**A Mechanistic Model for Mud Flocculation in Freshwater Rivers**

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**Abstract** The transport and deposition of mud in rivers are key processes in fluvial geomorphology and biogeochemical cycles. Recent work indicates that flocculation might regulate fluvial mud transport by increasing mud settling velocities, but we lack a calibrated mechanistic model for flocculation in freshwater rivers. Here, we developed and calibrated a semi-empirical model for floc diameter and settling velocity in rivers. We compiled a global data set of river suspended sediment concentration-depth profiles and inverted them for in situ settling velocity using the Rouse-Vanoni equation. On average, clay and silt (diameters <39 μm) are flocculated with settling velocity of 1.8 mm s\(^{-1}\) and floc diameter of 130 μm. Among model variables, Kolmogorov microscale has the strongest positive correlation with floc diameter, supporting the idea that turbulent shear limits floc size. Sediment Al/Si (a mineralogy proxy) has the strongest negative correlation with floc diameter and settling velocity, indicating the importance of clay abundance and composition for flocculation. Floc settling velocity increases with greater mud and organic matter concentrations, consistent with flocculation driven by particle collisions and binding by organic matter which is often concentrated in mud. Relative charge density (a salinity proxy) correlates with smaller floc settling velocities, a finding that might reflect the primary particle size distribution and physical hosting of organic matter. The calibrated model explains river floc settling velocity data within a factor of about two. Results highlight that flocculation can impact the fate of mud and particulate organic carbon, holding implications for global biogeochemical cycles.

**Plain Language Summary** The fate of fine sediment in rivers is important for understanding contaminant dispersal, organic carbon burial, and the construction of river floodplains and deltas. Individual grains of silt and clay dispersed in water settle under the pull of gravity at extremely slow rates. However, in natural rivers, these mud particles can aggregate together into larger structures called flocs, resulting in far faster settling rates. Here, we built on prior work from estuaries to develop a settling velocity model for flocculated mud in freshwater rivers. Our results demonstrate that mud settling velocity increases in rivers with less vigorous turbulence because turbulence can break flocs apart. Mud settling velocity also increases with greater concentrations of mud and particulate organic matter, which promote particle collisions and binding. Counterintuitively, settling velocity decreases with greater clay abundance and greater river water salinity, possibly due to how they affect organic matter in binding mud particles into flocs. Our results improve understanding of floc behavior in rivers and indicate potential links between the routing of mud and organic matter, river geomorphology, and global climate.

**1. Introduction**

Mud (grain diameter, \(D < 62.5 \mu m\)) dominates the sediment load carried by rivers globally (e.g., Baronas et al., 2020; Lupker et al., 2011) and its fate is important for our understanding of fluvial geomorphology and biogeochemical cycling. For example, mud-rich fluvial deposits are a major component of the rock record (Aller, 1998; McMahon & Davies, 2018; Zeichner et al., 2021). Mud cohesion increases bank strength in alluvial rivers, affecting river morphodynamics (e.g., Dunne & Jerolmack, 2020; Kleinhans et al., 2018; Lapôtre et al., 2019; Millar & Quick, 1998). Mud is also a primary carrier of organic carbon and pollutants because of its high specific surface area (e.g., France-Lanord & Derry, 1997; Galy et al., 2015; Pizzuto et al., 2014). Despite its importance, we lack well-tested mechanistic models for mud transport in rivers.

Mud in rivers has traditionally been treated as washload, or sediment that is too fine to regularly settle to and interact with the riverbed (Church, 2006; Garcia, 2008). In contrast, recent work suggests that flocculation—the aggregation of particles into composite structures called flocs—can enhance mud settling velocities and...
Figure 1. Schematic of a cross-section through a river water column illustrating physicochemical processes operating at different scales that could be important for mud flocculation in rivers. Key variables are turbulence (Kolmogorov microscale, $\eta$), volumetric mud concentration ($C_m$), sediment mineralogy (molar Al/Si of river suspended sediment), organic matter concentration (fraction of sediment surface covered by organic matter, $\theta$), and dissolved species concentrations (relative charge density of river water, $\Phi$). These variables affect the diameter, $D_f$, and settling velocity, $w_{s,floc}$, of flocs composed of primary particles with diameter $D_p$.

Experiments have also supported organic matter, dissolved species, and sediment concentration as important controls on flocculation in freshwater (Figure 1). Chase (1979) showed that the presence of organics increased floc settling velocity, a result attributed to the interaction of sediment surface coatings, organic chemistry, and dissolved solutes. Subsequent experiments showed that sediment concentration positively correlated with floc size while fluid shear rate affected floc size and settling velocity differently (e.g., Burban et al., 1990; Tsai et al., 1987).

More recent experiments examining the role of organics on flocculation in freshwater highlighted the importance of nutrients, biomass, and organic matter composition on floc size and settling velocity (Furukawa et al., 2014; Lee et al., 2017, 2019; Tang & Maggi, 2016; Zeichner et al., 2021). For instance, Zeichner et al. (2021) showed in experiments modeled after rivers that organic matter increased clay floc settling velocities by up to three orders of magnitude, depending on organic matter type and clay mineralogy.

Process-based flocculation theory is required to link field studies and experiments into a coherent framework. Floc population balance models use particle aggregation and breakage kernels, and have been successful at reproducing floc size distributions (e.g., Lick & Lick, 1988; Spicer & Pratsinis, 1996; Xu et al., 2008). These studies showed that sediment concentration and fluid shear enhance floc aggregation by increasing particle collision frequency, but greater shear causes floc breakage (Figure 1). Winterwerp (1998) introduced a simplified model (hereafter, the Winterwerp model) tracking a characteristic floc diameter (e.g., the median), making it more easily coupled to hydrodynamic models (e.g., Maggi, 2008; Son & Hsu, 2011; Winterwerp, 2002). The Winterwerp model includes the effects of fluid shear and sediment concentration, but subsumes other factors into coefficients that drastically affect mud transport dynamics in rivers (Bouchez, Métivier, et al., 2011; Lamb et al., 2020; Zeichner et al., 2021). Similar to sand, flocculated mud might be in a dynamic interchange between the flow and bed material (Lamb et al., 2020). Mud flocculation has been well-studied in estuarine and marine systems where flocs form in part because salinity promotes van der Waals attraction between particles (e.g., Hill et al., 2000; Mehta & Partheniades, 1975; Winterwerp, 2002, Figure 1). In addition, flow turbulence, sediment concentration, organic matter concentration, and clay mineralogy are important for estuarine and marine flocculation (e.g., Kranck & Milligan, 1980; Meade, 1972; Verney et al., 2009). In contrast to the wealth of studies on flocculation in saline environments, knowledge on flocculation in freshwater rivers is relatively limited (e.g., Bungartz & Wanner, 2004; Droppo et al., 1997; Droppo & Ongley, 1994).

Studies in rivers identified flow characteristics, organic matter concentration, and suspended sediment concentration as potential controls on floc size, settling velocity, and strength (Figure 1). Through microscopy of samples from Canadian rivers, Droppo and Ongley (1994) observed organic matrices binding together mineral sediment into flocs. They observed correlations between floc size and suspended sediment concentration, attached bacteria count, and particulate organic carbon concentration. Bungartz et al. (2006) characterized floc settling velocities at three transects along a lake outlet and found faster-settling flocs at higher discharge, a result they attributed to faster floc growth at higher flow turbulence. They also showed that settling patterns of suspended sediment and particulate organic carbon were similar, supporting the idea that flocculation controlled transport of both mineral sediment and organic carbon. Gerbersdorf et al. (2008) examined bed material composition in the Neckar River, Germany, and identified rich networks of microbe-derived extracellular polymeric substances (EPS). They found positive correlations between concentrations of EPS moieties and the critical shear stress for erosion, indicating that EPS can help stabilize bed sediment. Lamb et al. (2020) used a field data compilation to infer the presence of widespread mud flocculation in rivers. They showed that in situ particle settling velocity can be inferred by fitting the Rouse-Vanoni equation to grain-size-specific suspended sediment concentration-depth profiles. However, they did not explain the order-of-magnitude variation in the inferred floc settling velocities.
of the aggregation and breakage rates. The model describes well the equilibrium size of flocculated estuarine mud (Winterwerp, 1998) and flocs in saline laboratory experiments (e.g., Kuprenas et al., 2018; Maggi, 2009; Son & Hsu, 2008). However, these models have yet to be compared or adapted to flocculation in freshwater rivers.

