Freshwater Suspended Particulate Matter – Key Components and Processes in Floc Formation and Dynamics.

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ABSTRACT

Freshwater suspended particulate matter (SPM) plays an important role in many biogeochemical cycles and serves multiple ecosystem functions. Most SPM is present as complex floc-like aggregate structures composed of various minerals and organic matter from the molecular to the organism level. Flocs provide habitat for microbes and feed for larger organisms. They constitute microbial bioreactors, with prominent roles in carbon and inorganic nutrient cycles, and transport nutrients as well as pollutants, affecting sediments, inundation zones, and the ocean. Composition, structure, size and concentration of SPM flocs are subject to high spatiotemporal variability. Floc formation processes and compositional or morphological dynamics can be established around three crucial components: phyllosilicates, iron oxides/(oxy)hydroxides (FeOx) and microbial extracellular polymeric substances (EPS). These components and their interactions increase heterogeneity in surface properties, enhancing flocculation. Phyllosilicates exhibit intrinsic heterogeneities in surface charge and hydrophobicity. They are preferential substrates for precipitation or attachment of reactive FeOx. FeOx form patchy coatings on minerals, especially phyllosilicates, which increase surface charge heterogeneities. Both, phyllosilicates and FeOx strongly adsorb natural organic matter (NOM), preferentially certain EPS. EPS comprise various substances with heterogeneous properties that make them a sticky mixture enhancing flocculation. Microbial metabolism, and thus EPS release, is supported by the high adsorption capacity and favorable nutrient composition of phyllosilicates and FeOx supply essential Fe.

KEYWORDS: suspended particulate matter composition, phyllosilicates, iron oxides, extracellular polymeric substances, aggregation, flocculation

ABBREVIATIONS

SPM: suspended particulate matter; EPS: extracellular polymeric substances; FeOx: iron oxides and (oxy)hydroxides; HS: humic substances; NOM: natural organic matter; POM: particulate organic matter; DOM: dissolved organic matter; POC: particulate organic carbon; DOC: dissolved organic carbon; MW: molecular weight

1. INTRODUCTION

Freshwater suspended particulate matter (SPM) is an integral part of global geological, geochemical and biological cycles in the aquatic environment, due to its ubiquitous presence, mobility, and physicochemical properties (Eisma, 1993). About 10^9 - 10^{13} tons of SPM are discharged into the oceans every year (Beusen et al., 2005; Meybeck, 1982; Viers et al., 2009; Walling and Webb, 1987), supplying loads of inorganic (Martin and Meybeck, 1979) and organic (Meybeck, 1982) matter to the marine ecosystem. For most elements, particulate loads by far exceed dissolved ones (Jeandel and Oelkers, 2015; Meybeck, 1976), making riverine SPM the major nutrient-supply to the oceans (Beusen et al., 2005; Eisma, 1993; Jeandel and Oelkers, 2015). Substantial particulate carbon loads (Meybeck, 1982) indicate the importance of SPM in global carbon-cycling. About 44 % of the annual terrestrial C flux into rivers are returned to the atmosphere, ~22 % are buried in lake and reservoir sediments, and about one third reaches the ocean (Aufdenkampe et al., 2011), where salinity boosts aggregation and sedimentation (Eisma, 1993). Both, freshwater and marine sediments constitute important carbon sinks, and burial may subject SPM to diagenesis or hydrocarbon formation processes, closing the geological cycle (Eisma, 1993; Leithold et al., 2016).

Freshwater CO_2 release is partly attributed to colonized SPM flocs functioning as bioreactors (Figure 1). SPM pools elemental nutrients and organic substrates which fuel aquatic microbial production and attract microorganisms to attach (Grimm, 2017; Grossart and Ploug, 2000; Luef et al., 2009; Servais and Garnier, 2006). To access nutrients, microbes modify pH and redox potentials inside SPM and create a microenvironment with increased enzyme activity. During the degradation of organic matter biomass is built up, inorganic nutrients are recycled and partly released to the water together with labile organic substances, feeding free-living organisms (Grossart and Simon, 1998; Simon et al., 2002). Microbial biomass improves the nutritional value of SPM (Crump et al., 2017; Rosi-Marshall and Meyer, 2004) for grazing filter feeders (e.g. crustaceans, fish, whales), making SPM an essential part of the pelagic food web (Figure 1) (Zimmermann-Timm, 2002).

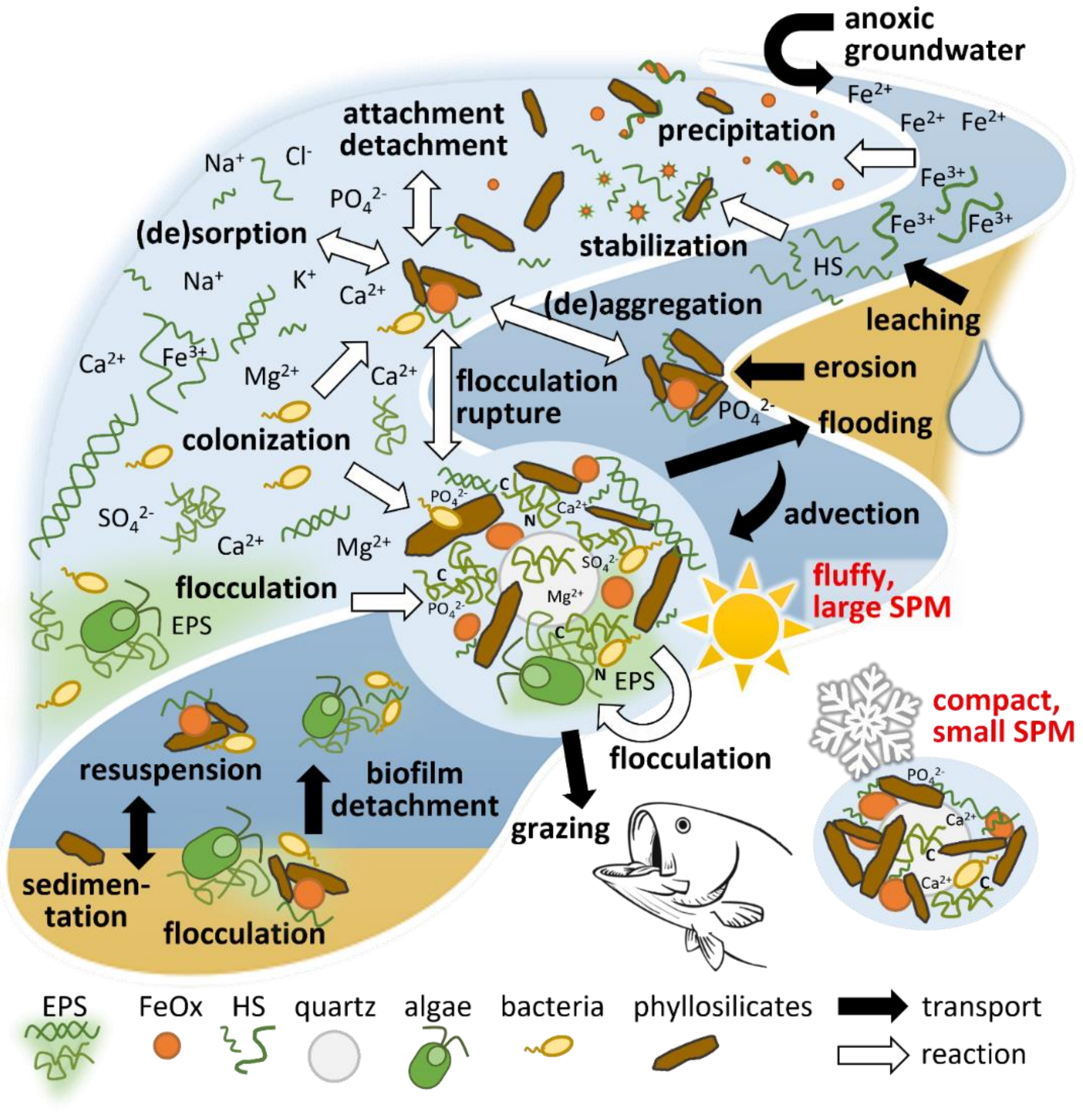

Figure 1. Overview on suspended particulate matter dynamics (EPS: extracellular polymeric substances, HS: humic substances, FeOx: iron oxides/(oxy)hydroxides).

SPM is mobile and connects the pelagic to the benthic zone by sedimentation and resuspension, rivers to lakes and oceans by advective transport, and terrestrial to aquatic environments via runoff/erosion and flooding (Figure 1) (Aufdenkampe et al., 2011; Zimmermann-Timm, 2002). Sedimentation is favored at slow flow and in zones of reduced turbulence (Eisma, 1993) and supplies nutrients to benthic organisms. Floc formation continues in sediments (Wotton, 2007; Zimmermann-Timm, 2002) until increased shear through high discharge in rivers, tidal impact in estuaries, or temperature/wind-driven mixing in lakes, (re)mobilizes SPM (Eisma, 1993). High concentrations of SPM can physically impair aquatic ecosystems. Increased turbidity hampers bioproduction due to reduced light and mechanical stress, and mineralization of organic-rich SPM upon deposition can induce oxygen shortage in poorly mixed waters (Bilotta and Brazier, 2008). Inundations supply SPM to riparian zones and floodplains (Adair et al., 2004; Brunet et al., 1994; Droppo et al., 2004), where nutrients may accumulate over several flood cycles (Adair et al., 2004; Leithold et al., 2016). SPM retention reduces eutrophication of river systems (Gordon et al., 2020) and nutrient discharge into the oceans (Leithold et al., 2016). SPM can as well act as vector for contaminants. Due to its physicochemical properties, it accumulates various dissolved organic (Guo et al., 2007; He et al., 2006; Patrolecco et al., 2010; Pohlert et al., 2011) and inorganic contaminants (Adamiec and Helios-Rybicka, 2002; Brugmann, 1995; Juracic et al., 1986; Vidmar et al., 2017) and governs their mobility, bioavailability and accumulation. More recently, SPM interactions (e.g. heteroaggregation) with particulate contaminants like engineered nanoparticles, micro-/nanoplastics, tire/break/road wear or soot received increased attention, as SPM governs their fate (e.g. Li et al., 2019; Oriekhova and Stoll, 2018; Praetorius et al., 2014; Sigmund et al., 2018; Surette and Nason, 2019; Wagner et al., 2018).

SPM is operationally defined and comprises any material that does not sediment under the given hydrodynamic and hydrochemical conditions, and is retained by filtration over 0.45 or 0.22 µm pore size membranes (Eisma, 1993). The filtrate is considered *dissolved*, and is sometimes further separated into *colloidal* (< 0.45 µm and > 1 kDa) and *truly dissolved* fractions (< 1 kDa) (e.g. Guo et al., 2004, 2007). SPM is highly complex and dynamic (Figure 1). It typically exhibits complex floc- or aggregate-like structures that integrate inorganic and organic components of allochthonous (aquagenic) and autochthonous (mainly pedogenic) origins (Droppo, 2001; Henning et al., 2001; Zimmermann-Timm, 2002). The inorganic fraction is dominated by minerals retrieved from catchment erosion or sediment resuspension, complemented with some authigenic precipitates (e.g. carbonates, oxides, sulfides), biogenic Ca- or Si-rich frustules and (exo)skeletons, or anthropogenic particles (e.g. fly ash, soot, wear and corrosion products, slag, talc). The organic fraction comprises a range of molecular-level labile to refractory substances, detrital plant or microbial fragments and living microorganisms (e.g. bacteria, algae, viruses, fungi, protozoa). (Droppo, 2001; Filella, 2007; Greiser, 1988; Ittekkot, 1988; Thomas and Meybeck, 1996; Zimmermann-Timm, 2002) Among truly dissolved, colloidal, suspended matter and sediments, SPM constitutes a structural and functional transition phase in constant exchange with all other phases (Droppo et al., 2004; Eisma, 1993; Wotton, 2007). SPM composition, structure, size, and concentration are dynamic in time and space, and depend on discharge (storm or base flow), season (bioproduction), catchment geology (slope, mineralogy), vegetation (quantity and quality of soil erosion and leachate), hydrochemistry (pH, concentration and composition of electrolytes and dissolved organic matter), as well as human impacts (e.g. river engineering, pollution, land use) (Eisma, 1993; Viers et al., 2009; Zimmermann-Timm, 2002).

