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# Physical and Ecological Controls on Freshwater Floc Trace Metal Dynamics

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Ⓢ *Supporting Information*

ABSTRACT: Significantly higher concentrations of Ag, As, Cu, Co, Ni, and Pb are found in suspended floc compared to surficial bed sediments for a freshwater beach in Lake Ontario. Contrasting observed element-specific bed sediment metal partitioning patterns, floc sequestration for all elements is dominated by one substrate: amorphous oxyhydroxides. More specifically, floc metal scavenging is controlled by floc biogeochemical architecture. Floc organics, largely living microbial cells and associated exopolymeric substances (EPS), act as scaffolds for the collection and/or templating of amorphous Fe oxyhydroxides. While interactions between floc organics and amorphous Fe oxyhydroxides affected floc sorption behavior, specific element affinities and competition for these limited substrates was important for overall floc partitioning. Further, assessment of metal dynamics during stormy conditions indicated energy-regime driven shifts in floc and bed sediment partitioning that were specifically linked to the exchange of floc and bed sedimentary materials. These novel results demonstrate that the microbial nature of floc formation exerts an important control on floc metal dynamics distinguishable from surficial bed sediments and that hydrologic energy-regime is an important factor to consider in overall floc metal behavior, especially in beach environments.
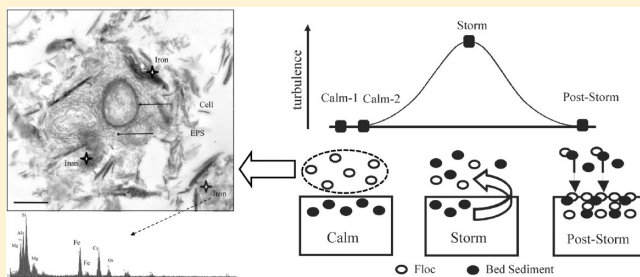
■ INTRODUCTION

Trace metal behavior in aquatic environments is controlled by dynamic interactions between aqueous and sedimentary compartments that reflect interactive environmental, substrate, and element specific influences. While many studies have assessed metal abundance and substrate associations in bed sediments (e.g., refs 1), few have investigated suspended floc metal dynamics.

Aquatic floc is a complex aggregate of fine-grained inorganic particles (e.g., clays, oxyhydroxide minerals, carbonates) held together by a network of extracellular polymeric substances (EPS) generated by floc-associated biological communities (e.g., bacteria, algae, fungi).[2,3] These suspended microbial microecosystems constantly interact with the surrounding water-column sequestering nutrients, organic material (e.g., detritus, humic and fulvic acids), and chemicals for development and growth.[2] Floc comprises the majority of suspended particulate matter (SPM) in aquatic environments[3] enabling comparison of our floc results with those determined for "SPM" referred to elsewhere in the literature. Although floc has been shown to be a significant metal sorbent,[4,5] its metal dynamics relative to bed sediments has not been assessed to date.

Microorganisms and associated EPS are important metal sorbents with the potential to significantly influence trace metal behavior (mobility, bioavailability, and toxicity) and contaminant cycling in the environment.[6,7] Internal redox gradients, within the diffusive microenvironment of floc,[8] may facilitate microbial catalysis of redox sensitive mineral precipitation-dissolution reactions (i.e., Fe/Mn oxides[9,10]) that could profoundly affect metal cycling, similar to sulfur redox cycling observed in other environmental microbial consortia.[11] Fe and Mn oxyhydroxides are well recognized to influence metal behavior in the environment.[12] Oxyhydroxides are ubiquitous in aquatic systems and tend to precipitate as surface coatings on other minerals and organic material including bacterial surfaces.[13,14] These minerals typically exist as nanoparticulates that have large surface areas relative to their volume resulting in considerable metal scavenging.[15] Although Fe/Mn oxyhydroxides and organic matter are both highly effective metal scavengers, these reactive substrates typically coexist and interact resulting in collective impacts on metal cycling, interactions that will be especially important within suspended floc. The underlying microbial nature of floc formation, its differing substrate composition, and its suspension within the water-column collectively suggest that floc metal abundances and partitioning will differ from that observed within bed sediments.

Further, interactive exchanges between suspended floc and bed sediment compartments driven by hydrologic energy-regime will affect solution and sedimentary compartment metal dynamics

and are likely to be particularly important in shallow beach environments. The role of sediment remobilization on floc metal concentrations has been investigated within marine coastal sediments (e.g., refs 16). However, very little is known about temporal chemistry and *in situ* metal partitioning of floc and its interactions with bed sediments within freshwater beach environments where the potential remobilization and exchange of contaminants may significantly degrade water quality and increase risk to aquatic organisms and public health.[17,18] While it is well-known that the hydrologic energy-regime mediates interactions between suspended floc (i.e., SPM) and bed sediment compartments,[19] the subsequent fate of metal contaminants associated with any exchange of sedimentary reactive constituents in freshwater aquatic systems remains undescribed.

The objectives of this field based study were to determine 1) metals Ag, Cu, Co, Ni, Pb, and metalloid As concentrations (collectively referred to as metals from here on) within suspended floc, bed sediment, and water-column aqueous compartments and 2) important reactive solid-phases for metal sequestration in suspended floc and bed sediment compartments under variable energy-regimes specifically within an urban freshwater beach.

