stream water was bi-modal with much of the mud existing as very small aggregates or unflocculated mud. Addition of the road way salt resulted in the formation of large flocs with a more uni-modal distribution and an overall increase in average size. Consequently, the suspension with road salts experienced a larger amount of settling within the tank. The reason for this enhanced flocculation is that, as ions concentration increases (particularly cations and more importantly divalent and multivalent cations), the thickness of the double layer decreases and allows for the attraction force to overcome the repulsion force, leading to formation of aggregates.

The contrast between flocs formed in the road salt experiments and those in the unaltered stream water is evident across all lower shear rates. For instance, at a shear rate of 35 s^{-1}, the median floc size in the experiment with mixed road salt was almost 40% higher than that in the unaltered stream water experiment. This was true even though a few larger flocs with $d_f > 150$ µm did form in the unaltered stream water experiment (Fig. 2.2). Size increases of this amount led to increases in settling velocity of 56% according to Equation 2.1, and a decrease in the advective transport length scale of the same amount. A stronger flocculation response (a larger increase in settling velocity and clearance rate of sediment from the mixing tank) than that due to the mixed salts was observed in the experiments with magnesium chloride and calcium chloride. The more pronounced effect is likely due to the divalent nature of magnesium and calcium cations compared to the monovalent sodium cations that are in the mixed road salt. The presence of more than one positive charge can also facilitate divalent cation bridging (DCB) and enhance flocculation (Sobeck and Higgins, 2002).

In all cases with salt, the calculated advective length scale based on typical conditions in Stroubles Creek were smaller than the advective distance of mud, 10 km, estimated by Pizzuto (2014) for the South River, Virginia, USA using concentration of sediment-bound mercury in sediment cores. While our estimates of this length scale are based on assumed hydraulic conditions, and do not consider re-entrainment of freshly deposited mud, the calculated values and measured change in floc sizes suggest that the addition of road salts at levels comparable to those that have been observed in southwest Virginia, USA, could potentially have an impact on the transport dynamics of mud in streams and rivers.

A broader implication of our study finding is that negative impacts of road salt on stream ecosystems may extend past that of toxic salinity levels for freshwater organisms. Sedimentation of fine sediment to streambeds is a leading cause of stream impairment (Wood and Armitage, 1997). In this study we have demonstrated that road salts have the potential to significantly increase floc size and thereby increase the settling velocity and deposition rates relative to suspensions unaffected by road salts. We propose that this increase in deposition rate could lead to an increase in the accumulation rate of fine sediment on river beds. While this proposition of increased net accumulation due to the increase in floc size was born out in our laboratory mixing tank experiments (with visual observations of deposition on the bottom of the tank being greater and OBS readings being lower for the cases with salts), our experiments cannot confirm whether or not the increase in deposition rate would ultimately lead to an increase in accumulation rate in natural streams. Resuspension rates within the tank and natural rivers are likely to differ. And it is possible that the potential of the stream to entrain deposited sediment could be significant enough to re-entrain any extra mud that makes it to the bed as a result of enhanced floc size.

While we find that our data suggest that the use of road salts has the potential to alter mud transport dynamics and accumulation rates in streambeds, we must also stress that additional work is needed to confirm or deny our proposition. As mentioned above, accumulation rate is the net outworking of both deposition rate and entrainment rate of sediment. Our study focused only on how the addition of road salt altered floc size and therefore the settling velocity and deposition rate of the mud in a laboratory tank. We did not measure accumulation or entrainment rates in the field. Furthermore, our experiments were conducted using mud and water samples only from one particular stream. It remains unknown as to how widespread the flocculation behavior of suspended stream mud in the presence of road salts that we observed is. Therefore, while our study points to a potential link between road salt use and the health of streams through the pathway of alterations to mud transport dynamics, it also is a call for additional work, particularly field studies, on this topic.

2.6 Acknowledgement

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Chapter 3

Salinity impacts on floc size and growth rate with and without natural organic matter

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Chapter 3 has been submitted to Journal Geophysical Research: Oceans. Revisions have been submitted to the journal.

3.1 Abstract

Due to the flocculation process, suspended mud aggregates carried by rivers to the coastal ocean are thought to undergo changes in size and shape in response to environmental drivers such as turbulence, sediment concentration, organic matter (OM), and salinity. Some have assumed that salt is necessary for floc formation, and that mud, therefore, reaches the estuary unflocculated. Yet mud flocs exist in freshwater systems long before the estuarine zone, likely due to the presence of OM acting as a floc-promoting binder. Therefore, it is important to consider how salinity affects flocculation, if at all, in the presence of OM. Here, we used experiments to examine the flocculation of a natural mud with and without OM. Results showed that the rate of floc growth and equilibrium size both increase with salinity regardless of the presence or absence of OM. However, the response of both to salinity was stronger when OM was present. In DI water, natural sediment with OM was seen to produce large flocs. However, the size distribution of the suspension tended to be bimodal. With the addition of salt, increasing amounts of unflocculated material became bound within flocs, producing a more unimodal size distribution. Here, the enhancing effects of salt were noticeable at even 0.5 ppt, and increases in salinity past 3 to 5 ppt only marginally increased the floc growth rate and final size. Data from the experiment were used to develop a salinity-dependent model to account for changes in floc growth rate and equilibrium size.

3.2 Introduction

3.2.1 Overview

Rivers undergo changes in flow physics, water chemistry, and organic constituents as they approach the end of their freshwater journey and transition to estuarine, and eventually, marine environments. The exact nature of the estuarine environment varies from river to river, but two key changes pertaining to the sediment transport dynamics of the system generally occur. The first is that the hydrodynamics of the system goes from being dominated by the gravitational body force and wall-bounded shear flow turbulence to a system that is also driven by tides, waves, density differences, and the initial inertia of the river upon entering the coastally-influenced zone. This causes a general decrease in the turbulent energy of the fluid and its ability to keep sediment in suspension. Another generality is that the salinity in the system increases from near 0 PSU upstream of the estuarine zone to approximately 35 PSU in fully marine conditions. The spatial-temporal nature of the salt transition varies depending on the fluvial, tidal, and bathymetry boundary conditions of the estuary, but an increase in salt level must take place.

Rivers deliver mixtures of sand and mud (clay and silts size particulate mineral and organic matter less than 63 microns in size that exhibit cohesive behavior) to estuarine zones, and the change in hydrodynamic, chemical, and organic quantities and constituents can all impact how sediment moves through the system and where sediment of different size fractions erodes or accumulates. Sand is primarily affected by hydrodynamics. Like with sand, a reduction in turbulent energy promotes the deposition of mud through the reduction in upward mixing forces on mud particles. However, mud can be influenced by the changes in hydrodynamics, salt levels, and biological processes through flocculation, which refers to continuous aggregation and breakup of muddy aggregates (Winterwerp, 1998). The reduction in turbulence can decrease the shear stress exerted on flocs and contribute to their growth. Changes in salt levels and the quantity and type of organic matter present in the water can further influence the size and density of mud flocs. Therefore, the physical, chemical, and biological conditions can all exert an influence on the settling speed of mud through the flocculation process. And while it has long been acknowledged that all three of these factors influence floc size, our ability to model floc size and settling velocity in dynamic conditions remains limited.

In this study, we examine the effects of salinity change within a turbulent suspension of varying intensity on the flocculation of mud both with and without natural organic matter. We then use the floc size and growth rate data obtained from the experiments to propose a simple model to account for the variations in salinity on a growth rate factor for flocs.

3.2.2 Background

Water salinity has long been deemed an influential factor in the flocculation of fine sediment (e.g., Odd, 1988). Fundamental to this understanding is the small mass of the fine sediment particles (which allows them to aggregate when close enough to each other) and the fact that the particles are often negatively charged due to the isomorphous substitution and preferential adsorption in their crystalline structure (Partheniades, 2009) or adsorption of low molecular weight (LMW) organic compounds (Tipping and Higgins, 1982; Tipping and Cooke, 1982). The negative charge causes a repulsion force that prevents the particles from getting close enough to aggregate. Increased salinity can promote flocculation by shrinking the electric double layer (EDL) that surrounds the charged clay minerals (Gregory and O'Melia, 1989). The EDL consists of a Stern layer that contains ions with a charge opposite to the clay mineral surface charge and a diffuse layer that contains free ions with a higher counterion concentration. When the ion concentration of water increases, both the Stern layer and the diffuse layer shrink, making it easier for particles to get close enough to each other for van der Waals forces to dominate and allow particles to aggregate and form flocs (Gregory and O'Melia, 1989). An extensive line of research has provided evidence for the growth-enhancing effects of salinity on the flocculation of cohesive sediment both in laboratory experiments and in field surveys.

Laboratory studies have generally reported that increased ion concentration of water leads to a growth in floc size and an associated increase in mud settling velocity. Edzwald et al. (1974) was one of the earliest attempts to quantify the effects of ion concentration in the water on suspensions of clay minerals such as kaolinite, illite, and montmorillonite. Based on their experiments, they reported enhanced aggregation for all clay suspensions with increased salinity. Further research has shown increase in floc size (e.g., Mietta et al., 2009a; Mikeš and Manning, 2010; Guo et al., 2021; Abolfazli and Strom, 2022) and settling velocity (e.g., Portela et al., 2013; Li et al., 2021). While added salt is generally acknowledged to increase the size and settling velocity of clay-based flocs in the laboratory, the effects of salinity increases have also been found to have a threshold past which further increases in salt concentration have little effect on floc properties. For instance, $S = 15$ ppt was reported by Mietta et al. (2009a), $S = 10$ ppt by Mikeš and Manning (2010), and $S = 7$ ppt by Guo et al. (2021) to be the concentration threshold for salinity effects.

It is difficult to isolate the effects of increased salinity on flocs in natural settings since other flocculation drivers such as turbulence, suspended sediment concentration, and the organic fraction of suspended sediment tend to co-vary along with salinity. Nevertheless, field studies have also generally described a positive, though less pronounced, relationship between salinity and floc size. In the Yangtze estuary, the largest flocs were observed in high slack water when salinity peaked and shear was lowest, while smaller flocs were found during flood and ebb tides when turbulence was stronger (Guo et al., 2017); whether the peak in floc sizes was due to changes in salinity or turbulence or was a result of larger material being advected into the sampling region is unknown. In the Ems Estuary, the largest flocs were observed in the seaward direction, where the suspended sediment concentration was not necessarily at its maximum (van Leussen, 2011). The presence of a halocline was suggested as the main driver for vertical variation in floc size in the Pearl River estuary by Zhang et al. (2020). However, the authors later argued that, although increased salinity is important in enhanced fluctuation, the density stratification due to saltwater intrusion played a stronger role in modulation of the floc size distribution in the Pearl River estuary (Zhang et al., 2021).

Another driver of cohesive sediment flocculation is organic matter (OM). OM is known to be a significant factor in aggregation dynamics of sediments and has been suggested to affect flocculation in freshwater (Droppo et al., 1997), estuarine (Eisma, 1986), and coastal (Fettweis et al., 2022) environments. In fact, Eisma (1986) proposed that OM was the first-order influence on floc size and that increases in salt concentration with an estuary have a minor to negligible effect. And, the laboratory experiments of Mietta et al. (2009a) showed that flocs formed from mud devoid of OM were smaller compared to those formed from mud with natural OM. Due to their structural complexity, and relatively larger size compared to clay crystals, OM can modify the characteristics and behavior of clay particles in a myriad of ways. Microorganisms or a part of their structure can be bound in and become a part of floc structure (Droppo et al., 1997; Droppo, 2001). They can change the surface charge of clay particles (Beckett and Le, 1990), act as a binder for clay particles due to their complex structure (Theng, 2012; Labille et al., 2005), or grow on the particles (Tang and Maggi, 2018; Shen et al., 2019). The OM present in freshwater can have terrestrial or autochthonous origin and thereby vary seasonally (Lee et al., 2019). Additionally, despite the historical assumption that cohesive sediment is unflocculated when transported in fluvial systems, an increasing body of observational (e.g., Droppo et al., 1997; Fox et al., 2014; MacDonald and Mullarney, 2015; Osborn et al., 2021), experimental (e.g., Abolfazli and Strom, 2022), and analytical (e.g., Lamb et al., 2020; Nghiem et al., 2022) evidence support the ubiquitous presence of flocs in rivers and streams. Without the presence of measurable salinity in most cases, the explanation for the presence of flocs in freshwater systems has been the presence of OM serving as a binder for the inorganic and organic components of the flocs.

To account for the influence of drivers such as OM and salinity on mud transport, one must have a mathematical model for floc size or settling velocity that can be integrated into a larger hydrodynamic and sediment transport framework (e.g., Winterwerp, 1998; Teeter, 2000; Verney et al., 2011; Sherwood et al., 2018; Tarpley et al., 2019). Recently, there has been a push to include the impact of OM on floc population models (e.g., Shen et al., 2019). However, models that account for alterations in the floc sizes or settling velocity brought on by changes in salinity are more limited, perhaps due to the lack of data suitable for model development. The two models that include a salinity effect are the approaches by Delft3D Deltras (2021) and Horemans et al. (2020). In Delft3D, the salinity effect is modeled directly on the settling velocity of the mud (i.e, floc size is not modeled). The Delft3D salinity-driven model assumes that settling velocity, w_s, approaches a maximum value as salinity increases and approaches a value past which increases in salt no longer influence floc size and settling velocity, S_{max}. Horemans et al. (2020) (hereafter, H20) takes a similar approach in that salinity effects are limited to a range of values below a cutoff or threshold salinity. But, rather than mapping these effects directly to the mud settling velocity, they propose a floc aggregation efficiency parameter, usually taken as a constant in floc size models, as a function of salinity. The equation for the efficiency parameter they developed was based on three data points from Edzwald et al. (1974) (hereafter referred to as E74), and using it allowed them to predict changes in floc size, and hence settling velocity, due to changes in estuarine salinity.

3.2.3 Study purpose

The studies discussed above point to the significance of both ion concentration of the water and OM in the flocculation of cohesive sediments. Either can likely independently influence flocculation, and it is unclear if the independent effects are linearly additive or if there are interactions between the two that override the other or provide a joint effect. Answering this question is particularly important for modeling of mud in natural environments because both cations and OM are always present in some form. In addition, while changes in salinity are thought to drive changes in flocculation rate and equilibrium size, efforts to parameterize and model its behavior in natural environments are scarce and not well tested or calibrated.

In this study, our first goal is to test the hypothesis that the positive correlation between increased aggregation rate and equilibrium floc size and increased salinity is more pronounced when organic matter is present. That is, we expect the effect of salinity change on mud flocs to be positively modulated by organic matter. The rationale for this hypothesis is that the presence of both salt and OM affects flocculation by changing the electric charges that are present on the ions, clay particles, and OM molecules and the alterations they make to the inter-particle interactions. This suggests that there exists a potential interaction between the different components of flocculation, i.e., sediment particles, ions, and OM. The specific questions we aim to answer in this study are: 1) is there a fundamental difference in the way natural mud flocs and those devoid of OM respond to an increase in salinity; and 2) is there a particular range of salt levels past which increases in salt in the suspension of either type of sediment no longer influence the flocculation properties? A broader question of consideration associated with our study is whether or not salt has any effect on a mud suspension if organic binders are already present and causing flocculation in freshwater rivers before they enter estuarine environments. The second goal of our study is to use data from the experiments to develop a method for including the impacts of changes in salinity within a Winterwerp (1998) type formulation for dynamic or equilibrium median floc size.

3.3 Materials and methods

3.3.1 Approach overview

To test our hypothesis, we measure the size distribution, equilibrium median size, and aggregation rate of mud flocs in a laboratory mixing chamber for three sets of experiments using OM-free kaolinite clay, natural sediment containing OM, and that same natural sediment treated to remove its organic content. Salinity and turbulent shear rate are varied across each of the three sets of experiments (Table 3.1). Data are collected with a floc camera to measure the size distribution of the particles in suspension and an optical backscatter sensor (OBS) is used to measure the turbidity. Comparisons between experiments with and without OM and across increasing salinities are used to test the hypothesis and answer the specific research questions. The turbulent shear rate during the experiments proceeds through step-downs in mixing rate to mimic the weakened turbulence conditions in a river plume, delta, or estuary. Below we present a detailed description of the mixing chamber, the camera system, the salt and sediment used in the experiments, and the experimental procedure.

Table 3.1: Experiments were conducted using three types of sediment at various salinity levels.

Experiment set	Sediment type	Salinities tested [ppt]
1	Kaolinite clay	0, 2, 10
2	Natural mud (natural OM)	0, 0.5, 1, 2, 3, 5, 10
3	Treated mud (devoid of OM)	0, 2, 10

3.3.2 Mixing chamber and data acquisition setup

The experiments were carried out in a 13 L mixing chamber (27.5 × 27.5 × 25 cm) equipped with an overhead stirrer motor connected to a paddle that allows the mixing rate and hence turbulent shear rate (G) to be adjusted within the chamber. G is a measure of the dissipation rate of turbulent kinetic energy, ϵ, and is defined as $G = \sqrt{\epsilon/\nu}$, where ν is the kinematic viscosity of water. G is a widely used parameter in modeling the flocculation process because turbulence drives both aggregation (due to increasing the likelihood of particle collision) and breakup of flocs (due to increased mechanical stress exerted on flocs) (e.g., Winterwerp, 1998; Lee et al., 2011). G was estimated using a relationship proposed by Logan (2012) based on tank and paddle geometry and paddle speed:

$$G = (\frac{52.3 C_D A s^3 R^3}{\nu V_T})^{1/2} \tag{3.1}$$

where C_D is the drag coefficient, A and R are the paddle area and radius, respectively, s is the paddle speed, ν is the fluid kinematic viscosity of water, and V_T is the volume of water in the chamber.

The mixing tank was also equipped with a camera system that consisted of a waterproof LED light source placed inside the tank and a camera placed outside of the tank. The camera records images of particles passing through the slit created by the light source and the wall of the mixing chamber (Figure 3.1). The system is capable of capturing images of flocs in the size range of approximately 5-1500 µm. Details on the mixing chamber and the camera system can be found in Tran and Strom (2017). The images captured by the camera were then organized using a Python script that was based on the procedure by Keyvani and Strom (2013) and processed in ImageJ to identify the particles present in each image. The particle, or floc, sizes were then extracted using the measured area of each particle as $d_f = \sqrt{4A_f/\pi}$, where d_f is the floc diameter or size, and A_f is the measured area of each floc. Associated floc volumes were calculated as: $V_f = \pi d_f^3/6$, where V_f is the floc volume. The identified particles or flocs were then sorted into log sized bins to produce floc size distributions based on floc volume and size statistics such as d_{50} (the median floc size by volume). Defining d_{50} by volume eliminates the need to assume a fractal dimension for flocs. Additionally, obtaining actual and real-time images of flocs with the camera system enabled us to visually compare the flocs formed in different conditions in addition to measuring their size (compared to the particle size and volume distribution estimation methods that are based on the principles of laser diffraction).

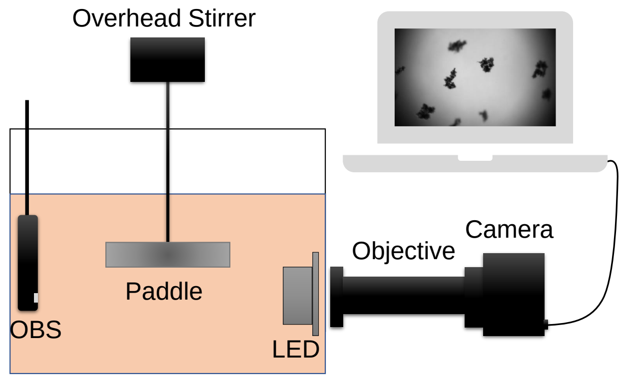

Figure 3.1: Schematic of the experimental setup.

3.3.3 Salt

Previous experimental flocculation studies have used different types of salt to represent sea salt; for example, salts used include table salt (sodium chloride) (e.g., Nasser and James, 2006), commercial aquarium salts (e.g., Tan et al., 2014), and a mixture of multiple salts (e.g., Edzwald et al., 1974). While all of these salt mixtures increase the ion concentration and salinity of water, it has been shown that in addition to the concentration of salt (i.e., ion concentration), the type of salt can be quite important in setting the flocculation behavior of mud (e.g., Abolfazli and Strom, 2022). Divalent and polyvalent cations (compared to monovalent ions), for instance, are more efficient in facilitating the bonds between the sediment particles mostly due to cation bridging effects (Theng, 2012; Lai et al., 2018). To recreate saline water as close as possible to seawater, we used an American Society for Testing and Materials (ASTM) grade sea salt substitute (Lake Products Company LLC, Florissant, MO, USA) in our experiments. This salt contains nine other constituents in addition to sodium chloride including magnesium chloride and sodium sulfate. Deionized (DI) water was used as the background water in all experiments to eliminate the effects of the ions that are already present in tap water and their potential variations over the period of the study.