Here, we built on the Winterwerp approach to develop a semi-empirical process-based model for mud flocculation in freshwater rivers. First, we proposed new forms for flocculation efficiency coefficients to explicitly cast floc diameter and settling velocity as functions of physicochemical variables that prior work has shown are important for flocculation in freshwater: turbulence, sediment concentration, sediment mineralogy, organic matter concentration, and dissolved ion concentration (Figure 1). Next, we calibrated the new model against field data. We compiled a global data set of river grain size-specific suspended sediment concentration-depth profiles and inverted them for in situ settling velocity using the Rouse-Vanoni equation (Lamb et al., 2020). Together with a river geochemistry data compilation, we fitted the model to help explain the variance in floc settling velocities. Finally, the results are discussed in the context of fluvial geomorphology, organic carbon, tectonics, and climate.

2. Model Development

2.1. Winterwerp Model

Winterwerp (1998) proposed a flocculation model in which fluid shear drives particle collisions and floc aggregation and breakage. The model casts the time rate of change of floc diameter, $D$ (or median $D_f$ for a floc size distribution) as the difference of floc aggregation and breakage rates:

$$\frac{dD_f}{dt} = \frac{k_A}{n_f\eta^2} C D_f \left( \frac{D_f}{D_p} \right)^{3-n_f} - \frac{k_B}{n_f\eta^2} \nu D_f \left( \frac{D_f}{D_p} \right)^{3-n_f} \left( \frac{\tau_y}{\tau_t} \right)^j \tag{1}$$

On the right-hand side of Equation (1), the first term is the floc aggregation rate, scaled by the aggregation efficiency, $k_A$ (dimensionless), and the second term is the floc breakage rate, scaled by the breakage efficiency, $k_B$ (dimensionless). The shear rate, $G$ (s$^{-1}$), quantifies fluid mixing and relates to the smallest turbulence length scale—the Kolmogorov microscale, $\eta = \sqrt{\nu/G}$ (m), where $\nu$ is the fluid kinematic viscosity (m$^2$ s$^{-1}$) (Tennekes & Lumley, 1972). Greater fluid mixing and volumetric sediment concentration, $C$ (volume sediment/total volume; dimensionless), drive more frequent collisions of primary particles with diameter $D_p$ (m) and thereby increase aggregation rate (Figure 1). Flocs break up if fluid shear is too high relative to floc strength, an effect that Winterwerp (1998) expressed in Equation (1) using the ratio of fluid stress on the floc, $\tau_y = \rho(\nu/\eta)^2$ (Pa), and floc strength, $\tau_f = F_y/D_f^2$ (Pa), where $\rho$ is fluid density (kg m$^{-3}$). $F_y$ is floc yield strength (in terms of force) and has been estimated to be of order $10^{-10}$ N (Matsuo & Unno, 1981). Floc fractal dimension, $n_f \in [1, 3]$ (dimensionless), describes floc structure assuming it is approximately self-similar (Kranenburg, 1994). Floc structure can vary from a linear string of particles ($n_f = 1$) to a solid, compact particle ($n_f = 3$). An average $n_f = 2$ is typical for natural flocs (e.g., Tambo & Watanabe, 1979; Winterwerp, 1998). In practice, $n_f$ describes the relationship between floc diameter and floc density by $R_f/R_s = (D_f/D_p)^{n_f/3}$ where $R_f$ is the floc submerged specific gravity (dimensionless) and $R_s$ is the submerged specific gravity of the primary particle sediment (dimensionless) (Kranenburg, 1994). Although the parameter $j$ in Equation (1) is an empirical constant, Winterwerp (1998) used $j = 0.5$ to ensure that floc settling velocity, floc diameter, and sediment concentration are linearly related to each other based on estuarine floc data. We retained $j$ as a fit parameter to maintain generality.

2.2. Modifications to the Winterwerp Model for River Flocs

We proposed changes to floc strength, and floc aggregation and breakage efficiencies to adapt the Winterwerp model to rivers.

2.2.1. Floc Strength

Experiments in freshwater have shown that, for constant $D_f$, floc settling velocity, $w_s/floc$, increases with larger mixing rate due to an increase in floc density (Burban et al., 1990). This behavior suggests that flow conditions during floc formation can affect floc strength, where more porous and lighter flocs are weaker because they have fewer interparticle contacts and vice versa. Bache (2004) proposed that floc strength, $\tau_f$, is a balance of local
turbulent kinetic energy per unit volume acting on the floc and the energy per unit volume required to rupture the floc:

\[ \tau_s = \frac{\rho}{30} \left( \frac{v}{\eta} \right)^2 \left( \frac{D_f}{\eta} \right)^2 \]

(2)

The power-law form of Equation (2) holds in general but the numerical constants apply for small \( D_f/\eta \) (Bache, 2004).

2.2.2. Floc Aggregation and Breakage Efficiencies

In the Winterwerp model, all contributions to flocculation outside of fluid shear and sediment concentration are captured in the constant floc aggregation and breakage efficiency terms, \( k_A \) and \( k_B \), respectively. We investigated whether \( k_A \) and \( k_B \) in rivers depend on organic matter concentration, sediment mineralogy, and dissolved ion concentration, as functions rather than fit constants.

Organic matter can adsorb onto sediment surfaces and form connective “bridges” between grains (Ruehrwein & Ward, 1952; Smellie & La Mer, 1958; Molski, 1989, Figure 1). In rivers, biogenic molecules like EPS can act as sticky media for bridging flocculation (Droppo & Ongley, 1994; Gerbersdorf et al., 2008; Larsen et al., 2009; Lee et al., 2019). Smellie and La Mer (1958) proposed a functional form of bridging flocculation efficiency,

\[ k_A, k_B^{-1} \propto \theta(1 - \theta) \]

(3)

in which \( \theta \) is the fraction of the sediment surface covered by a polymeric substance. We used Equation (3) and calculated \( \theta \) for organic matter (Section 3.3).

We accounted for sediment mineralogy using the molar elemental ratio Al/Si as a proxy variable (Figure 1). More intensely weathered rocks typically generate sediment with larger Al/Si because chemical weathering produces Al-rich clay minerals (e.g., Ito & Wagai, 2017; Jackson et al., 1948; Lupker et al., 2012). Mineralogy can affect flocculation because it determines the range of potential chemical interactions between particles through cation exchange capacity (CEC) and therefore the ability to attract cations in solution (Mehta & McAnally, 2008). Furthermore, cations can affect the ability of organic matter to adsorb to particle surfaces and the physical orientation of adsorbed organic matter (Galy et al., 2008; Mehta & McAnally, 2008). We used a simple power law model as a starting point,

\[ k_A \propto (\text{Al/Si})^{A_1} \]

(4)

\[ k_B \propto (\text{Al/Si})^{B_1} \]

(5)

where \( A_1 \) and \( B_1 \) are dimensionless fit constants.

Dissolved ions in river water might promote flocculation through the same mechanism as salinity by boosting the effectiveness of van der Waals attraction between particles (e.g., Seiphoori et al., 2021, Figure 1). To express ionic effects, we used a dimensionless parameter, \( \Phi \), to quantify the relative densities of charges in solution and on the sediment (Rommelfanger et al., 2020):

\[ \Phi = \frac{\lambda I}{\text{CEC} \rho_s L/2} \]

(6)

in which the Debye length, \( \lambda \) (m), is the average length from the particle in which an electrostatic effect from the charged surface is sustained, \( I \) is the solution ionic strength ((number ions) m\(^{-3}\)), CEC is the sediment CEC ((number ions) kg\(^{-1}\)), \( \rho_s \) is sediment density (kg m\(^{-3}\)), and \( L \) (m) is a grain length scale that is nominally the face length of a plate-shaped clay particle, which we set to \( D_p \). Physically, \( \Phi \) quantifies the ionic strength of river water relative to the ionic strength in a volume surrounding primary particles. As \( \Phi \) increases, the positive charge in the water within the Debye length overcomes the negative charge on the sediment surface and causes attraction between nearby sediment grains (Rommelfanger et al., 2020). We proposed power-law relations as starting points to relate \( \Phi \) and the flocculation efficiencies:

\[ k_A \propto \Phi^{A_2} \]

(7)

\[ k_B \propto \Phi^{B_2} \]

(8)
where $A_2$ and $B_2$ are dimensionless fit constants.