Different conceptions of SPM are reflected in the diversity of terms across disciplines. The most common ones are s*uspended sediments* (Droppo et al., 1998; Hillier, 2001; McConnachie and Petticrew, 2006; Pont et al., 2002), *suspended (particulate) matter* (Baalousha et al., 2019; Breitenbach et al., 1999; Le Meur et al., 2016; Ran et al., 2000), *(total) suspended solids* (Berger et al., 1996; Bilotta et al., 2012; Droppo and Ongley, 1994), which share the idea of a material suspended under given conditions. *Suspended sediments* stresses sedimentation and resuspension as a major SPM control but falls short of implying material inputs by runoff, soil-erosion and pelagic bioproduction. *Suspended solids* underlines the distinction from the dissolved phase, but dissolved substances are building blocks incorporated by adsorption or diffusion into SPM pores. Consequently, *suspended matter*, seems most comprehensive. Some less common terms are *seston* (Kernegger et al., 2009; Kondratieff and Simmons, 1985; McConnachie and Petticrew, 2006; Peduzzi and Luef, 2008) (from Greek *strain* or *filter*), which reflects the operational definition of SPM, and *composite (suspended sediment) particles* (Sinawi and Walling, 1996; Woodward and Walling, 2007) or *(suspended) cohesive sediments* (Garcia-Aragon et al., 2011; Shin et al., 2015; Zhang et al., 2013), which highlight its complex composition. *River snow* (Böckelmann, 2000; Neu, 2000) was introduced by microbial ecologists analogously to *marine snow* and emphasizes microbial impact yielding organic-rich fluffy structures, just as the term *floc*. *Aggregate*, in turn, describes mineral-dominated structures associated with soil origin.

So far, SPM in river systems has received much less attention as compared to estuarine and marine systems. In the light of recent research addressing particulate pollutants, a fundamental understanding of freshwater SPM is a prerequisite to assess the fate of these emerging contaminants in river systems. Knowledge about freshwater SPM is found in manuscripts from various disciplines, ranging from geosciences through microbiology and ecology to environmental sciences and modelling. There is no comprehensive review available on the formation of SPM in river systems which analyzed the plethora of information from these different disciplines. Many studies have considered SPM as substrate for contaminant interactions, controlling behaviour, fate and bioavailability of pollutants. In most cases SPM was treated as a black-box, constituting the particle-bound fraction of pollutants. Here we abandon this contaminant-centred view and focus on the characteristics and dynamics of SPM as pivotal micro-reactors in freshwater chemistry and ecology. The aim of this review is to analyze the complexity of freshwater SPM composition and identify the key components and mechanisms governing physicochemical floc formation processes with a focus on river systems. We elucidate the quantitative and qualitative mineralogical and organic composition of riverine SPM and identify components that play crucial structural-functional roles in SPM formation. The origins, flocculation-relevant properties and dynamic interactions of these SPM components are discussed in detail, and spatiotemporal dynamics affecting floc formation, morphology, and composition are explained (Figure 1).

2. COMPOSITION AND STRUCTURAL FEATURES OF RIVERINE SPM

With about 1 - 30 $\%_{wt}$ organic matter content, riverine SPM mass, not necessarily volume, is overall dominated by minerals, mainly phyllosilicates, carbonates, quartz, and feldspars. The organic matter content and its composition underlie seasonal and discharge-related dynamics. Generally, less bioavailable fulvic and humic-like substances dominate, but during periods of substantial bioproduction, easily biodegradable substances can constitute up to 70 $\%_{wt}$ of the organic matter in SPM.

2.1. Phyllosilicates dominate the mineral fraction.

Phyllosilicates and quartz are omnipresent in riverine SPM around the world (Table 1), followed by feldspars and carbonates reported in 24 and 21 out of 25 rivers, respectively. By mass (Table 1 (A)), phyllosilicates contribute 22 - 72 $\%_{wt}$ and carbonates up to 61 $\%_{wt}$. The carbonates fraction is more variable and sometimes absent, as they might dissolve with distance from the lithological source. Their presence is often related to an increased microbial activity (Breitenbach et al., 1999; Eidam et al., 1997; Sigleo and Helz, 1981) and artefacts from sample preparation, e.g.

precipitation, can distort the picture (Bibby and Webster-Brown, 2005; McGuire and Herman, 2015). Quartz represents 8 - 35 $\%_{\mathrm{wt}}$ and feldspars 4 - 41 $\%_{\mathrm{wt}}$. With increasing discharge, coarse grain-size classes increase their share in the SPM size distribution, often resulting in higher fractions of quartz (up to ~50 $\%_{\mathrm{wt}}$ (Slomberg et al., 2016)), feldspar or carbonates (Buffle et al., 1998; Henning et al., 2001; Hillier, 2001; Kravchishina et al., 2010; Lučić et al., 2021; Pont et al., 2002; Slomberg et al., 2016; Subramanian, 1979; Wall and Wilding, 1976). This grain size dependence is reflected in particle-number based SPM composition data (Table 1 (C)), where phyllosilicates amount to 66 - 89 $\%_{\mathrm{n}}$ and quartz only up to 9 $\%_{\mathrm{n}}$. Clays (e.g. illite, kaolinite, smectite, montmorillonite) are the prevalent phyllosilicates, with illite constituting 48 $\%_{\mathrm{wt}}$ of phyllosilicates and 24 $\%_{\mathrm{wt}}$ of the total minerals (SI-Table 1 (A)). Furthermore, chlorite, mica (muscovite, biotite) and mixed-layer silicates are common (SI-Table 1).

Finally, oxides and (oxy)hydroxides – predominantly those of iron – are frequently reported, but typically in low mass or number concentrations (Table 1). They appear to be mainly present as patchy coatings on aluminosilicates and sometimes other minerals, as evidenced by electron microscopy (Henning et al., 2001; Hirst et al., 2017; Le Meur et al., 2016; Poulton and Raiswell, 2005) or by a co-occurrence of Fe with Al, Si, Ca and other elements (Atteia et al., 1998; Chanudet and Filella, 2008; Hirst et al., 2017; Le Meur et al., 2016; Poulton and Raiswell, 2005; Sigleo and Helz, 1981), but also discrete iron oxide or (oxy)hydroxide particles (FeOx) are reported (Baken et al., 2013; Chanudet and Filella, 2008; Le Meur et al., 2016; Neubauer et al., 2013a; Poulton and Raiswell, 2005). Regarding mineralogy, amorphous phases and ferrihydrite dominate, but also goethite and hematite are frequently identified (Baken et al., 2013; Hirst et al., 2017; Kravchishina and Dara, 2014; Le Meur et al., 2016; Mao et al., 2010).

The mineral composition is of course coined by the catchment lithology and soil-types (Håkanson et al., 2005; Le Meur et al., 2016; Lučić et al., 2019; Pont et al., 2002), but was found to be quite constant throughout seasons and different flow regimes (Nachtnebel et al., 1998; Pont et al., 2002; Slomberg et al., 2016; Wall and Wilding, 1976), except for the mentioned grain-size relation (higher quartz, feldspar, carbonate concentrations in larger size fractions).

Table 1. Mineralogical composition of riverine SPM based on (A) semi-quantitative XRD, (B) qualitative XRD, (C) TEM.

	Ref.	**River**	**Quartz: Phyllosilicates**	**Quartz**	**Phyllo-silicates**	**Feldspars**	**Carbonates**	**FeOx**
(A) [%$_{wt}$]	(Wall and Wilding, 1976)	Maumee Catchment, USA	34:66	29±5	56±7.1		x	x
	(Eidam et al., 1997) a)	Odra, POL	34:66	16.9	32.3	9.2	6.2	7.7
	(Nachtnebel et al., 1998)	Danube, AUT	21:79 (15:85...30:70)	12.9 (8...17)	49.6 (34...64)	8.8 (5...12)	32.2 (16...46)	
		Inn, AUT	28:72 (18:82...45:55)	16.0 (10...22)	42.8 (27...58)	19.5 (8...39)	23.5 (6...34)	
		Salzach, AUT	21:79	12	46	12	30	
		Traun, AUT	21:79	13	48	6	33	
		Enns, AUT	24:76	10	31	5	54	
		Ybbs, AUT	38:63	18	30	6	45	
		Erlauf, AUT	24:76	10	31	2	56	
		Krems, AUT	24:76	14	44	42		
		Kamp, AUT	18:82	16	72	12		
		Traisen, AUT	30:70	14	33	3	50	
	(Ding et al., 2004)	Yangtze, CHN	29:71 (25:75...34:66)	21.9 (18.4...24.5)	54.4 (47.3...61.1)	13.8 (10.8...18.5)	10.0 (5.0...16.4)	
	(Kravchishina et al., 2010)	Severnaya Dvina Mouth, RUS	31:69 (12:88...51:49)	20.2 (9.0...28.8)	46.3 (25.3...68.3)	24.9 (17.3...41.2)	5.5 (3.6...8.7)	
	(Mao et al., 2010)	Changjiang, CHN	25:75 (20:80...31:69)	21.8 (19.4...25.3)	58.1 (45.8...68.2)	12.4 (6.3...20.3)	7.7 (2.6...14.4)	4.6 (4.3...5.2)
	(Ding et al., 2011)	Yellow River, CHN	27:73 (16:84...41:59)	18.8 (12.8...25.0)	52.1 (34.1...65.1)	16.7 (9.5...31.2)	10.5 (7.2...15.1)	1.3 (0...2.5)

	(Slomberg et al., 2016) [b]	Rhone, FRA	54:46 (54:46...55:45)	31 (28...34)	26 (23...29)	12.0	31 (25...37)	
	(Lučić et al., 2019)	Sava, HRV	43:57 (38:62...52:48)	25.9 (13.5...34.6)	33.1 (22.4...45.6)	7.7 (3.9...13.3)	36.1 (19.1...60.7)	
		ave. [$\%_{wt}$] [c] **min…max**	**29:71 (12:88...55:45)**	**17.6 (8.0...34.6)**	**43.1 (22.4...72)**	**12.0 (2...42)**	**29.9 (2.6...60.7)**	**4.5 (0...7.7)**
(B)	(Henning et al., 2001)	Odra, POL		x	x	x	x	x
	(Subramanian, 1979)	Major Indian Rivers		x	x	x		
	(Hillier, 2001)	Don, GBR		x	x	x	x	x
	(Bibby and Webster-Brown, 2005)	Pakuranga, East Tamaki, Puhinui; NZL		x	x	x		x
	(Sigleo and Helz, 1981)	Patuxent, USA						x
(C) [$\%_{n}$]	(Le Meur et al., 2016)	Moselle Catchment, FRA	6:94 (0:100...10:90)	4.4 (0...7.5)	73.6 (66...82)	x	x	19.9 (13...27)
	(Chanudet and Filella, 2008)	Aare, CHE	4:96 (0:100...12:88)	3.4 (0...9)	72.5 (68...77)	18.8 (13...22)	x	2.3 (0...4)
		Lütschine, CHE	5:95 (0:100...10:90)	4.3 (0...9)	78.5 (67...89)	5.6 (3...9)	x	4.6 (1...9)
		ave. [$\%_{n}$] [c] **min…max**	**5:95 (0:100...12:88)**	**4.0 (0...9)**	**74.9 (66...89)**	**12.3 (3...22)**		**8.9 (0...27)**

[a] original data included organic fraction; numbers were recalculated so that the total minerals represent 100 %

[b] only data for 0.5 - 1µm size fraction were included

[c] Averages should only provide orientation, as data are of different quality (regarding sampling frequencies and seasons).

2.2. Particulate organic matter (POM) fraction mostly below one third

Particulate organic matter (POM) denotes the organic mass fraction in SPM, distinguished from dissolved organic matter (DOM) by filtration (POM > 0.2 or > 0.45 µm). Sometimes colloidal organic matter (< 0.45 µm and > 1 kDa) is separated as well. This distinction is solely operational, since natural organic matter (NOM) constitutes a continuum, from molecules via detrital matter up to microorganisms, and the POM fraction integrates parts of all size-fractions.