■ MATERIALS AND METHODS

Study Site/Sampling Protocol. The study site, Toronto Sunnyside Beach, is an erosive manufactured sandy beach located on the north shore of Lake Ontario, Canada (43°38′21″N, 079°27′21′W); an urbanized region of more than 5 million people. The sampling campaign was designed to investigate temporal trends of suspended floc and bed sediment metal concentrations with associated geochemistry. *In situ* water-column measurements and sample collection occurred ~10 m from the shoreline on four sampling days under varying hydrologic conditions: July 21, 2009 (Calm-1), May 13, 2009 (Calm-2), May 14, 2009 (Storm), and May 13, 2008 (Post-Storm). For the purpose of this study, conditions at the beach were considered 'calm' when average and maximum wind speeds were less than 26 Km h^{-1}.[20] Mean and range of wind speeds on each sampling day and 48 h prior are outlined in Table S1, Supporting Information. Geochemical characterization and sample collection involved 1) *in situ* physicochemical profiling (°C, pH, O$_2$, and specific conductivity; Datasonde-Surveyor 4A, Hydrolab Corporation, TX) of the 1.2 m deep water-column; 2) collection of bed sediment (diver retrieved cores) and bulk floc (continuous field flow centrifugation (CFC), 0.5 m above sediment-water interface) for solid-phase metal analysis and mineralogy; 3) diver retrieved plankton chambers[21] used to collect floc from the same depth for ultrastructural imaging; and 4) collection of water samples (0.5 m above bed) for dissolved metal analysis and dissolved inorganic and organic carbon (DIC/DOC).[22]

Water-Column Collection/Analysis. All sampling equipment and sample containers for trace metal analysis were prepared by soaking in 10% (v/v) HCl for >24 h followed by eight rinses with ultra pure water (18.2Ωm cm^{-1}, Mili-Q, Millipore). Water samples for dissolved metal analysis were collected into acid washed syringes from an acid washed van dorn water sampler, filtered serially through a 0.45 and 0.2 μm sterile inline syringe filters and subsequently preserved with trace metal grade (TMG) HNO$_3$ to 2% v/v (Fisher). Field blanks were collected by flushing ultra pure water through an acid washed van dorn as well as serially syringe filtering (Acrodisc 0.45 and 0.2 μm) and

acidifying ultra pure water during each sampling period. Samples were kept in the dark and stored at 4 °C until analysis. Dissolved metal (<0.2 μm) concentrations [M]$_D$ were quantified by inductively coupled plasma mass spectrometry (ICP-MS (Ag, As, Cu, Co, Ni, Pb) PerkinElmer SCIEX ELAN 6100, Woodbridge, ON, Canada). [M]$_D$ are summarized in Table S1, along with procedural limits of quantification. Field blank analysis indicated no contamination for all elements. Unfiltered iron [Fe] was determined colorometrically using the FerroVer HACH method (Ultrospec 2000, UV/visible spectorophotometer, Pharmacia Biotech, Cambridge, U.K.). DIC/DOC samples were analyzed using a UV-persulfate TOC analyzer following the methods at the National Laboratory for Environmental Testing (NLET) Environment Canada (2009).

Floc Collection. Bulk suspended floc was collected using a continuous flow centrifuge (CFC, Westfalia Model KA). Water (>2000 L) was pumped (6 L min^{-1}) into stainless steel bowls, preleached with 10% EDTA solution prior to collection, with a rotational speed of 9470 rpm where >90% of the floc was recovered (assessed by weight comparison of CFC inflow and outflow filtered water samples on glass-fiber Whatman filters following the standard method 2540D[23]) and placed into acid clean 50 mL Falcon tubes. Floc samples were collected over 6—8 h 0.5 m above the sediment-water interface. Although centrifugation may facilitate colloid aggregation, unfiltered centrifuge inflow and outflow [M] showed no differences for detectable elements in solution (As, Co, Cu, Ni, Pb; $p < 0.05$), indicating no significant CFC associated colloidal artifacts were induced.

Bed Sediment Collection. Bed sediments were collected in acid washed polycarbonate core tubes (6 cm diameter, 45 cm length) and capped underwater by SCUBA divers to the keep sediment water-interface intact and to retain pore waters. Cores were collected within the vicinity but downstream of the CFC inflow to minimize sediment disturbance. Sediment cores were immediately extruded onshore and subsamples collected from the surface (0—0.5 cm) and mid core (5—7 cm) were immediately frozen on dry ice and stored at −20 °C until analysis. All bed sediment samples were composed of >98% sand sized particles on each sampling campaign and likely well-aerated at these surficial depths.[24]