### 2.3. River Floc Model

We substituted Equations (2) – (8) into Equation (1) to derive a modified semi-empirical model for floc diameter, $D_f$:

$$\frac{dD_f}{dt} = k'_A \theta(1-\theta)(\text{Al}/\text{Si})^{A_1} \Phi^{A_2} - k'_B \theta(1-\theta)\eta^2 v D_p \left( \frac{D_f}{D_p} \right)^{3-n_f} \left( \frac{\eta}{D_f} \right)^{2j}$$

in which $k'_A$ and $k'_B$ are new dimensionless constants that absorb all constant dimensionless parameters related to floc aggregation and breakage, respectively. At dynamic equilibrium, the time derivative of $D_f$ vanishes, resulting in

$$D_f = k\eta \left( C \theta^2 (1-\theta)^2 \right)^{\eta} (\text{Al}/\text{Si})^{\eta} \left( 1 - \frac{D_f}{D_p} \right)^{-\eta(3-n_f)}$$

in which $k = (k'_A/k'_B)^{1/(2j)}$, $q = -1/(2j)$, $r = (B_1 - A_1)/(2j)$, and $s = (B_2 - A_2)/(2j)$. We consolidated the unknown dimensionless coefficients and variables into the coefficient $k$, and exponents $q$, $r$, and $s$. $D_f$ appears on both sides of Equation (10), so we simplified the equation by assuming $D_f \gg D_p$:

$$D_f = k\eta \left( C \theta^2 (1-\theta)^2 \right)^{\eta} (\text{Al}/\text{Si})^{\eta}$$

The assumption $D_f \gg D_p$ makes $D_f$ independent of $D_p$ in Equation (11) and implies a model domain of validity of intermediate fluid shear such that $D_f$ does not converge to $D_p$. We validated the assumption through analysis of our field data compilation (Section 4.1). The equilibrium $D_f$ model is plausible in rivers because experiments and field studies have shown the time scale for unsteady floc behavior to reach equilibrium in river conditions is typically on the order of tens of minutes to hours, and most dynamic river processes (e.g., floods) have longer time scales (e.g., Bungartz et al., 2006; Garcia-Aragon et al., 2011).

Floc settling velocity, $w_{s,floc}$, relates to $D_f$ using an adaptation of the Stokes settling law for flocs (Strom & Keyvani, 2011; Winterwerp, 1998) as

$$w_{s,floc} = \frac{R_g D_f^2}{c_1 v} \left( \frac{D_f}{D_p} \right)^{n_f-1}$$

(12)

Substituting Equation (11) into Equation (12) yields a model for $w_{s,floc}$

$$w_{s,floc} = \frac{R_g D_p}{c_1 v} \left[ k \frac{\eta}{D_p} \left( C \theta^2 (1-\theta)^2 \right)^{\eta} (\text{Al}/\text{Si})^{\eta} \right]^{n_f-1}$$

(13)

Flocs have irregular shapes and variable porosity which complicate the relationship between floc diameter and settling velocity (van Leussen, 1988). In Equation (13), the effects of floc shape and porosity on $w_{s,floc}$ are captured in the dimensionless parameters $c_1$ and $n_f$. We held them constant at $c_1 = 20$ (Strom & Keyvani, 2011; Winterwerp, 1998) and $n_f = 2$ (Kranenburg, 1994; Tambo & Watanabe, 1979). Combining these assumptions with Equation (13) yields

$$w_{s,floc} = \frac{R_g D_p}{20v} k\eta \left( C \theta^2 (1-\theta)^2 \right)^{\eta} (\text{Al}/\text{Si})^{\eta}$$

(14)

Equation (14) demonstrates that different $c_1$ values do not affect model calibration because model fitting absorbs multiplicative constants into the prefactor $k$. However, different $n_f$ values affect model calibration because Equation (13) depends nonlinearly on $n_f$, an effect we explored in sensitivity tests (Section 4.2).
3. Field Data Methods

3.1. River Suspended Sediment Concentration-Depth Profiles

We compiled a data set of grain size-specific suspended sediment concentration-depth profiles containing 122 profiles from 12 rivers distributed globally (Table S1 in Supporting Information S1). We targeted datasets with suspended sediment concentration for multiple heights in the water column, laser-diffraction grain size analysis, water depth, and boundary shear velocity data. We used datasets analyzed by de Leeuw et al. (2020) and Lamb et al. (2020), and included additional datasets (Abraham et al., 2017; Baronas et al., 2020; Bouchez, 2022; Bouchez, Lupker et al., 2011, 2012; Dingle, 2021; Dingle et al., 2020) (Table S1 in Supporting Information S1).

Having a detailed grain size distribution for each suspended sediment sample is vital because it permits the construction of concentration-depth profiles for every grain size class (denoted i). We refer to these profiles as grain size-specific concentration-depth profiles. In other words, a single profile of suspended sediment samples yields as many grain size-specific concentration-depth profiles as there are measured grain size classes. We took advantage of grain size data to fit the Rouse-Vanoni equation and invert for in situ settling velocity as a function of the measured grain size (Figure 1). The measured grain sizes are those of unflocculated sediment (i.e., the primary particles) because size distribution measurements were made after dispersing the sediment (e.g., Baronas et al., 2020).

The Rouse-Vanoni equation is

\[ C_i(z) = C_{i0} \left( \frac{h - z}{h - h_b} \right)^{\beta_i} \]

(15)

in which the volumetric sediment concentration for the ith grain size class, \( C_i \), is a function of height from the bed, \( z \), water depth, \( h \), and a near-bed concentration, \( C_{i0} \), specified at a near-bed height, \( z = h_b \) (Rouse, 1937). The Rouse number (dimensionless) is

\[ p = \frac{w_s}{u_*} \beta \]

in which \( \kappa = 0.41 \) is the von Kármán constant (dimensionless), \( u_* \) (m s\(^{-1}\)) is the boundary shear velocity, \( w_s \) (m s\(^{-1}\)) is the sediment settling velocity, and \( \beta \) is the ratio of sediment and fluid diffusivities (Rouse, 1937) where \( i \) indexes the grain size class. Following de Leeuw et al. (2020) and Lamb et al. (2020), we fitted Equation (15) to the compiled grain size-specific concentration-depth profiles to estimate \( C_{i0} \) and \( p \) for each grain size class. We estimated \( p \) and \( C_{i0} \) (at \( z = h_b = 0.1 \) h) from fitting the log-transformed Equation (15) using ordinary least squares regression. We computed the 68% confidence intervals on the fitted \( p \), from the regression and discarded profiles in which the lower confidence bound on \( p \) is negative because these profiles do not follow Rouse-Vanoni theory for unknown reasons (e.g., non-equilibrium sediment transport, sampling and/or measurement errors).

We needed to specify \( u_* \) and \( \beta \) to estimate the grain size-specific in situ settling velocity, \( w_{si} \), from the fitted value of \( p \). We used \( u_* \) reported in the original data sources, which were measured concurrently with suspended sediment samples and typically calculated by fitting flow velocity profiles measured using an acoustic Doppler current profiler to the law of the wall (e.g., Wilcock, 1996). \( \beta \) is a major unknown in calculating settling velocities from fitted Rouse numbers (e.g., de Leeuw et al., 2020). Empirically, \( \beta \) is commonly found to increase with \( w_s/u_* \) (de Leeuw et al., 2020; Graf & Cellino, 2002; Santini et al., 2019; van Rijn, 1984). \( \beta < 1 \) corresponds to greater sediment concentration stratification compared to \( \beta = 1 \), which could result from turbulence damping due to suspended sediment-induced density stratification (Graf & Cellino, 2002; Wright & Parker, 2004; discussion in de Leeuw et al., 2020). The reasons for \( \beta > 1 \) are less clear, but might be linked to enhanced mixing from bedform-generated turbulence (Graf & Cellino, 2002) or the high vertical concentration gradient of fast-settling particles promoting sediment diffusion relative to eddy diffusion (Smith & McLean, 1977).

We followed de Leeuw et al. (2020) and empirically fitted functions for \( \beta \), using only suspended sand because we assumed sand was unflocculated and settled in situ at theoretical settling velocities. To calculate theoretical sand settling velocities, we used the Ferguson and Church (2004) model (that is,

\[ w_s = \frac{R_g D^2}{c_{sand} + \sqrt{0.75c_{sand} R_g D^2}} \]

with \( c_{sand} = 20 \) and \( c_{sand} = 1.1 \), which follows Stokes law for small particles and accounts for inertial affects for large particles. We calculated \( \beta \) using these theoretical sand settling velocities, \( u_* \), and the fitted \( p \). We found values of \( \beta \) and \( w_s/u_* \) that agree with previously proposed relations for \( \beta(w_s/u_*) \) (Figure 2). Next, we calibrated the power-law equation \( \beta \propto (w_s/u_*)^\gamma \) on the sand...
data within each concentration-depth profile, resulting in a fitted equation for each concentration-depth profile. The median coefficient of determination of the fits is 0.88, indicating a good fit. We assumed that the profile-specific functions \( \beta_i = \beta(w_i/u_s) \), calibrated on the sand data, were valid for the mud data and extrapolated the fitted \( \beta_i \) functions to calculate \( w_s \) for the mud size classes (Lamb et al., 2020). We did not explicitly account for the potential effect of hindered settling because 93% of concentration-depth profiles analyzed had mud concentration <5% solids by volume for which hindered settling and density-induced stratification are not expected to be important (Gratiot et al., 2005). However, if hindered settling affected the data, it is implicitly included in our fit values of \( \beta_i \).

