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Deicing Road Salts May Contribute to Impairment of Streambeds through Alterations to Sedimentation Processes

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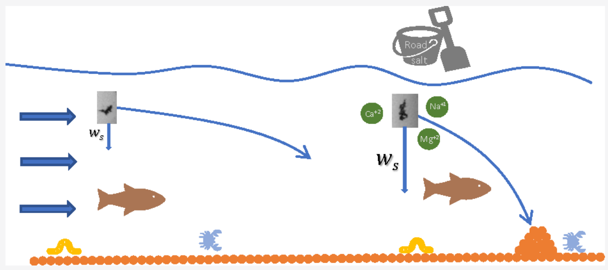
ABSTRACT: Deicing road salts have been increasingly used in the United States over the past 80 years. Previous studies have shown that these salts can have deteriorating effects on freshwater organisms. Here, we hypothesize that the introduction of road salts to streamwater can also boost aggregation 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.



KEYWORDS: *freshwater benthic organisms, flocculation, mud, road salt*

■ 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.[1,2] 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.[3] Roadway deicing salts generally contain sodium chloride, calcium chloride, and magnesium chloride (see Table S1 for a listing of the salt types used by different state departments of transportation in the eastern and midwestern US.) 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,[4] leading to concentrations that can, at times, be of the order of magnitude of the ion concentration in seawater.[5] Once mobilized in streams and rivers, the ions can ultimately enter groundwater[6] and lakes.[7] 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,[8] microinvertebrates,[9] macroinvertebrates,[10] and fish.[11,12] These effects can range from disrupted metabolism and reduced reproduction rate to increased mortality.[13]

While the direct effects of road salts on freshwater organisms have received extensive attention,[13] 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 poststorm 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

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velocity (and therefore deposition rate) of the mud fraction from its state in streamwater 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 in 1994[14] concluded that 90% of the fine sediment transported by six rivers in Canada was flocculated. Fox et al. in 2014[15] found two distinct size classes of suspended aggregates (i.e., 11−20 and 20−53 μm) in samples collected using a sediment trap in the Elkhorn Creek, Kentucky, USA. Furthermore, McLachlan et al. in 2017[16] 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. in 2020[17] 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[14] 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 waste-water 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[18] and larger flocs.[19] This phenomenon is thought to result from shrinkage of the electrical double layer (EDL) surrounding the particles due to increased ionic concentration.[20] 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 interparticle repulsion force and form aggregates. The resulting flocculation increases the size of mud flocs,[21,22] leading to higher settling velocities.[23]

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 a 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,[24] 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.[25] Accumulation of fine sediment can also make the substrate unstable (i.e., easily erodible) and unsuitable for some benthic organisms.[26] Microbial activity, as well as reduced water percolation, within the accumulated mud layer can cause oxygen depletion.[27] Fine sediment accumulation can also negatively affect habitat[28] and food[29] 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.[30] This outcome points to the direct influence of road salts on the chemical properties of the streamwater during winter and therefore, potentially, the deposition of mud within the stream.

■ MATERIALS AND METHODS

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 streamwater 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[31] due to soil erosion and bank instability.[32,33] 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 biogeochemistry (deionized water, unimpaired streamwater, streamwater with added calcium chloride, magnesium chloride, and a commercial deicing mixture).

Stroubles Creek. Stroubles Creek is an example of a stream with multiyear high-frequency SC data that has been shown to be impacted by road salts and experience general sedimentation impairment.[34] 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 poststorm SC values as high as 3921 μS cm^{-1}.[30] Stroubles Creek was used to provide sediment for the experiments and to define target SC values.

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 modeling of the cohesive sediment flocculation process[35] 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 was measured using a specially designed imaging system. The imaging system consists of a digital camera fitted with a 2× microscope lens placed outside of the tank and focused on a plane just inside the tank and a waterproofed LED light source. The LED was 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 from 2017.[36] Collected images were processed in ImageJ to identify particles and measure their area. A Python script, based on the method of Keyvani and Strom from 2013,[37] was used to obtain particle size distributions on the basis of the measured area of the identified particles. Turbidity within the mixing tank was continuously measured and recorded using an optical backscatter sensor (OBS).