Solid-Phase Sediment Metal Analysis. Floc and bed sediment samples were processed using a modified Tessier sequential extraction method using microwave digestion that distinguishes between amorphous and crystalline oxides.[25] Samples were homogenized prior to digestion and run in triplicate. Sediment associated metals were partitioned into six operationally defined sediment fractions: exchangeable (loosely bound); carbonates; amorphous Fe/Mn oxyhydroxides (easily reducible); crystalline Fe/Mn oxides (reducible); organics/sulfides (oxidizable); and residual (concentrated HNO$_3$ digestion). Reagents blanks were included during digestion to correct for procedural contamination. Matrix effects associated with ICP-MS were corrected using matrix-matched standard curves. Mean total floc and bed sediment metal concentrations {M}$_T$ (μmol g^{-1} dry weight) were determined by summing metal concentrations from the six sediment fractions. Variation in relative aqueous metal sorption by bulk floc was assessed by relative solid-solution distribution coefficients (K_d)

$$K_d = \{M\}_T/[M]_D \quad (1)$$

where {M}$_T$ is the total metal concentration (mol kg^{-1}) within the bulk sediment, and [M]$_D$ is the dissolved metal concentration

Table 1. Floc, Surface and Mid Sediment Total Metal Concentrations $\{M\}_T$ ($\mu mol g^{-1}$) $\pm$ 1 Standard Deviation and Percent (%) $\{M\}$ in Each of Six Operationally Defined Sediment Fractions (Exchangeable $\{M\}_E$, Carbonates $\{M\}_{CAR}$, Amorphous Fe/Mn Oxyhydroxides $\{M\}_A$, Crystalline Fe/Mn Oxides $\{M\}_C$, Organics $\{M\}_O$, Residual $\{M\}_R$).

		Ag			As			Co			Cu			Ni			Pb		
		Floc	Sur	Mid	Floc	Sur	Mid	Floc	Sur	Mid	Floc	Sur	Mid	Floc	Sur	Mid	Floc	Sur	Mid
	$\{M\}_T$	0.011	0.002	0.002	0.252	0.055	0.024	0.137	0.044	0.027	0.879	0.109	0.062	0.749	0.281	0.087	0.160	0.042	0.025
	$\pm$	0.001	0.000	0.000	0.009	0.007	0.007	0.006	0.002	0.001	0.039	0.011	0.003	0.065	0.016	0.005	0.006	0.002	0.001
	$\{M\}_E$	0	0	0	8	0	0	2	0	0	4	3	0	2	0	0	0	0	0
	$\{M\}_{CAR}$	0	0	0	18	5	11	19	16	13	2	5	5	11	26	30	40	33	20
Calm-1	$\{M\}_A$	75	0	0	17	6	8	29	5	6	15	2	2	17	13	13	43	8	13
	$\{M\}_C$	17	84	83	12	70	57	32	37	33	24	53	59	55	30	27	12	50	56
	$\{M\}_O$	3	6	7	8	4	7	5	7	15	40	14	15	6	6	8	2	2	2
	$\{M\}_R$	5	10	10	37	15	17	13	35	33	15	23	19	9	25	22	3	7	9
	$\{M\}_T$	0.012	0.006	0.003	0.137	0.045	0.050	0.148	0.028	0.050	0.603	0.048	0.071	0.492	0.074	0.101	0.140	0.010	0.027
	$\pm$	0.000	0.001	0.000	0.010	0.005	0.005	0.009	0.002	0.001	0.019	0.003	0.004	0.028	0.005	0.002	0.002	0.001	0.001
	$\{M\}_E$	0	0	0	4	0	0	0	0	0	2	2	0	1	0	0	0	0	0
	$\{M\}_{CAR}$	0	0	0	11	8	9	6	9	8	1	6	4	11	15	15	7	24	31
Calm-2	$\{M\}_A$	80	5	2	39	13	13	60	16	13	36	8	5	50	23	26	76	29	22
	$\{M\}_C$	17	60	88	36	68	65	21	45	38	18	57	52	20	38	33	14	38	39
	$\{M\}_O$	1	11	6	7	4	5	2	8	12	22	10	15	5	6	8	0	2	1
	$\{M\}_R$	2	24	4	3	7	8	11	22	29	21	17	24	13	18	18	3	7	7
	$\{M\}_T$	0.009	0.003	0.003	0.289	0.018	0.039	0.217	0.007	0.033	1.094	0.010	0.012	0.523	0.055	0.088	0.340	0.067	0.025
	$\pm$	0.001	0.001	0.000	0.028	0.004	0.001	0.022	0.002	0.002	0.065	0.001	0.001	0.047	0.006	0.003	0.039	0.013	0.001
	$\{M\}_E$	0	0	0	1	1	0	0	0	0	0	0	0	1	0	0	0	0	0
	$\{M\}_{CAR}$	0	0	0	5	12	9	7	5	10	2	0	5	10	17	15	7	22	22
Storm	$\{M\}_A$	0	0	0	5	14	16	3	4	9	1	0	0	10	25	19	18	31	26
	$\{M\}_C$	87	89	92	79	56	66	31	63	53	61	0	0	49	33	45	67	45	42
	$\{M\}_O$	6	7	4	2	7	3	48	15	8	17	36	22	7	9	7	2	0	3
	$\{M\}_R$	7	4	4	8	10	6	11	13	20	19	64	73	23	16	14	6	2	7
	$\{M\}_T$	7.347[a]	0.387[a]	0.112[a]	0.228	0.046	0.014	0.165	0.021	0.010	1.454	0.059	0.017	0.544	0.079	0.043	0.169	0.011	0.009
	$\pm$	0.367[a]	0.029[a]	0.012[a]	0.012	0.002	0.001	0.008	0.001	0.001	0.202	0.008	0.001	0.030	0.005	0.001	0.015	0.001	0.001
	$\{M\}_E$	0	0	0	18	0	0	4	0	0	6	19	0	3	0	0	0	2	0
	$\{M\}_{CAR}$	0	0	0	19	4	10	12	19	23	3	7	17	11	37	51	37	47	49
Post-Storm	$\{M\}_A$	64	39	23	38	37	46	47	37	39	32	25	49	43	30	29	48	37	38
	$\{M\}_C$	19	18	26	12	51	30	24	16	14	11	11	12	23	12	8	11	7	6
	$\{M\}_O$	8	8	14	9	5	8	5	7	6	29	20	4	5	6	2	1	2	2
	$\{M\}_R$	9	35	37	4	3	6	8	21	18	19	18	18	15	15	10	3	5	5