### 3.2. Extracting River Floc Data

We inferred floc settling velocity, \( w_{s, \text{floc}} \), by examining the relationship of particle diameter, \( D_p \), and the in situ settling velocity, \( w_s \), calculated from fitting the Rouse-Vanoni equation to the concentration-depth profile data. We found good agreement between the Rouse-estimated and predicted settling velocities for sand, but a continuous transition to a settling velocity plateau larger than the theoretical predictions for coarse silt and clay (Figure 3). We attributed the elevated settling velocity of coarse silt and clay to flocculation (Lamb et al., 2020). We found a best-fit two-part piecewise function to quantitatively describe these two settling regimes for each concentration-depth profile (Figure 3; see Text S1 in Supporting Information S1 for details on the fitting method). We termed the diameter at the regime transition the floc cutoff diameter, \( D_f \), and interpreted all sediment finer than \( D_f \) to be flocculated with a constant \( w_{s, \text{floc}} \) for each concentration-depth profile (Lamb et al., 2020, Figure 3).

Next, we computed the floc settling velocity, \( w_{s, \text{floc}} \), and primary particle diameter, \( D_p \), from the flocculated data (\( D < D_f \)). We computed \( w_{s, \text{floc}} \) as the mean in situ settling velocities for \( D < D_f \) (Figure 3). This method is oversimplified because it implies that all sediment in a given size class for \( D < D_f \) was flocculated and settling at the same rate. In reality, some sediment might not have been flocculated and there was likely a distribution of floc sizes and settling velocities in situ (Osborn et al., 2020, 2021), but these distributions cannot be constrained by our data. We also cannot constrain floc structure and the size distribution of the primary particles in individual flocs (e.g., a floc composed of mostly clay might have the same settling velocity as a smaller floc composed of coarse silt with finer sediment bound to its surface). \( D_f \) might vary with depth, so we calculated \( D_f \) as the median grain size for \( D < D_f \) using the depth-averaged concentration of each grain size class as relative weights (Figure 3). We propagated uncertainty to find the 68% confidence intervals for \( w_{s, \text{floc}} \) and \( D_f \) (Figure 3; Text S1 in Supporting Information S1). Some profiles had data gaps because of the data quality filtering (Section 3.1). We discarded concentration-depth profiles in which \( D_f \) was in a data gap greater than one order of magnitude in \( D_f \). 96 concentration-depth profiles, or about 79% of the initial profiles, remained after this filtering.

We estimated floc diameter, \( D_f \), from the flocc cutoff diameter, \( D_f \), which can be interpreted as the diameter of unflocculated grains that settle at the same rate as flocs (Figure 3). Therefore, Stokes law for unflocculated particles applied to \( D_f \) results in

\[
\Delta w_{s, \text{floc}} = \frac{R_g D_f^2}{c_1 v} \tag{16}
\]

combining Equations (12) and (16), we found...
$$D_f = D_p \left( \frac{D_{p}}{D_{f}} \right)^{\frac{2}{n_f - 1}}$$

We used Equation (17) with $n_f = 2$ to calculate $D_f$. We then combined Equations (11) and (17) to derive a model for $D_f$:

$$D_f = k(\eta D_p)^{1/2} \left( C \theta^2 (1 - \theta)^2 \right)^g (\text{Al/Si})^r \Phi^s$$

### 3.3. Estimating Other Variables

We used the depth-averaged volumetric mud concentration, $C_m$, as the representative sediment concentration in the model (Equations 11, 14 and 18) because we expect flocculation to mainly occur within mud. We found the model goodness-of-fit to be insensitive to the choice of total or mud concentration because they are correlated. We chose typical values for river water density, $\rho = 1000$ kg m$^{-3}$, sediment density, $\rho_s = 2650$ kg m$^{-3}$, and kinematic viscosity of water, $\nu = 10^{-6}$ m$^2$ s$^{-1}$. We calculated the Kolmogorov microscale using $\eta = \left[ \frac{(x_k \nu^3)}{(u'_h(h-z))}\right]^{1/4}$ for open-channel flow (Nezu & Nakagawa, 1993). The near-bed (at $z = h_b = 0.1 h$) and depth-averaged $\eta$ did not vary significantly from each other (within a factor of about 2), so we used the near-bed $\eta$ in our calculations.

Most data sources for the concentration-depth profiles do not have the requisite geochemical measurements to evaluate the floc model. To supplement, we compiled river geochemistry data from other sources for the same rivers (Table S2 in Supporting Information S1). We matched geochemical measurements to each profile by finding the closest measurements in terms of geographic distance and time of year, weighted equally. The median deviations of the concentration-depth profiles and matched geochemical measurements in time and space are about 4 days and 22 km (or about 54 channel widths). Although these sources of error are difficult to quantify, they should be considered together with the results.

Al/Si is commonly measured for suspended sediment samples, but almost all Al/Si values are measured in bulk without grain size distinction. We compiled and used bulk suspended sediment Al/Si measurements for fitting the model.

We compiled measurements of percent weight organic carbon of suspended sediment samples to estimate $\theta$, the average fraction of sediment covered by organic matter. We assumed cellulose organic matter composition (molar ratio C:H:O of 6:10:5) because it is the most abundant organic compound in the terrestrial biosphere (e.g., Brigham, 2018). We converted measured percent weight organic carbon into percent weight organic matter as cellulose, %OM, using molar mass ratios. Although organic matter usually adsorbs onto sediment in irregular patches (e.g., Ransom et al., 1997), we assumed for simplicity that the volume of organic matter, $V_{OM}$, is hosted uniformly on the surface of spherical grains with diameter $D_p$ in a shell with volume $V_{shell}$ and thickness $\delta$. With these assumptions, we obtained

$$\theta = \frac{V_{OM}}{V_{shell}} = \frac{(\%OM/100) \cdot \frac{\rho_s}{\rho_{OM}} D_p^3}{(D_p + \delta)^3 - D_p^3}$$

We assumed neutrally buoyant organic matter, $\rho_{OM} = 1000$ kg m$^{-3}$, and $\delta = 10^{-6}$ m (Barber et al., 2017; Hackley et al., 2017). Measurements of $\theta$ for river suspended sediment are unavailable, so we chose $\delta$ to obtain $\theta$ consistent with $\theta \sim 0.15$ for marine sediment (Bock & Mayer, 2000; Mayer, 1999).

To estimate relative charge density, $\Phi$, we compiled major ion concentrations in rivers (cations: Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$; anions: HCO$_3^-$, SO$_4^{2-}$, Cl$^-$). We calculated the molar ionic strength, $I$, using dissolved ion concentration measurements as $I = 0.5 \sum c_i z_i^2$ in which $c_i$ is the molar concentration of the $i$th ion and $z_i$ is its charge number. The Debye length, $\lambda$, is expressed as:

$$\lambda = \left( \frac{e_0 e k_B T}{2 \varepsilon_r \varepsilon_0 \text{cation}} \right)^{1/2}$$
\( \lambda \) is a function of vacuum permittivity, \( \varepsilon_0 = (8.854 \times 10^{-12} \text{ F m}^{-1}) \), dielectric constant of water, \( \varepsilon_\text{r} \) (dimensionless), Boltzmann constant, \( k_\text{B} = (1.381 \text{ J K}^{-1}) \), water temperature, \( T \) (°C), elementary charge magnitude, \( e \) \((=1.602 \times 10^{-19} \text{ C})\), cation charge number, \( z_\text{cation} \), and cation concentration, \( x_\text{cation} \) (Rommelfanger et al., 2020). We assumed \( T = 15^\circ\text{C} \) if it was not reported. We used a temperature-dependent formula to compute \( \varepsilon_\text{r} \) (Owen et al., 1961). We calculated \( z_\text{cation} \) from the reported cation concentrations and summed them to obtain \( x_\text{cation} \). Due to data gaps, we estimated sediment CEC (mol kg\(^{-1}\)) from the percent clay of the depth-averaged concentration for each profile using (Ersahin et al., 2006)

\[
\text{CEC} = 4.97 + 0.53 \%\text{clay}
\]  

(21)

in which \%\text{clay} is the percentage by weight of the total suspended sediment concentration with particle diameters smaller than 2 μm. Equation (21) assumes grain size is a suitable mineralogy proxy to compute CEC.

### 4. Results

#### 4.1. Floc and Physicochemical Parameters

Results for mud demonstrate an orders-of-magnitude departure of in situ settling velocities, inferred from concentration-depth profile fitting, from predicted settling velocities of unflocculated mud (Figure 4a). Physically, faster mud settling velocity causes a more stratified suspended mud concentration-depth profile (Figure 4b). For example, the Rouse-Vanoni equation predicts particles with \( D_p = 2 \) μm should be nearly uniformly mixed in the water column. However, the data show similar stratification between mud and sand profiles (Figure 4b). We interpreted elevated mud settling velocities as a signature of mud flocculation (Lamb et al., 2020).