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 μS cm^{-1}). Experiment 2 used unaltered streamwater, which is streamwater collected from a local unimpaired stream without the addition of salts. Experiments 3−5 used the same streamwater from the unimpaired stream as the second experiment (Table 1), but with salt added to reach the median wintertime SC in Stroubles Creek (i.e., 947 μS cm^{-1}).[30]

Table 1. Equilibrium Floc Size ($d_{50\mathrm{eq}}$) at Different Turbulent Shear Rates (G) for Different Experiments

		$d_{50\mathrm{eq}}$ [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

Water from Toms Creek was used as the baseline unaltered or unimpaired streamwater for Experiments 2−5. Toms Creek sits in the same county as Stroubles Creek (Montgomery County, VA) and is comparable in stream order (second), habitat, and stream power to Stroubles Creek, yet it meets water quality standards that Stroubles does not (sedimentation, *E. coli.*, and nitrates concentrations[38]). For this reason, Toms Creek has been used as a biological reference reach for Stroubles in restoration efforts.[39] The initial background SC of the collected water ranged from 116 to 147 μS cm^{-1} across experiments. The background SC levels in the Toms Creek samples were all significantly lower than the SC levels in Stroubles Creek, which has been impacted by the long-term effects of deicing salt use in its watershed.[40]

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, Overland Park, KS). 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, subsamples were extracted from the large unaltered and a 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 min. Following this period of floc growth from a sonicated state, the suspension was subjected to a high shear rate of 550 s^{-1} for 15 min to break the flocs down to a more natural, turbulence-generated initial condition.[36] 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 min of each step in G. Therefore, the last 35 min 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.

Settling Velocity and Advective Length Scale Calculations. The relationship in Strom and Keyvani from 2011[41] was used to estimate floc settling velocity on the basis of the size of the flocs as,

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

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.[35] We used b_1 and b_2 of 18 and 0.548, respectively.[41]

The advective length scale, L_{adv},

$$L_{\mathrm{adv}} = \frac{hU}{w_s} \tag{2}$$

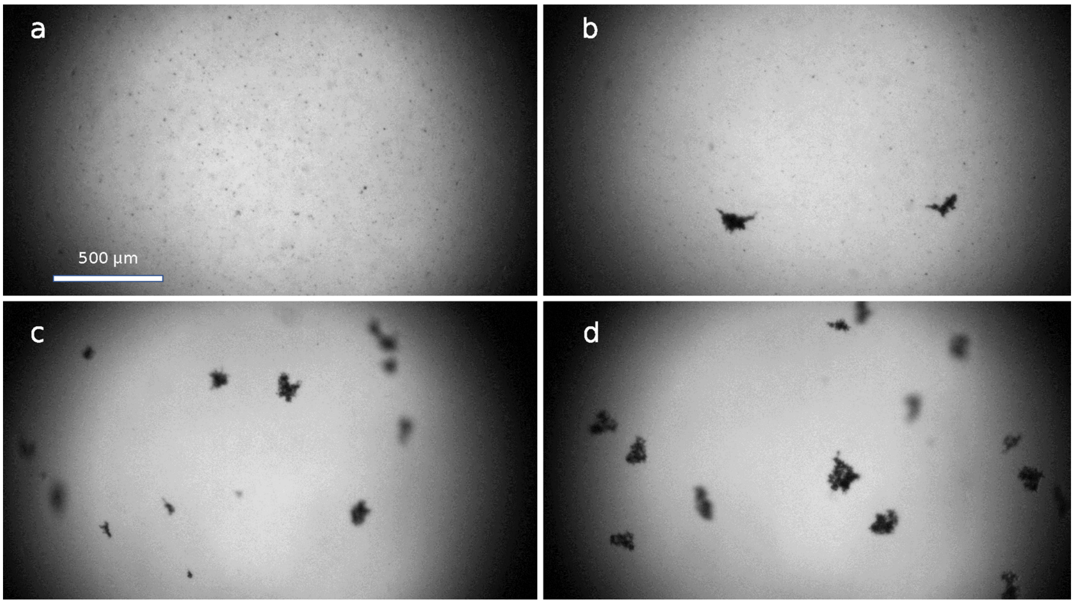

Figure 1. Sample images showing flocculated and unflocculated particles in (a) DI water, (b) unaltered streamwater, and water with (c) mixed road salt and (d) calcium chloride at the turbulent shear rate of 35 s^{-1}.

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 eq 2, h is the water column depth in the stream, U is average stream velocity, and w_s was calculated from eq 1.

RESULTS

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.