POM is typically determined as mass loss on ignition or applying conversion factors to particulate organic carbon (POC). The reported POM fractions in SPM of 9 rivers range from a few percent to above 30 $\%_{wt}$, with a median of 15 $\%_{wt}$ (Table 2). Employing the reported conversion factors 1.7 - 2.5 (Guo and Macdonald, 2006; Hillier, 2001; Wall and Wilding, 1976) to POC data (SI-Figure 1), 95 % of the reviewed 54 rivers fall within the range of 1.2 - 40 $\%_{wt}$ POM, with a median of 6.5 - 9.5 $\%_{wt.}$ The POM content was found to be inversely correlated with SPM size and reached its maximum in the smallest (1 - 0.2 µm) SPM subfraction (Ran et al., 2000). This is confirmed by 55 % of the total organic carbon load being colloidal (0.45 µm - 1 kDa) and 6 - 20 % particulate (> 0.45 µm), leaving 15 - 28 % in the truly dissolved fraction (< 1 kDa) (Guo et al., 2003; Guo and Macdonald, 2006).

Table 2. Reported POM fractions in riverine SPM. Data represent average (min…max).

Ref.	River	Sampling Period	SPM [mg/L]	POM [$\%_{wt}$]	Method $^{a)}$
(Mao et al., 2010)	Changjiang, CHN	1 year, monthly	48.2 (11.3…152)	10.9 (10.0…12.2)	LOI
(Ding et al., 2004)	Yangtze, CHN	1 week, July	283.9 (69.0…592)	10.2 (8.9…11.6)	LOI

(Eidam et al., 1997)	Odra, POL	1 year, bimonthly	17.0	33.0	LOI
(Sigleo and Helz, 1981)	Patuxent, USA	1 day, July	32.0	31.6	LOI
(Hillier, 2001)	Don, GBR	1 day, Sept. HQ (6 locations)	65.7 (14.0…143)	13.3 (10.4…15.2)	POC×1.84
		1 day, May LQ (7 locations)	8.0 (2.9…19.1)	23.1 (20.6…26.1)	
(Wall and Wilding, 1976)	Maumee, USA	5 months, weekly	0.45	5.5±0.9	POC×1.7
(Guo et al., 2003)	Chena, USA	1 month, several	5.0	17.3	POC×2.5
(Guo and Macdonald, 2006)	Yukon, USA	5 months, monthly	155.7 (53.0…331)	3.3 (1.3…6.0)	POC×2.5 [b]
(Ran et al., 2000)	Namoi, AUS	1 day, July	52.5	31.4 [c]	LOI
		median (min…max)		**15.3 (1.3…33.0)**	

[a] LOI = loss on ignition; POC = particulate organic carbon

[b] same factor as for Chena River located in the same area

[c] mass-weighted average for size fractions > 0.2 µm calculated from size fractionated data

Quantitative data on the composition of POM is scarce. Typically, easily biodegradable labile and hardly degradable refractory organic matter are distinguished. The labile fraction mainly comprises carbohydrates and protein-like substances, the refractory fraction represents mostly pedogenic, but also aquagenic fulvic or humic-like substances. The POC composition depends on the total SPM load (Ittekkot, 1988) (Table 3). Overall, refractory substances dominate with about 29 - 96 %. Average labile POC fractions of 13 major world rivers amount to 4.3 - 46.6 %, but local or seasonal maxima can be higher, e.g 71 % in river Lütschine (Chanudet and Filella, 2007). In the labile fraction protein-like substances mostly prevail over carbohydrates.

Table 3. Refractory (R-) and labile (L-) POC fractions in riverine SPM. L-POC includes carbohydrates (CH-C) and protein-like substances (Prot.-C). Data represent min…max (average).

Ref.	**River**	**Sampling Period**	**SPM fraction**	**L-POC [%]**		**R-POC [%]**
				CH-C [%]	**Prot.-C [%]**	
(Chanudet and Filella, 2007) a)	Aare, CHE	2 years	< 1.2 µm	17…61 (39)		39…83 (61)
(Chanudet and Filella, 2007) a)	Lütschine, CHE	2 years	< 1.2 µm	15…71 (42)		29…85 (58)
(Guo et al., 2003)	Chena, USA	1x, July	> 0.7 µm	34.2 b)	30.2	35.6 c)
(Servais and Garnier, 2006)	Seine, FRA	3 years	> 0.7 µm	13…52		48…87
(Panagiotopoulos et al., 2012)	Rhône, FRA	2 years	> 0.7 µm	23…32		68…77
(Mannino and Harvey, 2000)	Delaware, USA	1x, June	> 0.7 µm	20	31…34	46…49 d)
(Ittekkot and Laane, 1991)	13 world rivers e)	2 - 3 years	> 0.45 µm	4.3…46.6		53.4…95.7
		SPM [mg/L]	5 - 15	15	35	64.8
			15 - 50	17	29	53.4
			50 - 150	8	14	77.9
			150 - 500	5	7	88.2
			500 - 1500	7	11	81.2
			1500 - 5000	4.3		95.7
		total range		**4…71**		**29…96**
				5…34	**7…35**	

a) original data [mg L^{-1}] extracted from graph and converted to % of sum CH-C and R-POC

b) sum of C originating from polysaccharides, carboxylic acids, carbohydrates

c) sum of C related to refractory and “other” compounds

d) remaining fraction (non-polysaccharidic & non-amino acids)

e) Mackenzie, St. Lawrence, Magdalena, Orinoco, Parana, Niger, Zaire, Nile, Oragne, Indus, Ganges, Brahmaputra, Yangtze; averages across all rivers grouped by total SPM concentrations

2.3. POM content and composition are dynamic.

Whether the quality of POM is rather refractory or labile is related to the source of NOM. Refractory substances are mostly pedogenic humic substances (HS), predominantly fulvic acids, retrieved from catchment soils by leaching or erosion (Buffle et al., 1998), while labile carbohydrates and proteins, referred to as extracellular polymeric substances (EPS), mainly originate from aquatic microbial production (Droppo et al., 2004; Flemming and Wingender, 2010; Lee et al., 2019; Zimmermann-Timm, 2002) (Figure 1). Consequently, POM content and composition are linked to seasonal variations in primary production and discharge (Figure 2).

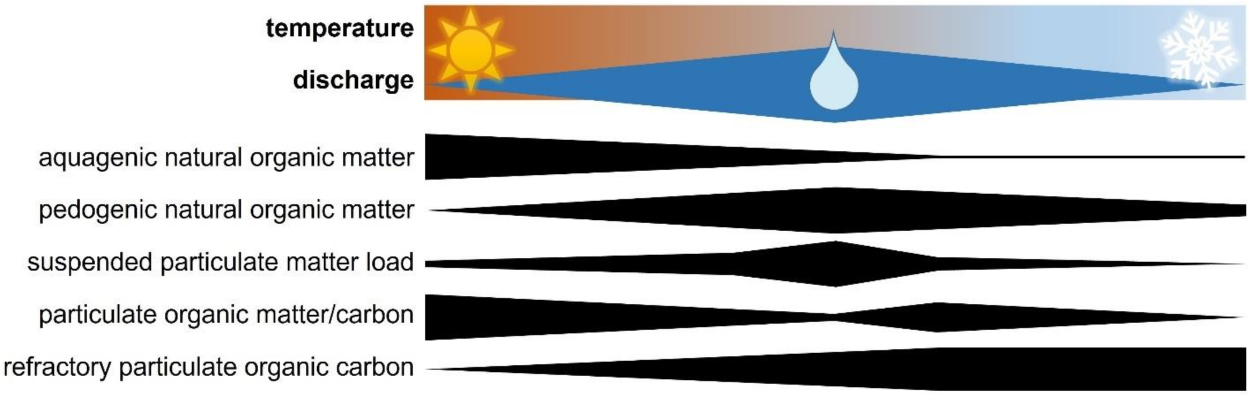

Figure 2. Seasonal and discharge-related dynamics in natural organic matter source, suspended particulate matter load and particulate organic carbon contents and composition (schematic).

Related to the dominant source of NOM, contrary seasonal patterns exist: temperate low-land rivers exhibit increased autochthonous microbial production and EPS release from spring through autumn, yielding high labile aquagenic POC fractions (Bukaveckas et al., 2019; Henning et al., 2001; Lučić et al., 2019; Servais and Garnier, 2006; Sigleo and Helz, 1981). Allochthonous (e.g. periglacial or arctic) systems are mainly fed by HS-type NOM leached from soils during wet seasons or snowmelt and exhibit organic carbon minima during dry summers (Chanudet and Filella, 2007; Guo et al., 2003; Guo and Macdonald, 2006; Onstad et al., 2000).

With increasing discharge, the SPM load increases and POC decreases (Bibby and Webster-Brown, 2005; Henning et al., 2001; Ittekkot and Laane, 1991; Le Meur et al., 2016; Lučić et al., 2019; Meybeck, 1981; Onstad et al., 2000). This is explained by dilution of the POC fraction in SPM with eroded or resuspended minerals (Bibby and Webster-Brown, 2005; Hillier, 2001), together with a reduced bioproduction through increased turbidity (Chanudet and Filella, 2007; Ittekkot and Laane, 1991). The first moderate flushes in spring or autumn, however, can increase POC by mobilizing sedimented organic detritus (Bibby and Webster-Brown, 2005; Chanudet and Filella, 2007; Guo and Macdonald, 2006; Henning et al., 2001). Discharge also affects organic matter quality. During storm-flow conditions soil-derived HS increase the refractory POC portion (Chanudet and Filella, 2007; Hillier, 2001; Ittekkot and Laane, 1991), whereas under low-flow conditions bioproduction increases the labile POC portion (Besemer et al., 2009; Hillier, 2001; Panagiotopoulos et al., 2012; Servais and Garnier, 2006).

The maximum POC values are frequently measured from spring to early summer (Chanudet and Filella, 2007; Henning et al., 2001; Servais and Garnier, 2006) at intermediate discharge (low runoff-to-precipitation ratios) and increased temperatures (Besemer et al., 2009; Onstad et al., 2000). In such conditions, inputs of soil-derived carbon and inorganic nutrients meet the onset of increasing bioproduction, while the shear suffices to resuspend (and avoid sedimentation of) light organic-rich fractions but not to mobilize minerals from the riverbed or banks.

2.5. Floc-like aggregates are the dominant SPM structure.

The primary mineral and organic constituents of SPM are hardly found isolated, but assembled in complex floc or aggregate-like structures (Bibby and Webster-Brown, 2005; Droppo, 2001; Henning et al., 2001; Kravchishina et al., 2010; Lučić et al., 2019; Nomizu et al., 1987; Wilkinson et al., 1997; Zimmermann-Timm, 2002), which constitute more than 90 % of the total SPM volume, 10 - 60 % by number (Droppo and Ongley, 1994; Droppo and Stone, 1994) and about 60 % by mass (Woodward and Walling, 2007).

Droppo and Ongley (1994) summarized three possible origins of floc or aggregate-like structures (1) soil-erosion supplying some water-stable aggregates, (2) flocculation within the river by physical, chemical and biological means, and (3) *hybrids* combining both. Traditionally, *flocs* referred to a riverine origin, whereas *aggregates* were considered soil-borne. Also structural differences were inferred: aggregates show higher density and compactness, lower porosity and rounder shape (Droppo et al., 2005; Woodward et al., 2002). A distinction within a river-water sample was, however, not possible (Droppo et al., 2005). Most soil aggregates (partially) disaggregate in rivers (Grangeon et al., 2014); heavier factions are incorporated into sediments or organic-rich sediment surface layers, from where they can be resuspended as flocs (Droppo and Stone, 1994), whereas light fractions stay suspended and form flocs or aggregate-floc hybrids in the water column (Droppo et al., 2005). Biofilm fragments that detach from their substratum also contribute to SPM (Wotton, 2011, 2007) and may capture minerals within their organic matrix while suspended (Figure 1). In this work, the term *floc* refers to any complex SPM structures.