3.3.4 Sediments

Kaolinite clay, natural mud, and natural mud devoid of OM were all used in the experiments. The first set of runs was conducted using kaolinite clay (ActiveMinerals, Maryland, USA). Kaolinite has less total negative charge compared to other common minerals found in freshwater sediment (e.g., montmorillonite and illite) due to smaller isomorphous substitution that takes place in its tetrahedral or octahedral sheets. Because of this, and also due to the presence of positive charges on its edges and negative charges on its surfaces, kaolinite can create flocs even in DI water (Partheniades, 2009). Natural sediments typically consist of various inorganic and organic components. The base sediment used in the second and third sets of experiments was fine bed sediment collected from Stroubles Creek, which is a stream in southwest Virginia, USA. The sediment was wet sieved to include only the material in the clay and silt size range (<62.5 µm). During the study, the natural mud was kept in a dark fridge at 4°C. The organic matter content of the mud was measured as 11.7% based on loss on ignition. The sediment used for the third set of experiments was the same as the one used for the second set except it was treated with sodium hypochlorite following Siregar et al. (2005) to remove OM content. Experiments with kaolinite clay, which is devoid of OM, enabled us to draw a comparison between the naturally OM-free flocs and the flocs formed from the treated fine sediment. Figure 3.2 shows the disaggregated size distribution of the kaolinite clay and bed sediment used in the experiments. All flocculation experiments were conducted at a sediment concentration of 100 mgL^{-1}. Pre-weighed dry kaolinite clay was used for the first set of experiments. For the second and third sets, we used wet sediments, the OBS, and a calibration between NTU and the mass concentration to set the experiments to the 100 mgL^{-1}. The calibration curve was produced by filtering, drying, and weighing disaggregated particles. For both the treated and untreated natural sediments, 55 NTU was found to produce a concentration of 100 mgL^{-1}.

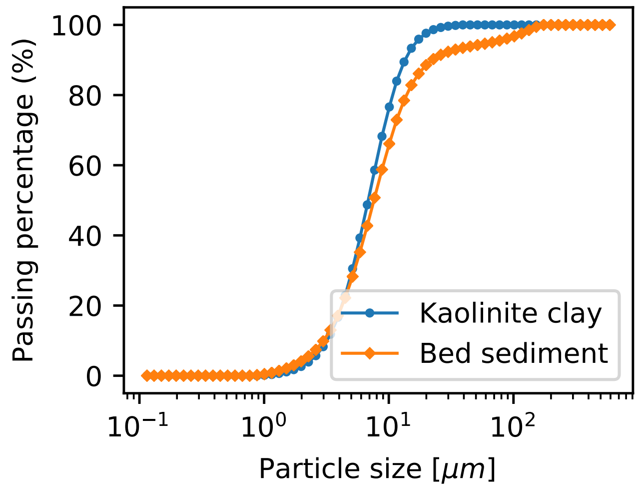

Figure 3.2: Disaggregated particle size distributions of kaolinite clay and bed sediment measured by the laser diffraction method.

3.3.5 Experimental procedure

In each experiment, the tank was first filled with 13 L of DI water, followed by the addition of salt (or no salt in the DI water experiments). In all three sets of experiments, the dry or wet sediment was added to 40 mL of DI water, and the mixture was sonicated for 15 minutes to break up any aggregates that may be present. Once the sonicated sediment was added to the tank, the experiments commenced with a 1-hr period of low turbulent shear (G = 35 s^{-1}) where flocs were allowed to grow from a sonicated state. We referred to this first hour as the initial growth (IG) phase. Flocs were then broken up during a high shear (HS) phase at G = 550 s^{-1} over a period of 15 minutes to allow the process of flocculation to start from a more natural state (from turbulence-generated and not sonicated particles). After the HS phase, the suspension was put under 5 periods of descending turbulent shear rates (i.e., G = 95, 70, 50, 35, and 20 s^{-1}, respectively) to mimic the range of shear a river could experience as it makes its way to the sea. For the kaolinite clay, each period lasted 90 minutes. For the natural sediment, these periods were 150-minutes long as we had previously observed that natural sediment required more time compared to kaolinite clay to reach equilibrium in size after each step-down phase.

3.4 Results

3.4.1 Overview

The floc size population was extracted from the images that were captured at a frequency of 1 Hz and grouped into 1-minute samples. The size distribution of each minute was then used to calculate the characteristic floc size statistics such as the d_{50} (median floc size by volume) as a function of time (Figure 3.3a). The d_{50} time series also provides the rate of change of the characteristic floc size as a function of G and S. Generally, flocs rapidly grew as soon as the sonicated sediment was added to the mixing chamber (Figure 3.3b). Flocs that form during this stage were then broken down during the high shear phase. From this point, they then increased in size again with each step-down in shear (Figure 3.3b). d_{50} was found to reach an equilibrium size faster at higher turbulence levels, and kaolinite reached equilibrium for a given shear rate faster than the natural mud. At the lowest shear rate ($G = 20$ s^{-1}) using natural mud, some of the flocs grew large enough to settle out of suspension. This led to a negative slope in the d_{50} time series in roughly the second half of the $G = 20$ s^{-1} stage (Figure 3.3). We present the results by sediment type in the following sections.

3.4.2 Kaolinite

In the DI water experiment ($S = 0$ ppt), the sonicated kaolinite clay readily flocculated once it was added to the mixing chamber (Figure 3.4), reaching a d_{50} of about 40 µm within the 1-hr initial growth phase. Flocs were found to be weak enough to notably break up during the high shear (HS) phase of the experiment but ultimately grew back up to about 45 µm in diameter at $G = 20$ s^{-1} by the end of the experiment (Figure 3.5).

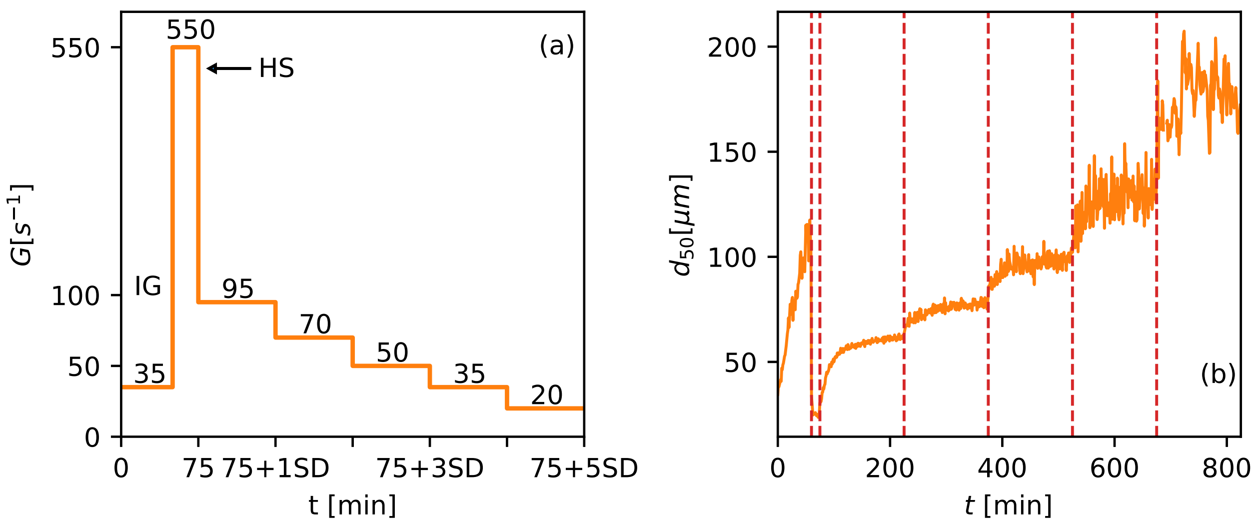

Figure 3.3: a) Time series of turbulent shear rate (G) for all the experiments. The step-down (SD) duration of each phase was 90 minutes in the kaolinite experiments and 150 minutes in the natural sediment experiments; b) floc d_{50} time series in the experiment with natural bed sediment at $S = 2$ ppt in response to variations in G.

The next two kaolinite experiments were conducted with added salt (Table 3.1). The presence of salt in the water caused a decrease in equilibrium floc size compared to the DI water experiment; in the experiment at $S = 2$ ppt, floc size increased to only 20 µm during the initial growth phase, and the d_{50} did not exceed 20 µm even at $G = 20$ s^{-1}. Although flocs were slightly larger in the experiment at $S = 10$ ppt compared to those at $S = 2$ ppt, they were still smaller compared to those in the DI water experiment at all turbulence levels (Figure 3.5).

The flocs' response to reduced turbulence during each step-down phase occurred quickly. New equilibrium sizes were reached at each new shear level within 20 minutes of the change in shear. To quantify their growth rate, we calculated $\Delta d_{50}/\Delta t$, which is the change of d_{50} over a specified duration of time, Δt (15 minutes for the kaolinite experiments), immediately after G was reduced at each step-down phase. The response was stronger in the DI water experiment, in which d_{50} increased at a rate of 0.2-0.4 µm min^{-1} at $G > 35$ s^{-1} and more than 0.5 µm min^{-1} at $G = 20$ s^{-1} (Figure 3.5). In comparison, in the salt experiments, d_{50}

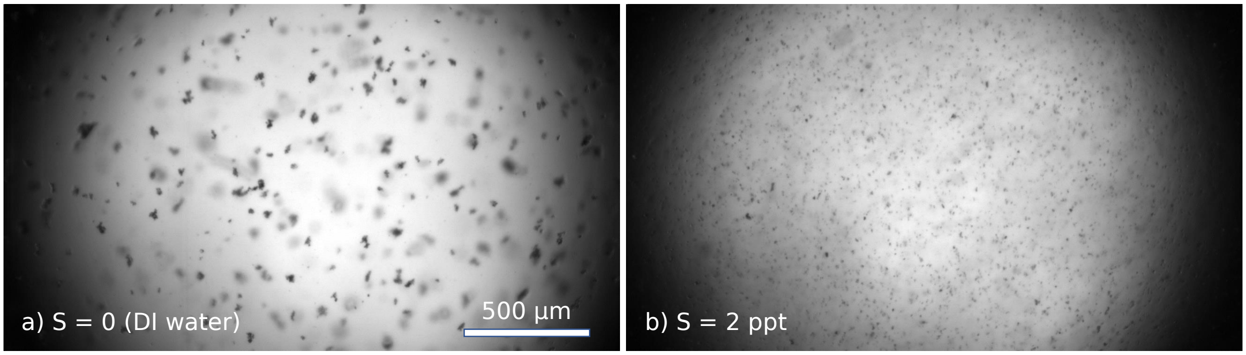

Figure 3.4: Snapshots of kaolinite flocs at equilibrium for a shear rate of $G = 35\ \mathrm{s}^{-1}$ in a) DI water and b) $S = 2$ ppt experiments.

increased by only a few µm at each step-down with $\Delta d_{50}/\Delta t$ never exceeding 0.2 µm min^{-1} at any turbulence level.

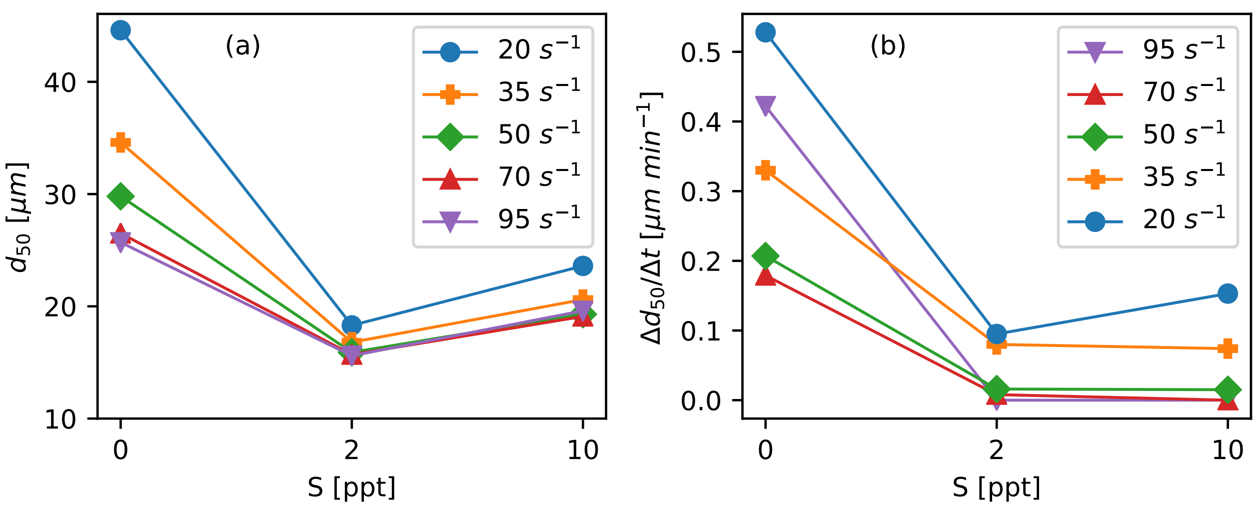

Figure 3.5: a) Kaolinite floc size at equilibrium (d_{50}) by salinity at different turbulent shear rates; b) rate of change of d_{50} in the first 15 minutes following each step-down phase by salinity at different turbulent shear rates.

3.4.3 Bed sediment with natural OM

Similar to the kaolinite experiments, we first examined the flocculation behavior of the natural bed sediment without the addition of salt using DI water ($S = 0$ ppt). In the absence of added salt, two distinct groups of suspended particles were observed across all shear rates. The larger of these two groups consisted of flocs in the >200 µm size range. The number of particles and total sediment volume in this larger group was, however, strongly outnumbered by particles in the second group, i.e., the smaller un- or less-flocculated particles (Figure 3.6a).

Six salt experiments were conducted at salinities ranging from S = 0.5 ppt to 10 ppt (Table 3.1). A key takeaway from these experiments is that it only took a very small increase in salinity to strongly enhanced the flocculation of natural mud such that at S = 0.5 ppt, the number of flocs were noticeably greater at all of the turbulence levels compared to the DI water experiments (Figure 3.6b).

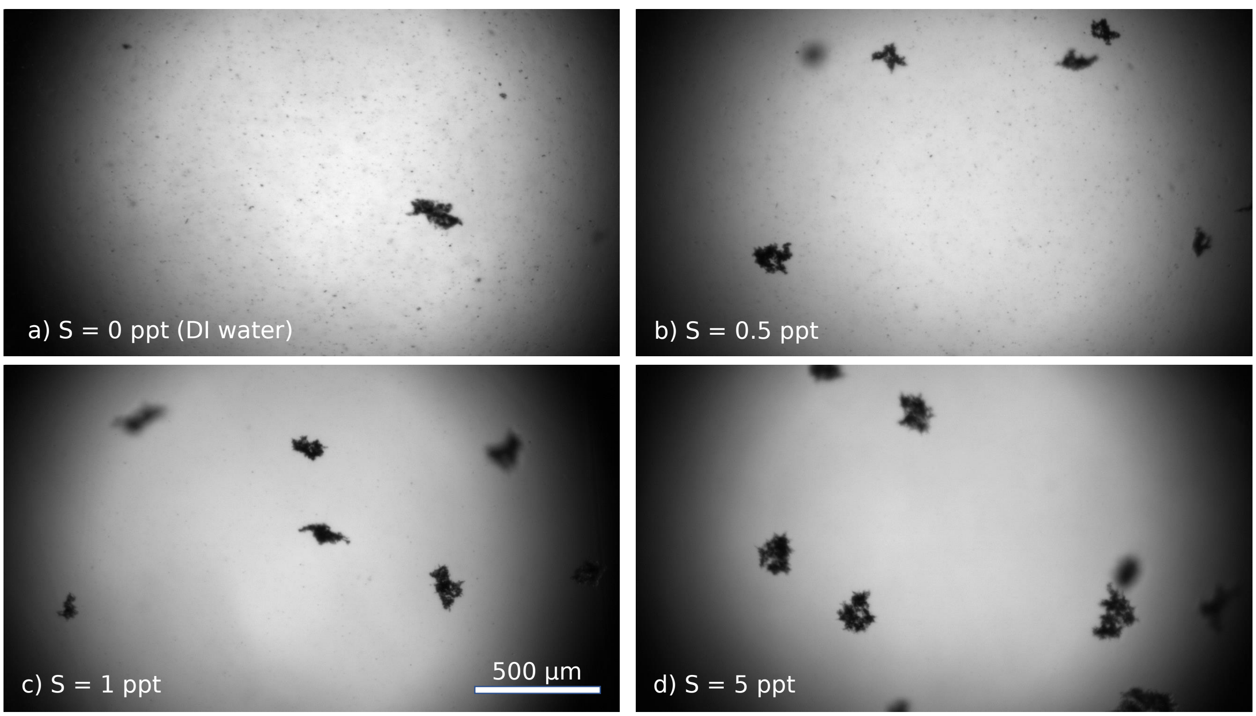

Figure 3.6: Snapshots of bed sediment flocs at equilibrium for a shear rate of $G = 35$ s^{-1} at different salinities.

The increase in d_{50} in response to increased salinity can be traced back to the aggregation of unaggregated particles and smaller flocs mostly in the 25-75 µm size range. That is, as salinity increased, the unaggregated particles became more and more integrated into the floc structure. The loss of fine material is evident in the images as the background of small dispersed particles in DI water reduces with salinity (Figure 3.6). The change in floc population in response to increased salinity is also evident in the particle size distribution (PSD) (Figure C.2). While some relatively large flocs with the size of >200 µm did form in DI water, the fraction of discrete unaggregated particles was notably larger than those in the experiment at $S = 0.5$ ppt. The PSD moved towards larger particle sizes as salinity increased, leading to a larger d_{50}.

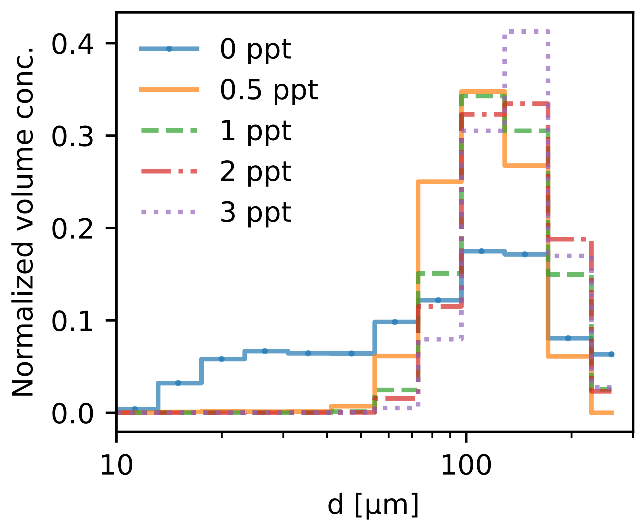

Figure 3.7: Normalized volume concentration distributions at equilibrium for a shear rate of $G = 35\ \mathrm{s}^{-1}$.

The equilibrium floc size (d_{50}) increased notably from the DI water experiment to $S =$ 0.5 ppt, and then to 1 ppt, 2 ppt, and 3 ppt. These enhancing effects of increased salinity, however, were found to be most evident at $S \leq 3$ ppt, and a further increase in salinity from 3 ppt to 5 ppt and then to 10 ppt did not result in notable increases in d_{50} (Figure 3.8). The stronger effects of increased salinity at lower salinity levels were observed at all shear levels.

Salinity affected not only the equilibrium floc sizes but also the growth rate of flocs in response to each reduction in turbulent shear rate (Figure 3.8b). While in DI water the equilibrium floc size increased at a very slow pace (or decreased as some larger flocs with

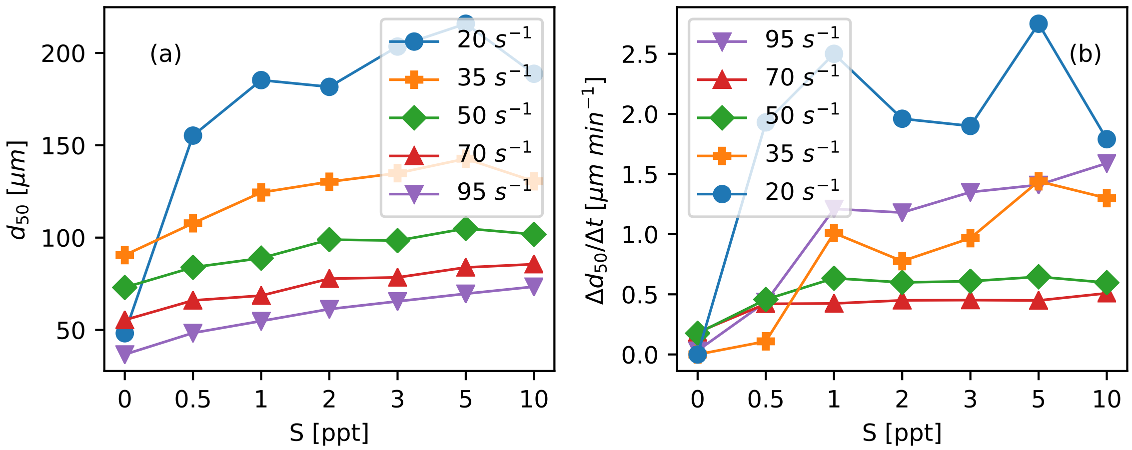

Figure 3.8: a) Mud floc size at equilibrium (d_{50}) by salinity at different turbulent shear rates; b) rate of change of d_{50} in the first 20 minutes following each step-down phase by salinity at different turbulent shear rates.

diameters of roughly >250 µm settled out of the suspension), the presence of salt at the level of only 0.5 ppt in water increased the flocculation rate by as much as 2 µm min^{-1} at $G = 20$ s^{-1}. Similar to the equilibrium floc size, the enhancing effects of salinity on flocculation rate had a threshold, and the strongest effects were found at S≤5 ppt.