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 nondimensionalized with depth, and κ is the von Karman constant. Considering an average channel slope of 0.0023 m m^{-1} in Stroubles Creek,[42] 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 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, streamwater (Figure 1). When suspended in DI water, the mud particles formed few aggregates and instead tended to remain as discrete particles of diameter <30 μm (Figure 1a). Mud particles in the unaltered, or unimpaired, streamwater created a few relatively large flocs (some larger than 100 μm in diameter). However, these larger flocs were significantly outnumbered by smaller particles (Figure 1b). In the experiments with a 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 Figure 1b,c). These effects were found to be stronger in the experiments with calcium chloride (Figure 1d) and magnesium chloride (no image shown in the figure) compared to the mixed road salt (Figure 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 (Figure 2). In the DI water experiment, the majority of the particles were smaller than 50 μm. The particle size distribution shifted slightly toward the larger sizes in unaltered streamwater with some flocs with size of >150 μm forming in the mixing tank. However, a significant number of particles were still in the unaggregated form. With an increase in SC as a result of the

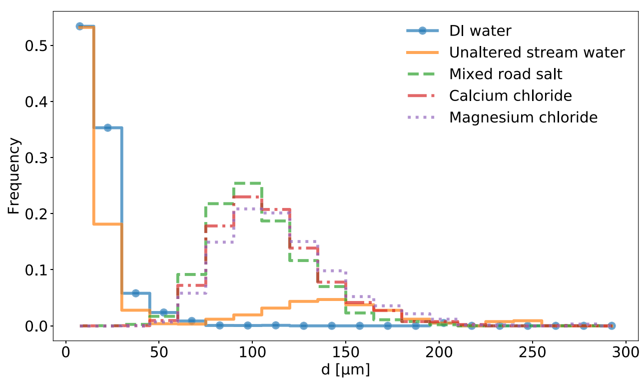

Figure 2. Volume-weighted normalized particle size distribution across different experiments at equilibrium at the turbulent shear rate of 35 s^{-1}.

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addition of road salt, the fraction of discrete and unaggregated particles decreased substantially, shifting the particle size distribution toward 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 streamflow rate and turbulence might impact the floc sizes with different salt types. All findings were consistent with what can be seen in sample images (Figure 1) and particle size distributions (Figure 2) from the G = 35 s^{-1} case. The addition of road salts decreased the number of small unaggregated 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 1.

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.[43]

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 h 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 (Figure 3a). Comparatively, the experiments with DI water and unaltered streamwater 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 streamflow (for example the lowermost Mississippi River.[44])

In the settling test with decaying turbulence (mixer turned off), the DI water lost about 1% of its initial turbidity over a 15 min period (Figure 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

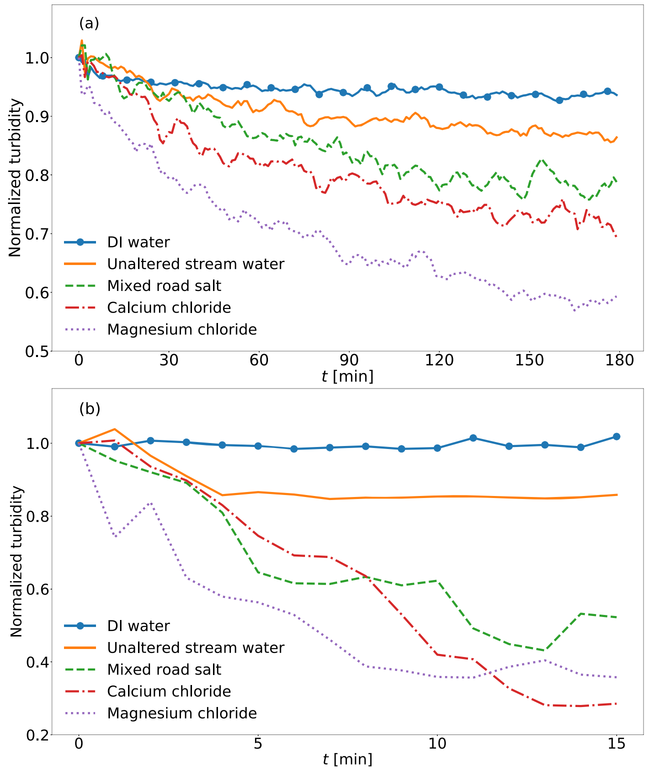

Figure 3. Time series of normalized turbidity at (a) turbulent shear rate of 20 s^{-1} and (b) stagnant water.

streamwater 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.