The formation and stability of flocs depends on the constituents' physicochemical surface properties, which give rise to short-range interaction forces. Based on particle aggregation theory (Elimelech et al., 1995; Gregory, 2005), electrostatic forces arising from the constituents' structural charge or ionized functional groups, as well as van der Waals and hydrophobic attractions are most relevant. Organic molecules may also favor flocculation, acting as bridges between particles or inducing surface charge heterogeneities or neutralization upon adsorption (Buffle et al., 1998).

3. CRUCIAL STRUCTURAL-FUNCTIONAL SPM COMPONENTS

The major physicochemical processes driving SPM floc formation can be established around three crucial structural-functional components due to their physicochemical surface properties: EPS, FeOx, and phyllosilicates (Figure 1).

3.1. Microbial EPS-type NOM is the “glue” in SPM flocs.

NOM is omnipresent in aquatic systems and no solely mineral associations are found in riverine SPM samples (Droppo, 2001; Droppo et al., 1997). Different types of NOM exhibit different flocculation potentials (Buffle et al., 1998; Wilkinson et al., 1997) depending on their molecular characteristics and the degree of particle surface coverage (Buffle et al., 1998; Philippe and Schaumann, 2014; X. Wang et al., 2021). Adsorbed rigid, high-MW molecules may form bridges to other particles, while low-MW and flexible molecules flatten on the particle surface but may induce flocculation via charge neutralization, or patchy particle surface coverage (electrostatic patches). Particles are stabilized against flocculation if fully coated by highly charged, low-MW molecules, or by large, rigid molecules, inducing steric hindrance.

An early conceptual model of complex SPM flocs (Greiser 1988, cited in Henning et al., 2001) already stressed the importance of organic gels, binding other particles. Evidence of network-like and fibrillar organic structures was found in numerous electron microscopy images of natural SPM

(Buffle and Leppard, 1995; Chanudet and Filella, 2007; Droppo et al., 1997; Filella et al., 1993; Henning et al., 2001, 2000; Lartiges et al., 2001; Liss et al., 1996; Neu, 2000; Perret et al., 1994) and a relation between seasonal increase of microbial activity and increased network density – involving thicker, longer, more branched organic fibrils – was observed (Chanudet and Filella, 2007; Henning et al., 2001). These fibrils were concluded to consist of macromolecular microbial EPS (Filella et al., 1993; Leppard, 1997) and pores in SPM were found mostly filled with EPS (Liss et al., 1996; Neu, 2000; Wheatland et al., 2017). At times of high microbial activity, a matrix of macromolecular EPS integrates mineral particles, yielding large fluffy flocs; while in winter, when pedogenic HS is the major NOM source, SPM is dominated by small, compact, mineral-rich flocs and single mineral grains (Böckelmann, 2000; Droppo and Ongley, 1994; Henning et al., 2001; Sigleo and Helz, 1981; Walling and Phillips, 2004) (Figure 1).

Although certain EPS (e.g. highly charged alginate) could stabilize particles, microbial EPS overall enhance flocculation (Lee et al., 2019; Srivastava et al., 2018; Stone and Droppo, 1994; Wotton, 2011). EPS comprise a diverse mix of substances (mainly polysaccharides, proteins, lipids, DNA), with highly heterogeneous physicochemical properties that allows for various interactions with mineral surfaces and with each other. Different EPS preferentially sorb to different mineral surfaces resulting in fractionation (Aufdenkampe et al., 2001; Cao et al., 2011; Gu, 1992; Hedges and Hare, 1987; Lin et al., 2016; Xinran Liu et al., 2013; Yeasmin et al., 2014). Heterogeneities may even persist on a particle level: On goethite, EPS formed nano-scaled patches enriched in different subfractions (proteins, lipids, polysaccharides), suggesting that patches exhibit distinct physicochemical properties (Xinran Liu et al., 2013).

3.1.2. Microbial EPS are a diverse mix of substances.

The origin of EPS is mostly linked to microbes, such as bacteria and microalgae (Figure 1), but also fungi and archaea (Droppo et al., 2004; Flemming and Wingender, 2010; Zimmermann-Timm, 2002) or larger organisms contribute – from insect silk up to fish mucus (Wotton, 2011). EPS are dominated by polysaccharides and a previously underestimated share of proteins (Flemming and Wingender, 2010; Laspidou, 2002), complemented by some extracellular DNA, lipids and fragments of all these (peptides, amino- and nucleic acids, sugars) (Flemming and Wingender, 2010). Here we consider EPS the sum of biopolymers released by microorganisms, (a) actively as part of their metabolic activities (exudates) or (b) passively upon cell lysis (intracellular substances) or during cell decomposition (structural biopolymers) (Laspidou, 2002).

Active exudation serves purposes of attachment/detachment to/from surfaces or each other; protection from toxic components, UV-radiation, oxidation, desiccation or mechanical stress; nutrition through exoenzymes, capture of nutrients and particles in the EPS matrix or use of EPS as substrate; and establishment of microenvironments with physicochemical gradients (Flemming and Wingender, 2010). Most exudates are either matrix-forming polysaccharides (e.g. xanthan, pullulan, dextran, alginate (Buffle et al., 1998)) or enzymatic proteins (Flemming and Wingender, 2010, 2001). Matrix polysaccharides are long molecular chains that may associate to form fine strands attached to cells or complex networks surrounding cells (Sutherland, 2001) and are comparatively resistant to degradation (Flemming and Wingender, 2001). Enzymatic proteins cleave organic matter, yielding bioavailable low-MW products, or degrade the EPS matrix, allowing detachment (Flemming and Wingender, 2010). Some lipopeptides are exuded as well (Flemming and Wingender, 2010), they render surfaces more hydrophobic (e.g. serrawettin) or hydrophilic (e.g. surfactin, viscosin), aiding attachment or detachment (Neu, 1996). More recently, the active exudation of DNA, which forms grid- or network-like filament structures, was attributed an attachment function (Flemming and Wingender, 2010).

Upon cell death or lysis, intracellular substances, including reserve polysaccharides (e.g. glycogen) proteins and DNA, are set free and are mostly subject to quick degradation (Buffle et al., 1998; Flemming and Wingender, 2010). Cell hulls decay more slowly and release structural biopolymers: mainly polysaccharidic cell-wall components (cellulose, hemicellulose, pectin, mucopolysaccharides, peptidoglycan (Buffle et al., 1998)) and non-enzymatic proteins (from cytoskeleton filaments, fimbria, pili, flagella or cell-wall components), but also cell-wall associated lipids (phospholipids, glycolipids or lipopolysaccharides) and some extracellular cell-surface bound substances (e.g. proteins such as carbohydrate-binding lectins or amyloids, which aid cell-to-surface attachment) (Flemming and Wingender, 2010).

3.1.3. Heterogeneous molecular characteristics confer stickiness to EPS

There are neutral as well as charged EPS. Anionic character mostly results from carboxyl-groups (in uronic acid and ketal-linked pyruvate), and partly from inorganic groups such as phosphate (e.g. in DNA or phospholipids) or sulphate (e.g. in cyanobacterial EPS), while cationic character arises mostly from amino groups. Most polysaccharides are polyanionic heteropolysaccharides (e.g. alginate, xanthan, colonic acid), while homopolysaccharides such as fructans and glucans are usually neutral (e.g. cellulose, pullulan, dextran, levan). Proteins are ampholytic, as they consist of basic and acidic amino acids carrying carboxyl- and amino groups (Flemming and Wingender, 2010; Sutherland, 2001). Polycationic EPS, exuded by some gram-positive bacteria (Vu et al., 2009), are rare (an example being adhesin) and the hydrophilic moieties of lipid-type amphophiles (phospholipids, glycolipids and lipopolysaccharides) can exhibit either charge condition (Neu, 1996). Charged EPS interact with particle surfaces through electrostatic interactions, H-bonding or ion-bridging (Philippe and Schaumann, 2014). Cationic amino groups for example sorb to negatively charged basal planes of montmorillonite, illite or kaolinite, while anionic carboxyl-groups and phosphate groups (on phospholipids, phosphorylated proteins or DNA) prefer mostly positive Fe- or Al-(hydr)oxide surfaces and phyllosilicate edges, or require ion-bridges (Cao et al., 2011; Gu, 1992; Hedges and Hare, 1987; Lin et al., 2016; Xinran Liu et al., 2013; Yeasmin et al., 2014). Compared to carboxyl-rich pedogenic HS, negative charge densities of most aquagenic EPS are low, which eases interactions with mostly negative mineral surfaces (Buffle et al., 1998), and charge heterogeneities within the EPS mix or even on single EPS molecules (e.g proteins) favor flocculation.

Another relevant property is hydrophobicity (Philippe and Schaumann, 2014). Most polysaccharides and proteins, as well as DNA are hydrophilic. Hydrophobicity increases with increasing acyl-groups (e.g. acetyl-, lactyl-, succinyl-, propionyl-), alkyl-groups (e.g. methyl-, ethyl-), hydrophobic amine and benzyl-groups. (Flemming and Wingender, 2010; Hong et al., 2018; Neu, 1996; Sutherland, 2001) Some EPS exhibit hydrophilic and hydrophobic regions (e.g. emulsan, a highly acetylated polysaccharide, allowing detachment from hydrophobic surfaces) or hydrophobic moieties (e.g. phospholipids, glycolipids, lipopolysaccharides) (Neu, 1996). Hydrophobic interactions let hydrophobic parts of EPS molecules flatten on particle surfaces, as modelled for negative montmorillonite basal planes (Henao and Mazeau, 2008), while hydrophilic side chains (e.g. carrying charged carboxyl- or hydroxyl-groups) extend and may induce flocculation (Henao and Mazeau, 2008; Labille et al., 2005). This reveals the importance of structural EPS features like molecular weight, structural flexibility/rigidity and conformation.

Rigid, high-MW EPS have a higher chance to induce bridging flocculation, as they extend from the particle surface into the water where electrostatic forces become negligible. A full coating by rigid biopolymers, however, prevents flocculation through steric hindrance. (Buffle et al., 1998) Rigid, high-MW EPS mainly comprise structural biopolymers (e.g. cell-wall components) and polysaccharidic exudates, but also DNA (Buffle et al., 1998). Polysaccharide primary structures are long molecular chains, either branched for most heteropolysaccharides or linear for many homopolysaccharides (Sutherland, 1990). Their rigidity depends on the types of linkages between their monomers: 1,3-β- or 1,4-β-linkages confer rigidity (e.g. the cellulosic backbone in xanthan), while other linkages may yield more flexible structures (e.g. 1,2-α- or 1,6-α-linkages in dextran) (Sletmoen et al., 2003; Sutherland, 2001). Highly charged EPS behave rigid because they strongly bind water (sometimes up to 80 %) (Buffle et al., 1998). Some EPS can also self-assemble in rigid supramolecular structures via (1) H-bonding, as between hydroxyl- or methyl-groups, (2) electrostatic or (cation-induced) ionic interactions, as on carboxyl- or sulfate groups, (3) molecular "chain-chain" van der Waals interactions (Kunhi Mouvenchery et al., 2012; Sutherland, 2001). The most common secondary conformation of polysaccharidic exudates (and DNA) in environmental conditions are rigid double or triple helices, yielding long, thin, fibrous structures in single strands or networks (Sutherland, 2001).

With a MW of 10^4-10^5 g mol^{-1}, fibrils reach a thickness of a few nm and a length up to the µm-range. Nano-sized minerals can attach to fibril segments with favorable characteristics and act as connectors between fibrils, yielding large, loose flocs. (Buffle et al., 1998) Polysaccharides can also form gels, which can bind particles. Gelling is favored by carboxyl-groups that allow bridging by multivalent cations (e.g. in gellan or alginate). Increasing acylation, in turn, renders polysaccharides more hydrophobic, which inhibits interactions with ions, weakening gels and promoting flexible random coil structures. Weak gels will not persist in rivers as they dissolve in excess solvent. (Sutherland, 2001) Flexible polymers often exhibit globular appearance and easily change conformation, which lets them flatten on the particle surface and excludes bridging, but they may induce aggregation via electrostatic patch formation or charge neutralization (Buffle et al., 1998; Gregory, 2005). Flexible EPS comprise proteins, intracellular reserve polysaccharides and aquagenic refractory organic matter (i.e. recalcitrant fragments and recombinations of degradation products of microbial cells) (Buffle et al., 1998).