We estimated the floc cutoff diameter, \( D_f \), primary particle diameter, \( D_p \), floc diameter, \( D_f \), and floc settling velocity, \( w_s,\text{floc} \), for each concentration-depth profile using our piecewise function fits in \( D_w,\text{floc} \) space (summarized in Table 1). The medians indicate that suspended sediment in rivers with diameter smaller than \( D_f = 39 \) μm (half the interquartile range, IQR/2 = 22 μm) is flocculated into aggregates with diameter \( D_f = 130 \) μm (IQR/2 = 100 μm), settling rates of \( w_s,\text{floc} = 1.8 \text{ mm s}^{-1} \) (IQR/2 = 1.7 mm s\(^{-1}\)), and primary particle diameter of \( D_p = 12 \) μm (IQR/2 = 4.5 μm). The estimated \( w_s,\text{floc} \) and \( D_f \) indicate a median floc density of \( \rho_\text{floc} = 1100 \text{ kg m}^{-3} \) (IQR/2 = 160 kg m\(^{-3}\)) using Equation (12). As expected, the \( \rho_\text{floc} \) estimates are much smaller than the mineral sediment density (\( \rho_s = 2650 \text{ kg m}^{-3} \)) because flocs contain lighter organic matter and pores. We found
Table 1

<table>
<thead>
<tr>
<th>Variable</th>
<th>Median</th>
<th>IQR/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Floc cutoff diameter, D_f (μm)</td>
<td>39</td>
<td>22</td>
</tr>
<tr>
<td>Floc settling velocity, w_floc (mm s^-1)</td>
<td>1.8</td>
<td>1.7</td>
</tr>
<tr>
<td>Floc diameter, D_f (μm)</td>
<td>130</td>
<td>100</td>
</tr>
<tr>
<td>Primary particle diameter, D_p (μm)</td>
<td>12</td>
<td>4.5</td>
</tr>
<tr>
<td>Floc density, ρ_floc (kg m^-3)</td>
<td>1100</td>
<td>160</td>
</tr>
<tr>
<td>Kolmogorov microscale, η (μm)</td>
<td>170</td>
<td>26</td>
</tr>
<tr>
<td>Depth-averaged mud volumetric concentration, C_m</td>
<td>1.8 × 10^{-3}</td>
<td>4.7 × 10^{-3}</td>
</tr>
<tr>
<td>Fraction of sediment surface covered by organic matter, θ</td>
<td>0.070</td>
<td>0.039</td>
</tr>
<tr>
<td>Suspended sediment Al/Si [molar ratio]</td>
<td>0.23</td>
<td>0.081</td>
</tr>
<tr>
<td>Relative charge density, Φ</td>
<td>2.9 × 10^{-8}</td>
<td>3.4 × 10^{-8}</td>
</tr>
</tbody>
</table>

Note. We used half the interquartile range (IQR/2) as a robust measure of spread.

$D_f/D_p = 0.097$ (IQR/2 = 0.057), resulting in a negligible difference between Equations (10) and (11) and justifying the assumption of $D_f \gg D_p$ in the model derivation (Figure 5).

Our finding of $D_f = 39$ μm is similar to the finding of $D_f = 40$ μm by Lamb et al. (2020) even though they used a different method to calculate $D_f$. Tests with different $D_f$ formulations also demonstrate limited effect on $w_f$ and yield the same general pattern of in situ settling velocity versus particle diameter (Text S2; Figure S1 in Supporting Information S1). Although in situ river floc data are rare, Osborn et al. (2020) deployed an in situ camera in the Mississippi river and observed flocs with $D_f$ of 70–130 μm, a range also consistent with our $D_f$ estimates.

The Kolmogorov microscale, η, has been proposed as an upper bound on floc diameter, $D_f$, because flocs can be efficiently broken by turbulence once they grow to the size of the smallest eddies (e.g., Kuprenas et al., 1979; Tambo & Hozumi, 1979; van Leussen, 1988). We found a narrow range of η in our compilation with a typical value of 200 μm (Figure 6a). $D_f$ estimates are typically of the same scale or smaller than η, indicating that η might limit $D_f$ (Figure 5). However, the data suggest that floc size is not strictly turbulence-limited and can increase beyond η (36% of the data), perhaps due to other physicochemical factors that can be explained by the model (see discussion in Section 4.3) and/or uncertainties in calculating $D_f$ (Equation 17; Section 4.2). Conversely, the cases in which $D_f$ is smaller than η motivate examining effects of sediment concentration and mineralogy, organic matter, and water chemistry on flocculation (Section 4.2).

4.2. Floc Model Calibration

We used sediment Al/Si, depth-averaged volumetric mud concentration, $C_m$, fraction of sediment surface covered by organic matter, θ, relative charge density, Φ, and primary particle diameter, $D_p$, as independent variables to calibrate the model (Figure 6). Sediment Al/Si ranges from 0.2 to 0.5 (molar ratio) and generally increases with river drainage area (Figure 6b)—a pattern that could reflect production of more Al-rich clay minerals with progressive silicate weathering downstream (e.g., Lupker et al., 2012; West et al., 2005). Depth-averaged volumetric mud concentration, $C_m$, varies widely across rivers on the order of $10^{-5}$ to $10^{-2}$, a range that likely reflects regional variation in catchment lithology, sediment supply, and transport capacity (Figure 6c). The fraction of sediment surface covered by organic matter, θ, is typically close to 0.1 (Figure 6d). The relative charge density, Φ, largely varies between $10^{-8}$ and $10^{-7}$ for our data compilation (Figure 6e) and is a function of weathering contributions to river water ion concentration and electrostatic properties of sediment. Primary particle diameter, $D_p$, generally...
decreases with drainage area (Figure 6f), consistent with downstream grain size fining due to sorting and abrasion (Paola et al., 1992).

We fitted the floc diameter, settling velocity, and cutoff diameter models (Equations 11, 14, and 18) to our $D_f$, $w_{s,\text{floc}}$, and $D_t$ estimates, respectively (Figure 7; Table 2). The calibrated models with best-fit parameters are:

$$D_t = 0.0187(\eta D_p)^{1/2}(C_m \theta^2 (1 - \theta)^2)^{0.0797}(\text{Al}/\text{Si})^{-0.792}\Phi^{-0.211}$$  \hspace{1cm} (22)

$$w_{s,\text{floc}} = \frac{R_g D_p}{20\nu} 0.0284(\eta C_m \theta^2 (1 - \theta)^2)^{0.162}(\text{Al}/\text{Si})^{-2.22}/\Phi^{-0.133}$$  \hspace{1cm} (23)

$$D_f = 3.50 \times 10^{-4} \eta (C_m \theta^2 (1 - \theta)^2)^{0.142}(\text{Al}/\text{Si})^{-1.58}/\Phi^{-0.422}$$  \hspace{1cm} (24)

Figure 6. Boxplots of model input variables classified by river. Boxplots that appear as a horizontal line segment contain only a single data point. River names are ordered by increasing drainage area at the sample collection point, measured using HydroSHEDS digital elevation data (Lehner et al., 2008). Amazon Basin Rivers are plotted separately in order of increasing drainage area.
The majority of the profiles in our compilation was sampled in lowland alluvial rivers, so application of the calibrated model is most appropriate for those settings. The high model goodness-of-fit supports the equilibrium floc assumption in the model (Figure 7; Table 2).