3.4.4 Treated bed sediment with OM removed

Mud floc size and structure were clearly different when the treated sediment was used in the flocculation experiments. Interestingly, in the experiment with no added salt (DI water), the treated bed sediment devoid of OM did not form any visible flocs, and the suspended particles retained their sonicated dispersed form (Figure 3.9a).

It was only in the presence of salt that treated sediment started to aggregate and form flocs. In the experiment at $S = 2$ ppt, small flocs with the size of <20 µm formed immediately after the sonicated sediment was added to the mixing tank. However, d_{50} of the flocs never exceeded 30 µm during any of the shear step-downs (Figure 3.10). Similar behavior was observed in the experiment with $S = 10$ ppt. Although the size and growth rate of flocs were slightly greater compared to those in the experiment with $S = 2$ ppt, their d_{50} hardly reached 35 µm even at $G = 20$ s^{-1}.

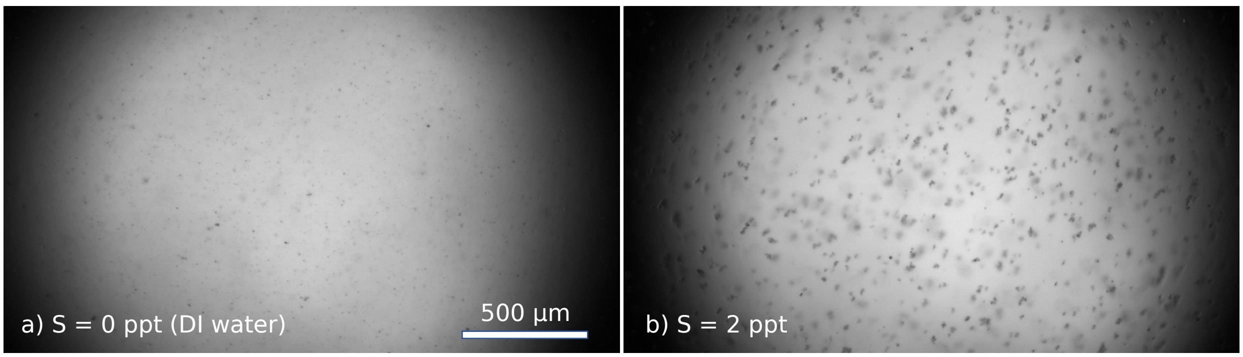

Figure 3.9: Snapshots of treated sediment flocs at equilibrium for a shear rate of $G = 35$ s^{-1} in a) DI water and b) $S = 2$ ppt experiments.

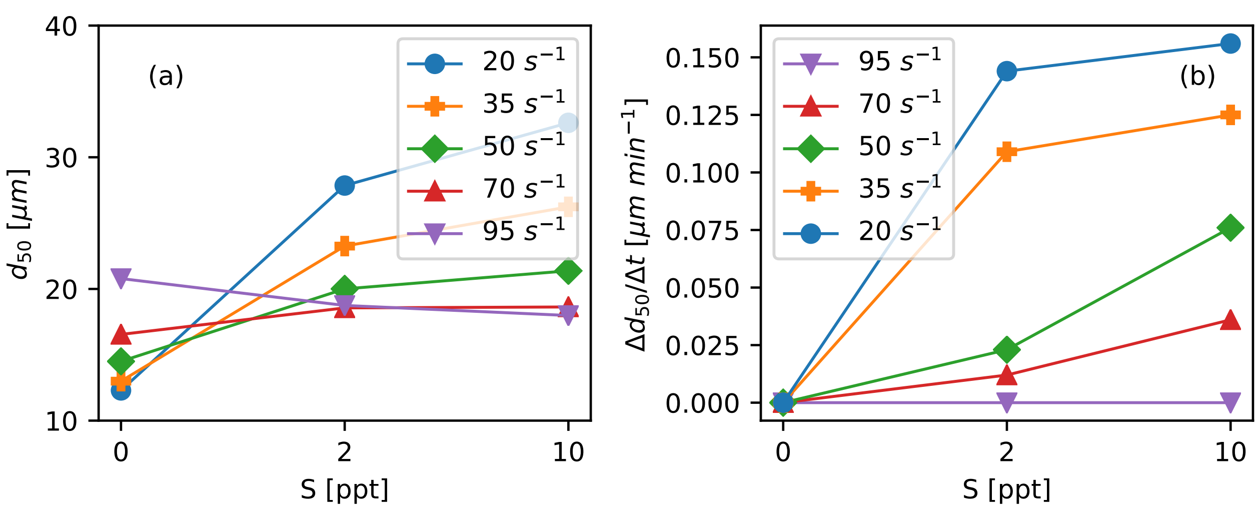

Figure 3.10: a) Treated mud floc size at equilibrium (d_{50}) by salinity at different turbulent shear rates; b) rate of change of d_{50} in the first 15 minutes following each step-down phase by salinity at different turbulent shear rates.

3.5 Discussion

3.5.1 Organic matter and flocculation of natural mud

Gums such as xanthan gum, guar gum, and chitosan are often used in laboratory experiments looking to study the role of organic material on flocculation (e.g., Zhang et al., 2013; Furukawa et al., 2014; Zeichner et al., 2021). In this study, we used an alternative approach by removing OM from natural sediment rather than adding gum to the suspension.

Our experiments revealed a stark difference between flocs formed from natural unaltered bed sediment (which contains OM) and flocs that form from suspensions of the same sediment after it has been treated to remove the organics (OM-free). Figure 3.12 visually highlights this distinction. In the images, salinity, shear rate, and base inorganic sediment components are identical in panels (a) and (b). The only item that is different is the OM content. Untreated bed sediment formed larger flocs, where most mud particles were incorporated into the floc structure. The incorporation of discrete particles caused the background to be clearer, resulting in more defined and darker flocs in the images due to their higher contrast with the clearer background. In comparison, flocs were smaller in the treated sediment experiment. The difference we observed in floc size is greater than that reported by Mietta et al. (2009a), where the increase in floc size from OM-devoid mud to OM-containing mud was limited to < 30 µm at $G = 35$ s^{-1}. The flocs formed from the OM-free mud were also more transparent and fragile than the OM-containing flocs. These differences between the sediment that contained OM and that devoid of OM were present at all salinity and turbulence levels that were tested.

TThe strong flocculation-enhancing role of the OM that is naturally present in freshwater sediment has been attributed to the structure and weight of OM molecules and, therefore, behavior when interacting with sediment particles. Organic biopolymers, such as the extracellular polymeric substances (EPS), contain numerous charged or uncharged groups in their structure, all contributing to the forces between the organic and inorganic components of the mud (Lai et al., 2018). The uncharged groups of biopolymers can interact with the negatively-charged surface of clay minerals through the van der Waals forces. Hydrogen bonds can occur between the basal hydroxyl surface of silicates such as kaolinite and polar groups of biopolymers (Theng, 2012). Cationic groups of the polymers can further interact with clay mineral surfaces through electrostatic forces, while the anionic groups can attach to negatively charged surfaces of clay minerals through polyvalent cations acting as a bridge between the two (Philippe and Schaumann, 2014). All of these interactions can lead to a complex looped structure of OM-sediment bonds in the floc structure (Figure 3.11). The role of OM in flocculation is not limited to forming the general size and shape of flocs as a whole. The presence of OM can also alter the nature of the primary particles, i.e., those particles that are the base-level building blocks of flocs. At this level, sediment particles and OM can firmly bind, thereby increasing the size of these building blocks (Fall et al., 2021). When OM is absent from the sediment, flocs form by absorption of differently charged sections of mineral structure (such as positively charged edges and negatively charged faces of kaolinite) (Partheniades, 2009) or due to polyvalent cation bridging between two negatively-charged clay particles (Mietta et al., 2009a) or shrinking of the EDL and the resulting net attractive van der Waals forces (Spielman, 1978). In all of these cases, the structure of the flocs is different from the flocs that contain OM (Figure 3.12).

3.5.2 Salinity and flocculation

Salinity has historically been considered a driving factor in the flocculation of mud deposition in estuarine zones (e.g., Odd, 1988). Our results support the idea that the presence of salt increases both the rate of aggregation and the equilibrium size of mud flocs formed from fluvial bed sediment. While this general trend or principle is in line with historic un-

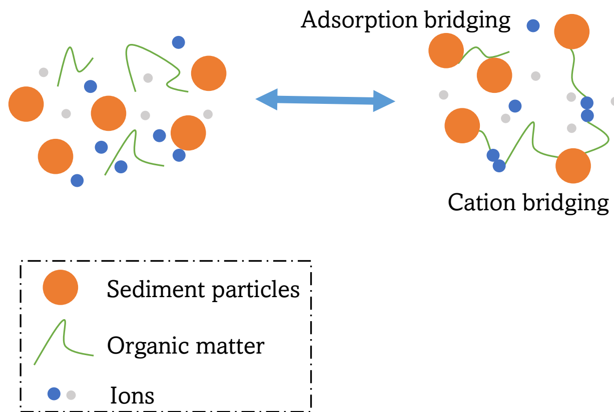

Figure 3.11: Mechanisms of sediment-OM interactions.

derstanding, the experiments presented here offer three more refined points of consideration to this general trend and observation regarding salt and its role in the flocculation of natural mud.

First, it appears to us that the primary role of salt is to make it easier for unaggregated small particles to flocculate with existing flocs or each other. Our experiments did not show flocs with salt and no flocs without salt. For the untreated natural bed sediment, we still observed the formation of flocs even without the addition of any salt, i.e., flocs were present in the pure DI water experiment (Figure 3.6a). However, a notable fraction of the suspended matter did remain in a discrete, unaggregated state, and the presence of flocs and unaggregated material resulted in a bimodal PSD (Figure C.2). We expect that the existence of flocs with a diameter of >200 µm was most likely driven by OM, particularly macromolecules that contain multiple charges that act as a binder for sediment particles because identical experiments with the treated bed sediment (OM removed) in DI water did not produce any flocs (Figure 3.9). Considering the role of salt on the PSD then, the primary role of the salt in the natural sediment case was to change the PSD from a bimodal (unflocculated and flocculated) distribution to one that is more uni-modal (flocculated); or to change the fraction of material in suspension that resides in larger flocs.

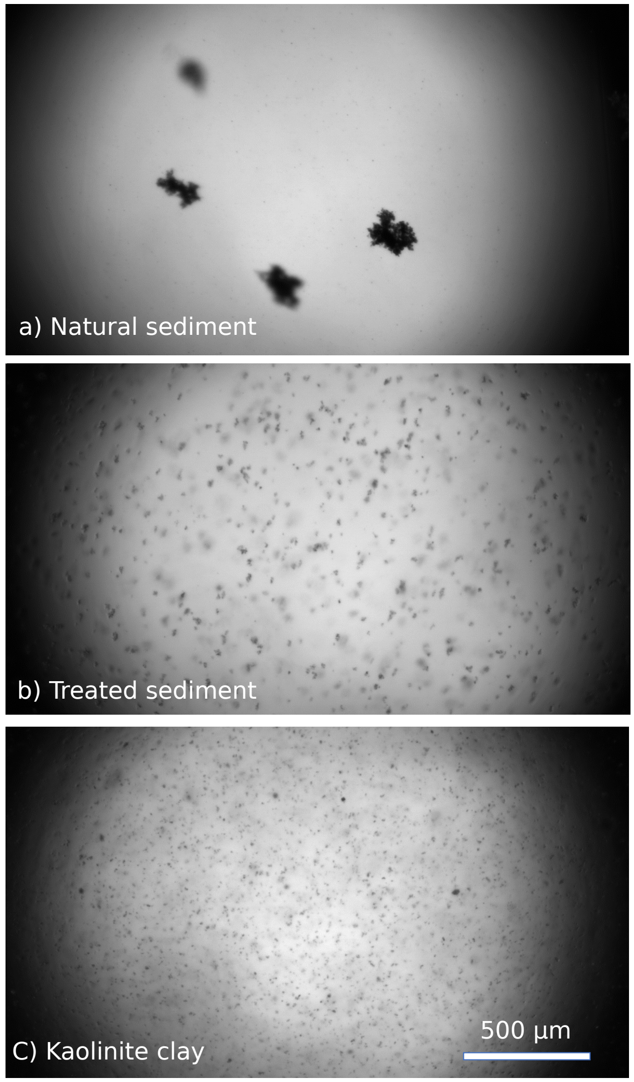

Figure 3.12: Snapshots of flocs formed from a) natural bed sediment, b) treated bed sediment, and c) kaolinite clay all at equilibrium and $S = 2$ ppt, $G = 35$ s^{-1}, and $C = 100$ mgL^{-1}.

Second, the PSD for the natural bed sediment with OM had a stronger response to increases in salt than the PSD for the bed sediment without OM. That is, the presence of OM did not override or remove a flocculation response to changes in salinity. Instead, it enhanced them. Without OM present, floc sizes increased in response to an increase in salinity. But the change in size, as represented by d_{50}, was limited to a change of approximately 10 to 15 µm from $S = 0$ ppt to 20 $S = 10$ µm (Figure 3.10); translated to settling velocity of approximately 0.03 mms^{-1} difference. In contrast, flocs formed with the untreated bed sediment experienced a change in d_{50} of 50 to 150+ µm with the addition of salt depending on shear rate (Figure 3.8); a change of almost 0.5 mms^{-1} in terms of settling velocity for $G = 35$ s^{-1}. We suspect that increasing salinity had less of an effect on the treated sediment because when OM is removed, the electrically charged points of contact that can cause aggregation of particles are limited to the charged sediment surfaces, with the complex structures of biopolymers being no longer present (Theng, 2012).

Third, very small changes in initial salinity, going from 0 to 0.5 ppt, exerted a marked influence on both the equilibrium PSD and rate of growth of the suspended natural bed sediment (Figures C.2 and 3.8). And, relative increases past $S = 3$ ppt had little influence on either the equilibrium PSD or growth rate. The lack of response in the growth rate or equilibrium PSD after $S = 3$ ppt suggests that at this salinity, there are already enough ions to effectively shrink the EDL and promote flocculation. A limit to the flocculation-enhancing effects of increased ion concentration of water have also been reported previously in the literature, for instance $S = 10$ ppt (Mikeš and Manning, 2010), 15 ppt (Mikeš and Manning, 2010), or 7 ppt (Guo et al., 2021). This threshold concept has also been implemented in computational models. For instance, Delft3D assumes settling velocity, w_s, approaches $w_{s,max}$ as salinity approaches S_{max} (Deltras, 2021), while Horemans et al. (2020) assumes that aggregation parameter of flocs, k'_A reaches a maximum as S approaches a prescribed maximum.

While the above points are about the natural mud that contained OM, we have to make two comments about the sediment samples that did not contain OM and behaved in some aspect differently than natural mud. With kaolinite, the smaller floc sizes in the salt experiments compared to the DI experiment are likely due to the differences in floc structures in these two cases. In DI water, kaolinite particles form random particle-to-particle bonds via the van der Waals forces. In the absence of ions, on the other hand, the positively-charged edges and the negatively-charged faces bond through electrostatic forces (Partheniades, 2009). With treated mud, the reversal of effect of G on d_{50} between $S = 0$ and 2 ppt is likely due to the absence of flocculation at $S = 0$ ppt (Figure 3.10). At $S = 0$ ppt, instead of breaking up the flocs, greater G kept the silt particles larger than 20 microns in suspension. On the other hand, at $S = 2$ ppt, at which flocculation did occur, higher shear led to break-up of flocs and, consequently, smaller particle size. This was most likely also the case with the untreated mud but was obscured by flocs larger than 100 µm.

One of the broader questions we wanted to consider with our study was whether or not salt has any effect on a mud suspension if organic binders are already present and causing flocculation in freshwater rivers. While the experiments do not definitively answer this question, we do believe that the experiments offer a few points of consideration that we then use to speculate on flocculation dynamics in natural rivers.

The experiments show that the presence of organics increases the response of the mud suspension PSD to the presence of salt. They also show that flocs can form without the presence of added salt and that the flocculation-promoting elements of added salt are strongest at very low salinities. Clearly, rivers carry different types and amounts of organic matter. And it has been amply shown that mud in fluvial settings is flocculated (e.g., Droppo et al., 1997; Droppo, 2001; Osborn et al., 2021). Our experiments in DI water showed that it is possible for flocs to form in pure DI water in the presence of natural organic matter. However, the fraction of the mud that was contained in flocs was low until some salt ions were added. For at least the case of Osborn et al. (2021) (and other unpublished data we have in different rivers in the USA), the flocculation state of the mud upstream of any measurable saltwater intrusion has tended to be larger than what we observed in the DI water case in the experiment presented in this study. In fact, compared to DI water, fresh stream water was shown to result in a greater degree of flocculation of bed sediment (Abolfazli and Strom, 2022). Together these observations suggest to us that the ions present in natural stream water, upstream of any saltwater intrusion, can sufficiently aid in promoting flocculation when organic matter is present. We, therefore, expect that flocs in rivers are governed not just by the organic matter, but also by other ions, salt or otherwise, that may be present. As a result, one can imagine a case where the organic matter and background ions, i.e., non-saltwater-intrusion-related ions, are sufficient to promote the flocculation of a large fraction of the mud load. However, our findings suggest the effects of salinity on modulating the fraction of mud flocculated or the overall floc PSD to be limited to the head of a well-mixed estuary or to the fresh-saltwater interface in a vertically stratified salt wedge system.

As a final note, given the complex interaction between clay minerals, OM, and ions, we speculate that the order in which OM and ions are added to the clay affects the flocculation process. In the present study, we added salt to mud that already contained OM to mimic the increase in ion concentration as freshwater mud experiences higher levels of salinity as it approaches estuaries and oceans or experiences a spike in ion concentration due to deicing salt runoff (Abolfazli and Strom, 2022).

3.5.3 How applicable are these findings to coastal mud?

Our experiments were conducted using natural mud gathered from a local stream in the Valley and Ridge province of Virginia, i.e., Stroubles Creek. Stroubles Creek is a tributary to the New River, which in turn is a tributary to the Mississippi River. Sediment found in the creek can ultimately make its way to the Gulf Coast region, and spikes in salinity do occur in the creek following runoff of roadway deicing salts during winter (Lakoba et al., 2021; Abolfazli and Strom, 2022). Therefore exploring the role of organic matter and salinity on the flocculation of Stroubles Creek mud specifically has utility for understanding its transport dynamics. Nevertheless, it is reasonable to question how broadly applicable the experimental results are to other muds — and in particular, muds that are more proximally located to coastal zones where changes in salinity are more eminent.

As one step towards more broadly testing the response of different muds to changes in salinity both with and without natural organic material, we conducted experiments similar to those outlined in the methods and results for the Stroubles Creek mud using mud obtained from the bed of the main channel of the Mississippi River near Venice, LA. The mud was collected as part of a larger project in January 2021 using a Shipek grab sampler. Tests were run on the treated (OM removed) and natural (no removal of OM) muds in DI water and DI water with enough salt added to bring the salinity to 2 ppt. Images of the suspension are shown in Figure 3.13. Images and floc size measurements indicate that the general behavior concerning salts and organic matter for the Mississippi River mud was the same as that of the Stroubles Creek mud. The unaltered mud in DI water produced a bimodal distribution with a few larger flocs and many smaller aggregates and unflocculated particles (Figure 3.13a). Adding salt resulted in a much higher degree of flocculation, a more unimodal distribution, and an overall larger median size (Figure 3.13b). Without OM (i.e., for the treated case) no large flocs formed in DI water at $S = 0$ ppt (Figure 3.13c). The addition of salt led to a more flocculated state, but floc sizes were smaller than those produced at the same shear and salinity level but with the presence of OM (Figure 3.13d). The primary difference that we observed between the Mississippi River mud flocs and the Stroubles Creek mud flocs was that the Stroubles Creek mud flocs were, on average, larger and optically denser than the Mississippi River mud flocs for the OM tests at 2 ppt. We expect that this is due to higher levels of organic matter present in the fresh Stroubles Creek mud relative to the older Mississippi River sample.

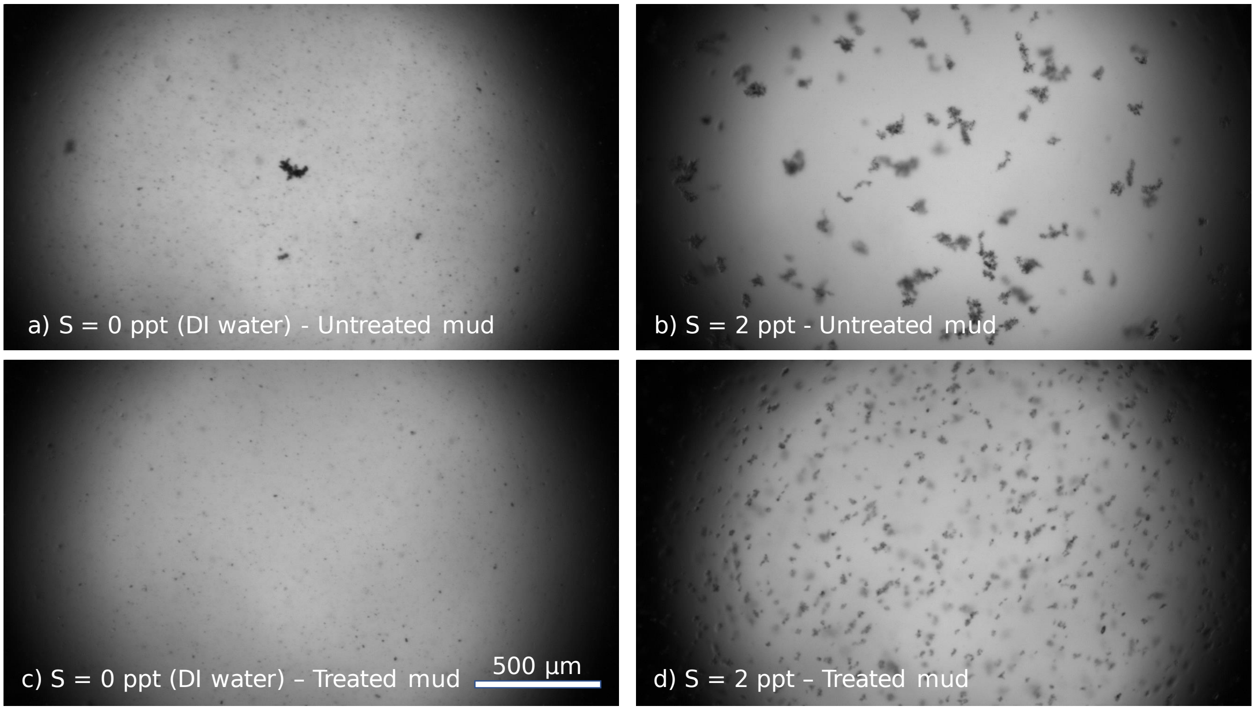

Figure 3.13: Snapshots of flocs formed from Mississippi River mud at equilibrium for a shear rate of $G = 35$ s^{-1} and concentration of $C = 100$ mgL^{-1}.