3.1.4. Colonization favors flocculation and vice versa

SPM is enriched in EPS as evidenced by low C:N ratios. N-rich microbially derived organic matter is highest in the fine SPM fraction (< 63 μm) (Hatten et al., 2012; Spencer et al., 2016) and decreases from the colloidal (1 kDa-0.45 μm) to the truly dissolved (< 1 kDa) fractions, as shares of C-rich pedogenic HS and aquagenic refractory organic matter increase (Besemer et al., 2009; Guo et al., 2003; Guo and Macdonald, 2006; Mannino and Harvey, 2000). In coarser SPM fractions (> 250 μm or > 63 μm) C:N ratios increase with increasing vascular plant detritus (Hatten et al., 2012; Johnson et al., 2018; Rowland et al., 2017; Spencer et al., 2016). Accumulation of EPS in SPM can result from (1) colonizing microbes releasing EPS into the flocs, or (2) preferential adsorption of dissolved EPS inducing mineral flocculation (Figure 1).

Microbes can be free-living, obligatory or facultatively SPM-attached (Zimmermann-Timm, 2002). Imaging of natural SPM evidences floc-internal presence of microbes (Liss et al., 1996; Neu, 2000; Wheatland et al., 2017), with bacteria and microalgae dominating (Neu, 2000). The most prominent microalgae in SPM are green algae and diatoms. Bacteria are mainly β-Proteobacteria, accounting for > 70 % of the DAPI-stained cells throughout the year, followed by γ- and α-Proteobacteria, Cytophaga and Flavobacteria (mainly in spring), some sulfate reducers and Planctomycetes (Böckelmann, 2000), as well as cyanobacteria (Lee et al., 2017). Both, bacteria and algae were attributed a positive effect on SPM floc size (Berger et al., 1996; Droppo and Ongley, 1994; Grossart and Simon, 1998; Kondratieff and Simmons, 1985; Wörner et al., 2002; Zimmermann, 1997). Bacteria exhibited the strongest correlation with floc size and were also correlated to phytoplankton concentrations (Wörner et al., 2002; Zimmermann, 1997). Associations between bacteria and algae are mutualistic: bacteria use labile algal EPS as substrate, and algae benefit from inorganic N-fixation and reductive dissolution of Fe by bacteria (Flemming and Wingender, 2001; Srivastava et al., 2018 and refs. therein). Since free-living and attached bacteria are equally correlated to SPM floc size (Zimmermann, 1997), attachment is not a prerequisite for microbially induced flocculation (Figure 1).

On average up to 50 and 60 % (by number) of the particles in the Danube and Danube Channel were non-colonized (Berger et al., 1996) and up to 25 % in River Elbe (Zimmermann, 1997), comprising mainly single mineral particles and small aggregates (Berger et al., 1996; Zimmermann-Timm, 2002). In lab studies, bacteria were the first colonizers of fresh aggregates, forming the base of the microbial food web (Wörner et al., 2000). Low numbers of bacteria are even present in autumn-winter SPM, which completely lacked algae and exhibited smaller, more compact floc-structures than spring-summer SPM (Böckelmann, 2000) (Figure 1). In winter, bacteria sustain themselves on pedogenic HS (Besemer et al., 2009), until phytoplankton blooms and related algal EPS release foster free-living and attached bacteria (Besemer et al., 2009; Crump et al., 2017; Wörner et al., 2002; Zimmermann-Timm, 2002; Zimmermann, 1997). Dissolved, labile EPS get quickly depleted by preferential adsorption to mineral-surfaces (Aufdenkampe et al., 2001; Cao et al., 2011; Lin et al., 2016) and mineralization through free-living bacteria and nutrient limitation makes particle-attachment beneficial (Hoppe, 1984; Sutherland, 2001).

Motile microbes actively colonize SPM, others attach passively upon collision (Zimmermann-Timm, 2002). The latter is enhanced by starvation-induced release of adhesive EPS (Stehr et al., 1995; Sutherland, 2001) and by high SPM concentrations (Wörner et al., 2002). The favorable nutrient composition of SPM, fosters microbial growth (Hoppe, 1984; Zimmermann-Timm, 2002). Heterotrophic bacteria access nutrients exuding EPS (Srivastava et al., 2018 and refs. therein), such as exoenzymes to degrade organics and ligands to dissolve minerals. Spatial proximity of substrates allows a more efficient use of exoenzymes (Servais and Garnier, 2006) and SPM-attached bacteria achieve about three times higher growth-rates than free-living ones (Hoppe, 1984; Luef et al., 2009; Servais and Garnier, 2006). Once the substrate becomes refractory (ageing of SPM) (Grossart and Ploug, 2000), nutrient limitation induces further EPS release and flocculation (Figure 1) (He et al., 2017; Sutherland, 2001).

Preferential adsorption of dissolved EPS also yields enrichment within SPM (Aufdenkampe et al., 2001; Cao et al., 2011; Lin et al., 2016; Xinran Liu et al., 2013). With increasing microbial activity in spring or during algal blooms, EPS release induces a shift in DOC composition, with an increase of larger biopolymers (> 20 kDa) (Lee et al., 2019); increased MW of proteinaceous substances, and lower MW of aromatic compounds (Lee et al., 2015) (Lee et al., 2019). Simultaneously, the potential of filtered (1.2 µm) river water to flocculate kaolinite suspensions increased (Lee et al., 2017, 2019). The fine SPM fraction is coined by aluminosilicate and FeOx primary particles with a high specific surface area (Markussen et al., 2016; Poulton and Raiswell, 2005). Phyllosilicates (e.g. illite, montmorillonite and kaolinite) enrich N from basic proteins, while FeOx preferentially adsorb P-containing nucleic acids, phospholipids or phosphorylated proteins, as well as carboxylate-rich polysaccharides and acidic proteins (Cao et al., 2011; Gu, 1992; Hedges and Hare, 1987; Lin et al., 2016; Xinran Liu et al., 2013; Omoike et al., 2004; Yeasmin et al., 2014; Zhang et al., 2021). EPS induced flocculation generates a favorable substrate for pioneering bacteria (Flemming and Wingender, 2001; Wotton, 2011 and refs. therein). Indeed, small aggregates of clay-sized minerals exhibit the highest bacterial density and activity (Berger et al., 1996; Crump and Baross, 2000; Edwards, 1987; Kondratieff and Simmons, 1985), which again promotes flocculation.

3.1.5. Pedogenic HS counteract EPS.

Flocculation by dissolved EPS is in competition with stabilization by soil-derived HS (Guo et al., 2003; Guo and Macdonald, 2006) (Figure 1). Pedogenic HS typically constitute the largest NOM fraction in fresh waters, with 40 - 80 % of NOM being fulvic acids and < 5 - 10 % humic acids. Fulvic compounds exhibit a low MW (0.5 - 5 kg mol^{-1}) and high maximum charge densities (-6 to -11 meq g^{-1}). Humics are larger, with lower charge density, higher hydrophobicity, C:O and C:H ratios, but else similar. (Buffle et al., 1998) The highly negative charge of HS results from many carboxyl-groups, which are deprotonated at environmental pH values. HS are generally thought to electrostatically stabilize colloids against aggregation, as adsorption increases negative charge of mineral surfaces or induces charge reversal of positively charged surfaces (Buffle et al., 1998; Reinhardt and Wilkinson, 2004; Srivastava et al., 2018). Adsorption of low-MW HS is kinetically favorable, but their hydrophilicity eases desorption and HS will be replaced by higher-MW, aromatic, hydrophobic NOM, the adsorption of which is thermodynamically favored (Philippe and Schaumann, 2014). Therefore, the flocculation potential of river water decreases after rain events, when soil-derived HS increase their share compared to EPS (Lee et al., 2017, 2019). The addition of EPS-like substances to HS-stabilized montmorillonite, in turn, triggers slow aggregation of HS-coated montmorillonite (Wilkinson et al., 1997).

3.2. Iron oxides and (oxy)hydroxides (FeOx) are the "cement" in SPM flocs.

Due to their physicochemical properties, FeOx play a crucial role in SPM floc formation (Praetorius et al., 2020), acting as aggregating agent or cementing agent, analogously to their role in soil aggregates (Filella, 2007). FeOx can be of soil origin, reaching rivers with soil aggregates or as crusts on mineral surfaces, or form and transform in-situ through redox-driven dissolution and precipitation reactions (Davison and De Vitre, 2019) (Figure 1). Precipitation initially yields amorphous and poorly crystalline FeOx, like ferrihydrite or lepidocrocite (Guo and Barnard, 2013; Vindedahl et al., 2016). This so-called labile FeOx fraction was found positively correlated to SPM floc size (Markussen et al., 2016), as it exhibits a high specific surface area and reactivity (Davison and De Vitre, 2019; Hirst et al., 2017; Jilbert et al., 2018). Dissolution and reprecipitation, however, can transform labile FeOx into more cryctalline goethite, while hematite requires dry and warm conditions to form and indicates soil origin (Davison and De Vitre, 2019; Guo and Barnard, 2013). With points of zero charge mostly above pH 7 up to 9 (Kosmulski, 2014), bare FeOx surfaces are expected to be positively charged in many rivers (Salminen et al., 2005), favoring association with negatively charged minerals and NOM. Indeed, only 3-8 % of the total Fe in four river water samples were discrete positively charged FeOx colloids (filtration < 1 µm) and most Fe was associated with SPM (1-10 µm) and with colloidal (< 1 µm) HS or aluminosilicates (Hiraide et al., 1988b).

The morphology of FeOx also plays a role. On electron microscopy images of SPM, FeOx appear as patchy precipitates, rather than uniform coatings, on clay-mineral basal planes and fill surface pits on coarser aluminosilicates (Baalousha et al., 2019; Hirst et al., 2017; Le Meur et al., 2016; Poulton and Raiswell, 2005). Isolated discrete larger FeOx are rarely observed (Hirst et al., 2017; Le Meur et al., 2016; Poulton and Raiswell, 2005). However, small nano-sized spherical particles, as related to ferrihydrite (Davison and De Vitre, 2019; Guo and Barnard, 2013), are common (Allard et al., 2004; Buffle et al., 1998; Hirst et al., 2017; Perret et al., 2000; Poulton and Raiswell, 2005; Tipping et al., 1981). Those occur in the colloidal fraction associated with NOM (Allard et al., 2004; Hiraide et al., 1988b; Perret et al., 2000), and in the SPM fraction as homoaggregates, or heteroaggregates with aluminosilicates, carbonates, sulfates or quartz (Baalousha et al., 2019; Buffle et al., 1998; Hiraide et al., 1988a; Hirst et al., 2017; Neubauer et al., 2013a; Nomizu et al., 1987). Moreover hair-like Fe-rich structures were reported (Le Meur et al., 2016). As nano-sized precipitates or particles attached to other mineral surfaces increase surface heterogeneities, the typical FeOx morphologies support SPM floc formation.

3.2.1. Reactivity of FeOx surfaces favors aggregation and flocculation processes.

Due to (1) the dominance of labile FeOx phases and (2) a high density in (positively charged) surface hydroxyl-groups, most FeOx surfaces are highly reactive. The transformation of amorphous and poorly crystalline FeOx into crystalline phases is limited by stabilization through ligation, and by relatively short residence times in rivers (as compared to soils) (Davison and De Vitre, 2019; Guo and Barnard, 2013). Consequently, labile, reactive FeOx phases with high specific surface area predominate (Guo and Barnard, 2013; Hirst et al., 2017; Vindedahl et al., 2016 and refs. therein). Labile FeOx can be stabilized (Figure 1) by NOM and inorganic ligands, like silicates or phosphates (Baalousha et al., 2019; Cameron and Liss, 1984), or by precipitation or attachment onto phyllosilicates (Arias, 1995; Schwertmann, 1988; Wei et al., 2011). The surface chemistry of FeOx is governed by hydroxyl-groups, exhibiting pH-dependent variable charge (Vindedahl et al., 2016 and refs. therein). Due to their high points of zero charge, FeOx surfaces are a major contributor of positive surface charge in SPM.