Although the three models are dependent, we fitted the regressions independently of each other because the \( D_w \), \( w_{s,floc} \), and \( D_f \) models each include different assumptions. The \( D_f \) model is the most direct evaluation of the proposed model parameters because we directly estimated \( D_f \) from the concentration-depth profiles (Figure 3) and it is independent of \( c_1 \) (Equations 17 and 18), yielding the highest goodness-of-fit among the models (coefficient of determination, \( R^2 = 0.685 \); root mean square error, RMSE = 26.91 μm). We assumed \( n_f = 2 \) to derive the \( D_f \) model (Equation 17), but model calibrations with different choices of constant \( n_f \) show that \( n_f \) has a negligible effect on overall goodness-of-fit and minimal effect on calibrated model exponents (Text S3; Figure S2 in Supporting Information S1). Similarly to \( D_w \), we estimated \( w_{s,floc} \) directly (Figure 3) and assumed \( n_w = 2 \) to derive the model (Equation 14). But, in addition, we assumed a constant \( c_1 = 20 \) (Ferguson & Church, 2004; Strom & Keyvani, 2011) to derive the \( w_{s,floc} \) model (Equation 14), leading to a reduction in the goodness-of-fit (\( R^2 = 0.611; \) RMSE = 2.03 mm s\(^{-1}\)) compared to the \( D_f \) model. In contrast to the direct \( D_w \) and \( w_{s,floc} \) estimates, \( D_f \) was calculated from \( w_{s,floc} \) or \( D_w \). We assumed \( n_f = 2 \) to calculate \( D_f \) from \( D_w \) (Equation 17), causing a relatively large drop in goodness-of-fit (\( R^2 = 0.357; \) RMSE = 227.1 μm) relative to both the \( D_f \) and \( w_{s,floc} \) models despite the fact that the \( D_f \) model is independent of \( c_1 \) and \( n_f \) (Equation 11). The differences in goodness-of-fit between the three models indicate the importance of constraining \( c_1 \) and \( n_f \) which depend on floc shape and structure (Maggi et al., 2007; Strom & Keyvani, 2011). We calculated the ratio of model predictions and data and took quantiles at 16%, 50% (median), and 84% to characterize the deviation of predictions from the data. We computed quantiles of this ratio at \([0.60 (16%), 1.1 (50%), \) and 1.5 (84%)] for \( D_f \), \([0.48, 1.0, \) and 2.1] for \( w_{s,floc} \), and \([0.36, 1.2, \) and 2.1] for \( D_w \). These results show that the model explains the data within factors of about 1.7 for \( D_f \), 2 for \( w_{s,floc} \), and 2.5 for \( D_w \) (Figure 7).

All model exponents (\( q, r, \) and \( s \)) are significantly different than 0 according to the 95% confidence interval (0.05 significance level) except for the exponent of \( \Phi \) in the \( w_{s,floc} \) model (Table 2). The reason for the statistical insignificance of \( \Phi \) in the \( w_{s,floc} \) model is unclear, but might be related to errors in assuming constant \( c_1 \) or in matching geochemical measurements to the concentration-depth profiles. The statistical significance of the remaining parameters supports the hypothesis that organic matter, sediment concentration and mineralogy, water chemistry, and turbulence are important predictors of floc properties in rivers.

### 4.3. Floc Model Dependencies and Interpretation

To isolate the effect of individual parameters on floc settling velocity, we plotted each parameter against the \( w_{s,floc} \) data normalized by all other model terms (Figure 8). We also divided by the median for each normalized quantity to provide comparable scales. The gross trends between individual parameters and \( w_{s,floc} \) are similar to those for \( D_f \) and \( D_w \) (Figures S3 and S4 in Supporting Information S1).

The Kolmogorov microscale, \( \eta_t \), expresses the effect of turbulence on flocs and is predicted to have a positive linear relationship with \( w_{s,floc} \) and \( D_f \) (Figure 8a; Figure S4a in Supporting Information S1: Winterwerp, 1998). We tested the plausibility of the relationship between (normalized) \( w_{s,floc} \) and \( \eta_t \) (e.g., the trend in Figure 8a) using...
regression $F$-tests of the linear relation and an alternative power-law relation. We found a statistically significant linear relationship between normalized $w_{s,floc}$ and $\eta$ ($p$-value $= 7.8 \times 10^{-10}$) and a statistically insignificant power-law relationship ($p$-value $= 0.33$). The linearity between $D_f$ and $\eta$ agrees with the steady-state equilibrium form of the Winterwerp model (Kuprenas et al., 2018; Winterwerp, 1998).

Mud concentration, $C_m$, displays a positive sublinear trend with $w_{s,floc}$ (exponent $= 0.162 \pm 0.0905$; Figure 8b) in contrast to the linear trend predicted by the equilibrium model of Winterwerp (1998). The equilibrium Winterwerp model predicts a linear trend between sediment concentration and floc settling velocity because greater sediment concentration results in proportionally greater interparticle collisions. However, there is a different scaling relation in our model because we allowed the exponent $j$, which controls the importance of floc strength on the floc breakup rate, to vary (Equations 10 and 11). Inspecting Equation (11), linearity between $C_m$ and $w_{s,floc}$ occurs only when $j = -0.5$, or $D_f \propto (\tau_f/\tau_i)^{0.5}$, while our calibration indicates that $j = -3.09$, or $D_f \propto (\tau_f/\tau_i)^{−0.6}$, which in turn reveals $(\tau_i/\tau_f)^{0.09} \propto (D_f/\eta)^{−2}$. Thus, our calibrated model indicates that the floc breakup rate becomes very large when $D_f > \eta$—much more so than in the Winterwerp model. This finding is consistent with the limiting effect of $\eta$ on floc size proposed by Kuprenas et al. (2018). But in contrast to their work, our model does not feature a built-in turbulence limit. Rather, $D_f$ can exceed $\eta$, but the rapid breakage rates for large flocs make $D_f >> \eta$ less likely. In our equilibrium model, the strong dependence of $D_f$ on $\eta$ effectively reduces the strengths of dependency on the other input variables. In the case of $C_m$, fluid shear stresses inhibit the efficiency of sediment concentration to drive floc growth. Thus, although the aggregation rate still depends linearly on $C_m$ in our model, we found a sublinear dependence on $C_m$ for floc diameter and settling velocity.

Organic matter affects flocculation through the fractional cover of organic matter on the surface of sediment grains, $\theta$, according to the function $(\theta^2 (1-\theta)^y)$ with an exponent, $q = 0.162 \pm 0.0905$, identical to that of $C_m$ (Figure 8c). The shared exponent, $q$, indicates an analogous interpretation: turbulence can promote floc breakage and disrupt the ability of organic matter to facilitate bonding between particle surfaces. Most data display $\theta < 0.5$, a regime in which the function $\theta (1-\theta)$ increases with $\theta$. In this domain, the model predicts that increased loading of organic matter promotes larger $w_{s,floc}$ because the areas of bare sediment and organic matter become more comparable for binding. The positive sublinear exponent implies that increasing organic matter coverage on sediment causes a much larger enhancement of floc size at low $\theta$ compared to high $\theta$ (but still less than 0.5). Thus, the addition of even small amounts of organic matter to an organics-poor system can trigger an appreciable flocculation response, consistent with experiment results (Zeichner et al., 2021).

The model predicts a reverse effect for organics-rich systems, but the sparsity of data for $\theta > 0.5$ precludes confirmation of this behavior.

Sediment Al/Si shows a decreasing trend with $w_{s,floc}$ (exponent $r = −2.22 \pm 0.916$; Figure 8d). The negative relationship with Al/Si is surprising because Al/Si is typically treated as a clay abundance proxy and clay is expected to be the grain size fraction most susceptible to flocculation (e.g., Mehta & Partheniades, 1977; Van Leussen, 1988). Equation (10) shows that $r = (B_i−A_i)/(2j)$ where $A_i$ and $B_i$ are the respective power-law aggregation and breakage exponents (Equations 4 and 5). We found $j = −3.09$, $r = −2.22$, and hence $B_i−A_i \cong 13.7$, which indicates that the negative trend between Al/Si and $w_{s,floc}$ occurs because the breakage rate exponent exceeds the aggregation rate exponent ($B_i > A_i$). We expect that $A_i$ is positive because Al/Si is correlated with higher clay mineral abundance, and clays with stronger surface charges promote flocculation (Mehta & McAnally, 2008; van Olphen and Hsu, 1977). If $A_i > 0$, then our analysis implies that $B_i > 13.7$. In other words, the floc breakage rate is increasingly sensitive to Al/Si at greater values of Al/Si. We speculated two explanations. First, Equation (16) shows that $w_{s,floc} \propto A_i^j$, suggesting that the inclusion of progressively coarser sediment into flocs has a strong control on increasing floc settling velocity and vice versa. Clay might flocculate more readily than coarser sediment because it is more cohesive, so greater clay abundance (correlated with greater Al/Si) might cause clay-rich flocs and exclude coarser grain sizes (smaller $D_f$) thus reducing floc settling velocity. For a given floc size, flocs composed of smaller, high Al/Si primary particles must necessarily have more interparticle contacts and thus may be more fragile and prone to breakage in a turbulent fluid. We found evidence for this idea in the fact that (normalized) floc cutoff diameter varies inversely with Al/Si, indicating coarser grain sizes were increasingly excluded from flocs at higher Al/Si (Figure 9a).