3.5.4 Modeling the influence of salinity on floc size

Efforts to include salinity as a driver of mud flocculation using simple models have been made before. However, these models have been developed with sparse data in the less than 5 ppt salinity range (e.g., Horemans et al., 2020; Deltras, 2021). Here we examine the model of Horemans et al. (2020) using data from the natural mud runs in our experiment, and we also propose our own model for a salinity-dependent aggregation efficiency parameter within the Winterwerp (1998) modeling framework.

At equilibrium, the Lagrangian form of the Winterwerp (1998) floc size equation yields the following expression:

$$d_{50} = d_p + \frac{k_A C}{k_B \sqrt{G}} \tag{3.2}$$

where d_p is the disaggregated primary or constituent particle size, C is the mass concentration of sediment, and k_A and k_B are the aggregation and breakup coefficients defined as:

$$k_A = \frac{k'_A}{n_f} \frac{d_p^{n_f - 3}}{\rho_s} \tag{3.3}$$

and,

$$k_B = \frac{k'_B}{n_f} d_p^{-p} \left(\frac{\mu}{F_y} \right)^q \tag{3.4}$$

In Eq. 3.3 and 3.4, n_f is the fractal dimension of the flocs, ρ_s density of the dry unflocculated sediment, μ is the dynamic viscosity of the water, F_y is the yield strength of the flocs, k'_A and k'_B are dimensionless aggregation and breakup efficiency coefficients, and p and q are model parameters. Through a scaling argument, p is typically taken to be $p = 3 - n_f$ (Winterwerp, 1998; Kuprenas et al., 2018). Following further scaling arguments, based on settling tests in stagnant water columns, Winterwerp (1998) took $q = 0.5$. Here we use the reasoning of Kuprenas et al. (2018) and set q to be a simple function of the size of the flocs relative to the Kolmogorov microscale, $\eta = \sqrt{G/\nu}$:

$$q = c_1 + c_2 \frac{d_{50}}{\eta} \tag{3.5}$$

where c_1 and c_2 are constant coefficients. The proposed formulation ensures k_B increases as d_{50} approaches η. In calculations, we used meters, kilograms, and seconds.

Similar to Horemans et al. (2020), we expect that one way to capture the influence of salt on the growth rate and equilibrium size of mud flocs is to seek out a relationship for the aggregation efficiency parameter, k'_A, expressed as a function of S in ppt. To do this, we back-calculated values of k'_A in Eq. 3.3 using Eq. 3.2, 3.4, and 3.5 and measured or known floc sizes, d_{50}, primary particles, $d_p = 8$ µm, shear rates, G, and sediment concentration,

$C = 0.1$ gL^{-1}. For the calculations, we also used the following set of model parameters: $n_f = 2$, $\rho_s = 2500$ kgm^{-3} (slightly smaller than the typical 2650 kgm^{-3} for clay to account for the organic matter present in the mud), $\mu = 1\times10^{-3}$ NSm^{-2}, $F_y = 10^{-10}$ N, $c_1 = c_2 = 0.5$, and $k'_B = 1.16 \times 10^{-6}$ (Kuprenas et al., 2018).

Our back-calculated k'_A increased with S (the values obtained are represented by box plots in Figure 3.14). Following Horemans et al. (2020), we averaged all calculated k'_A for each salinity and then fit a hyperbolic tangent function through the average. The result of this process yielded:

$$\frac{k'_A}{k'_{A0}} = 0.4 + 1.2[1 + \tanh(S - 0.55)] \tag{3.6}$$

where $k'_{A0} = 0.05$ denotes k'_A at $S = 0$ ppt Eq. 3.6 has a total residual sum of squares (RSS) of 0.064 and a $R^2 = 0.73$ when using the average k'_A for each S.

Overall, our data suggest a similar functional shape in the relationship between k'_A and S as that Horemans et al. (2020) and the Delft3D models. However, our data show a slight increase in the response of k'_A to increasing S and one that occurs at a lower salinity. For example, the change in k'_A with S in our case all occurs before a change in k'_A is predicted by the Horemans et al. (2020) model (Figure 3.14).

While our aim was to provide a functionality between k'_A and S, the data did show that k'_A was also affected by G. In the analysis, we present here we have grouped all of the variations with G at a single salinity value (reflective in the box-plots in Figure 3.14) into an average. However, we did observe a systematic increase in k'_A increased with a decrease in G. It should also be noted that it is possible that the equilibrium floc sizes are underestimated at the lowest shear rate in our experiments (i.e., $G = 20$ s^{-1}) due to the settling of a small fraction of the flocs.

With the natural mud used in our experiment, most of the change in floc size and growth

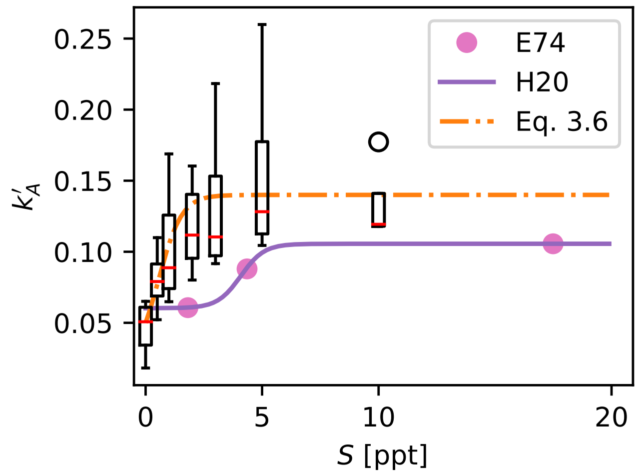

Figure 3.14: A comparison between our model for k'_A (Eq. 3.6 with $k'_{A0} = 0.05$) and that of Horemans et al. (2020) (H20). Boxplots show the spread of our back-calculated k'_A over G values at each salinity. E74 depicts the data from Edzwald et al. (1974).

rate occurred at salinities below 5 ppt with the positive effects of salinity on enhancing k'_A being evident even at salinities as low as 0.5 ppt. While the model predicts a reversible response with S, one would expect the physical process to not be perfectly reversible. Additional data are needed with other natural sediment mixtures to better understand the level of generality that our data and Eq. 3.6 reflect.

3.6 Conclusion

Our experiments reveal a strong interaction between organic matter and salinity in driving the flocculation dynamic of natural mud. Moving from DI water to salinities of 10 ppt increased the equilibrium floc size and growth rate of flocs formed in natural sediment both with and without natural organic matter. Without organic matter, flocs were limited in size to 20 to 30 µm even at 10 ppt. With natural OM present, a limited number of large flocs formed even in pure DI water. However, the fraction of material flocculated remained low, resulting in a bimodal suspended particle size distribution. Adding just a small amount of salt to bring salinity to 0.5 ppt notably increased the fraction of flocculated material and changed the particle size distribution from bimodal to unimodal. Increases in salt up to 3 to 5 ppt decreased the number of unflocculated particles further and increased floc sizes such that the average reached between 100 and 200 µm depending on the shear level. Increases in salinity past this level led to only marginal increases in floc size for a given shear rate. The data suggest that both organic material and ions associated with river or estuarine water are likely present if high degrees of flocculation, with flocs on the order of 100 µm and larger, are observed. The data also suggest that very low levels of salinity (e.g., 0.5 ppt) are needed to enhance floc size. It is therefore likely that large salinity-driven changes to the floc size distribution in nature are limited to the head of a well-mixed estuary or to the fresh-saltwater interface in a vertically stratified salt wedge system in rivers with low background freshwater ion concentration. Change in floc growth and equilibrium size brought on by salinity changes in the presence of natural mud and OM can be captured with a salinity-dependent aggregation efficiency parameter in a Winterwerp (1998) type formulation.

3.7 Acknowledgments

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Chapter 4

Flocculation state of mud in the lowermost Mississippi River: a laboratory study

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Chapter 4 is draft of a manuscript in preparation to be submitted to Frontiers in Earth Science.

4.1 Abstract

Muddy sediment constitutes a major fraction of the suspended sediment mass carried by the Mississippi River through its lower reaches. Thus, adequate knowledge of sediment transport dynamics of the suspended mud in the lower Mississippi River is critical in devising efficient coastal management plans on the coastal Louisiana. We conducted laboratory experiments on the sediment suspended in the water column in the lower reaches of the Mississippi River to provide further insight into the behavior of mud flocs. In particular, we examined how the floc size distribution responded to changing environmental factors such as turbulent energy, sediment concentration, and changes in salinity during the summer and winter; and we compare data from laboratory tank experiments to *in situ* observations. Turbulence shear rate, a measure of the river hydrodynamic energy, was found to be the most influential factor in determining mud floc size. Flocculation was not found to be strongly dependent on sediment concentration, and flocs larger than 100 µm formed in sediment concentrations as low as 20 mgL^{-1}. An artificial increase in salinity generated by adding salts to river water suspensions did not lead to a considerable increase in floc size. However, the addition of water collected from the Gulf of Mexico to freshwater river suspensions did notably enhance the fraction of material bound up within large flocs, producing larger overall median sizes. We speculate that the effects of Gulf of Mexico water originate from its biomatter composition. No meaningful difference between summertime and wintertime floc size was observed. Compared to *in situ* floc size measurements, values measured in the laboratory were larger in winter and smaller in summer.

4.2 Introduction

Sediment carried by rivers to deltas and estuaries plays a major role in shaping the ecosystem and geomorphology of coastal regions. Fine muddy sediments, those with a diameter smaller than 63 µm, can constitute a significant fraction of the total mass delivered by large, lowland rivers to the coastal regions. These fine sediments have a unique characteristic that separates them from sand or gravel in that they can undergo continuous aggregation and breakup cycles whereby the suspended particles aggregate or disaggregate to grow or shrink in size. This process is known as flocculation. Flocculation alters the shape and size and, therefore, the settling velocity of mud particles (e.g., Eisma, 1986; Droppo and Ongley, 1994). Settling velocity is the primary sediment-dependent parameter that determines the vertical concentration profile of mud, the fate of sediment before it deposits on the bed, and its resuspension behavior once it deposits (e.g., Ross and Mehta, 1989; Lamb et al., 2020).

Research into the flocculation behavior of mud has historically focused on saltwater and brackish water settings. The rationale for this focus on saltwater has been the observation of thick layers of deposited mud in estuarine regions, where muddy freshwater mixes with salty seawater (e.g., Gibbs, 1985; Eisma, 1986). This is backed by the knowledge we have that: 1) fine sediment particles are inherently charged and surrounded by layers of water molecules that inhibit the aggregation of these particles, and 2) ions (anions and more so cations) shrink these layers, making the sediment particles easier to aggregate (Gregory and O'Melia, 1989). However, a line of research has shown that freshwater flocs do indeed exist, and are responsible for a significant fraction of mud transport in fluvial systems. This has been accomplished either by imaging the suspended sediment or analyzing the sediment concentration profiles in various fluvial systems (e.g., Droppo et al., 1997; Droppo, 2001; Lamb et al., 2020; Osborn et al., 2021; Nghiem et al., 2022; Osborn et al., 2023).

The Mississippi River is the largest river in the United States both by length and discharge. It carries an estimated annual load of 200-500 million tons of sediment down to the coastal region of Louisiana (Blum and Roberts, 2009) and therefore plays a significant role in both shaping the coastal landscape of the region and influencing the marine ecosystems in the northern Gulf of Mexico (GoM). These areas are drawing increasing attention because of their high sea level rise (compared to the global average), subsidence, and the increasing frequency of tropical storms and river floods all of which threaten the livelihood of coastal communities and the economy of the region (Britsch and Dunbar, 1993; Chan and Zoback, 2007; Ingebritsen and Galloway, 2014). These compounding threats have led to the development and implementation of coastal management plans aimed at mitigating these adverse effects. For instance, in the state of Louisiana, the "Coastal Master Plan" aims to reduce flood risks and support the infrastructure that is necessary for a healthy and functioning coast (Sprague and Nelson, 2023). An integral part of these plans is the installation of sediment diversions that would re-connect the Mississippi River and its suspended sediment with the surrounding bays, marshes, and floodplains in a controlled way to facilitate subaerial land growth and marsh nourishment. The sediment diversion plans cannot succeed without a sufficient understanding of the nature of the sediment carried by the Mississippi River. Over 90% of the Mississippi River sediment reaching the GoM is estimated to be mud (Allison et al., 2012). Therefore, knowledge about the flocculation behavior of the suspended mud in the lower Mississippi River plays an important role in devising effective coastal management and restoration plans that rely heavily on assessing the fate of the sediment transported to the US GoM coasts.

This laboratory study was conducted during two field campaigns in the summer of 2020 and winter of 2021 when river discharge and suspended sediment concentration were approximately equal between seasons. During the field surveys, we used an *in-situ* floc camera system (i.e., the FlocARAZI (Osborn et al., 2021)) to examine the flocculation state of the sediment suspended in the lower freshwater reaches of the Mississippi River, as well as the spatial and seasonal variations in the flocculation state (Osborn et al., 2023). While the *in-situ* observations are valuable in accessing the state of mud flocculation, they can only provide snapshots of the flocs at a particular place and time. As such, the data are limited in their ability to explore the evolution of the size distribution as environmental drivers vary temporally and/or spatially. Thus, to provide additional comprehensive insight into the dynamics of mud flocs in the lower Mississippi River, we conducted laboratory experiments to investigate the response of mud floc size distributions to variations in environmental conditions such as turbulent energy levels and salinity.

In particular, we pursue three objectives in this study. The first is to determine the drivers that are most influential in setting the size distribution of suspended mud in the fluvial to marine transition (FtMT) zone where turbulence, salinity, and sediment concentration all co-vary. These drivers have been historically known to affect flocculation but the knowledge of the extent to which each on their own and together affects flocculation in natural settings, and in particular within the FtMT zone of the Mississippi River, is still lacking. Because of this, a clear method to account for changes in mud flocs and their influence on sediment transport dynamics in various conditions or through a dynamic region such as the FtMT is not available. For example, in a classic model by Winterwerp (1998), equilibrium median floc size by volume, d_{50eq}, increases linearly with sediment concentration (C) and decreases linearly with $\sqrt{G}$, where G is turbulence shear rate. However, new experiments have called into question the linear dependence of floc size with C in turbulent suspensions (Tran et al., 2018). Furthermore, the model does not dynamically account for changes in salinity or organic matter. Additionally, in the floc population model by Verney et al. (2011), which was later implemented in Coupled-Ocean-Atmosphere-Wave (COAWST) by Sherwood et al. (2018), the effect of turbulent shear is again included but any salinity (S) or organic matter effect can only be accounted for using a tunable aggregation parameter. Alternatively, Delft3D includes the effects of salinity by setting the overall mud settling velocity to be a function of salinity while the effect of turbulence in floc aggregation and breakup is not accounted for (Deltras, 2021). In this study, to determine the dependence of equilibrium d_{50} of the mud flocs suspended in the lower Mississippi River on these environmental drivers, experiments were designed so that they include a wide range of suspended sediment concentrations, turbulence shear rates, and salinity levels while using the Mississippi River water and natural suspended sediment suspended.

The flocculation process involves the aggregation and breakup of assemblages of inorganic and organic particles (e.g., Mehta, 1986). The balance between these two processes can lead to an equilibrium in the floc population. However, the timescale over which floc populations evolve is not yet well understood. The second question that we aim to answer is, therefore, whether flocs are in equilibrium with their immediate environment. If so, what are the time scales over which flocs respond to the variations in their environment.

Laboratory experiments can provide data on mud flocs that are more controlled compared to field observations and can capture the time evolution of the floc population rather than snapshots that are often provided by field observations. Such data can greatly contribute to efforts on flocculation model development and calibration. The downside with laboratory experiments is that they inevitably study flocs in a simulated environment rather than the natural environment in which flocs form and travel. Conducting the laboratory experiment as a part of a larger project that included *in-situ* observations (Osborn et al., 2021, 2023) provided us with an excellent opportunity to examine if the experiments conducted in flocculation tanks are translatable to natural systems. If so, repeatable flocculation experiments can be used to provide realistic data that are helpful for flocculation model parameterization and calibration. The third goal of the study was, therefore, to determine whether the floc characteristics in the flocculation tank experiments are comparable to those observed in the field.

To answer the research questions, we conducted laboratory experiments on the suspended mud in the lower Mississippi River. The experiments were conducted in a flocculation chamber that provided a controlled environment to examine the floc size distribution over time.

4.3 Materials and methods

4.3.1 Overview

Laboratory experiments were conducted in a flocculation chamber using water and sediment samples from the Mississippi River and Gulf of Mexico to study behavior of mud flocs under different environmental conditions. Data were collected on floc size distribution and turbidity of the suspension.

4.3.2 Study location and sampling method

The water samples, which contained suspended sediment, were primarily collected from the Mississippi River main channel at Venice, Louisiana, the Southwest Pass of the Mississippi River, and near the Bonnet Carré Spillway (BCS) upstream of New Orleans, Louisiana (Figure 4.1).

4.3.3 Water and mud samples

At the end of each day of field sampling, the water samples were collected and taken back onshore, put in a fridge overnight, and experimented on the following day. The total suspended solid concentration varied across the experiments due to the nature of the sampling method used. To estimate the concentration of the suspension, its turbidity was recorded using an optical backscatter sensor (OBS), and a suspended sediment concentration (SSC)-turbidity calibration curve was developed after filtering the suspension and drying and weighing the

Figure 4.1: Water and sediment sampling locations in the lower Mississippi River and Bonnet Carre Spillway, Louisiana. Map from Google Earth; Retrieved on 04/01/2023.

filters. The calibration curve allowed for the conversion of the turbidity recordings to SSC values.

4.3.4 Flocculation chamber and camera system

Water samples that were collected from the Mississippi River were put into a 13 L mixing tank. The mixing tank was equipped with an overhead mixer and a paddle that allowed for varying turbulence shear rates within the tank. A camera system, consisting of a camera, an objective, and a LED light source was used to capture floc images while in suspension (Figure 4.2). The flocculation chamber is described in detail in Tran and Strom (2017). The floc images were then grouped in Python based on a script by Keyvani and Strom (2013). The grouped images were then processed using ImageJ to identify flocs and measure their sizes. Ultimately, the sizes were passed back to the automated Python code to obtain floc size distribution and calculate a representative median floc size by volume (d_{50}). The floc sizes were calculated using the measured area of each floc as $d_f = \sqrt{4A_f/\pi}$, where d_f is the floc diameter, and A_f is the measured area of each floc. The corresponding volume for flocs were calculated as $V_f = \pi d_f^3/6$, where V_f is the floc volume.

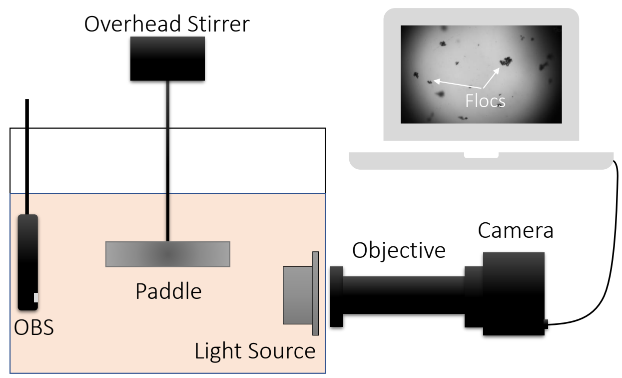

Figure 4.2: A schematic of the experimental setup.

4.3.5 Experimental design

Two main sets of experiments were carried out: 1.Salinity-focused experiments and 2. Turbulence-focused experiments. Table 4.1 shows a summary of the experiments.

Salinity-focused experiments

Three sets of experiments were designed to examine the effects of increased salinity on flocs, which is driven by the mixing of freshwater and saltwater in the FtMT zone. The first set looked at the evolution of flocs in freshwater. In the second set of experiments, salt was added to the suspension in increments to mimic the increase in the salinity of the water. In the summer 2020 experiments, table salt (NaCl) was used. In the winter 2021 experiments, we used an ASTM-grade sea salt substitute (Lake Products Company LLC, Florissant, MO, USA). In addition to its main component, NaCl, the sea salt contains nine other chemicals that provide a number of mono- and divalent ions other than Na^{+1} and Cl^{-1}. The objective was to produce water that is as close as possible to seawater in terms of ion concentrations as we have previously shown that the type of ions present in water is also important in mud flocculation (Abolfazli and Strom, 2022).