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 eq 1. These suspension average values of w_s for G = 35 s^{-1} are presented in Table 2. The highest settling velocities belonged to the experiment with magnesium chloride where the calculated settling velocity was just above 1 mm s^{-1}. The settling velocity for the experiment with unaltered streamwater 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 streamflow. The advective length scale, $L_{adv} = h\, U/w_s$, 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 the resuspension of deposited sediment or input from tributaries or the land surface. Here, L_{adv} is calculated for

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Table 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

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 poststorm 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 streamwater to 7.1 km for magnesium chloride and 7.6 km for calcium chloride (Table 2). For the same flow conditions, the 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 3–400 km that was calculated using a formulation similar to eq 2 for sediment travel distance in rivers in Intermountain West at near bankfull discharge.[45]

■ DISCUSSION AND CONCLUSION

The presence of road salt in the streamwater 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 (Figure 1). Flocs did exist in the natural or unaltered streamwater without the addition of salt. However, the distribution of particle sizes in the unaltered streamwater was bimodal with much of the mud existing as very small aggregates or unflocculated mud. The addition of the road way salt resulted in the formation of large flocs with a more unimodal 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 the formation of aggregates.

The contrast between flocs formed in the road salt experiments and those in the unaltered streamwater 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 streamwater experiment. This was true even though a few larger flocs with d_f > 150 μm did form in the unaltered streamwater experiment (Figure 2). Size increases of this amount led to increases in settling velocity of 56% according to eq 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.[46]

In all cases with salt, the calculated advective length scale based on typical conditions in Stroubles Creek was smaller than the advective distance of mud, 10 km, estimated by Pizzuto in 2014[47] 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.[48] 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

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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.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.1c00300.

Table of different types of road salts used in different states (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) USGS Scientific Investigations Report 2009–5236: Effects of Highway Road Salting on the Water Quality of Selected Streams in Chittenden County, Vermont, November 2005–2007. https://pubs.usgs.gov/sir/2009/5236/ (accessed 2021-06-26).

(2) Bagenstose, K. Heavy road salt use in winter is a growing problem, scientists say. https://www.usatoday.com/story/news/nation/2019/12/24/winter-weather-road-salt-use-problems/2741286001/ (accessed 2021-06-29).

(3) Mineral Commodity Summaries 2020; U.S. Geological Survey, 2020.

(4) Jackson, R. B.; Jobbagy, E. G. From icy roads to salty streams. *Proc. Natl. Acad. Sci. U. S. A.* **2005**, *102*, 14487–14488.

(5) Kaushal, S. S.; Groffman, P. M.; Likens, G. E.; Belt, K. T.; Stack, W. P.; Kelly, V. R.; Band, L. E.; Fisher, G. T. Increased salinization of fresh water in the northeastern United States. *Proc. Natl. Acad. Sci. U. S. A.* **2005**, *102*, 13517–13520.

(6) Williams, D. D.; Williams, N. E.; Cao, Y. Road salt contamination of groundwater in a major metropolitan area and development of a biological index to monitor its impact. *Water Res.* **2000**, *34*, 127–138.

(7) Novotny, E. V.; Murphy, D.; Stefan, H. G. Increase of urban lake salinity by road deicing salt. *Sci. Total Environ.* **2008**, *406*, 131–144.

(8) Sarma, S. S. S.; Nandini, S.; Morales-Ventura, J.; Delgado-Martínez, I.; González-Valverde, L. Effects of NaCl salinity on the population dynamics of freshwater zooplankton (rotifers and cladocerans). *Aquat. Ecol.* **2006**, *40*, 349.

(9) Kefford, B. J.; Fields, E. J.; Clay, C.; Nugegoda, D. Salinity tolerance of riverine microinvertebrates from the southern Murray-Darling Basin. *Mar. Freshwater Res.* **2007**, *58*, 1019–1031.

(10) Shenton, M. D.; Nichols, S. J.; Bray, J. P.; Moulding, B. J. G.; Kefford, B. J. The Effects of Road De-icing Salts on Water Quality and Macroinvertebrates in Australian Alpine Areas. *Arch. Environ. Contam. Toxicol.*, in press, **2021**.

(11) Tollefsen, K. E.; Song, Y.; Kleiven, M.; Mahrosh, U.; Meland, S.; Rosseland, B. O.; Teien, H.-C. Transcriptional changes in Atlantic salmon (Salmo salar) after embryonic exposure to road salt. *Aquat. Toxicol.* **2015**, *169*, 58–68.