[a] values in nmolg^{-1}

(mol L^{-1}) within the water-column.[26] Bed sediment porewater concentrations were not available, thus K_ds for the surficial bed sediments were not calculated for comparison. $[M]_D$ below detection on particular sampling periods were assigned the limit of quantification to generate K_ds (Co, Pb; Table S1). $[Ag]_D$ was consistently below detection limits, thus no floc Ag K_ds were calculated.

Statistical Analysis. All statistical analyses were performed using PASW version 18.0 (SPSS Inc., Chicago, Illinois, U.S.A). Multiple linear regression analysis identified the main variables influencing $\{M\}_T$ (floc and bed), metal concentration within individual solid-phase fractions, and $[M]_D$. *T*-tests were applied to test for significant differences of mean $\{M\}_T$ between floc and surficial bed sediment. Unless otherwise indicated, for all statistical tests a sample size of $n = 6$ and a significance level of $\alpha = 0.05$ was applied.

Sediment Composition. Mean sediment weights were determined by drying (80 °C) triplicates of sediment samples until consistent weight. Mean bulk organic content $\{OM\}$ of floc/sediment samples was estimated by loss on ignition (%LOI, 550 °C 2 h) and carbonate content $\{carbonate\}$ estimated by further heating (%carbonates, 950 °C 1 h). Total extracted Fe and Mn from extraction steps 3 and 4 (Fe quantified by colorimetric analysis; Mn quantified by ICP-MS) were used to estimate the concentration of amorphous Fe/Mn oxyhydroxide $\{Fe\}_A/\{Mn\}_A$ and crystalline Fe/Mn oxide $\{Fe\}_C/\{Mn\}_C$ substrates, respectively. The relative metal scavenging efficiency of each specific sediment substrate was assessed through calculation of concentration factors CF

$$CF = \{M\}_{sediment\ fraction} / \{substrate\} \qquad (2)$$

where $\{M\}_{sediment\ fraction}$ is the metal concentration ($\mu mol\ g^{-1}$) within a specific sediment fraction, and $\{substrate\}$ is the estimated concentration of that substrate within the bulk sediment ($g g^{-1}$).

X-ray diffractometry (XRD) was used to determine bulk mineralogical composition of floc and bed sediments (Siemens D5005 X-ray diffractometer). Bulk XRD analysis identified the main crystalline components of both floc and bed sediments as silicates (quartz and albite) and calcite minerals on each sampling campaign.