Due to our limited access to the GoM during the field surveys, only a few experiments were dedicated to examining the effects of saltwater collected from the GoM on freshwater flocs. These experiments aimed to provide the most realistic environment to study the exposure of freshwater flocs to marine saltwater. In these experiments, the water collected from the Gulf of Mexico was added to the suspended sediment collected from the main channel of the Mississippi River.

Turbulence-focused experiments

Turbulence variable experiments aimed to simulate the reduction in turbulence progressing down river through the distributary channels and into wider and saltier embayments. In these experiments, turbulence was reduced over time in a stepwise manner while other drivers were kept constant.

Table 4.1: Experimental conditions during summer and winter.

Summer				Winter			
Exp.	Range of G [s^{-1}]	Range of S [PSU]	Salt type	Exp.	Range of G [s^{-1}]	Range of S [PSU]	Salt type
1	20-95	2.2-4.5	Table	1	20-95	0	-
2	20-95	0-4.3	Table	2	20-95	0-1	ASTM
3	20-95	14.6	GoM	3	20-95	4.6	ASTM
4	20-95	0-17.2	Table	4	20-95	4.8-8.8	ASTM
5	10-95	0	-	5	20-50	13.3	GoM
6	10-95	0	-	6	20-95	11.7	GoM
7	70	1.9-26.1	Table	7	70	0-9.1	ASTM
8	70	2.2-24	Table	8	70	0-9.2	ASTM
9	70	0-13.5	Table	9	70	4.7	ASTM
10	70	1.2	Table	10	95	4.7	ASTM
11	70	0-13.4	Table	11	70	11.4	GoM
12	70	0-13	Table	12	70	0	-

4.4 Results

4.4.1 Effects of environmental drivers on flocs

Here, we looked at the changes in floc characteristics driven by variations in three environmental drivers, namely salinity, suspended sediment concentration, and turbulence by examining equilibrium conditions first. We then present data on the rates of change of the floc size distribution. Figure 4.3 shows examples of the captured floc images.

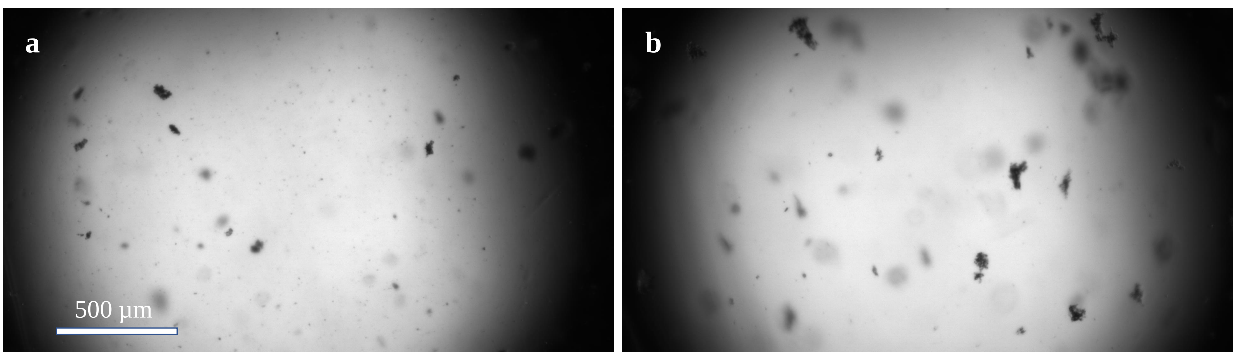

Figure 4.3: Examples of captured floc images at a) $G = 50$ s^{-1} and $S = 1$ PSU and b) $G = 50$ s^{-1} and $S = 13.3$ PSU.

Salinity

An increase in salinity obtained by adding salts in increments did not lead to a pronounced change in floc size population or d_{50} even up to S values of more than 26 PSU. Figure 4.4 shows three examples of the salinity experiments, all of which commenced with unaltered freshwater. Only three examples of the salinity experiments are shown here, but similar behavior was observed across all other salinity experiments for which table or ASTM salt was added.

While increased salinity through the addition of table salt and ASTM sea salts to the Mississippi River freshwater suspensions did not enhance flocculation, adding water from the

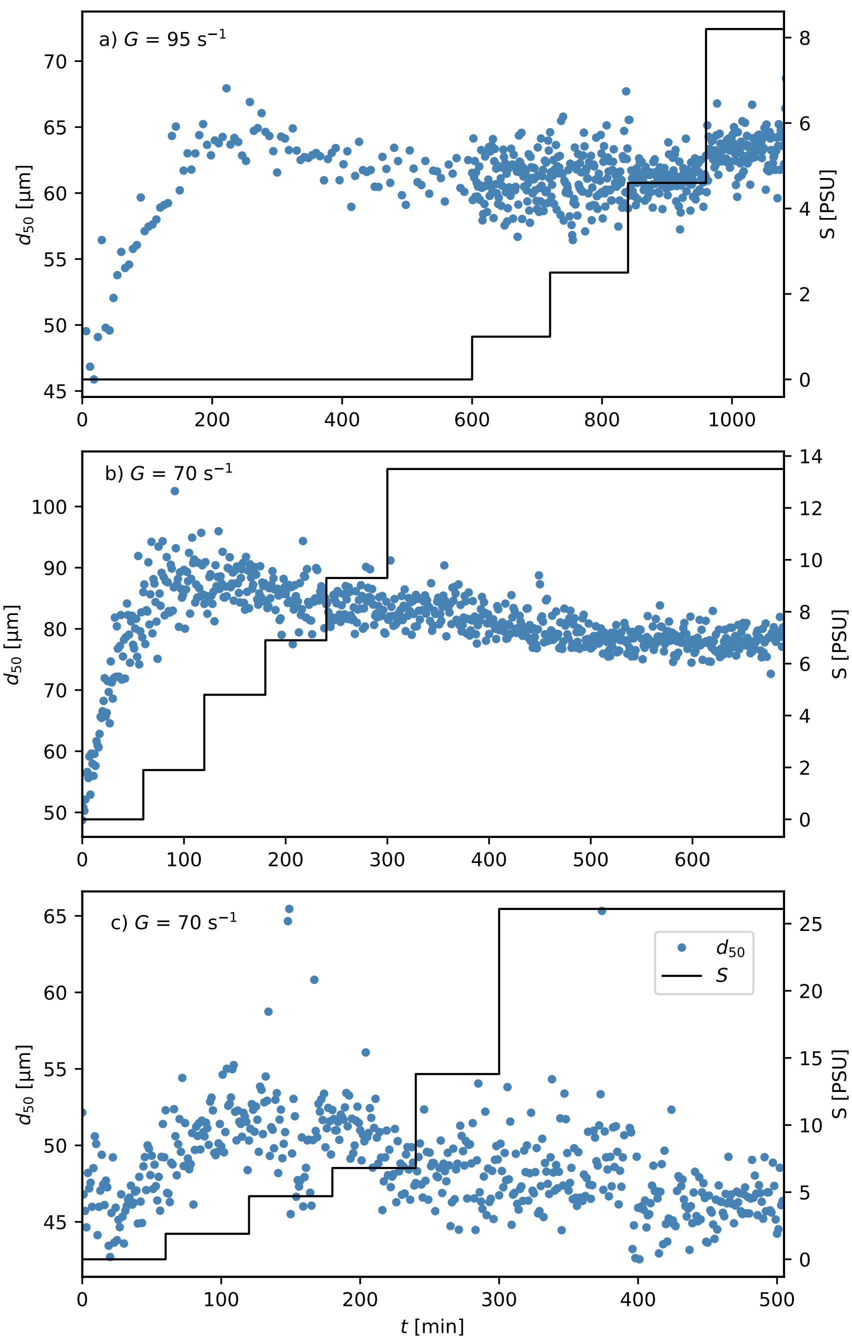

Figure 4.4: d_{50} time series in three salinity-variable experiments. Stepwise increase in the salinity of the water was achieved by the addition of salt to the flocculation chamber. Panel a shows an experiment conducted using ASTM salt in winter 2021, and panels b-c show experiments conducted using table salt in summer 2020.

GoM did promote a substantial change in the suspended particle size distribution. Namely, adding the GoM water caused the disaggregated particles to become incorporated into flocs. This led to tightening of the size distribution and moving it towards larger particle sizes (Figure 4.5).

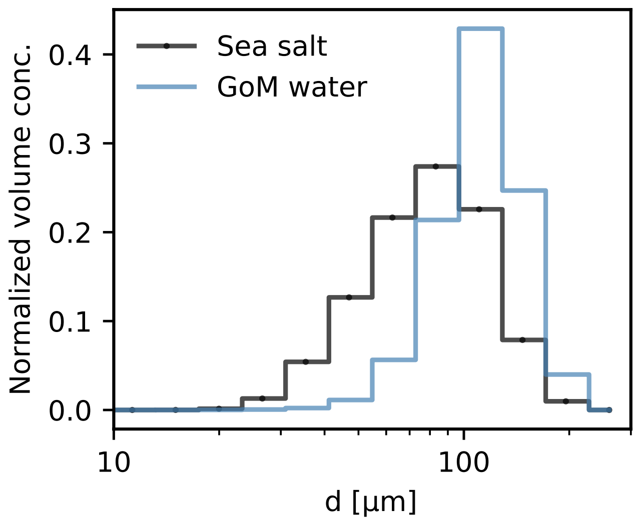

Figure 4.5: Normalized volume concentration distributions at equilibrium for a shear rate of $G = 20$ s^{-1}. Salinity measurements for the sea salt and GoM experiments were 4.8 and 11.3 PSU, respectively.

Sediment concentration

Figure 4.6 shows the equilibrium d_{50} values extracted from the time series data as a function of SSC. The corresponding G values are also shown because G can have a strong effect on d_{50} and because we generally observe a decrease in SSC due to settling of the suspended sediment at lower G values.

SSC ranged between 14 mgL^{-1} and 213 mgL^{-1} across the experiments, with SSC being < 75 mgL^{-1} in the majority of the them. The equilibrium d_{50} values ranged between 45 and 115 μm. The largest equilibrium d_{50} were at lower SSC values, which also had the lowest G (i.e., 20 s^{-1}). No systematic relationship was observed between d_{50} and SSC within each G

group. Regardless of G, the largest flocs were generally observed at SSC of <50 $\mathrm{mgL^{-1}}$.

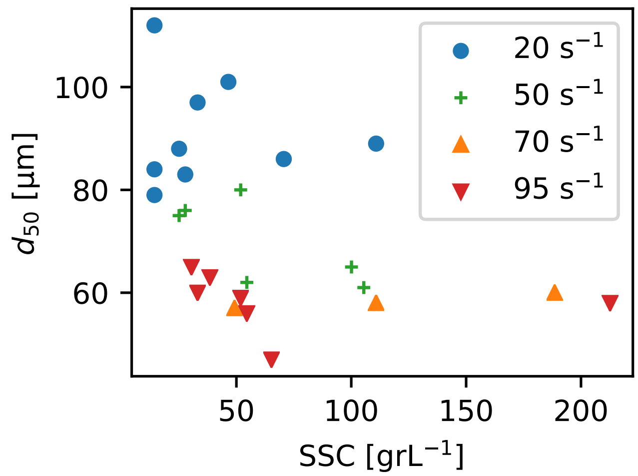

Figure 4.6: Equilibrium d_{50} versus SSC. Colors and markers indicate shear rate (G).

Turbulence

Figure 4.7 shows an example of floc size and turbidity time series in a turbulence-focused experiments. The largest flocs (those with the size of > 100 µm) formed at the lowest shear rate in the experiments (i.e., $G = 20\ \mathrm{s^{-1}}$). At this shear rate, the average equilibrium d_{50} across all experiments was 97 µm. As G increased to 50 $\mathrm{s^{-1}}$, average equilibrium d_{50} decreased to 71 µm. The average equilibrium d_{50} was 51 µm (considering an unusually small d_{50} of 31 µm in one of the experiments) at $G = 70\ \mathrm{s^{-1}}$ and 57 µm at $G = 95\ \mathrm{s^{-1}}$.

4.4.2 Floc growth and breakup time scales

The results presented in the sections above correspond to when flocs had reached an equilibrium. But how fast equilibrium is reached during times of growth (decreasing shear) and breakup (increasing shear) is also important since flocs need some time to respond to changes in shear rate. Although the time to equilibrium varied across experiments, flocs generally reached an equilibrium in size over a period of <7 hrs following the high shear stage (i.e.,

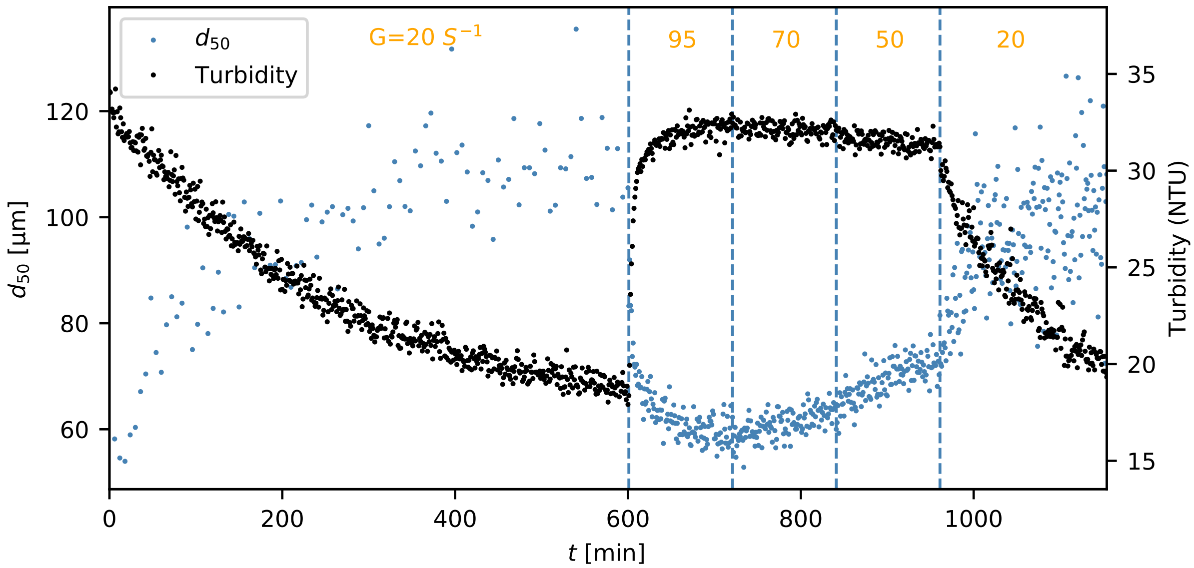

Figure 4.7: Time series of d_{50} and turbidity during a turbulence-variable experiment.

$G = 550\ \mathrm{s}^{-1}$) (Figure 4.8a). The time to equilibrium was shorter in the case of breakup such that flocs reached an equilibrium in size with their new higher shear environment within approximately 30 minutes (Figure 4.8b).

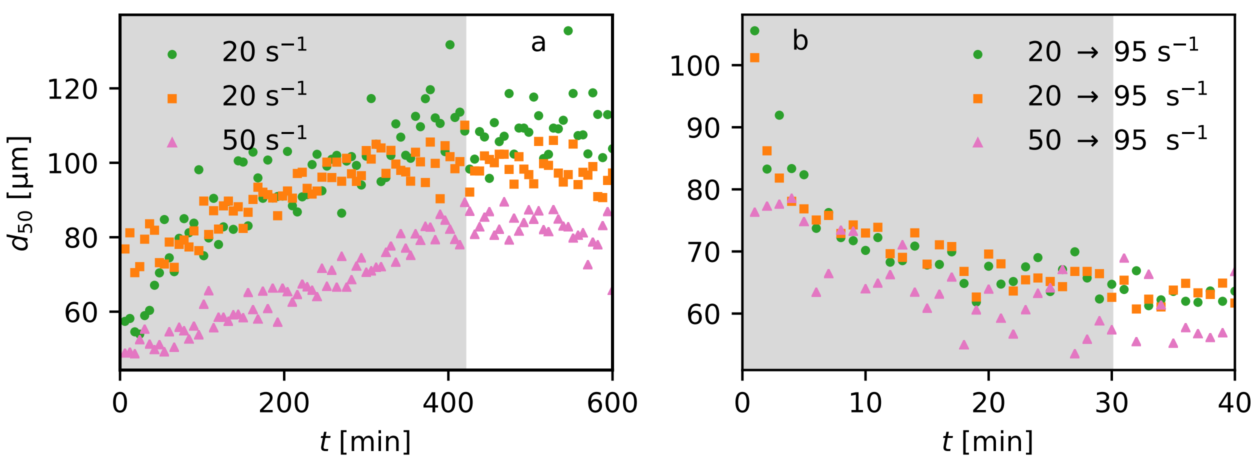

Figure 4.8: Timeseries of d_{50} illustrating the time flocs need to reach an equilibrium in size during a) growth following reduced turbulent shear from a dissaggregated condition and b) breakup during increased shear.

4.4.3 Comparison between laboratory and field measurements

Figure 4.9 shows a comparison between laboratory-obtained data and those from FlocARAZI. The wintertime laboratory-derived average d_{50} values were greater than those from FlocARAZI. In the summer, on the other hand, the FlocARAZI d_{50} values were greater. The seasonal variations in equilibrium d_{50} were less pronounced in the laboratory than in the field. That is, the FlocARAZI d_{50} values encompassed the laboratory values.

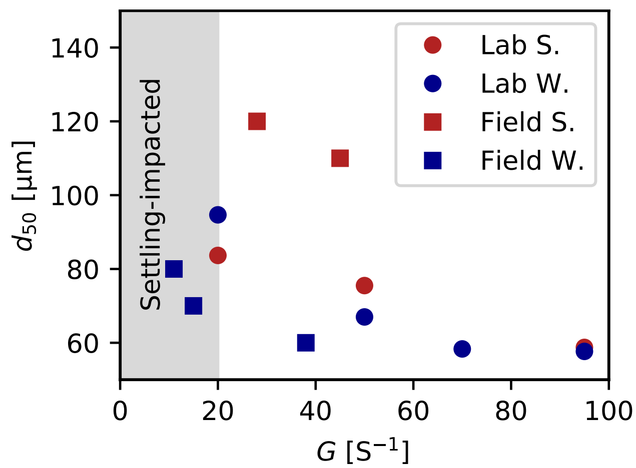

Figure 4.9: Comparison between average equilibrium d_{50} values by turbulent shear rate obtained from the laboratory experiments and FlocARAZI. "S." and "W." denote summertime and wintertime values, respectively.

4.5 Discussion

4.5.1 Drivers of the Mississippi River floc dynamics

Mud flocculation can be influenced by many factors relating to hydrodynamic, chemical, biological, and sediment properties. In this study, we investigated the effects of three main drivers of floc dynamics, i.e., turbulence, salinity, and suspended sediment concentration on Mississippi River flocs.

Due to the limitations to exert exact control on SSC in our experiments due to 1) being restricted to the amount of sediment that was suspended in the collected water samples and 2) a fraction of flocs settling out of suspension, particularly at the lower shear rate, we examined how floc sizes vary by SSC while taking G into consideration (Figure 4.6). While the presence of suspended mud particles is essential to the formation of mud flocs, our experiments did not show a strong dependence of floc size on SSC. Across all of our experiments, and regardless of G, the largest equilibrium d_{50} was found to be at lower SSC values. These relatively low SSC values generally corresponded to low G values, in which a fraction of particles had settled out of the suspension. This means that the largest flocs can form at lower shear rates even when as much as 75% of the suspended sediment has settled out of the suspension and suggests that mud flocculation in the Mississippi River is not sediment limited.

Increased salinity is thought to enhance mud flocculation. Here, an artificial increase in salinity, either via the addition of table salt or sea salt, was found to have no notable effect on the mud flocs, at least at shear rates of 20, 50, 70 and 95 s^{-1}. Floc sizes did not grow with the addition of salts. This result was unexpected and is in contrast to what we have observed in other laboratory studies (Abolfazli and Strom, 2022, 2023), where the mud did respond to increased salinity through the addition of salts to DI and natural stream water, leading to enhanced flocculation.

In our previous experiments, mud was added to pre-mixed saltwater (Abolfazli and Strom, 2022, 2023). Whereas in the experiments on the Mississippi River water suspension, salt was added to a pre-mixed river water suspension. Therefore, we considered that one possible reason for a lack of response to increased salinity with the Mississippi River suspended might have been due to the order in which sediment or salt was added to the water. Therefore, we ran an additional test using mud collected from the bed of the main channel of the Mississippi River at Venice, Louisiana to test if the order in which sediment and salt are added (sediment into salt water vs salt into a freshwater mud suspension) can alter the flocculation response. The sediment was not the sediment present in the water column during the field sampling similar to the sediment test and discussed above, but was instead obtained from the bed during the 2021 winter survey. In these ancillary tests with the mud from the bed of the main channel, we allowed for the mud to reach an equilibrium with its freshwater environment (one test with deionized water and one with water collected from Stroubles Creek, a stream in southwest Virginia, USA with strong biological activity) and then added salts to the suspension sequentially to bring the salinity to 2 and 4 PSU. We did this at shear rates of 35 and 70 s^{-1}. In all cases, we observed a response to the added salts in that flocs grew in size with the addition of salts up to 4 PSU. The response was notably stronger in the case of stream water and at lower shear rates. Because we observed an increase in floc size with the addition of salt (regardless of the order in which the salt was added and regardless of shear rate), we conclude that the lack of response, or growth in floc size, in the Mississippi River water experiments with the addition of table or ASTM sea salt was not due to the fact that we added salt to a river water mixture instead of adding sediment to a saltwater mixture. Nor was it because the mixing rate was too high to allow for flocs to grow at a given shear rate with the addition of salt.