(12) Hintz, W. D.; Relyea, R. A. Impacts of road deicing salts on the early-life growth and development of a stream salmonid: Salt type matters. *Environ. Pollut.* **2017**, *223*, 409–415.

(13) Hintz, W. D.; Relyea, R. A. A review of the species, community, and ecosystem impacts of road salt salinisation in fresh waters. *Freshwater Biol.* **2019**, *64*, 1081–1097.

(14) Droppo, I. G.; Ongley, E. D. Flocculation of suspended sediment in rivers of southeastern Canada. *Water Res.* **1994**, *28*, 1799–1809.

(15) Fox, J.; Ford, W.; Strom, K.; Villarini, G.; Meehan, M. Benthic control upon the morphology of transported fine sediments in a low-gradient stream. *Hydrological Processes* **2014**, *28*, 3776–3788.

(16) McLachlan, R. L.; Ogston, A. S.; Allison, M. A. Implications of tidally-varying bed stress and intermittent estuarine stratification on fine-sediment dynamics through the Mekong's tidal river to estuarine reach. *Cont. Shelf Res.* **2017**, *147*, 27–37.

(17) Lamb, M. P.; de Leeuw, J.; Fischer, W. W.; Moodie, A. J.; Venditti, J. G.; Nittrouer, J. A.; Haught, D.; Parker, G. Mud in rivers transported as flocculated and suspended bed material. *Nat. Geosci.* **2020**, *13*, 566–570.

(18) Edzwald, J. K.; Upchurch, J. B.; O'Melia, C. R. Coagulation in estuaries. *Environ. Sci. Technol.* **1974**, *8*, 58–63.

(19) Mietta, F.; Chassagne, C.; Manning, A. J.; Winterwerp, J. C. Influence of shear rate, organic matter content, pH and salinity on mud flocculation. *Ocean Dynamics* **2009**, *59*, 751–763.

(20) van Olphen, H. Internal mutual flocculation in clay suspensions. *J. Colloid Sci.* **1964**, *19*, 313–322.

(21) Mietta, F.; Chassagne, C.; Winterwerp, J. C. Shear-induced flocculation of a suspension of kaolinite as function of pH and salt concentration. *J. Colloid Interface Sci.* **2009**, *336*, 134–141.

(22) van Leussen, W. The variability of settling velocities of suspended fine-grained sediment in the Ems estuary. *J. Sea Res.* **1999**, *41*, 109–118.

(23) Portela, L. I.; Ramos, S.; Teixeira, A. T. Effect of salinity on the settling velocity of fine sediments of a harbour basin. *J. Coastal Res.* **2013**, *165*, 1188–1193.

(24) U.S. Environmental Protection Agency. National Rivers and Streams Assessment 2013–2014 Report. https://www.epa.gov/national-aquatic-resource-surveys/national-rivers-and-streams-assessment-2013-2014-report (accessed 2021-06-24).

(25) Conroy, E.; Turner, J. N.; Rymszewicz, A.; Bruen, M.; O'Sullivan, J. J.; Lawler, D. M.; Stafford, S.; Kelly-Quinn, M. Further insights into the responses of macroinvertebrate species to burial by sediment. *Hydrobiologia* **2018**, *805*, 399–411.