Microscopy. Diver retrieved plankton chambers samples were prepared following a 4-fold multistep technique to enhance visualization of cells and EPS material[8] for ultrastructure using transmission electron microscopy (TEM). Ultrathin sections were imaged in transmission mode at an accelerated voltage of 80 kV using a JEOL 1200 Ex II TEMSCAN scanning transmission electron microscope. Floc and bed sediment microbial viability was assessed using the LIVE/DEAD BacLight nucleic acid staining technique. Bulk floc and sediments (~10 mg) were resuspended in 1 mL of 0.085% NaCl solution, and 0.5 μL of LIVE/DEAD BacLight staining solution was added to the mixture, incubated for 15 min in the dark and spotting on gelatin-coated slides [0.25% gelatin and 0.01% KCr(SO$_4$)$_2$]. Slides were viewed using Leica LEITZ DMRX epifluorescence microscope equipped with an
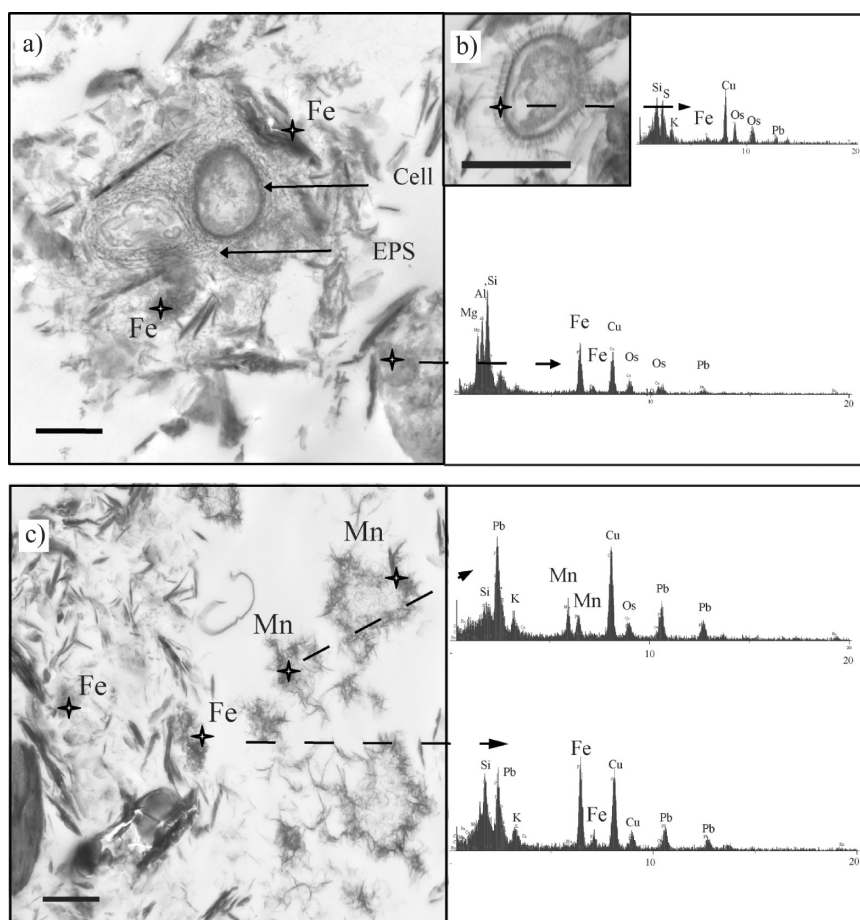
Figure 1. TEM image of calm-floc (a) exhibiting bacteria (species unknown) with EPS and cell walls (b) associated with Fe. TEM image of storm-floc exhibiting large mineral component rich in Mn and Fe (c). Scale represents 500 nm. Peaks of Cu, Os, and Pb are an artifact of sample preparation and grid.

HBO 100-W mercury arc lamp [Leica Microsystems (Canada), Richmond Hill, ON] equipped with 525/50, 645/75 nm barriers and 470/40, 560/40 nm excitation filters.

■ RESULTS AND DISCUSSION

(A). Suspended Floc and Bed Sediment Metal Dynamics. Suspended floc metal concentrations $\{M\}_T$ were significantly higher than those of bed sediments for all elements analyzed during four sampling campaigns (Table 1) despite their close proximity (floc collected here <0.5 m above bed). Mean floc $\{M\}_T$ ranged across the six elements analyzed (four sampling campaigns) from Cu (highest observed concentrations) to Ag (lowest observed concentrations): $\{Cu\}_T$ (1.0 μmol g^{-1}) > $\{Ni\}_T$ (0.58 μmol g^{-1}) > $\{As\}_T$ (0.23 μmol g^{-1}) > $\{Pb\}_T$ (0.20 μmol g^{-1}) > $\{Co\}_T$ (0.17 μmol g^{-1}) > $\{Ag\}_T$ (0.01 μmol g^{-1}) exceeding provincial sediment quality guidelines (SQG) at the lowest effect level as well as natural Great Lake background levels for metals.[27] In contrast, surficial bed sediment mean $\{M\}_T$ did not exceed SQG: $\{Ni\}_T$ (0.12 μmol g^{-1}) > $\{Cu\}_T$ (0.06 μmol g^{-1}) > $\{As\}_T$ (0.04 μmol g^{-1}) > $\{Co\}_T = \{Pb\}_T$ (0.03 μmol g^{-1}) > $\{Ag\}_T$ (0.003 μmol g^{-1}). Floc thus concentrated metals 4−18 times that observed in the surficial bed sediments. These results suggest discretely different metal scavenging behavior between these two sediment compartments that exist in close proximity. This ability of floc to sequester large quantities of

metal contaminants relative to bottom sediments has been demonstrated in the literature.[28−30]