At low DOC concentrations, positively charged bare FeOx tend to heteroaggregate with negatively charged minerals like phyllosilicates or quartz (Figure 1) (Hiraide et al., 1988b; Tombácz et al., 2004; Vindedahl et al., 2016). Composites may exhibit overall negative charge (Hiraide et al., 1988b), but attached FeOx particles, just as FeOx surface precipitates, can constitute positively charged patches (Arias, 1995; Baalousha et al., 2019; Hirst et al., 2017; Le Meur et al., 2016; Poulton and Raiswell, 2005) that favor further aggregation through surface-charge heterogeneities (Arias, 1995; Elimelech et al., 2000; Smith et al., 2015; Yates et al., 2005). Nano-sized FeOx particles may distribute on negative surfaces (Smith et al., 2015) and act as adhesives between them (Tombácz et al., 2004; Z. Wang et al., 2021), whereby size differences allow optimal particle bridging and clustering (Smith et al., 2015; Yates et al., 2005).

FeOx strongly interact with NOM. Nano-sized FeOx can connect large rigid EPS fibrils to loose networks (Buffle et al., 1998), similar to structures observed in natural freshwaters (Allard et al., 2004; Hirst et al., 2017; Perret et al., 2000). Patchy distributions of NOM blebs or smears on mineral surfaces were attributed to underlying FeOx patches (Poulton and Raiswell, 2005). Analogously, FeOx patches or nanoparticles sitting on mineral surfaces may be favorable interaction sites for NOM-induced flocculation (Figure 1). The major adsorption mechanisms include electrostatic interactions, and ligand-exchange reactions between FeOx hydroxyl-groups and NOM carboxyl-groups (Gu et al., 1995). Due to a higher hydroxyl-group density, FeOx adsorb NOM more strongly than aluminosilicates (kaolinite) or quartz, (Hiraide et al., 1988a; Meier et al., 1999). Moreover, NOM exhibits a higher affinity for Fe-OH and Al-OH groups than for Si-OH (Meier et al., 1999; Tombácz et al., 2004; Vázquez-Ortega et al., 2014).

The high density of (positive) hydroxyl-groups allows FeOx to induce aggregation even in the presence of highly negative HS (Baalousha et al., 2008; Mylon et al., 2004), low concentrations of which suffice to fully stabilize phyllosilicates (Kretzschmar et al., 1998; Tarchitzky et al., 1993). Governed by the degree of FeOx surface covered, aggregation occurs when patchy HS coverage induces surface charge heterogeneities or when increased coverage yields charge neutralization; at very high HS concentrations charge reversal results in electrostatic stabilization (Baalousha, 2009; Tombácz et al., 2004; Vindedahl et al., 2016). Stabilization yields negatively charged humic-FeOx colloids (Hiraide et al., 1988b; Tipping et al., 1981; Tipping and Heaton, 1983) (Figure 1). Aggregation by HS proceeds slowly and yields small, compact aggregate structures (Baalousha et al., 2008; Buffle et al., 1998; Mylon et al., 2004; Tipping et al., 1981). Slow aggregation driven by FeOx can, thus, explain smaller and more compact SPM aggregate structures observed in winter when HS are the dominant NOM source (Figure 1).

3.2.2. FeOx precipitation and morphology are governed by heterogeneous oxidation

Autochthonous FeOx form when waters rich in dissolved Fe get supersaturated upon hydrochemical transitions (Guo and Barnard, 2013). Generally, abiotic oxidation dominates over biotic or biotically mediated oxidation (Baken et al., 2013; Bullen et al., 2001; Davison and De Vitre, 2019). The latter proceeds in floc microenvironments or sediment redox transitions, where at low pH, biota may outcompete abiotic oxidation (Davison and De Vitre, 2019).

High amounts of FeOx form when (1) anoxic Fe(II)-rich groundwaters or soil porewaters discharge into oxic rivers (Allard et al., 2011; Baken et al., 2013; Bullen et al., 2001), or (2) waters rich in NOM-complexed Fe(III) (e.g. draining wetlands or forest areas) mix with higher-pH, low-DOC waters (Allard et al., 2011; Hirst et al., 2017; Neubauer et al., 2013a) (Figure 3). Inflowing anoxic waters supply dissolved Fe(II) which quickly oxidizes, hydrolyzes and precipitates (Bullen et al., 2001; van der Grift et al., 2014 and refs. therein). At low pH and high DOC, Fe(II) oxidation is slow and Fe(III) strongly complexed by NOM, suppressing precipitation (Allard et al., 2011; Karlsson and Persson, 2012; Neubauer et al., 2013a; van der Grift et al., 2014). DOC decrease and pH increase, however, induce hydrolysis and precipitation (Figure 3) (Neubauer et al., 2013a, 2013b). Season and discharge can impact the source of dissolved Fe: Soil-derived Fe(III)-NOM complexes increase after rain events (Guan et al., 2015; Herzog et al., 2020; Ingri et al., 2006), and contributions of Fe(II)-rich groundwater can increase at winter-baseflow, when slower oxidation at lower temperatures favors extension of the redox-cline into the surface water (Ingri et al., 2006; van der Grift et al., 2014).

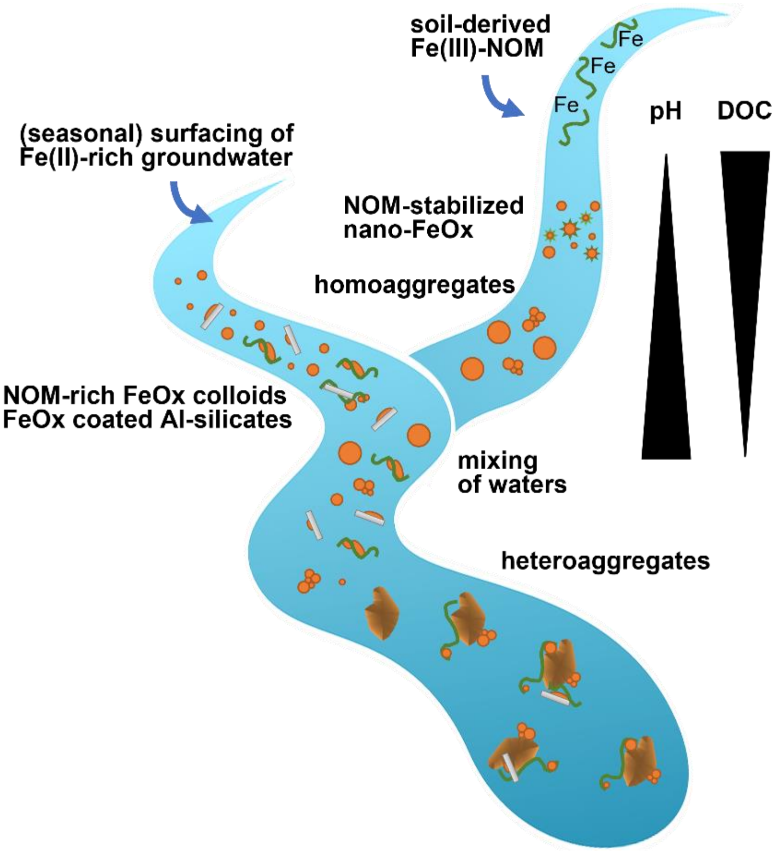

Figure 3. Heterogeneous oxidation governs morphology and reactivity of iron oxides/(oxy)hydroxides (FeOx) (NOM: natural organic matter, DOC: dissolved organic carbon).

The dominance of nano-sized FeOx and patchy coatings results from heterogeneous oxidation (Teutsch et al., 2005), which involves adsorption of Fe(II); Subsequent oxidation creates an unstable Fe(III) surface complex which hydrolyzes and precipitates. When anoxic groundwater enters a river, anoxia extends into the hyporheic zone (Baken et al., 2013; Ingri et al., 2006; Teutsch et al., 2005; van der Grift et al., 2014), supplying Fe(II) to the sediments, where it sorbs to minerals and NOM (Figure 3). Similarely, microbial reduction in organic-rich, anoxic sediment layers generates Fe(II), which diffuses and adsorbs to surface sediments. In most rivers and oligotrophic lakes reducing conditions start below the sediment surface, in eutrophic systems or stratified lakes anoxia may extend into the water (Davison and De Vitre, 2019), where suspended minerals and NOM offer further adsorption sites. When the groundwater table drops or surface-sediments get resuspended, adsorbed Fe(II) is oxidized and precipitates (Gerhardt and Schink, 2005). Some oxidation even proceeds under anoxic conditions, as catalyzed by the sorbate, e.g. NOM (Daugherty et al., 2017) or phyllosilicates (Van Groeningen et al., 2020), or by microorganisms (Bryce et al., 2018).

The affinity of dissolevd Fe for Al-OH groups and NOM favors FeOx patches on aluminosilicates (Baalousha et al., 2019; Hirst et al., 2017; Le Meur et al., 2016; Poulton and Raiswell, 2005) and organic-rich FeOx colloids (Buffle et al., 1989; Hiraide et al., 1988b; Perret et al., 2000; Tipping et al., 1981) (Figure 3). The morphology and surface properties of the latter are influenced by NOM type, Fe:C ratios, inorganic ligands and ionic strength (Ahmad et al., 2020; Cismasu et al., 2011; Liao et al., 2017; Mikutta et al., 2014; Perret et al., 2000). FeOx granules (10 - 50 nm) on EPS networks (Benedetti et al., 2003; Hirst et al., 2017; Perret et al., 2000) may nucleate at low Fe:C and high ionic strength, when Fe cannot fully coat EPS as other ions compete for complexation (Perret et al., 2000). Hair-like or fibrous FeOx (Fortin et al., 1993; Le Meur et al., 2017) can be related to biotic origin (Fleming et al., 2014) or FeOx-coated EPS formed at high Fe:C and low ionic strength (Perret et al., 2000).

Nucleation of FeOx on clay-attached NOM provides an alternative explanation for FeOx granules (10 - 20 nm) seaming clay edges attached via NOM (Poulton and Raiswell, 2005), which the authors attributed to aggregation of NOM-coated FeOx with positively charged clay edges. Larger (100 - 500 nm), C-rich FeOx globules (Buffle et al., 1989; Mavrocordatos et al., 2000; Perret et al., 2000; Tipping et al., 1981) were related to HS-type NOM, high Fe:C and low ionic strength (Perret et al., 2000). They result from co-precipitatation with NOM (Guénet et al., 2017;

Mikutta et al., 2014; Neubauer et al., 2013b) and subsequent homoaggregation of < 10 nm ferrihydrite (Figure 3) (Cismasu et al., 2011; Fortin et al., 1993; Hirst et al., 2017; von Gunten and Schneider, 1991). Incorporation of HS or negatively charged inorganic ligands (e.g. silicates, phosphates) can lower the point of zero charge or even impose negative charge to FeOx (Liao et al., 2017; Mikutta et al., 2014; Saleh and Jones, 1984), affecting their reactivity and aggregation behaviour (Liao et al., 2017; von Gunten and Schneider, 1991).

3.3. Phyllosilicates are a major substrate for floc formation processes.

Being one of the most abundant SPM constituents, phyllosilicates constitute the scaffold for floc formation processes (Figure 1). Five interaction mechanisms can be discerned (Figure 4) in which phyllosilicates play a key role through intrinsic surface heterogeneities, a high affinity for NOM, as a preferential substrate for reactive FeOx coatings, and as substrate for microbial growth.