Furthermore, the additional experiment that was used to test whether or not a suspension might respond to added salt alone after flocs had already formed provided an additional insight that corroborated with the study of Abolfazli and Strom (2023). That insight is that the addition of organic matter can enhance the effect of salt in producing large, unimodal size distributions. Essentially, the presence of organic matter boosts the flocculation-enhancing potential of added salts by creating entangled complexes of organic, inorganic, and ionic material.

Although an increase in salinity through the addition of salts did not results in floc growth within the Mississippi River water, adding water collected from the brackish sections of the Mississippi River plume did notably enhance the incorporation of discrete unflocculated particles into flocs and increase the overall average floc size. Given that we did not observe similar enhancements even with the addition of ASTM-specific sea salt to the Mississippi River freshwater, we speculate that the flocculation-enhancing effects of the brackish water were due not only to a change in ion concentration and composition but also, and perhaps primarily, due to a change in the type of organic matter present. Organic matter is present in the Mississippi River, but its composition might not be as conducive to promoting aggregation as the algae-rich water found in the fresh and saltwater mixing zone.

The Mississippi River is extremely nutrient-rich. So much so that it has been historically linked to eutrophication Turner and Rabalais (1994) and the formation of a vast dead zone in the northern GoM (Rabalais et al., 2002). The dead zone is the hypoxic region harmful to marine life the forms due to algae blooms and their subsequent degradation. When the nutrients reach the nutrient-deprived marine microorganisms, a spike in production of biomatter is inevitable (Cloern et al., 2014). Therefore we speculate that the most important contribution of the seawater to the freshwater mixture was not the presence of salt as much as it was the presence of algal material. Long strands of algae in the saltwater were visually evident in the images captured by the camera during summer. These microorganisms can both produce binding agents that enhance aggregation of suspended particles (Figure 4.10a) and become entangled in the floc structure itself (Figure 4.10b). A similar increase but in the vertical chlorophyll-a concentration was observed along a salt wedge where the interaction between freshwater and seawater occurs in the Yura Estuary, Japan by Watanabe et al. (2014).

Another reason for the weakened effects of salinity in our experiments can be the differences in scale between the flocculation tank and the Mississippi River. We observed that a fraction of the flocs larger than 120 µm settle out of the suspension particularly at lower turbulent shear rate (i.e., $G = 20$ s^{-1}). This is different with the Mississippi River in which

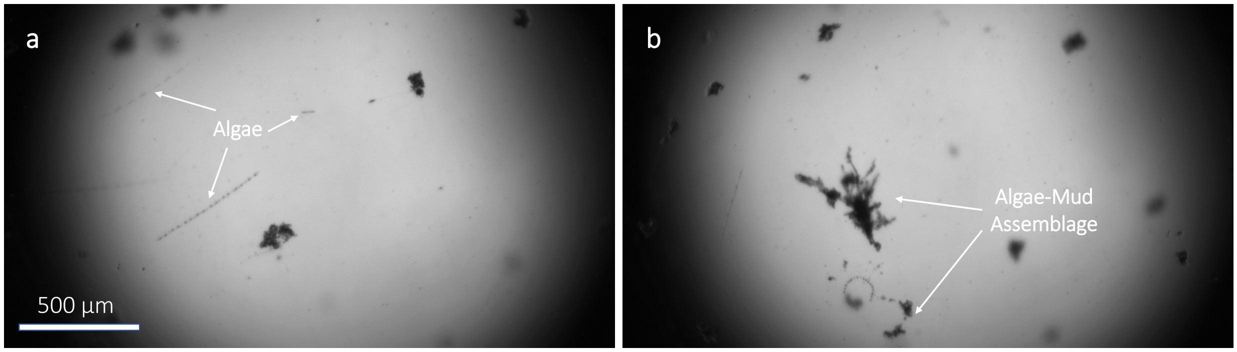

Figure 4.10: a) Algae in the water sample collected from GoM and b) their entanglement in floc structure both enhancing mud flocculation.

vertical eddies and circulations keep flocs in suspension longer. Although our experience show that our flocculation tank setup is capable of keeping flocs with d_{50} in the range of 180-220 µm in suspension, the presence of silt particles in the Mississippi River flocs is likely to cause them to be heavier and harder to keep in suspension at lower shear rates.

The strongest effect on equilibrium floc size was the turbulent shear rate in the tank. Considering that river hydrodynamics plays a major role in both bringing unflocculated particles together and breaking flocs up due to mechanical stress, it is reasonable to assume that turbulence has the first order effects on floc size. We found that a simplified Winterwerp (1998) model for d_{50eq}, in which d_{50eq} is not a function of SSC and can be written only as a function of $G^{-1/2}$ can adequately capture the dependency of equilibrium floc d_{50} on G (Figure 4.11).

4.5.2 Seasonality in floc size

Osborn et al. (2023) showed that, all else being considered, flocs imaged using FlocARAZI in the Mississippi River were larger in summer than in winter. This was attributed to the temperature-driven effects on the type and concentration of the organic matter in the water that can promote mud flocculation more in summer than in winter. However, in the

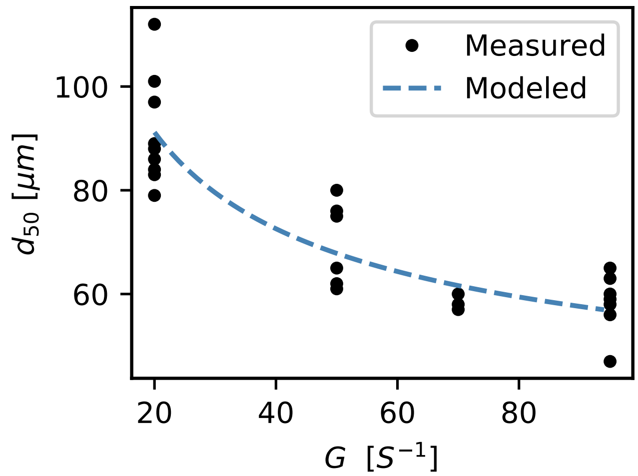

Figure 4.11: d_{50eq} by G at different experiments. The dashed blue line depicts a Winterwerp (1998) type model for d_{50eq} fitted to data.

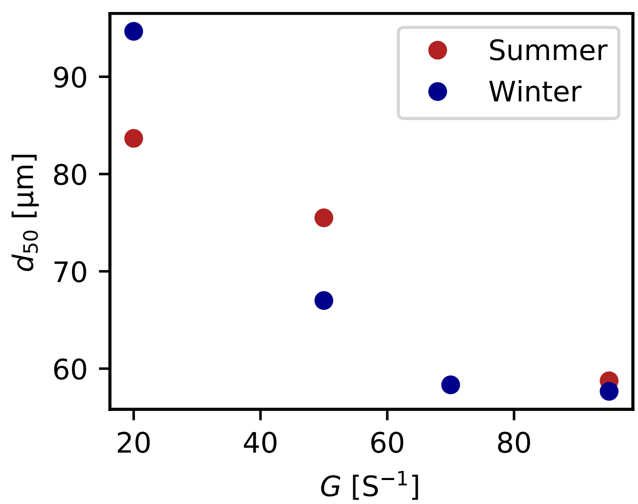

Figure 4.12: Comparison between summertime and wintertime equilibrium d_{50} by G.

laboratory experiments, the average summertime and wintertime equilibrium floc size at the shear rate of $G = 20$ s^{-1} were 96 and 103 μm, respectively (Figure 4.12). At $G = 50$ s^{-1}, the wintertime and summertime average equilibrium floc size at were comparable (70 μm in winter compared to 71 μm in summer). Similarly at $G = 95$ s^{-1}, the wintertime average equilibrium floc size was 59 μm compared to 56 μm during summer. Taken together, we conclude that the seasonal effect on floc size observed in the *in-situ* sampling was not present in the tank experiments. This might be partly due to the fact that we conducted our experiments at room temperature (19-21°C). While we expect that the organic and ion concentration of the water in the river was the same as that in the tank, perhaps the binding mechanism is dependent on temperature in some way.

4.5.3 Time scales in mud floc dynamics

Computational ocean circulation and wave models solve the discretized fluid dynamics and wave equation over time and space increments. The time increment in which the equations are solved should be selected so that the dynamics of the system are reasonably captured. The same goes for the modeling of sediment dynamics in such coupled computational models. Time steps for mud flocculation dynamic should be short enough to capture the general breakup-aggregation cycle that mud particles go through. On the other hand, if we assume that at each time step flocs are in complete equilibrium with their environment (velocity field, salinity, sediment concentration, and organic matter), algebraic equations can be used to determine the state of flocs at a point in time without the need for knowledge of their prior state (obtained through the solution of a differential equation). We observed that Mississippi River mud flocs needed a number of hours to grow from a dissaggregated state and reach an equilibrium in size (Figure 4.8). This was shorter in the case of breakup where flocs experienced an increase in turbulent shear. This highlights the need to ensure the flocculation models implemented in coupled model are temporally resolved enough to capture floc dynamics.

4.6 Conclusion

Given the rapid changes in global climate and, inevitably, geomorphology of northern coasts of the GoM, knowledge on the flocculation dynamics of the suspended mud in the lowest reaches of the Mississippi River is more critical than ever in devising efficient coastal preservation and restoration plans. In this study, we presented the findings of a series of experiments conducted during two field campaigns in the lower Mississippi River in 2020 and 2021. We found that river hydrodynamics is the main factor in driving the size of the suspended mud floc size. While increased salinity did not significantly affect mud flocculation, the GoM water was very effective in enhancing flocculation and increasing the floc size. Considering that we did not observe a similar response in flocculation with addition of salt, it is reasonable to expect that the organic matter native to the FtMT zone contributes greatly to the incorporation of suspended particles into flocs, formation of flocs > 150 µm in size, and enhanced deposition of suspended mud in this regions. As opposed to the finding of Osborn et al. (2023), no systematic difference was found between summertime and wintertime floc sizes, most likely due to the experimental conditions. Compared to sea salt, these effects are more realistic as salty ocean water is what the suspended sediment encounters in estuaries.

Chapter 5

Discussion

Studying the transport behavior of mud is critical since it constitutes a major fraction of the sediment carried by rivers. More and more research has shown that mud particles are often transported in the form of flocs and rarely in a disaggregated state (e.g., Lamb et al., 2020; Osborn et al., 2021, 2023). Therefore, the study of mud flocculation is essential to better understanding and predicting mud transport. The aim of this dissertation was to investigate key drivers of mud flocculation dynamics within the context of upstream freshwater settings within the fluvial system down to the system's terminus where fresh and marine waters mix.

One aim of this research was to investigate the flocculation state of mud in local streams within the upper portions of the Mississippi River basin. Specifically, I sought to measure the size distribution of suspended mud in local streams without the introduction of additional salts to determine if mud was flocculated or unflocculated. Extrapolating from this work one might ask the question of how prevalent mud flocs are throughout the basin more broadly and/or in other basins. Clearly, more work needs to be done to answer that question completely; however, at least for the Mississippi River basin, mud appears to exist in flocculated form throughout from the headwaters down through the delta. This was studied by examining snapshots of the flocculation state of the mud transported by the streams and rivers over the Mississippi River basin (Figure 5.1). A study of water column samples collected from streams in Southwestern Virginia, which ultimately drain in the Mississippi River, all indicated that the suspended mud is notably flocculated (Figure 5.2). These observations were not limited to the Valley and Ridge Province of southwest Virginia as our group had similar observations using FlocARAZI (Osborn et al., 2021) in fall 2020 in the upper Mississippi River in Oquawka, Illinois (Figure 5.3a). The *in-situ* observations of Osborn et al. (2023) in the lower Mississippi River also confirmed the flocculated state of suspended mud in the freshwater reaches of the lowermost Mississippi River (Figure 5.3b).

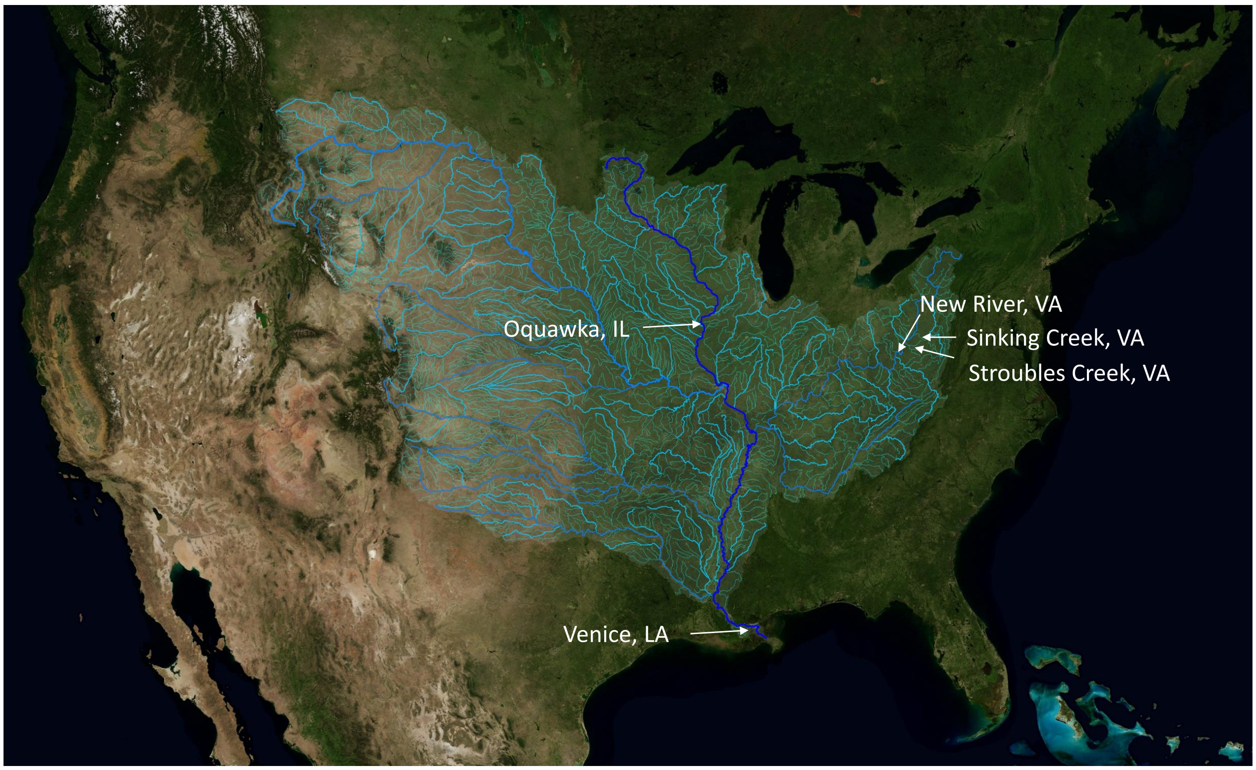

Figure 5.1: Locations of the water samples collected or *in-situ* observations made to investigate the flocculation state of the Mississippi River basin flocs (Mississippi River basin map from NASA's Scientific Visualization Studio).

If mud is mostly flocculated throughout the fluvial system, due to biomatter and background ion concentration, then a logical question might be, is there any chemical effect on flocs when exposed to higher ion concentration due to encounter with marine-derived water or roadway salts (freshwater salinization syndrome)? To answer this question, mud from Stroubles Creeks, a stream in southwest Virginia, was studied. While it was found to be mostly flocculated in water with specific conductance of 200 µScm^{-1} (Figure 5.2b), it still strongly responded to the elevated levels of specific conductance of water that had been

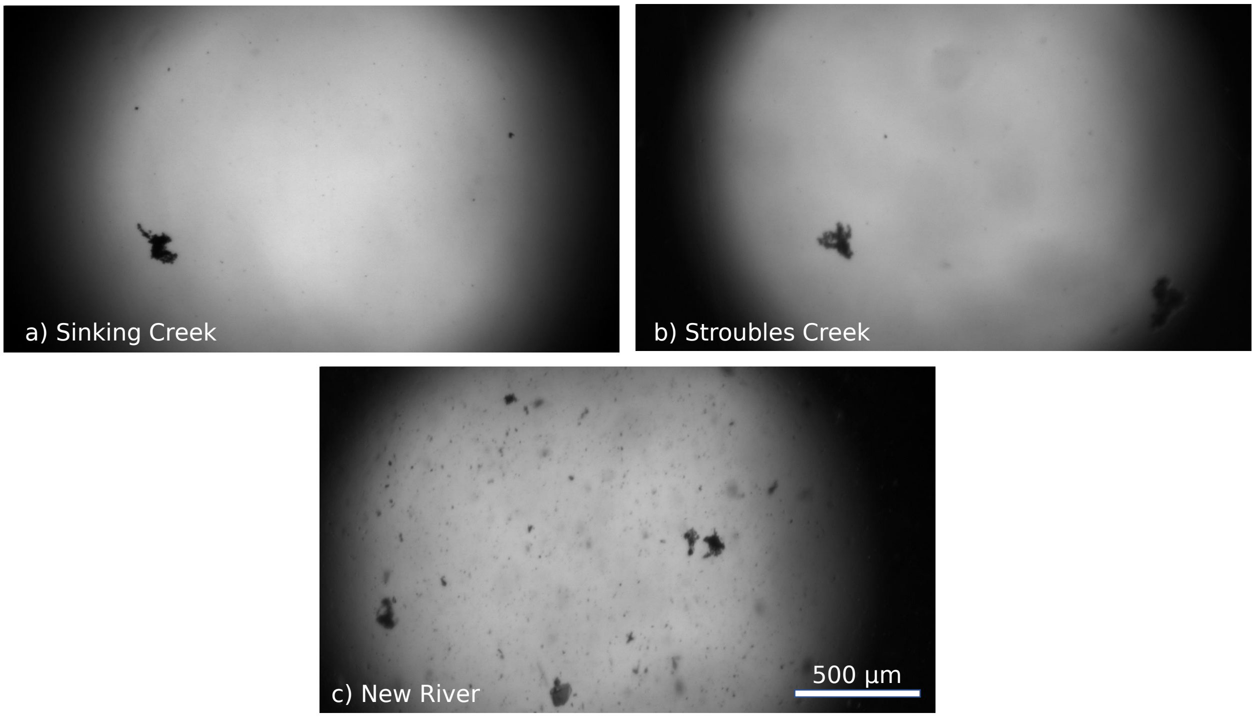

Figure 5.2: Mud flocs observed in the Valley and Ridge province in southwestern Virginia.

previously observed post winter storms due to deicing road salt runoff. The effects were strong enough to increase the floc size and thereby decrease the advective length scale by up to 40% relative to the unaltered stream water. This shows that the onset of the freshwater salinization syndrome (e.g., Kaushal et al., 2018) in the Mississippi River basin could alter transport rates and bed accumulation rates of mud even in smaller tributaries far upstream of any marine intrusion. Additionally, since fine sediment is considered a pollutant in fluvial benthic ecosystems (e.g., Burdon et al., 2013), mud flocculation due to the application of roadway salts should be taken into consideration in the assessment of negative environmental impacts of deicing salts.

An interesting, and unexpected outcome, of this research, is the finding that salt influences on the floc size distribution is strongly influenced by the presence or absence, and likely type, of organic matter (likely both dissolved and particulate). Experiments that were

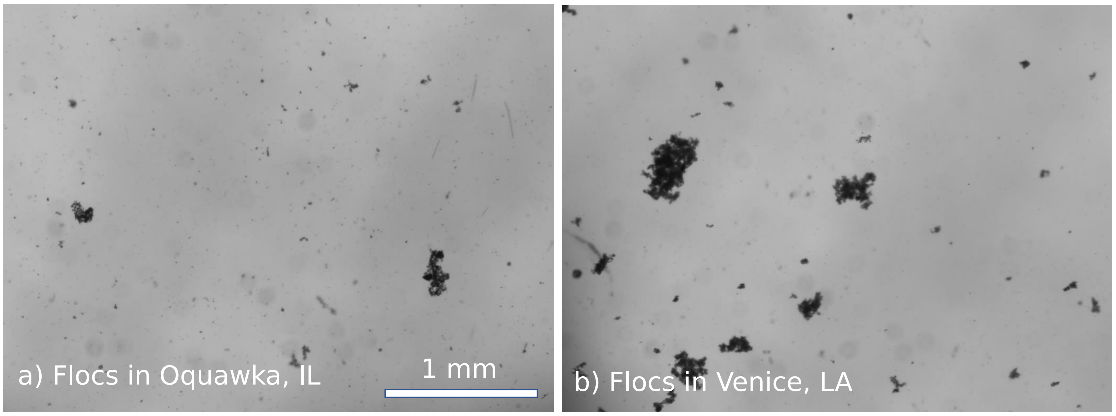

Figure 5.3: Sample mud flocs observed at a) Oquawka, IL about 1,900 river miles upstream of the Mississippi River mouth, and b) Venice, LA

conducted using the mud that was treated to remove its organic content showed that the treated sediment still responded to the increased salinity but in a clearly weaker manner, pointing to the strong contribution of organic matter in salinity-enhanced mud flocculation (Chapter 3). Additionally, in Chapter 4, I showed that sediment that was suspended in stream water with high organic content displayed a response to increased salinity beyond what was observed with the same sediment sample in organic matter-free water. That is, floc sizes increased to a greater extent when salt was added when the background organic levels were higher (Chapter 4).