Floc Metal Sorption Behavior. The observed variation in mean floc $\{M\}_T$ were not correlated with system physicochemical parameters ($[M]_D$, pH, temperature, O_2, specific conductivity, DIC/DOC) commonly observed to control solid-phase metal concentrations.[28,31,32] However, solution physico-chemistry within the floc environment (0.5 m above bed sediments) remained relatively constant across the four sampling periods (i.e., circumneutral pH, oxygenated water, <5 °C variation; Table S1). Under these static conditions typically important controlling physicochemical parameters, floc metal uptake was instead found to be strongly correlated to the mass of two key floc sorbent-phases: 1) amorphous Fe oxyhydroxides $\{Fe\}_A$ and 2) organic matter $\{OM\}$. Distribution coefficients (K_d) were significantly and positively correlated with either floc $\{Fe\}_A$ (Cu, Ni, and Co) or floc $\{OM\}$ (Pb and As) (Figure S1, Supporting Information). This indicates a greater sorption of these elements to floc from solution with increasing concentrations of these two floc substrates. Although Mn amorphous oxyhydroxides are important sorbents for metal sequestration,[25,33,34] floc $\{Mn\}_A$ did not predict floc metal distribution coefficients in this study. The importance of Fe oxyhydroxides and organic matter in controlling solid-solution metal distributions has been widely reported in literature,[35−37] and thus our results are entirely consistent with the metal reactive nature of these substrates. Organic
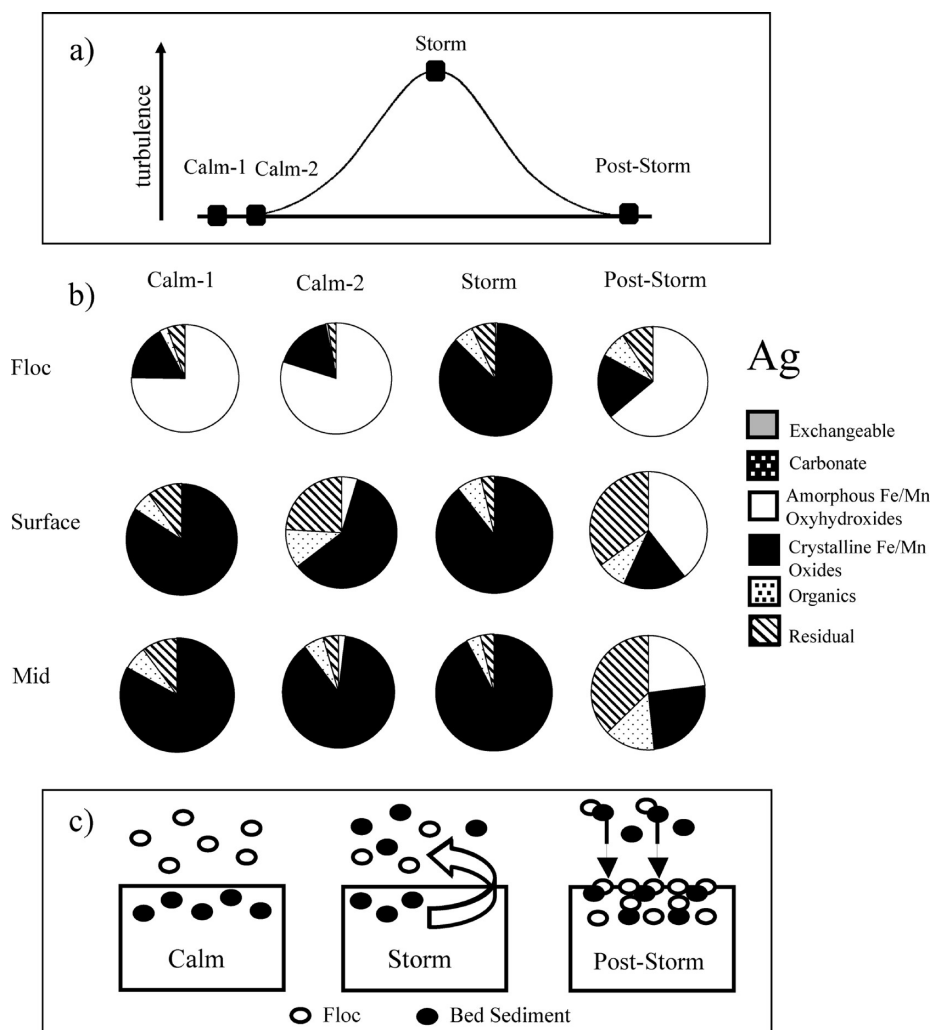
Figure 2. Under variable energy-regimes (a), relative proportion of Ag observed in each of six extraction steps of floc and bed sediments (b). Schematic diagram of floc-bed interactions (c).

components are commonly reported to be important metal sorbents in aquatic systems.[33,38] However, in contrast to bed sedimentary organics which typically contain a greater proportion of dead, decomposing organic matter, our results indicate that floc organics were largely comprised of a viable microbial community and associated EPS fibrils as evidenced by Live/Dead (Figure S2, Supporting Information) and high-resolution TEM imaging (Figure 1). This finding is consistent with previous investigations of floc organics, where microbial cells and EPS dominate floc structure[3,8] and exhibit reactive surfaces that are efficient at scavenging trace metals.[4,6] The highly "viable" nature of floc organic matter contrasts organic matter within the bed sediments that reveals far fewer living cells (Figure S2). Thus floc organics may be playing several roles facilitating floc metal scavenging such as provision of greater surface area to volume ratio and thus exposure of reactive metal sorption sites as well as collection/templating of reactive amorphous Fe oxyhydroxide minerals and metabolically induced micro-environments.