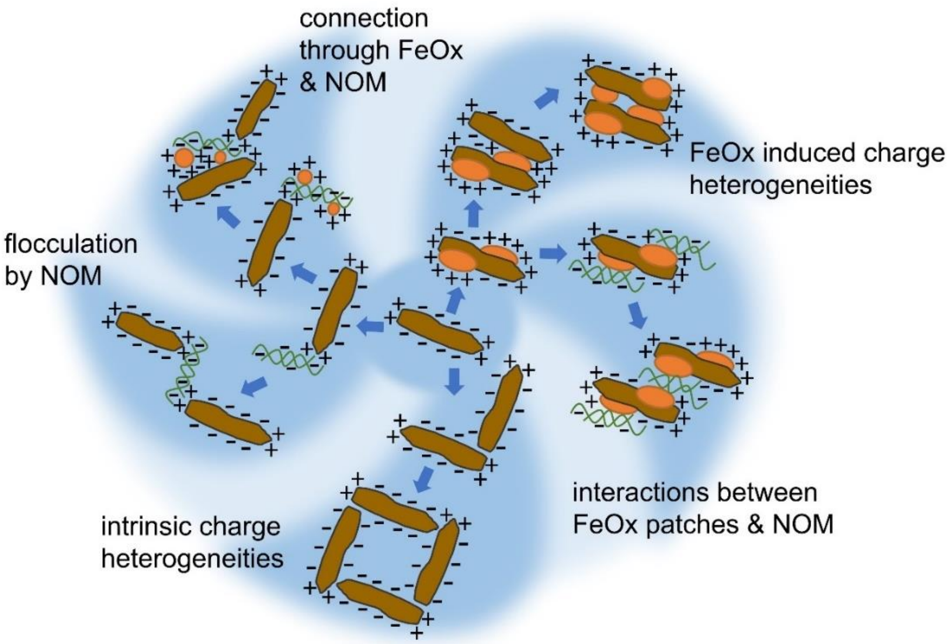

Figure 4. Interaction mechanisms involving phyllosilicates (NOM: natural organic matter, FeOx: iron oxides/(oxy)hydroxides).

3.3.1. Phyllosilicate surface heterogeneities favor aggregation and EPS-flocculation.

At the edges or surface defects, phyllosilicates carry reactive surface hydroxyl-groups, mostly Si-OH and Al-OH, but also some Mg-OH. Those exhibit pH-dependent, variable surface charge, while unimpaired basal planes exhibit permanent negative charge due to isomorphic substitution of Si^{4+} with Al^{3+} and Fe^{3+}, or Al^{3+} with Mg^{2+} and Fe^{2+} in the crystal lattice (Preocanin et al., 2016). Zero charge conditions for phyllosilicate edges were reported at $pH \geq 7.5$ (for chlorite, kaolinite, talc, muscovite) (Kosmulski, 2001; Yin et al., 2013). A higher density of Mg-OH and Al-OH groups at the edges favors positive edge charge as they are more easily protonated than Si-OH (Xiandong Liu et al., 2013; Tournassat et al., 2016; Yin et al., 2013). The intrinsic surface charge heterogeneities of phyllosilicates favor (edge-to-face) aggregation (Figure 4) especially at lower pH when edge-group protonation is more pronounced.

A close correlation of the organic C content in SPM with Al contents and specific surface area (Poulton and Raiswell, 2005) indicates interactions of NOM with phyllosilicates. Phyllosilicate hydroxyl-groups are prone to adsorb NOM. Negatively charged, low-MW HS coat positive edge groups and stabilize phyllosilicates (Kretzschmar et al., 1998; Tarchitzky et al., 1993), while EPS typically induce flocculation (Labille et al., 2005; Lee et al., 2017; Zhang et al., 2013). Due to their heterogeneous properties, phyllosilicates preferentially interact with similarly diverse EPS. Surface charge heterogeneity allows electrostatic interactions of anionic NOM groups (e.g. carboxyl- or phosphate) with phyllosilicate edges, and of cationic (amino) groups with phyllosilicate basal planes (Cao et al., 2011; Hedges and Hare, 1987; Lin et al., 2016; Yeasmin et al., 2014). Since the basal planes exhibit increasing hydrophobicity with lower degrees of isomorphic substitution (e.g. montmorillonite < illite < kaolinite < talc), while the edges are usually hydrophilic (Yin, 2012), hydrophobic interactions with NOM occur on basal planes (Henao and Mazeau, 2008). The high specific surface area and cation exchange capacity of phyllosilicates additionally supports weaker NOM interactions, like H-bonding and cation bridging at lower pH and in the presence of divalent cations (mainly Ca^{2+}) (Cao et al., 2011; Philippe and Schaumann, 2014).

3.3.2. Phyllosilicates are a preferential substrate for reactive FeOx coatings.

The visual evidence of frequent FeOx coatings on aluminosilicates mentioned earlier, is supported by positive correlations of reactive Fe with Al contents, with decreasing SPM constituent particle size and with increasing specific surface area (Markussen et al., 2016; Poulton and Raiswell, 2005). Aluminosilicates constitute a preferential substrate for precipitation or attachment of FeOx in patches, and support formation and persistence of labile reactive FeOx. FeOx patches yield surface charge heterogeneities, and reactivity enhances NOM interactions, favoring incorporation of FeOx-carrying aluminosilicates into SPM.

Ligation by reactive mineral surface groups can catalyze oxidation of adsorbed Fe(II) by water (Géhin et al., 2007; Van Groeningen et al., 2020), allowing for oxidative precipitation of adsorbed Fe(II) even below saturation and under strictly anoxic conditions (Géhin et al., 2007; Mikutta et al., 2009; Van Groeningen et al., 2020). Al-OH or Mg-OH groups at edges or surface defects of phyllosilicates (e.g. montmorillonite) constitute such catalysts (Géhin et al., 2007). Due to a limited availability of these sites, low Fe(II) surface loadings yielded higher oxidized Fe(III) fractions than high loadings (Van Groeningen et al., 2020). Aluminosilicate surface pits filled by FeOx provide visual evidence (Poulton and Raiswell, 2005). Below-saturation precipitation of FeOx in anoxic conditions also occurred on Al- and Fe-oxides (goethite), but not on quartz, and a stronger adsorption of Fe(II) suggests a higher affinity for Al-OH and Fe-OH than Si-OH (Mikutta et al., 2009). As phyllosilicates are way more abundant than metal(hydr)oxides, they will be the relevant substrates for surface-catalyzed FeOx precipitation, but FeOx patches themselves may facilitate further precipitation.

Attachment of FeOx to phyllosilicates behaves similarly, as indicated by ferrihydrite granules sitting in surface defects of montmorillonite after mixing (Yan et al., 2021). Electrostatic interactions favor attachment of FeOx (ferrihydrite) to phyllosilicate basal planes at low to circumneutral pH (Yong and Ohtsubo, 1987). Only high loadings yielded a full coating, else ferrihydrite distributed in patches of particles or aggregates centered around certain kaolinite surface sites (Jones and Saleh, 1987). Again, specific interactions with high affinity sites can be concluded.

As shown for FeOx surface precipitates on kaolinite (Arias, 1995; Wei et al., 2011) as well as for ferrihydrite particles being mixed with different clay minerals (Schwertmann, 1988), phyllosilicates (as opposed to quartz) increase lability, reactivity and specific surface area of FeOx, and inhibit or slow their crystallization. The authors hypothesized that (1) dissolved Si or Al released from phyllosilicates inhibits or retards FeOx crystallization, (2) reactive clay surfaces hamper FeOx crystallization more than silicates (in line with the above), (3) the cementing action between phyllosilicates and amorphous FeOx inhibits dissolution-precipitation reactions and structural rearrangement of FeOx into crystalline forms (Arias, 1995; Schwertmann, 1988; Wei et al., 2011).

3.3.4. Phyllosilicates support microbial nutrition.

Due to their high specific surface areas and ion exchange capacities, phyllosilicates adsorb nutrients and organic substrates, supporting microbial growth (Cuadros, 2017; Henning et al., 2001; Liss et al., 1996). Phyllosilicates offer hydrophilic and hydrophobic surfaces, easing microbe attachment, and microbes exude EPS to attach and access nutrients, fostering typical organo-mineral aggregates (Cuadros, 2017). 3D-nanotomography imaging of riverine SPM shows complex porous structures of clay minerals and few larger grains being colonized by microorganisms (Wheatland et al., 2017). So-called house-of-cards structures are actively constructed from phyllosilicates, EPS, and some FeOx, constituting the microbial "minimal nutritional sphere" (Lunsdorf et al., 2000). In this context, phyllosilicates are also thought to eliminate harmful waste products by adsorption. Microbes prefer nutrient-rich (e.g. smectite) and easily leachable clays: montmorillonite benefitted microbial activity more than kaolinite, as probably related to their adsorption capacity (Cuadros, 2017 and refs. therein). Moreover, microbes can mediate precipitation of low-crystallinity, Si-Al-Fe-containing clay minerals. Functional groups on cell walls and EPS (negative carboxyl-, hydroxyl-, phosphoryl- and positive amino groups) thereby provide sorption and nucleation sites. A detailed review of these and other microbe-mineral interactions (e.g. transformation, weathering, dissolution, leaching of clays) is given in Cuadros (2017).

4. CONCLUSION

In this review we elucidated how the most important physicochemical SPM floc formation processes are governed by three crucial structural-functional SPM components, i.e., EPS, FeOx, and phyllosilicates. These components contribute to an overall heterogeneity in physicochemical surface properties, which favors their association in complex flocs or aggregates. Other materials are rather inert (e.g. quartz), or play similar roles but are less abundant, like Mn- or Al-oxides/(oxy)hydroxides.

Flocculating EPS counteract stabilizing HS.

EPS, as opposed to HS, promote heterogeneity in physicochemical surface properties upon adsorption. They comprise substances spanning a wide range of molecular weights, various degrees of rigidity and hydrophobicity, and diverse functional groups and charge densities. Heterogeneity favors EPS-induced flocculation through

- (multivalent-ion assisted) bridging by large rigid EPS,
- charge heterogeneities within coatings through fractionated sorption or patchy coatings,
- charge neutralization allowing predominance of weak interaction forces such as van der Waals and hydrophobic forces.

Highly degraded HS are more homogeneous regarding flocculation-relevant properties. They mainly comprise low-MW fulvic and to a lesser extent high-MW humic acids, exhibiting high densities in negatively charged carboxyl-groups, which yield homogeneous, highly negative coatings that electrostatically stabilize minerals against flocculation. Due to their antagonistic roles flocculation or stabilization depend on the relative concentrations of HS and EPS.

Phyllosilicates constitute the base for SPM floc formation.

Phyllosilicates dominate the mineral mass fraction in SPM. Due to their heterogeneous surface properties, they provide the base for FeOx- and EPS-enhanced floc formation processes. Both, Fe, and organic C contents in SPM are closely correlated to phyllosilicates. Phyllosilicates exhibit intrinsic surface charge heterogeneities, with structural permanent negative charge on the basal planes and pH-dependent variable charge at the edges and surface defects. Edges are hydrophilic, while basal planes are more hydrophobic, and edges as well as surface pits exhibit increased densities of reactive hydroxyl groups. These properties allow phyllosilicates

- to undergo electrostatic edge-to-face aggregation,
- to interact with NOM, preferentially EPS, and
- to act as preferential substrate for FeOx attachment or surface-precipitation.

FeOx increase surface charge heterogeneities and reactivity of phyllosilicates.

Interactions between FeOx and phyllosilicates increase phyllosilicate surface charge heterogeneity and FeOx reactivity, favoring flocculation. Attachment or precipitation of FeOx yields patchy coatings on phyllosilicates, since dissolved Fe as well as FeOx particles are preferentially ligated by surface-pit or edge hydroxyl-groups. Additionally, bare FeOx can electrostatically interact with phyllosilicate basal planes, due to mostly positive surface charge at circumneutral pH. Association with phyllosilicates stabilizes labile FeOx phases against crystallization, keeping them reactive and their specific surface area high. Consequently, FeOx-carrying phyllosilicates enhance flocculation

- through surface charge heterogeneities arising from patchy distributions of FeOx precipitates or granules;
- through a phyllosilicate-mediated increased reactivity of FeOx, favoring interactions with NOM and mineral surfaces.

NOM strongly interacts with both, FeOx and phyllosilicates.

Phyllosilicates and FeOx strongly adsorb NOM, whereby EPS are preferentially adsorbed.