Of all the environmental factors that affect mud flocculation, which one is the most influential in driving the flocculation of suspended in the Lower Mississippi River? To answer this question, flocculation data were collected using water samples collected from the river during two field campaigns in the lowermost Mississippi River. Findings showed that flocculation in the Mississippi River is not sediment-limited, and flocs with d_{50}>115 µm formed at sediment concentrations of as low as 30 mgL^{-1}. Increasing the salinity of the water by adding salts did not strongly enhance flocculation. However, the mixture of suspended freshwater sediment and the salty water collected from the Gulf of Mexico did lead to the incorporation of loose particles in the floc structure and greater average floc sizes. This is possibly due to the strong effects of the biomatter that occurs in the mixing zone. The mixing zone provides a unique environment where nutrients from the river with predominantly agricultural runoff reaches the nutrient-deprived marine organisms (Rabalais et al., 2002). This causes a strong spike in primary production that has been also linked to the creation of hypoxic dead zones in coastal waters. Turbulence was also found to be a major factor in the flocculation of the Mississippi River suspended mud across all experiments, which is in line with our *in-situ* observations in the river.

How should one conceive of or model the influence of flocculation on suspended mud in the fluvial and estuarine systems? Flocs are always present due to the presence of organic matter that leads to complex clay-biopolymer interactions. Using a pure unflocculated settling velocity will likely underpredict the settling rate of mud throughout the system. For salinity levels less than 0.5 ppt, this study has found that suspended mud have a wider, or even bimodal, particle size distribution. Increasing salt and organic matter content moves the floc size distribution towards a more unimodal one. Average floc sizes of 60 to 180 µm (and therefore settling velocity of 1-2 mms^{-1}) depending on the states of turbulent shear, organic matter type and contents, and salts (Abolfazli and Strom, 2022, 2023; Osborn et al., 2023) can be thought as a reasonable representative for floc size, and based on the observations of Osborn et al. (2023), it is likely reasonable to characterize the entire reach with a single cross-sectionally averaged suspended floc size distribution.

Can we propose a simple equilibrium-type model that provides reasonable sizes for mud in fluvial and estuarine systems? More research needs to be done to develop a comprehensive knowledge of the equilibrium state of natural mud. However, I observed that in agreement with the Winterwerp (1998) type model, equilibrium floc size is inversely related with square root of shear rate, i.e., $\sqrt{G}$. In contrast to that model, equilibrium floc size was not found to be a function of suspended sediment concentration. The model presented here for the aggregation potential of flocs with a focus on the salinity range of $S = 0 - 10$ ppt showed the most evident increase in floc size in the $S = 0 - 3$ ppt range, indicating a potential threshold for salinity effects. As discussed above, I also observed that the effects of salinity depend on organic matter so that mud flocs can be roughly grouped into three categories of organic matter-free flocs, flocs moderately impacted by organic matter, and flocs strongly impacted by organic matter, each with a representative size larger than the former.

Chapter 6

Conclusion

6.1 Summary

This dissertation focused on mud flocculation dynamics over the Mississippi River basin and its geomorphological and ecological implications. Particularly, since flocs were found to exist over the basin wherever *in-situ* measurements were made or where samples were collected, the aim was to investigate the interplay between organic matter, salinity, and turbulent shear within the freshwater and FtMT zones of the Mississippi River basin. The importance of mud flocculation in urban streams and its potential role in the degradation of benthic ecosystems was addressed in Chapter 2. An increase in specific conductance of water due to the application of deicing road salts was found to greatly affect the flocculation dynamics of freshwater flocs and their transport behavior, increasing floc size and settling rate.

Establishing that increased salinity even in the ranges of $S < 1$ ppt can notably enhance mud flocculation, and considering the lack of calibrated models for lower ranges of salinity, a model was proposed for salinity effects on aggregation efficiency of mud flocs (Chapter 3). The model was based on experimental data that were specifically designed to be resolved over lower salinity levels ($S < 3$ ppt). It was also shown that flocs' response to increased salinity is stronger in the presence of naturally-occurring organic matter in mud, which points to the complex interaction between the ions and the biomatter in facilitating the aggregation of mud particles.

Chapter 4 of this dissertation focused on identifying the drivers that are the most important in the flocculation behavior of mud flocs in the lower Mississippi River. Flocculation was not found to be sediment-limited in the lower Mississippi River. The addition of water collected from the Gulf of Mexico strongly enhanced the flocculation of the suspended mud, while an artificial increase in the salinity of freshwater by adding salts did not produce similar results. This can be due to the presence of organic matter specific to the mixing zone, where nutrient-deprived marine organisms have access to nutrient-rich Mississippi River water. Turbulence was found to be the most influential factor in the flocculation state of the Lower Mississippi River mud, which was in line with the *in-situ* measurements from our group.

6.2 Limitations and future works

Mud flocculation is a process that involves several parameters with complicated interdependencies. This dissertation aimed to investigate mud flocculation in a number of scenarios that have substantial implications for coastal geomorphology and ecosystem health. Below are suggestions for future studies attempting to fill out the remaining pieces of the flocculation puzzle.

Characterizing the composition of the organic matter present in the fluvial and the FtMT zones and their spatial gradients (both longitudinal and vertical) will greatly help investigate the correlation between flocculation and settling rate of mud flocs and the potential dominance of certain organic compounds. For example, methods such as fluorescence spectroscopy, which was used in Appendix C, are capable of characterizing different types of organic matter that are known to enhance or hinder mud flocculation (Lee et al., 2019). For example, while many researchers have suggested that EPS is the primary type of organic matter responsible for promoting binding in flocs, no standard method for quantifying EPS in floc studies exists. One major step forward would be for the community to determine a set procedure for characterizing and quantifying the organic constituents so as to allow for better linking between mud floc characteristics and organic material.

Utilizing recently-developed three-dimensional image acquisition techniques, such as X-ray microCT (e.g., Spencer et al., 2022), in controlled experiments and sampling multiple flocs over time can help characterize floc structures and their evolution in response to environmental drivers, as well as the configuration of mineral and organic components within flocs. Bridging the two- and three-dimensional floc world such as interpreting three-dimensional fractal geometry of flocs from two-dimensional images can also be helpful (Maggi and Winterwerp, 2004).

The use of a mixing chamber that allowed for controlling the drivers of flocculation was a point of strength in this dissertation. However, the settling that occurred during some of the lower shear rate experiments prevented us from capturing the evolution of the floc population at shear rates less than 20 s^{-1}. One way to overcome this might be by enlarging the scale of the experimental apparatus. Although taller water columns and grid-generated turbulent flow have been used in past flocculation studies, such setups obtain floc images in a stagnant column (e.g., Tang and Maggi, 2015). Capturing floc images in a turbulent suspension at different depths in a tall water column could potentially improve our ability to capture data on flocculation behavior at low shear rates.

This study focused on flocculation in the Mississippi River basin. How broadly the results apply to other river basins is not known. Although flocs have been found in various environments, the nature of the sediment (mineral and organic matter) clearly plays a major role in flocculation. Expanding the mud floc dataset by experimenting on mud samples from the headwaters to the estuaries across other geological regions at different turbulence conditions while characterizing organic matter type and content would be a great step forward to develop a universal floc model for the fluvial and FtMT environments.

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Appendices

Appendix A

Measuring suspended mud flocs in the laboratory: a comparison between two methods

Appendix A has been published in the proceeding of River Flow 2020 (10th Conference on Fluvial Hydraulics).

A.1 Introduction

Transport and deposition of the fine muddy sediment present in marine and riverine environments is strongly modulated by flocculation. Flocculation is the aggregation and breakup of these muddy sediments that yields flocs with size, shape, and density different than its original constituent particles. The process of flocculation is affected by variables such as the sediment type and concentration, salinity, and flow condition. Determining the size of the flocs is critical as it is the major factor influencing the movement and behavior of flocs in different flow conditions.

Flocs are difficult to measure due to their small size, dependence on the environment that they form in, and inherent fragility. Various experimental methods have been used to measure and characterize flocs. A method that has been extensively used in the literature is to transfer sediment suspensions to a settling column using a syringe (e.g., Gratiot and Manning, 2004), hand pipette (e.g., Manning and Dyer, 1999; Mooneyham and Strom, 2018), or peristaltic pump (e.g., Jarvis et al., 2005b) and obtain images from the suspension within the settling column. However, these sample delivery methods can be destructive to floc structure and yield inaccurate measurements. Imaging flocs in their own turbulent environment in which they have formed and evolved can be a relatively more accurate approach for floc size measurements. Therefore, to be as least intrusive to flocs as possible in the imaging process, efforts have been made to utilize methods that allow for capturing floc images *in-situ* (e.g., Smith and Friedrichs, 2011; Keyvani and Strom, 2014; MacDonald and Mullarney, 2015; Tran and Strom, 2017). A major drawback in this method is that as the suspended sediment concentration (SSC) increases, it becomes more difficult to process floc images due to the extensive overlap of flocs in the obtained images (Tran et al., 2018), and the measurements become less reliable. This may necessitate transfer and dilution of the suspension sample into a second environment, where the imaging and measurement takes place. However, it is not clear how consistent the measurements from these two methods are. The study we present in this paper is a comparison between the floc sizes obtained from *in-situ* and transferred measurement methods under different suspension concentrations and shear rates. For this purpose, a series of four experiments were conducted to compare floc sizes measured using these two different methods. The remainder of this appendix is organized as follows. Section A.2 describes sample preparation procedure and the floc imaging and processing methods. Section A.3 presents the results. Section A.4 is discussion and conclusion.

A.2 Materials and methods

The experiments we conducted consisted of the use of two floc measurement methods. The first method was implemented in a 13 L mixing tank with dimensions of 27.5×27.5×25 cm.

A paddle mixer with variable speed was used to create turbulent shear in the tank. Salt was added to the background water to achieve the salinity of 8 ppt. A mixture of 80% kaolinite and 20% montmorillonite (by dry mass) was used to mimic natural mud. Before adding the sediment to the clear water in the mixing tank, it was well mixed in a beaker and then sonicated for 15 minutes to break down any potential flocs. Once the sonicated sediment mixture was added to the tank, imaging of the suspension was commenced at a frequency of 1 Hz.

In the second method, 3 mL samples from the mixing tank suspension were collected with a pipette and transferred to a 80 mL settling chamber. The settling chamber contained water with a salinity that matched that of the mixing tank. Every effort was made to transfer the suspension to the settling chamber in as little time as possible while introducing the least possible perturbation to the floc mixture. Sample delivery from the mixing tank to the settling chamber commenced 12 hours after the initiation of the mixing tank experiment to make sure that flocs in the tank were no longer changing size with time. Multiple samples were transferred to the settling chamber during each experiment. The still image capture rate in the settling chamber was also set to 1 Hz. The experiments were conducted at two different sediment concentrations (C) (i.e., $C = 100$ and 300 mgL^{-1}) and two different shear rates (G) (i.e., $G = 50$ and 95 s^{-1}), resulting in four different experimental conditions (Table A.1). Three replicates were performed for each condition. The exception to this rule was Experiment 2, in which six replicates where conducted. The camera systems used for the mixing tank and the settling chamber both provided a length to pixel ratio of 1.3 µm:1 pixel, allowing for measurement of flocs in the size range of 10-1000 µm. More details about the camera system can be found in Tran and Strom (2017). Floc images obtained from the mixing tank and the settling chamber were then processed using the procedures of Keyvani and Strom (2013) to obtain floc size distribution. Figure A.1 shows a schematic of the experimental setup.

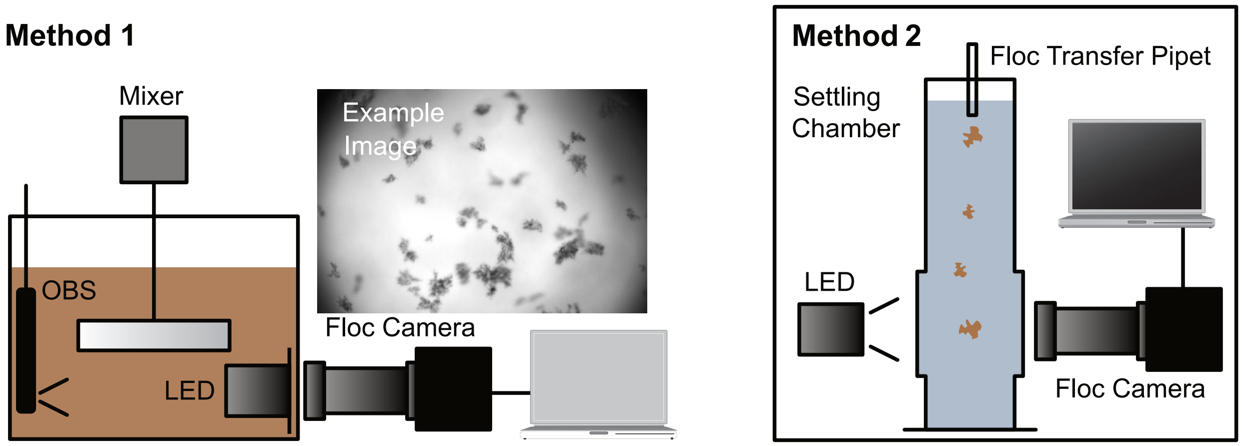

Figure A.1: A schematic of the two experimental setups.

Table A.1: Description of the experiments.

Experiment	Sediment Concentration [mgL^{-1}]	Shear Rate [s^{-1}]	Number of Replicates
1	100	50	3
2	300	50	6
3	100	95	3
4	300	95	3

A.3 Results

Continuous collection of floc images enabled us to investigate how floc sizes evolve within the mixing tank and to produce a time series of different size distribution statistics such as the floc d_{50} (Figure A.2a). There is an evident peak in floc size around minute 5 followed by a decline down to equilibrium. The floc size reached equilibrium after about 12 hr, which is when the suspension samples were transferred from the mixing tank to the settling chamber. Figure A.2a shows the floc size measured in the settling chamber in Experiment 1. In this experiment, floc size in the settling chamber was slightly smaller than those from the mixing tank (Table 2). The percentage difference between the the d_{50} measured using the two methods is

$$\Delta d_{50} = \left(\frac{d_{50mix} - d_{50set}}{d_{50mix}} \right) \times 100 \tag{A.1}$$

where d_{50mix} and d_{50set} are d_{50} measured in the mixing tank and settling chamber, respectively. Δd_{50} in Experiment 1 ranged between 1.0 to 3.7 in different replicates with an average of about 3, which means that on average, d_{50} was $\approx 3\%$ smaller in the settling chamber when compared to the mixing tank. Positive values for Δd_{50} in all the replicates shows smaller d_{50} in the settling chamber.

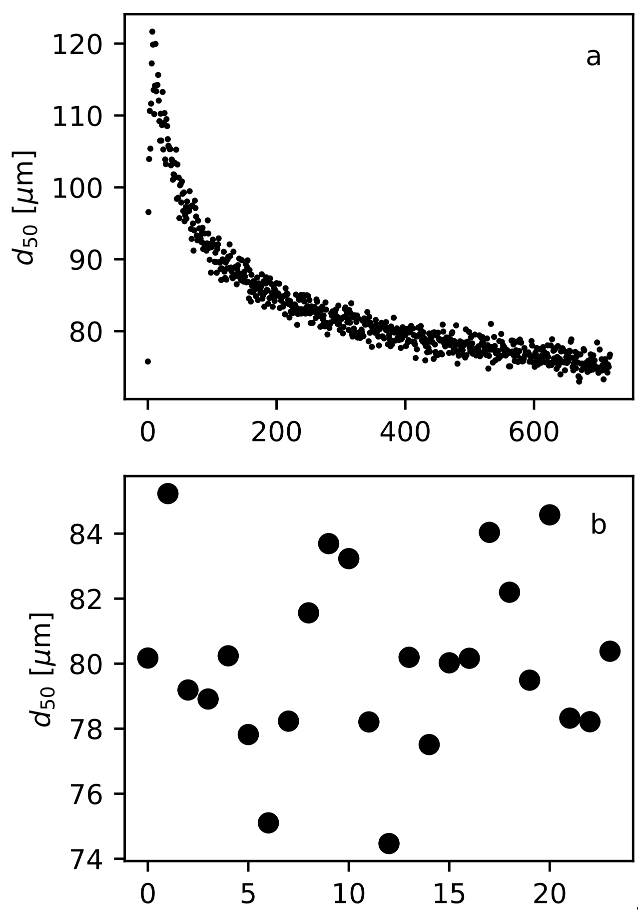

Figure A.2: Time series of d_{50} from Experiment 1 as measured in a) the mixing tank (method 1) and b) the settling chamber (method 2).

Experiment 2 had a larger sediment concentration compared to Experiment 1 at the

Table A.2: d_{50} measured in Experiment 1 ($C = 100$ mgL^{-1} and $G = 50$ s^{-1}).

Replicate	Mixing Tank d_{50mix} [µm]	Settling Chamber d_{50set} [µm]	d_{50mix}-d_{50set} [µm]	Δd_{50} [%]
1	103	102	1	1.0
2	114	110	4	3.5
3	106	102	4	3.7

same shear rate. Increasing the concentration of the sediments from 100 mgL^{-1} to 300 mgL^{-1} increased the average equilibrium d_{50} from 108 µm (Table A.2) to 124 µm (Table 3). Similar to Experiment 1 ($C = 100$ mgL^{-1} and $G = 50$ s^{-1}), floc size measured in the settling chamber were generally consistent among the replicates. Sizes ranged from 112 to 138 µm in the mixing tank and from 104 and 120 µm in the settling chamber (Table A.3). On average, d_{50} measured in the settling chamber was about 12% smaller than that measured in the mixing tank.

Table A.3: d_{50} measured in Experiment 2 ($C = 300$ mgL^{-1} and $G = 50$ s^{-1}).

Replicate	Mixing Tank d_{50mix} [µm]	Settling Chamber d_{50set} [µm]	d_{50mix}-d_{50set} [µm]	Δd_{50} [%]
1	122	105	17	13.9
2	119	113	6	13.4
3	132	116	16	12.1
4	121	105	16	13.2
5	112	104	8	7.1
6	138	120	18	13.0

An increase in shear rate from $G = 50$ to 95 s^{-1} led to a reduction in the equilibrium floc size in both the $C = 100$ mgL^{-1} and 300 mgL^{-1} experiments due to increased floc breakup (Experiments 3 and 4 compared to Experiments 1 and 2). The average equilibrium d_{50} across the replicates decreased from 108 µm (Table A.2) to 73 µm (Table A.4) at 100 mgL^{-1} and from 124 µm (Table A.3) to 82 µm (Table A.5) at 300 mgL^{-1} when the shear rate in the mixing chamber was increased from 50 s^{-1} to 95 s^{-1}. At the shear rate of 95 s^{-1}, the highest difference between d_{50} measured in the mixing tank and settling chamber was at the concentration of 100 mgL^{-1} (Table A.4), where the average measured d_{50} was about 5% less than that in the mixing tank. The average measured d_{50} at the concentration of 300 mgL^{-1} was interestingly the same as that measured in mixing chamber (Table A.5), the differences did exist for individual replicates.

Table A.4: d_{50} measured in Experiment 3 (C = 100 mgL^{-1} and G = 95 s^{-1}).

Replicate	Mixing Tank d_{50mix} [µm]	Settling Chamber d_{50set} [µm]	d_{50mix}-d_{50set} [µm]	Δd_{50} [%]
1	76	77	-1	-1.3
2	69	66	3	4.3
3	74	66	8	10.8

Table A.5: d_{50} measured in Experiment 4 (C = 300 mgL^{-1} and G = 95 s^{-1}).

Replicate	Mixing Tank d_{50mix} [µm]	Settling Chamber d_{50set} [µm]	d_{50mix}-d_{50set} [µm]	Δd_{50} [%]
1	79	80	-1	-1.2
2	80	87	-7	-8.7
3	88	80	8	9.1

A.4 Discussion and conclusion

We conducted four experiments with multiple replicates to compare the d_{50} measurements in the larger mixing tank and the smaller settling chamber. The d_{50} averaged over the replicates was reasonably consistent between the two methods in each experiment. Results generally indicate that transferring the sediment suspension from the mixing tank to the settling chamber results in smaller d_{50}, likely due to the breakup of some flocs. If we consider the average of the replicates as an indication of how the two measurement methods compare, Experiment 4 with the suspended sediment concentration of 300 mgL^{-1} and shear rate of 95 s^{-1}

yielded the best agreement (Table A.5). This could possibly be due to higher floc aggregation rate in the settling chamber, allowing flocs that had broken up some in the transfer process to grow. In this experiment, the relatively high floc concentration facilitates floc collisions that results in the aggregation of flocs. This is obvious in the first and second replicates of the experiment in which the d_{50} measured in the settling chamber were in fact greater than that measured in the mixing tank. The third replicate, however, indicates that d_{50} was smaller in the settling chamber. The variability among the replicates was consistent between mixing tank and settling chamber (9 and 7 µm, respectively). Experiment 1 showed the next best consistency between the floc sizes measured using the two methods with the average d_{50} in the settling chamber being only about 3% smaller than that in the mixing tank (Table A.2) with 11 and 8 µm variability within replicates in mixing tank and settling chamber, respectively. This suggests that the flocs were not large enough to undergo substantial breakup when they were being transferred. This conclusion is somewhat consistent with the results of Experiment 2. This experiment had the largest equilibrium d_{50} in the mixing tank and showed the greatest difference between the measurements conducted in the two chambers (Table A.3). In this experiment, the d_{50} measured in the settling chamber was in average 12% smaller than that in the mixing tank, suggesting a more significant breakup rate when the relatively large flocs were being transferred. The greatest variability among replicates was also in this experiment (26 and 16 µm in mixing tank and settling chamber, respectively). In Experiment 3, due to the relatively low sediment concentration and high shear rate, flocs had the smallest equilibrium d_{50} (Table A.4) and yet they underwent some degree of breakup with no significant aggregation in the settling chamber. In this experiment, d_{50} measured in the settling chamber was about 5% smaller than that in the mixing tank. Small floc size was in line with the small variability among replicates (7 and 11 µm in mixing tank and settling chamber, respectively).