Floc-Metal Partitioning. Assessment of metal partitioning of floc metal-reactive phases indicated that floc amorphous oxyhydroxides retained the largest proportion of Ag, Pb, Co, Ni, As, and Cu, up to 80%, 76%, 60%, 50%, 39%, and 36% of floc $\{M\}_T$

across the four sampling campaigns, respectively (Figure 2; Table 1). Further, floc $\{M\}_A$ were an order of magnitude greater than within the bed (Table 1) and generally exhibited a greater $\{Fe\}_A$ scavenging efficiency (CF) 50−100% of the time, depending on the element (Table S2, Supporting Information). For example, a gram of floc Fe amorphous oxyhydroxides retained up to 32 times the amount of Cu compared to the observed Cu concentration associated with a gram of amorphous Fe oxyhydroxides within surficial bed sediments. This result highlights factors contributing to a higher relative scavenging capacity of floc amorphous oxyhydroxides, such as the relative degree of amorphicity, the physical nature of the oxyhydroxides, i.e. surface coatings,[13,14] the relatively higher surface area to volume ratio of floc[4,8] and the occurrence of floc suspended within an oxygenated, circumneutral water-column, which collectively favor greater amorphous Fe oxyhydroxides abundances within floc and greater associated metal sorptive capabilities. In contrast, amorphous Fe oxyhydroxides within bed sediments are likely to be consumed by Fe reducing bacteria and/or aged into more crystalline Fe oxide minerals, such as hematite and/or goethite,[10,39] which are relatively less reactive[40] but tend to dominate bed sediment geochemistry. Indeed, in contrast to the floc, the crystalline Fe/Mn oxides were the most important

metal sequestration phase in the surficial bed sediment compartment (Figure 2; Table 1). While previous studies have demonstrated the importance of oxides and oxyhydroxides for scavenging metal,[33,38,41] this study is the first to our knowledge to identify a compartment dependent control on metal sequestration of floc amorphous oxyhydroxides and surficial bed sediment crystalline oxides.

Consistent with a more favorable sorptive environment of suspended floc relative to bed sediments, our results indicate the exchangeable fraction (metal loosely held by electrostatic attraction) sequestered floc Ni, Co, Cu, and As (Table 1). Floc $\{Ni\}_E$, $\{Cu\}_E$, and $\{As\}_E$ (up to 0.016, 0.087, and 0.041 μmol g^{-1}, respectively) were within the same magnitude as bed $\{Ni\}_T$, $\{Cu\}_T$, and $\{As\}_T$. Further, $\{As\}_E$ are among the first reported for floc and are important as they indicate higher labile As concentrations within the water-column than those reported for $\{As\}_E$ in bed sediments (e.g., ref 42). Bed sediment $\{M\}_E$ observed in this study were negligible for all elements analyzed (Table 1). Given that suspended floc is a highly mobile compartment, an exchangeable fraction has important ecological and human health implications for floc as a transport vector of easily liberated metal contaminants within freshwater beach environments. Our results also indicate that prediction of solution metal behavior likely requires characterization of floc metal abundances and distributions.

Organic matter was a major constituent of floc, comprising 10−33% by mass versus 1% within the bed (Table S1). Although floc $\{OM\}$ was an important predictor of aqueous-floc distribution, sequential extraction results somewhat surprisingly indicated that the organic fraction was generally not responsible for significant metal retention (Table 1). Cu was the sole exception to this trend. The organic fraction retained up to 49% of floc $\{Cu\}_T$, an association previously documented in both floc and bed sediments.[38,43] In contrast to the results observed for amorphous Fe oxyhydroxides, a gram of floc organic matter was generally not more reactive than a gram of surficial bed sediment organic carbon. In fact, a gram of floc organic carbon was often less effective at concentrating metal compared to bed organic carbon (bed CF exceeded floc CF 75% of the time, exception of Cu; Table S2). We interpret these results as indicating floc organics (mostly live cells and EPS) act as a scaffold for the accumulation of the key floc metal reactive sorbent-phase, amorphous Fe oxyhydroxides, rather than as a direct metal scavenging phase. Consistent with this hypothesis, TEM-EDS analysis revealed peaks of Fe specifically localized to surfaces of floc EPS fibrils and surrounding microbial cells (Figure 1). Associations of Fe with organics within floc have been commonly observed.[4,8] Here, however, our results demonstrate potential linkages between floc organics, Fe entrapment, and metal dynamics. Moreover, results show that flocs with greater $\{OM\}$ generally contained greater $\{Fe\}_A$ abundances (Table S1) consistent with our suggested scaffolding role of floc organic matter enabling the formation and/or collection of amorphous Fe oxyhydroxides rather than direct metal sequestration. However, when combined with our results for floc K_ds, these partitioning results indicate that interactions between floc organics and amorphous Fe oxyhydroxides occur that affect initial metal uptake from solution and sorbent sequestration. For instance, while the distribution of Cu between suspended floc and the solution phase is significantly controlled by the abundance of floc $\{Fe\}_A$ (Figure S1), the partitioning results indicate that it is bound by the floc organics themselves (Table 1).

Based on these results, we hypothesize competitive binding for limited substrate sites within floc either by other elements outcompeting Cu for limited amorphous Fe oxyhydroxide sites or Cu out competing other elements for limited organic sites. Interestingly while both floc Pb and As K_ds are best predicted by floc $\{OM\}$ indicating that the greater the floc organic concentrations (Figure S1), the greater sorption of these elements to the floc from solution occurs; neither of these elements are significantly bound to the floc organics themselves (Table 1). The intimate and, we believe, architectural association of floc organics and amorphous Fe oxyhydroxides drives overall floc metal uptake; however, variation in element concentrations and specific element affinities for these likely limited substrates within this competitive sorptive environment are also apparent.