A second possible reason for the greater sensitivity of floc breakup to larger Al/Si could be tied to the prevalence of a flat orientation of adsorbed organic matter on sediment. This orientation might be common in sedi-
ment with high specific surface area, like high Al/Si clay, because they have more adsorption sites to increase the chance of organic matter adsorbing to multiple sites on the same grain. However, a flat orientation is less effective for flocculation due to the lower probability of organic matter interacting with nearby particles (Gregory, 1978; Healy & La Mer, 1962). Thus, clay might have diminished sensitivity of floc aggregation to Al/Si (smaller $A_j$) and weaker floc structure (larger $B_j$). A flat orientation might also be less effective at capturing and retaining larger grains in flocs. Polymer chemistry and structure could also play a role by setting the binding strength to

Figure 8. Individual parameters plotted against floc settling velocity, $w_{s, \text{floc}}$, data normalized by the effects of all other predictors in the fitted $w_{s, \text{floc}}$ model (Equation 23). In all panels, the solid line, labeled in panel a, indicates the fitted relationship (Table 2). In panel b, the dashed line is the prediction from the equilibrium Winterwerp model. Error bars represent the propagated 68% confidence interval.
surface sites through mineralogy-specific interactions (Furukawa et al., 2014; Hemingway et al., 2019; Zeichner et al., 2021).

The relative charge density, $\Phi$, displays a negative correlation with $w_{s,floc}$ (exponent $s = -0.133 \pm 0.253$; Figure 8e). This relationship opposes the conventional idea that greater salinity enhances flocculation (e.g., Mehta & McAnally, 2008; van Leussen, 1988). The exponent on $\Phi$ is defined as $s = (B - A)/(2j)$ (Equation 10) where $A$ and $B$ are the respective power-law aggregation and breakage exponents (Equations 7 and 8). Similar to the rationale for interpreting Al/Si, we estimated $j = -3.09$ so we must have $B > A$. We again expected $A > 0$ because greater ionic strength and $\Phi$ typically increase the ability of van der Waals attraction to aggregate sediment grains in the perspective of salinity-driven flocculation (Mehta & McAnally, 2008; Seiphoori et al., 2021). Assuming $A > 0$, we have $B > 0.82$. Although flocs are more sensitive to breakage with increasing salinity only if $B > 1$, we expected that $B$ indeed exceeds 1 because $B > 1$ is consistent with the $D_t$ and $D_f$ models where the estimated $s$ is statistically significant. We propose that salinity could have similar interactions as Al/Si on floc size and settling velocity. First, greater ionic strength should primarily affect the flocculation of clay, on which negative surface charges are concentrated compared to coarser grain sizes. However, the bulk of mud in rivers is silt, for which ionic effects should be weaker (Table 2). Thus, larger $\Phi$ might preferentially flocculate clay, rather than silt, leading to more fragile flocs with a greater number of contact points. The inverse relationship between $D_t$ and $\Phi$ is consistent with clay enrichment by excluding coarser silt from flocs at larger $\Phi$ (Figure 9b). Second, higher $\Phi$ could affect the physical organic matter orientation and organic matter binding capacity on sediment (e.g., through competition of ions and organic matter for binding sites on sediment surfaces).

In summary, the model calibration reveals that, out of the fitted parameters, $D_t$, $w_{s,floc}$, and $D_f$ in rivers are most sensitive to sediment Al/Si and relative charge density, $\Phi$, because their exponent magnitudes are largest (Table 2). This fact should not be interpreted to mean that $C_m$ and $\theta$ are less important mechanistically for flocculation because these variables might be correlated, a possibility that is masked in our calibration. The model also depends on $\eta$ to a relatively large positive power ($0.5$ for $D_t$; $1$ for $w_{s,floc}$, and $D_f$) based on theory.

### 5. Discussion

Our results show that mud flocculation is widespread in rivers from geographically diverse regions spanning heterogeneous catchment lithologies and climates. Here we considered how flocculation might interplay with mud transport kinematics, channel morphology, organic carbon, tectonics, and climate.
Figure 10. Empirical cumulative distribution function of river floc settling velocity estimates from the suspended sediment concentration-depth profile data compilation. The vertical lines indicate possible bounds on floc settling velocity in rivers: at 1-μm clay and at Kolmogorov microscale, \( n \), of 200 μm typical of rivers and assuming solid particles (\( n = 3 \)). We computed the settling velocity bounds using the model of Ferguson and Church (2004) (Section 3.1).

5.1. Mud Transport Kinematics

Flocculation in rivers greatly increases mud settling velocity up to orders-of-magnitude larger than rates for individual particles (Figure 4a). The total range of observed floc settling velocities is likely set by the primary particle diameter and Kolmogorov microscale. The minimum floc settling velocity simply occurs in the limit of increasingly fewer primary particles until the floc converges to a single particle settling according to Stokes theory. For an upper bound, prior work suggests that the Kolmogorov microscale sets the maximum floc diameter (e.g., Coufort et al., 2005; Kumar et al., 2010; Kuprenas et al., 2018). Our data compilation indicates a typical Kolmogorov microscale of 200 μm with a relatively narrow distribution across different rivers (Figures 5 and 6; Table 1), from which we calculated a maximal floc settling velocity assuming a solid particle (\( n = 3 \); Figure 10). Our data support the plausibility of these bounds because they bracket all of our floc settling velocity observations (Figure 10).

Enhanced mud settling velocity due to flocculation reduces mud advective transport lengths, with implications for setting the spatial distribution and rates of mud accretion and retention in depositional zones (e.g., floodplains, deltas, wetlands). The enhanced settling velocity of mud flocs might also cause mud to be exchanged between the flow and bed as suspended bed-material load rather than washload in alluvial rivers (Lamb et al., 2020). As a result, a dynamic equilibrium of suspended mud in rivers could lead to predictive mud flux models based on bed grain size distribution as are common for cohesionless sediment (Lamb et al., 2020; Ma et al., 2020).

5.2. River Channel-Scale Geomorphology

We found Kolmogorov microscale to be an important predictor of floc parameters relative to other factors, scaling linearly with floc settling velocity and diameter (Table 2). Channel hydraulic geometry (e.g., water depth and channel slope) controls the observed variation in shear velocity and Kolmogorov microscale between sites. Extremes in shear velocity inhibit mud flocculation because more intense turbulence reduces Kolmogorov microscale and less turbulent flows are less effective at suspending sediment and driving particle collisions. All else being equal, floc diameter and settling velocity might peak at moderate flows and shear velocities leading to higher relative contribution to mud accretion at those conditions. For example, repeat concentration-depth profiles sampled from 2012 to 2014 in the Fraser river show, at an intermediate flow, maximum floc settling velocity about 2.5 times greater than that at the lowest and highest flows (Environment Canada, 2021; Haught et al., 2017, Figure 11). Discharge also covaries with other biogeochemical factors in rivers, complicating the relationship between discharge and floc properties. For instance, floods tend to dilute dissolved load concentrations (e.g., Torres et al., 2015), which could promote larger flocs and offset floc breakage.

Faster mud settling due to flocculation could contribute to finer channel-proximal deposits during overbank flow (Zeichner et al., 2021), and might help explain the existence of muddy levees (e.g., Adams et al., 2004; Nicholas & Walling, 1996). More cohesive channel-proximal deposits strengthen banks and limit channel lateral migration rates (Ielpi & Lapôtre, 2019; Peakall et al., 2007; van Dijk et al., 2013), thereby establishing a morphodynamic feedback between mud deposition and the long-term evolution of channel and floodplain morphology (Dunne & Jerolmack, 2020; Lapôtre et al., 2019). Mud flocculation could thus be an important control on equilibrium channel width in lowland alluvial rivers and river planform geometry. Over geologic time, mud flocculation could influence the development of alluvial stratigraphic architecture (Mackey & Bridge, 1995; Nicholas & Walling, 1996). More cohesive banks might favor aggradation and avulsion rather than lateral migration, leading to a mudrock-dominated alluvial architecture with sparse

Figure 11. Comparison of mean flow velocity and floc settling velocity, estimated from our data compilation, for the Fraser River (Haught et al., 2017). We calculated mean flow velocity from continuity using channel width and depth (Haught et al., 2017) and water discharge at the Mission gaging station (station number 08MH024; Environment Canada, 2021).
sandy channel bodies rather than laterally extensive amalgamated channel belts (Jerolmack & Mohrig, 2007; Zeichner et al., 2021).

More accurate modeling of flocculation across floodplains with relatively slow flow likely requires the time-dependent flocculation model (Equation 9), rather than the equilibrium model on which we focused here for channels. The importance of using the unsteady model relies on the relative timescales of variation in Kolmogorov microscale and floc equilibration to local conditions, which we expect are comparable to each other in floodplains. Key parameters ($n_j, j', k_s', A_1, A_2, B_1, B_2$) remain to be evaluated in the time-dependent model in rivers.