(26) Richards, C.; Bacon, K. L. Influence of Fine Sediment on Macroinvertebrate Colonization of Surface and Hyporheic Stream Substrates. *The Great Basin Naturalist* **1994**, *54* (2), 106−113.
(27) Pretty, J. L.; Hildrew, A. G.; Trimmer, M. Nutrient dynamics in relation to surface-subsurface hydrological exchange in a groundwater fed chalk stream. *J. Hydrol.* **2006**, *330*, 84−100.
(28) Burdon, F. J.; McIntosh, A. R.; Harding, J. S. Habitat loss drives threshold response of benthic invertebrate communities to deposited sediment in agricultural streams. *Ecological Applications* **2013**, *23*, 1036−1047.
(29) Suttle, K. B.; Power, M. E.; Levine, J. M.; McNeely, C. How Fine Sediment in Riverbeds Impairs Growth and Survival of Juvenile Salmonids. *Ecological Applications* **2004**, *14*, 969−974.
(30) Lakoba, V.; Wind, L.; DeVilbiss, S.; Lofton, M.; Bretz, K.; Weinheimer, A.; Moore, C.; Baciocco, C.; Hotchkiss, E.; Hession, W. C. Salt Dilution and Flushing Dynamics of an Impaired Agricultural-Urban Stream. *ACS ES&T Water* **2021**, *1*, 407−416.
(31) Inamdar, S.; Johnson, E.; Rowland, R.; Warner, D.; Walter, R.; Merritts, D. Freeze-thaw processes and intense rainfall: the one-two punch for high sediment and nutrient loads from mid-Atlantic watersheds. *Biogeochemistry* **2018**, *141*, 333−349.
(32) Couper, P. R.; Maddock, I. P. Subaerial river bank erosion processes and their interaction with other bank erosion mechanisms on the River Arrow, Warwickshire, UK. *Earth Surf. Processes Landforms* **2001**, *26*, 631−646.
(33) Ferrick, M. G.; Gatto, L. W. Quantifying the effect of a freeze-thaw cycle on soil erosion: laboratory experiments. *Earth Surf. Processes Landforms* **2005**, *30*, 1305−1326.
(34) Integrated Report | Virginia DEQ. https://www.deq.virginia.gov/water/water-quality/assessments/integrated-report (accessed 2021-06-21).
(35) Winterwerp, J. C. A simple model for turbulence induced flocculation of cohesive sediment. *Journal of hydraulic research* **1998**, *36*, 309−326.
(36) Tran, D.; Strom, K. Suspended clays and silts: Are they independent or dependent fractions when it comes to settling in a turbulent suspension? *Cont. Shelf Res.* **2017**, *138*, 81−94.
(37) Keyvani, A.; Strom, K. A fully-automated image processing technique to improve measurement of suspended particles and flocs by removing out-of-focus objects. *Comput. Geosci.* **2013**, *52*, 189−198.
(38) Gronwald, F.; Kenny, J.; Adams, E.; Delgoshaei, P.; Younos, T.; Lohani, V. K. Water quality assessment of a mixed land use watershed. *2008 NSF REU Proceedings of Research*; Virginia Tech, 2008; p 47.
(39) Stroubles Creek IP Steering Committee; Virginia Tech Department of Biological Systems Engineering; Virginia Water Resources Research Center. *Upper Stroubles Creek Watershed TMDL Implementation Plan Montgomery County, Virginia*; Virginia Tech, 2006.
(40) Hession, W. C.; Lehmann, L. T.; Wind, L. L.; Lofton, M. E. High-frequency time series of stage height, stream discharge, and water quality (specific conductivity, dissolved oxygen, pH, temperature, turbidity) for Stroubles Creek in Blacksburg, Virginia, USA 2013−2018. https://portal.edirepository.org/nis/mapbrowse?packageid=edi.510.1 (accessed 2021-06-21).
(41) Strom, K.; Keyvani, A. An explicit full-range settling velocity equation for mud flocs. *J. Sediment. Res.* **2011**, *81*, 921−934.
(42) Azinheira, D. L.; Scott, D. T.; Hession, W.; Hester, E. T. Comparison of effects of inset floodplains and hyporheic exchange induced by in-stream structures on solute retention. *Water Resour. Res.* **2014**, *50*, 6168−6190.
(43) Skalak, K.; Pizzuto, J. The distribution and residence time of suspended sediment stored within the channel margins of a gravel-bed bedrock river. *Earth Surf. Processes Landforms* **2010**, *35*, 435−446.
(44) MacDonald, D. G.; Goodman, L.; Hetland, R. D. Turbulent dissipation in a near-field river plume: A comparison of control volume and microstructure observations with a numerical model. *J. Geophys. Res.* **2007**, *112*, 1−13.
(45) Whiting, P. J.; Matisoff, G.; Fornes, W.; Soster, F. M. Suspended sediment sources and transport distances in the Yellowstone River basin. *Geol. Soc. Am. Bull.* **2005**, *117*, 515−529.
(46) Sobeck, D. C.; Higgins, M. J. Examination of three theories for mechanisms of cation-induced bioflocculation. *Water Res.* **2002**, *36*, 527−538.
(47) Pizzuto, J. E. Long-term storage and transport length scale of fine sediment: Analysis of a mercury release into a river. *Geophys. Res. Lett.* **2014**, *41*, 5875−5882.
(48) Wood, P. J.; Armitage, P. D. Biological Effects of Fine Sediment in the Lotic Environment. *Environ. Manage.* **1997**, *21*, 203−217.

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