(B). Energy-Regime Metal Dynamics. Given the substantive differences in both abundance and substrate associations of metals observed between floc and surficial bed sediments, it would be expected that interactions of these two sedimentary compartments would lead to dynamic shifts in metal behavior. Indeed, a comparison of floc and bed sediment metal partitioning observed during low-energy and storm conditions indicated that interactions of these two compartments led to shifts in substrate composition and associated metal behavior both when energy-regimes were sufficient to mobilize bed sediments into suspension as well as post storm, when materials subsequently settled out of suspension into the surficial bed sedimentary compartment. Low-energy periods (Calm-1, Calm-2) revealed distinctly different metal partitioning patterns between floc and bed sediments (Figure 2; Table 1). For these sampling periods, metal sequestration in floc was dominated by the amorphous oxyhydroxide fraction while the crystalline oxide fraction controlled bed metal dynamics, as discussed previously. In contrast, under storm-conditions, floc-partitioning patterns resembled that of bed sediments i.e. loss of the floc-signature in suspension. Metal sequestration in both floc and bed sediments was dominated by the crystalline oxide fraction (Figure 2; Table 1) indicating that hydrologically driven mobilization of bed sediments, and associated crystalline oxide-signature, overwhelmed the distinct floc amorphous Fe oxyhydroxide metal signature observed under low-energy periods. Mobilization of bed sediments was evidenced not only by a 100 times increase in suspended sediment concentrations during the storm but also increased $\{Fe\}_C$ and $\{Mn\}_C$ within storm collected floc (Table S1). TEM visualization of storm-floc revealed a greater proportion of inorganic particles compared to that of calm-floc (Figure 1), and TEM-EDS analysis indicated a distinct Mn marker within the inorganic particles. Further, imaging revealed far less biological structure to storm-floc aggregates, in particular fewer EPS fibrils associated with microbial cells. Together, these results reflect a distinct shift in floc aggregate structure, substrate composition, and associated metal-partitioning behavior during periods of hydrological mixing of floc-bed sedimentary compartments.

Storm-floc (i.e., including mobilized surficial bed sediments in the floc compartment) K_ds were also distinctly different from that of calm-floc in that they were greater for all metals, with the exception of Co, and did not correlate with either $\{Fe\}_A$ or $\{OM\}$ (Figure S1). These results indicate that nonsaturated differentially metal reactive substrates from the bed sediments are present in storm-floc altering both K_ds as well as partitioning patterns to that of calm-floc. Specifically, crystalline Fe oxides mobilized from the bed increased floc metal uptake, as evidenced

2162

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by storm-floc $\{Fe\}_C$ CFs that were substantively greater than those determined for the previous day calm-floc (Table S2). These results indicate energy-regime driven mobilization of nonmetal-saturated bed sedimentary crystalline Fe oxide provides a dynamic mechanism for enhanced floc metal uptake during high energy-regimes in nearshore beach environments.

Further, mobilized crystalline oxides also provide new surfaces for flocculation during periods of mixing. Flocculation, through physical collision, chemical (electrochemical) and/or biological means,[44,45] generates new aggregates of combined floc-bed substrates that would likely settle together when energy levels subsides. Newly generated floc deposition appears evident in our results by the emergence of a floc amorphous-partitioning signature in the bed compartment (Figure 2; Table 1), along with an observed spike of $\{Fe\}_A$ in the surficial bed sediments poststorm consistent with formation and entrainment of this more amorphous material once energy-regimes drop, settling this material into the surficial bed sediments (Table S1). As bed sediments remain undisturbed, the new supply of floc amorphous Fe oxyhydroxides may age into more crystalline oxide minerals, incorporating any bound metals into its solid structure[39] thus regenerating the crystalline oxide signature characteristic of the bed compartment under low-energy conditions. In contrast, regeneration of amorphous-partitioning in the floc compartment poststorm (Figure 2; Table 1) indicates return of "microbial floc" dominated by EPS-amorphous Fe oxyhydroxides and distinct metal behavior (substrate control on K_ds and amorphous-partitioning signature) as larger particles quickly redeposit. Therefore, floc collected under low-energy conditions is a unique microbially controlled sedimentary compartment in aquatic systems that cannot be regarded simply as bed sediments in suspension. It is the largely living microbial cells and EPS components that play a key structural role in floc metal behavior specifically through the biomineralization and/or collection of amorphous Fe oxyhydroxides, ultimately creating a distinctly different solid with different metal partitioning than bed sedimentary materials. These results indicate that floc is an important metal repository in aquatic systems that will not be well modeled by bed sediments, even when floc is in close proximity to surficial bed sediments (0.5 m above bed in this study). Further, the exchange of floc and bed sedimentary materials driven by hydrologic energy-regime will dynamically impact metal behavior of these two compartments, and, as such, freshwater beach environments are likely highly active metal systems.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Table S1, site physcio-chemical parameters and floc/bed substrate composition; Table S2, floc/bed $\{Fe\}_A$, $\{Fe\}_C$, and $\{OM\}$ CFs; Figure S1, floc K_ds; Figure S2, floc/bed Live/Dead images. This material is available free of charge via the Internet at http://pubs.acs.org.

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