5.3. Organic Carbon

Organic carbon flux in rivers is closely tied to mud because its high specific surface area provides ample sites to host particulate organic carbon (France-Lanord & Derry, 1997; Galy et al., 2008; Schlünz & Schneider, 2000). We found that binding of organic matter to mud is an important predictor for floc diameter and settling velocity through $\theta$. The functional form of $\theta$ in the model indicates an optimum for the largest and fastest-settling flocs at $\theta = 0.5$. The bulk of our $\theta$ estimates lies in the regime of $\theta < 0.5$ in which increasing organic cover leads to larger floc size and settling velocity (Figure 6d). In this regime, the model predicts that river suspended sediment with greater organic carbon concentration form larger, faster-settling flocs. Thus, there is potential for a feedback in net depositional zones whereby higher organic carbon concentration causes faster floc and organic carbon settling rates, which increase carbon preservation potential (Galy et al., 2007; Hartnett et al., 1998; Torres et al., 2020).

Field and laboratory flocculation studies have indicated that organic matter composition can be important for determining the degree to which organic matter affects flocculation (e.g., Furukawa et al., 2014; Lee et al., 2017; Zeichner et al., 2021), an effect not accounted for in our model. Previous work suggested that bacteria-derived EPS tends to encourage flocculation because its molecular composition and structure can generate a chain-like physical orientation when adsorbed on sediment, while aromatic-rich materials tend to discourage flocculation because they coat sediment evenly and limit interparticle contact between organic matter and bare sediment surfaces (Furukawa et al., 2014; Healy & La Mer, 1962; Lee et al., 2019). Shifts in organic matter composition and/or abundance (i.e., due to changes in terrestrial vegetation, algal productivity, hillslope input of organic detritus) and the covariation of such factors due to climate change and human activity (e.g., Li et al., 2021) could trigger changes in flocculation. Floods are an additional catchment-specific factor for organic matter because floods of different magnitude can source different parts of the catchment (e.g., Dunne & Black, 1970) with different types of organic matter (Golombek et al., 2021).

Our results indicate that greater river water ionic strength, through $\Phi$, reduces floc size in rivers. However, as rivers approach the ocean in estuaries, it is well known that the increasing salinity typically enhances flocculation. The salinity to induce flocculation usually occurs at a few parts per thousand (e.g., Drake, 1976; Einstein & Krone, 1962; Whitehouse et al., 2013), which is an order of magnitude larger than the values measured in rivers in our compilation (median salinity of 0.2 parts per thousand). Given that flocculation appears common in rivers, there could be a process transition from organics-mediated flocculation in freshwater to salinity-mediated flocculation in estuaries. In line with this view, Eisma et al. (1991) analyzed C isotope ratios of suspended sediment organic matter and found a transition in organic matter from freshwater-to marine-origin entering the Gironde estuary. In contrast, data from the Rhine and Elbe estuaries show that organic matter binding river flocs persisted in estuaries and led to minimal change in floc size in estuaries (Eisma et al., 1982; Puls & Kühl, 1986).

5.4. Climate, Tectonics, and Lithology

Climate, tectonics, and lithology affect chemical weathering and the delivery of weathering products (solids and solutes) to rivers, setting the chemical composition of sediment and river water (Hilton & West, 2020; West et al., 2005). In our model, these basinwide geochemical effects are expressed in Al/Si, $\Phi$, and $\theta$. Weathering-limited catchments (e.g., in rapidly uplifting mountains) yield fresher, less weathered sediment with smaller Al/Si and supply fewer dissolved ions (smaller $\Phi$) to a river system (West et al., 2005). The rock and soil composition of source areas can also affect the composition and concentration of dissolved species in river water, which both contribute to $\Phi$. Organic matter concentration in rivers might be higher in areas with more humid climates and/or relatively younger organics-rich soils and promote flocculation because of greater biological productivity and $\theta$ (Galy et al., 2015). Tectonic uplift, in concert with climate, could enhance mountain export of sediment
load, weathering products, and nutrients, which could also promote biological productivity (Geider et al., 2001; Godard et al., 2014; Raymo & Ruddiman, 1992).

With climate warming, rivers might source more weathering products and dissolved ions (Li et al., 2016; Perron, 2017), reducing the settling velocity of mud flocs in rivers. Warming could also change the magnitudes of sediment and organic carbon supply to rivers because of changes in catchment erosion rates (e.g., Perron, 2017) and biological productivity (e.g., Godard et al., 2014). These scenarios could alter the rates of mud and organic carbon delivery to floodplains via flocs and could be explored using our calibrated model.

6. Conclusion

Evidence from a global river suspended sediment data compilation shows that mud flocculation in rivers is common. Results from fitting the Rouse-Vanoni equation to grain size-specific concentration-depth profiles show, on average, that mud flocs in rivers have diameter of 130 μm, settle at a rate of 1.8 mm s⁻¹, and are composed of primary particles smaller than 39 μm (clay and silt). We proposed and verified a semi-empirical model for floc diameter and settling velocity in rivers. The calibrated model explains the estimated river floc settling velocities within a factor of about two. Out of the variables considered, sediment Al/Si has the strongest negative correlation with a fitted model exponent −2.22 ± 0.916. Kolmogorov microscale has the strongest positive correlation because it scales linearly with floc settling velocity. Higher floc settling velocity also scales with smaller relative charge density of river water compared to sediment (exponent −0.133 ± 0.253) and larger mud concentration and organic matter coverage on sediment grains (shared exponent 0.162 ± 0.0905). These relationships highlight the key role of geochemical interactions between primary particles and organic matter. Our model predicts a turbulence control for which floc diameter is generally smaller than the Kolmogorov microscale because floc breakage rate rapidly increases at large floc diameter, but floc diameter can exceed the microscale depending on the effects of the other predictor variables. The model dependencies imply that allogenic controls can affect floc properties, mud and organic carbon accretion in floodplains, and fluvial morphodynamics, resulting in possible new links between mud transport, tectonics, climate, and the global carbon cycle.

Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al/Si</td>
<td>aluminum-silicon molar ratio of suspended sediment, dimensionless</td>
</tr>
<tr>
<td>C</td>
<td>Volumetric sediment concentration, dimensionless</td>
</tr>
<tr>
<td>C_{bi}</td>
<td>Volumetric near-bed sediment concentration for i-th grain size class, dimensionless</td>
</tr>
<tr>
<td>C_{m}</td>
<td>Volumetric depth-averaged mud concentration, dimensionless</td>
</tr>
<tr>
<td>D</td>
<td>Particle diameter (unflocculated sediment), m</td>
</tr>
<tr>
<td>D_f</td>
<td>Floc diameter, m</td>
</tr>
<tr>
<td>D_p</td>
<td>Primary particle diameter, m</td>
</tr>
<tr>
<td>D_t</td>
<td>Floc cutoff diameter, m</td>
</tr>
<tr>
<td>e</td>
<td>Elementary charge magnitude (= 1.602 × 10⁻¹⁹), C</td>
</tr>
<tr>
<td>g</td>
<td>Gravitational acceleration (= 9.81 m s⁻²), m s⁻²</td>
</tr>
<tr>
<td>h</td>
<td>River water depth, m</td>
</tr>
<tr>
<td>h_b</td>
<td>Near-bed reference height, m</td>
</tr>
<tr>
<td>k</td>
<td>Calibrated model prefactor constant, dimensionless</td>
</tr>
<tr>
<td>k_A</td>
<td>Floc aggregation efficiency, dimensionless</td>
</tr>
<tr>
<td>k_B</td>
<td>Floc breakage efficiency, dimensionless</td>
</tr>
<tr>
<td>k_{BM}</td>
<td>Boltzmann constant (= 1.381), J K⁻¹</td>
</tr>
<tr>
<td>n_f</td>
<td>Floc fractal dimension (= 2), dimensionless</td>
</tr>
<tr>
<td>p_i</td>
<td>Rouse number for i-th grain size class, dimensionless</td>
</tr>
<tr>
<td>q</td>
<td>Calibrated model exponent of C_{m} \theta (1 - \theta)^2 term, dimensionless</td>
</tr>
<tr>
<td>r</td>
<td>Calibrated model exponent of Al/Si term, dimensionless</td>
</tr>
<tr>
<td>s</td>
<td>Calibrated model exponent of \Phi term, dimensionless</td>
</tr>
<tr>
<td>u_s</td>
<td>Shear velocity, m s⁻¹</td>
</tr>
<tr>
<td>w_{s,floc}</td>
<td>Floc settling velocity, m s⁻¹</td>
</tr>
<tr>
<td>w_{si}</td>
<td>In situ particle settling velocity for i-th grain size class, m s⁻¹</td>
</tr>
</tbody>
</table>
Acknowledgments

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Data Availability Statement

The suspended sediment concentration-depth profile, grain size distribution, and geochemical data used in this paper are freely available in the respective original publications. The authors are grateful to J. Bouchet, E. Dingle, and J. Shelley for sharing data used in this paper. Derived data are available online at https://doi.org/10.22002/D1.8962.

References