Although the d_{50} measured in the settling chamber was generally smaller than that in the mixing tank, it does not mean that the transfer methods cannot be used for floc size quantification. The maximum average difference in floc size between the two methods in the experiments was about 12%. This suggests that in cases that floc suspension cannot be imaged within the mixing tank due to high sediment concentration, transferring floc samples to a second environment can be considered a viable option. However, such measurements might be made more accurate by adding in a correction factor that depends on the sediment concentration and flow properties. It also should be noted that we initially observed significant differences between the measurements obtained from the two methods. That is, it was only after refining the sample delivery method and the image processing procedure that the floc size measurements in the settling chamber were close to those in the mixing tank. For the sample delivery procedure, great care was taken not to disturb the flocs. For the image processing procedure, once the images were obtained from the dilution chamber, they were manually inspected, and the images that did not contain any flocs or those with out-of-focus flocs were deleted.

Knowing the size distribution of flocs is important in accurately modelling floc transport and deposition in riverine and marine environments. This study was a step towards understanding the sensitivity of floc size quantification between two different measurements techniques that are widely used in the literature. We found that d_{50} measured *in-situ* in the mixing tank can be different and was generally larger than that measured in a smaller settling chamber. We also found that it is possible for the differences between the methods to be a function of suspension concentration and shear rate. Future research can be focused on comparison between floc sizes obtained using other floc measurement techniques and the potential effect of sediment composition.

Appendix B

Effects of ion composition of water on flocculation

B.1 Introduction

Salinity has historically been considered to be a major driver of mud flocculation. Researchers, therefore, have used different methods to increase the salinity of water in cohesive sediment flocculation studies. Table salt, a mixture of various salts representing sea salt, and sea water have all been used to replicate the increase in ion concentration of water as river water mixes with saltwater. However, it is still unclear how these different compositions of ions can influence the process of flocculation. This research aimed to investigate how the floc sizes compare when using different types of salts to enhance flocculation.

B.2 Materials and methods

Three different types of salt were used to assess their potential in enhancing flocculation of cohesive sediment. These salts include table salt (sodium chloride), epsom salt (magnesium sulfate), and an ASTM grade sea salt that contains 9 other compounds in addition to sodium chloride. Two types of sediments were used in each set of experiments. One set of experiments used the mud collected from Stroubles Creek. The second set of experiments used a kaolinite+xanthan gum (XG) mixture. Table B.1 shows a summary of the experiments.

Experiments were conducted in the flocculation chamber, where floc images were captured. The images were then analyzed to obtain floc size distribution.

Table B.1: Summary of experiments.

Experiment	Sediment type	Sediment concentration [mgL^{-1}]	Salt type	Salinity [ppt]
1	Bed sediment	100	Table salt	2
2	Bed sediment	100	Epsom salt	2
3	Bed sediment	100	Sea salt	2
4	Kaolinite+XG	100	Table salt	2
5	Kaolinite+XG	100	Epsom salt	2
6	Kaolinite+XG	100	Sea salt	2

B.3 Results

In the bed sediment experiments, both sea salt and epsom salt enhanced flocculation more than table salt so that flocs were on average 25 µm smaller in the table salt experiment compared to the sea salt and epsom salt experiments (Figure B.1). Epsom salt was found to have a stronger impact on the initial growth of the flocs both when the sonicated mud was added to the tank and after the flocs had undergone the high shear phase.

The behavior of the kaolinite+XG mixture in different salts experiments were similar to that of the bed sediment. Epsom salt facilitated the aggregation of disaggregated particles more evidently than sea salt or table salt (Figure B.2). The effects of table salt on promoting flocculation was weaker than the two other salts.

B.4 Discussion and conclusion

Cohesive sediment flocculation studies have used various types of salt or mixture of salts to mimic the increase in salinity of river freshwater as it mixes with seawater. Here, it was

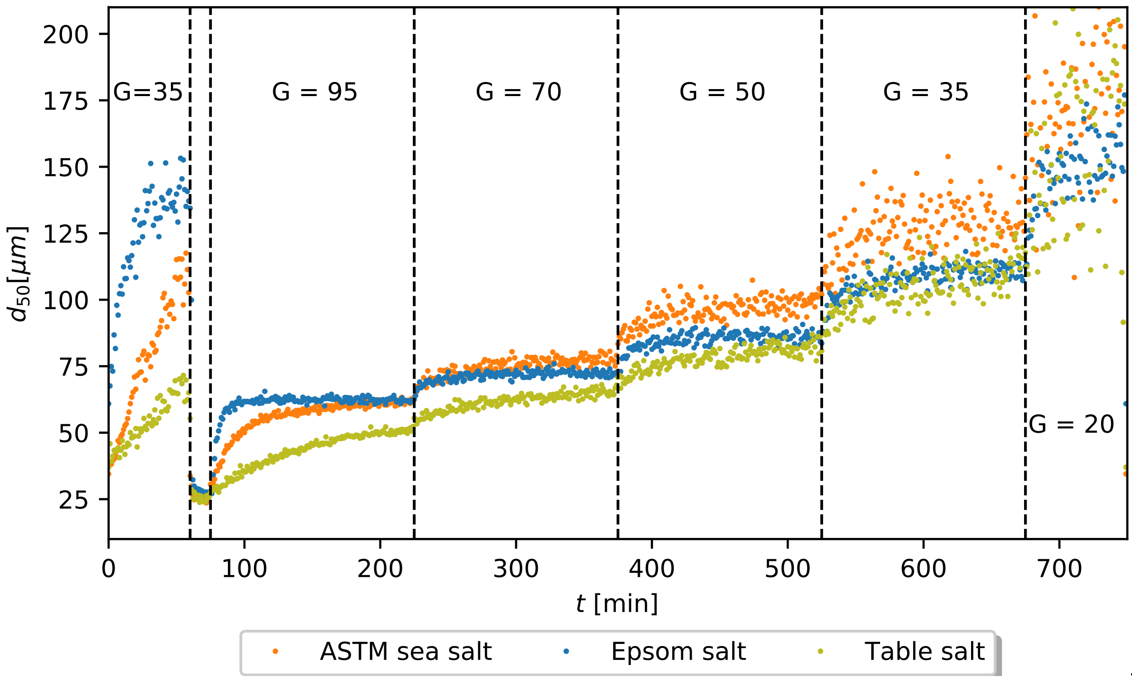

Figure B.1: Time series of d_{50} in the bed sediment experiments. Values for G are in s^{-1}.

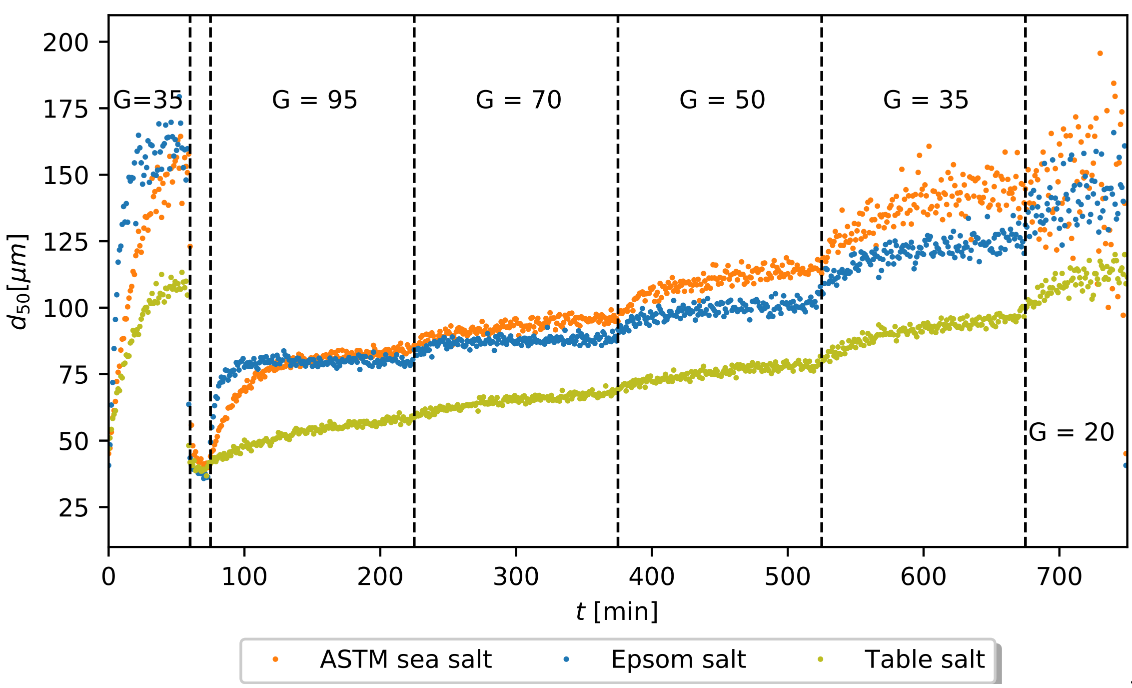

Figure B.2: Time series of d_{50} in the kaolinite experiments. Values for G are in s^{-1}.

shown that the flocculation-enhancing effects of both epsom salt and sea salt are stronger than table salt. This was observed for both bed mud and kaolinite+XG mixture. This is likely due to the presence of divalent cations in epsom salt and sea salt that are known to promote flocculation stronger than monovalent cations due to their cation bridging effects.

Given the differences observed in the effects of different types of salt on flocculation, it is recommended that the sea salt is used in mud flocculation studies so that the ion composition of water is consistent with that of sea water.

Appendix C

Can organic gums be suitable representatives of natural organic matter in mud flocculation studies?

C.1 Introduction

Laboratory studies have been used to produce controlled data on mud flocculation. The data can be used for calibrating sediment transport models. A problem that laboratory studies face is that mud experiments are not necessarily repeatable because the organic content of mud can vary across experiments even if the mud samples are similar. A solution to this problem has been to use commercially available organic matter as a representative of the organic matter that is naturally occurring in mud. Guar gum, xanthan gum, and chitosan gum have all been used in flocculation studies. However, it is not clear whether the type and the concentration of the artificial organic matter used in the experiments can suitably represent the natural organic matter.

To answer this question, in this research, comparisons were made between natural and laboratory-made flocs were made using flocculation experiments. In these sets of experiments, mud samples were collected from local streams and bodies of water and the size of mud flocs and the components of the organic matter were compared against those created with kaolinite and different concentrations of xanthan gum.

C.2 Materials and methods

Four mud samples were collected from Stroubles Creek, Toms Creek, Duck Pond, and the New River. With the laboratory-made flocs, kaolinite clay was used for the clay and xanthan gum was uses as a representative for organic matter (Table C.1). In contrast to guar gum that has plant origin, xanthan gum is derived from a species of bacteria known as Xanthomonas campestris. All of the natural mud experiments were conducted at a concentration of 100 mgL^{-1}. All the kaolinite experiments were also all conducted at a concentration of 100 mgL^{-1} with the difference that the amount of kaolinite clay was adjusted so that the concentration of Sediment+OM remains at 100 mgL^{-1}. In all experiments, salinity was set to 2 ppt by adding ASTM sea salt to the suspension. Flocculation experiments were conducted in the flocculation chamber, where the shear rate was reduced in a stepwise manner. Floc images were captured and analyzed to calculate the size distribution of flocs and d_{50}. PARAFAC model analysis was performed on excitation-emission matrix spectroscopy (EEMS) data to characterize the components organic matter (Cory and McKnight, 2005). Bound and soluble EPS were extracted following DuBois et al. (1956). For the soluble EPS, 10 gr of sediment was added to the conical tube. Nanopure water was added to the tube to get a 10 mL suspension. The samples was then mixed for 1 hr and then centrifuged at 4 ℃ at 3500 g for 10 min. The upper water was then extracted. For the bound EPS, resin was first activated using phosphate buffered saline. It was then mixed with the mud and water for 1 hr and then centrifuged at 4 ℃ at 3500 g for 10 min. The upper water was then extracted.

C.3 Results

Analysing the floc images over the each experiment yielded a timeseries for d_{50}. Figure C.1 shows the d_{50} timeseries for different experiments. Among the kaolinite+XG experiments,

Table C.1: Summary of experiments.

	Experiment	Sediment+OM Concentration [mgL^{-1}]	XG Concentration [mgL^{-1}]	Salinity [ppt]
1	Toms Creek	100	0	2
2	Stroubles Creek	100	0	2
3	New River	100	0	2
4	Duck Pond	100	0	2
5	Kaolinite clay	100	0.5	2
6	Kaolinite clay	100	1	2
7	Kaolinite clay	100	2	2

the experiment with 0.5 mgL^{-1} had the smallest d_{50}, while the d_{50} values between the 1 and 2 mgL^{-1} were not notably different.

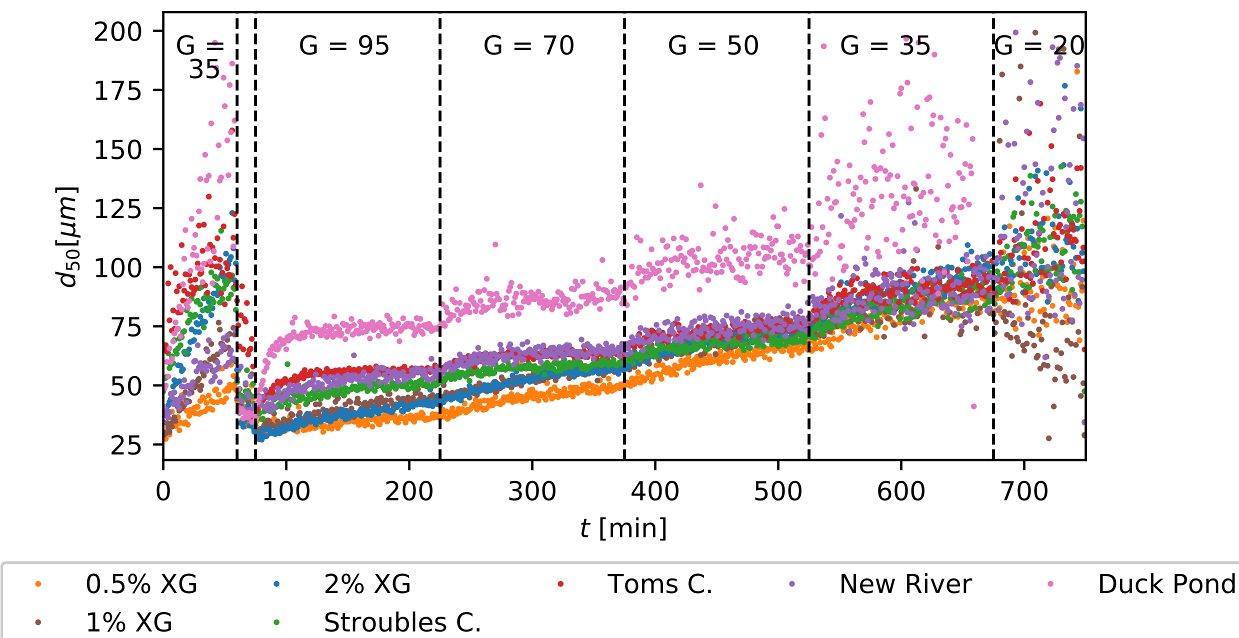

Figure C.1: Time series of d_{50}. Values for G are in s^{-1}.

Expect for the Dock Pond flocs, volume concentration of flocs for the remaining three natural samples were comparable to that of kaolinite and xanthan gum floc (Figure C.2).

Tables C.2 and C.3 show the organic matter components derived from the PARAFAC model. Among the components shown, the C8 and C13 components represent Tryptophan

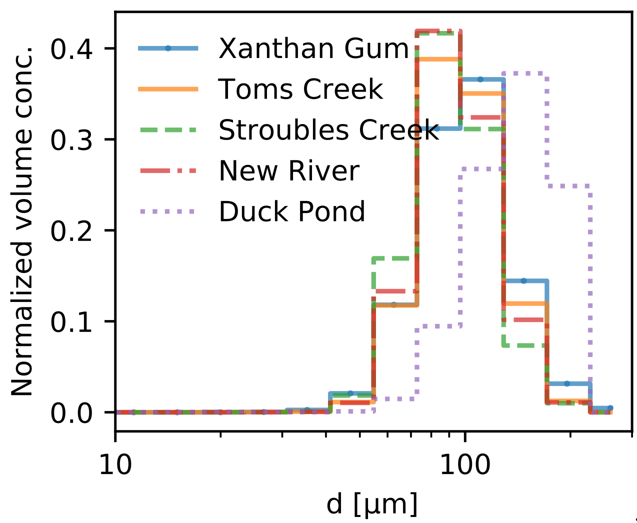

Figure C.2: Normalized volume concentration distributions at equilibrium for shear rate of $G = 35\ s^{-1}$.

and Tyrosine that are known to enhance mud flocculation (Lee et al., 2019). The sum of C8 and C13 components is reflected as %Protein. Xanthan gum by 33.3% had the largest % Protein across all analyzed samples, while Duck Pond by 13.1% had the largest % Protein among the natural samples.

Table C.2: Organic matter component loadings calculated by the PARAFAC model. "B" and "S" denote bound and soluble components of the organic matter, respectively.

Sample	%C1	%C2	%C3	%C4	%C5	%C6	%C7
Toms S	3.9%	28.7%	2.4%	17.5%	1.2%	2.8%	3.0%
Stroubles S	5.2%	33.0%	2.1%	17.2%	2.2%	6.3%	3.4%
New River S	6.4%	32.9%	3.3%	14.0%	1.9%	5.0%	4.1%
Duck Pond S	5.0%	29.4%	2.5%	12.1%	1.1%	5.3%	3.8%
Toms B	2.8%	25.6%	0.0%	26.4%	2.9%	4.1%	1.1%
Stroubles B	1.7%	23.4%	0.0%	28.4%	2.3%	1.9%	0.7%
New River B	5.3%	29.5%	0.1%	26.0%	4.3%	7.2%	1.0%
Duck Pond B	3.6%	21.8%	1.1%	19.9%	2.7%	5.1%	2.0%
Xanthan Gum	1.9%	3.0%	0.0%	26.3%	0.1%	0.0%	1.7%

Table C.3: Organic matter component loadings (Cont.).

Sample	%C8	%C9	%C10	%C11	%C12	%C13	%Protein
Toms S	5.7%	1.8%	0.0%	4.3%	25.5%	3.2%	8.9%
Stroubles S	1.8%	2.1%	0.0%	7.5%	16.2%	3.1%	4.8%
New River S	2.1%	1.5%	0.2%	7.8%	16.0%	4.6%	6.7%
Duck Pond S	7.8%	2.3%	0.0%	6.6%	24.1%	0.0%	7.8%
Toms B	6.8%	1.3%	0.0%	0.9%	28.2%	0.0%	6.8%
Stroubles B	7.8%	1.3%	0.0%	0.0%	32.6%	0.0%	7.8%
New River B	3.0%	0.5%	0.2%	5.3%	16.1%	1.4%	4.5%
Duck Pond B	13.1%	1.4%	0.0%	5.0%	24.2%	0.0%	13.1%
Xanthan Gum	33.3%	0.0%	0.0%	0.0%	33.8%	0.0%	33.3%

C.4 Discussion and conclusion

By providing linkage between mud particles and altering their surface charge, organic matter is known to strongly affect both freshwater and saltwater mud flocculation. Organic gums have been used in laboratory experiments to mimic their effects in flocculation. However, it is not clear how well these organic gums represent the biomatter that naturally occurs in mud. Here, we used a PARAFAC model on the EEMS analysis data to characterize the type of organic matter present in natural mud and Xanthan gum samples. Xanthan gum contained the highest protein fraction among the analyzed samples. The protein fraction consists of tryptophan and tyrosine components, which are linked to enhanced mud flocculation. Among the natural samples, the sample from Duck Pond had the highest protein fraction. This is most likely the reasons for the floc size being the largest the Duck Pond experiments compared to the other natural samples.

The analysis presented here shows that xanthan gum can reasonably represent natural organic matter in mud flocculation context. The flocs formed from the kaolinite+XG mixture at 2% XG to kaolinite ratio had an equilibrium d_{50} that was close to those from bed sediment. This translates to a XG concentration of 2 mgL^{-1}, which is within the range of 1-3 mgL^{-1} for particulate organic matter concentration that we have obtained in local streams.