- Negatively charged and hydrophobic phyllosilicate basal planes preferentially adsorb cationic amino groups (on basic amino acids) and hydrophobic parts (e.g. acyl-groups).
- FeOx and clay edges strongly interact with anionic carboxyl-groups (on polysaccharides, acidic amino acids, or HS) and phosphate groups (on phospholipids, phosphorylated proteins, or nucleic acids).

Preferential adsorption of EPS on FeOx and phyllosilicates supports flocculation mechanisms involving EPS. At high concentrations of HS, however, the affinity of HS carboxyl-groups for hydroxyl-groups on FeOx and phyllosilicate edges yields full coating and electrostatic stabilization. Due to their high hydroxyl-group density, FeOx can still allow for some degree of flocculation at elevated HS concentrations.

The high affinity between NOM and Fe can induce co-precipitation, whereby NOM-type and concentration impact morphology and reactivity of FeOx precipitates. Fully Fe-coated EPS yield elongated fibrous FeOx, while at lower Fe:EPS ratios nano-sized FeOx granules nucleate on EPS. HS promote globular co-precipitates with negative surface charge due to the high density of carboxyl-groups in HS.

Phyllosilicate-FeOx-NOM associations form the base floc unit.

Favorable interactions between the single components entail association of all three components, forming the base floc unit. Processes favoring phyllosilicate-FeOx-NOM associations include

- small FeOx granules connecting NOM or phyllosilicate-attached NOM,
- FeOx precipitates nucleating directly on phyllosilicate-attached NOM,

- reactive FeOx precipitates/granules on phyllosilicates favoring NOM interactions,
- NOM coated FeOx attaching to phyllosilicate edges.

Phyllosilicate-FeOx-NOM associations are a favorable substrate for microbial colonization. They pool essential inorganic nutrients and organic substrates, as their high specific surface area and cation exchange capacity favor adsorption. Microbial colonization triggers flocculation through EPS release at different stages. Adhesive EPS aid attachment, attached microbes exude ligands or enzymatic EPS to access nutrients, and when the substrate becomes refractory, starvation induces further EPS release. Additionally, dissolved EPS preferentially interact with FeOx and phyllosilicates and flocculate new phyllosilicate-FeOx-NOM associations that provide fresh substrate for microbial colonization.

Flocculation dynamics are governed by EPS and FeOx concentrations.

Large, fluffy flocs form at times of high bioproduction when EPS-release is high. Their loose structure is supported by high contents of fibril- or network-like organic EPS, and hosts bacteria and microalgae. At low temperatures or after rain events high fractions of soil-leached HS decrease the flocculation potential of river waters. Small, compact, aggregate-like SPM, inhabited by few bacteria, and single mineral grains are dominant. FeOx may induce slow formation of compact aggregates despite elevated HS concentrations. The content of labile, reactive FeOx is positively related to SPM floc size, as they constitute aggregating and cementing agents as well as an essential Fe source to microbes. Authigenic FeOx formation also exhibits seasonal fluctuations depending on the dominant Fe source. At (winter) baseflow higher shares of Fe(II)-rich anoxic groundwater may increase precipitation, while soil-derived Fe-NOM complexes increase after rain events.

SPM is an important part of many biogeochemical cycles and provides multiple ecosystem services. It functions as habitat and feed, as bioreactor involved in element cycling impacting aquatic food chains up to climate change, and as transport vehicle for nutrients and pollutants affecting freshwaters, sediments, inundation zones, and the ocean. Analyzing the scientific wealth of more than 220 publications from several decades of research and various scientific disciplines it could be shown that freshwater floc formation processes and structural dynamics involve three crucial components: phyllosilicates, FeOx and NOM. Associations of these components constitute the base SPM-type present throughout the year, even at low temperatures. During rain events SPM flocs are diluted by eroded minerals, which, upon recovery of bioproduction, are flocculated by dissolved EPS to form fresh SPM base units. With increasing temperatures and microbial growth, SPM is colonized and flocculated to large, fluffy EPS-rich flocs, microhabitats which provide multiple crucial services to the global element cycles.

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REFERENCES

Adair, E.C., Binkley, D., Andersen, D.C., 2004. Patterns of nitrogen accumulation and cycling in riparian floodplain ecosystems along the Green and Yampa rivers. Oecologia 139, 108–116. doi:10.1007/s00442-004-1486-6

Adamiec, E., Helios-Rybicka, E., 2002. Distribution of Pollutants in the Odra River System Part V. Assessment of Total and Mobile Heavy Metals Content in the Suspended Matter and Sediments of the Odra River System and Recommendations for River Chemical Monitoring. Polish J. Environ. Stud. 11, 675–688.

Ahmad, A., Rutten, S., Eikelboom, M., de Waal, L., Bruning, H., Bhattacharya, P., van der Wal, A., 2020. Impact of phosphate, silicate and natural organic matter on the size of Fe(III) precipitates and arsenate co-precipitation efficiency in calcium containing water. Sep. Purif.

Technol. 235, 116117. doi:10.1016/j.seppur.2019.116117

Allard, T., Menguy, N., Salomon, J., Calligaro, T., Weber, T., Calas, G., Benedetti, M.F., 2004. Revealing forms of iron in river-borne material from major tropical rivers of the Amazon Basin (Brazil). Geochim. Cosmochim. Acta 68, 3079–3094. doi:10.1016/j.gca.2004.01.014

Allard, T., Weber, T., Bellot, C., Damblans, C., Bardy, M., Bueno, G., Nascimento, N.R., Fritsch, E., Benedetti, M.F., 2011. Tracing source and evolution of suspended particles in the Rio Negro Basin (Brazil) using chemical species of iron. Chem. Geol. 280, 79–88. doi:10.1016/j.chemgeo.2010.10.018

Arias, M., 1995. Effects of Iron and Aluminium Oxides on the Colloidal and Surface Properties of Kaolin. Clays Clay Miner. 43, 406–416. doi:10.1346/CCMN.1995.0430403

Atteia, O., Perret, D., Adatte, T., Kozel, R., Rossi, P., 1998. Characterization of natural colloids from a river and spring in a karstic basin. Environ. Geol. 34, 257–269. doi:10.1007/s002540050277

Aufdenkampe, A.K., Hedges, J.I., Richey, J.E., Krusche, A. V., Llerena, C.A., 2001. Sorptive fractionation of dissolved organic nitrogen and amino acids onto fine sediments within the Amazon Basin. Limnol. Oceanogr. 46, 1921–1935. doi:10.4319/lo.2001.46.8.1921

Aufdenkampe, A.K., Mayorga, E., Raymond, P.A., Melack, J.M., Doney, S.C., Alin, S.R., Aalto, R.E., Yoo, K., 2011. Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere. Front. Ecol. Environ. 9, 53–60. doi:10.1890/100014

Baalousha, M., 2009. Aggregation and disaggregation of iron oxide nanoparticles: Influence of particle concentration, pH and natural organic matter. Sci. Total Environ. 407, 2093–2101. doi:10.1016/j.scitotenv.2008.11.022

Baalousha, M., Manciulea, A., Cumberland, S., Kendall, K., Lead, J.R., 2008. Aggregation and Surface Properties of Iron Oxide Nanoparticles: Influence of pH and Natural Organic Matter. Environ. Toxicol. Chem. 27, 1875. doi:10.1897/07-559.1

Baalousha, M., Stoll, S., Motelica-Heino, M., Guigues, N., Braibant, G., Huneau, F., Le Coustumer, P., 2019. Suspended particulate matter determines physical speciation of Fe, Mn, and trace metals in surface waters of Loire watershed. Environ. Sci. Pollut. Res. 26, 5251–5266. doi:10.1007/s11356-018-1416-5

Baken, S., Sjöstedt, C., Gustafsson, J.P., Seuntjens, P., Desmet, N., De Schutter, J., Smolders, E., 2013. Characterisation of hydrous ferric oxides derived from iron-rich groundwaters and their contribution to the suspended sediment of streams. Appl. Geochemistry 39, 59–68. doi:10.1016/j.apgeochem.2013.09.013

Benedetti, M.F., Ranville, J.F., Allard, T., Bednar, A.J., Menguy, N., 2003. The iron status in colloidal matter from the Rio Negro, Brasil. Colloids Surfaces A Physicochem. Eng. Asp. 217, 1–9. doi:10.1016/S0927-7757(02)00553-8

Berger, B., Hoch, B., Kavka, G., Herndl, G., 1996. Bacterial colonization of suspended solids in the River Danube. Aquat. Microb. Ecol. 10, 37–44. doi:10.3354/ame010037

Besemer, K., Luef, B., Preiner, S., Eichberger, B., Agis, M., Peduzzi, P., 2009. Sources and composition of organic matter for bacterial growth in a large European river floodplain system (Danube, Austria). Org. Geochem. 40, 321–331. doi:10.1016/j.orggeochem.2008.12.005

Beusen, A.H.W., Dekkers, A.L.M., Bouwman, A.F., Ludwig, W., Harrison, J., 2005. Estimation of global river transport of sediments and associated particulate C, N, and P. Global Biogeochem. Cycles 19, n/a-n/a. doi:10.1029/2005GB002453

Bibby, R.L., Webster-Brown, J.G., 2005. Characterisation of urban catchment suspended particulate matter (Auckland region, New Zealand); a comparison with non-urban SPM. Sci. Total Environ. 343, 177–197. doi:10.1016/j.scitotenv.2004.09.041

Bilotta, G.S., Brazier, R.E., 2008. Understanding the influence of suspended solids on water quality and aquatic biota. Water Res. 42, 2849–2861. doi:10.1016/j.watres.2008.03.018

Bilotta, G.S., Burnside, N.G., Cheek, L., Dunbar, M.J., Grove, M.K., Harrison, C., Joyce, C., Peacock, C., Davy-Bowker, J., 2012. Developing environment-specific water quality guidelines for suspended particulate matter. Water Res. 46, 2324–2332. doi:10.1016/j.watres.2012.01.055

Böckelmann, U., 2000. Characterization of the microbial community of lotic organic aggregates ('river snow') in the Elbe River of Germany by cultivation and molecular methods. FEMS Microbiol. Ecol. 33, 157–170. doi:10.1016/S0168-6496(00)00056-8

Breitenbach, E., Lampe, R., Leipe, T., 1999. Investigations on Mineralogical and Chemical Composition of Suspended Particulate Matter (SPM) in the Odra Estuary. Acta Hydrochim. Hydrobiol. 27, 298–302. doi:10.1002/(SICI)1521-401X(199911)27:5<298::AID-AHEH298>3.0.CO;2-B

Brugmann, L., 1995. Metals in sediments and suspended matter of the river Elbe. Sci. Total Environ. 159, 53–65. doi:10.1016/0048-9697(94)04252-I

Brunet, R.C., Pinay, G., Gazelle, F., Roques, L., 1994. Role of the floodplain and riparian zone in suspended matter and nitrogen retention in the adour river, south-west France. Regul. Rivers Res. Manag. 9, 55–63. doi:10.1002/rrr.3450090106

Bryce, C., Blackwell, N., Schmidt, C., Otte, J., Huang, Y.-M., Kleindienst, S., Tomaszewski, E., Schad, M., Warter, V., Peng, C., Byrne, J.M., Kappler, A., 2018. Microbial anaerobic Fe(II) oxidation - Ecology, mechanisms and environmental implications. Environ. Microbiol. 20, 3462–3483. doi:10.1111/1462-2920.14328

Buffle, J., De Vitre, R.R., Perret, D., Leppard, G.G., 1989. Physico-chemical characteristics of a colloidal iron phosphate species formed at the oxic-anoxic interface of a eutrophic lake. Geochim. Cosmochim. Acta 53, 399–408. doi:10.1016/0016-7037(89)90391-8

Buffle, J., Leppard, G.G., 1995. Characterization of Aquatic Colloids and Macromolecules. 1. Structure and Behavior of Colloidal Material. Environ. Sci. Technol. 29, 2169–2175. doi:10.1021/es00009a004

Buffle, J., Wilkinson, K.J., Stoll, S., Filella, M., Zhang, J., 1998. A Generalized Description of Aquatic Colloidal Interactions: The Three-colloidal Component Approach. Environ. Sci. Technol. 32, 2887–2899. doi:10.1021/es980217h

Bukaveckas, P.A., Katarzyte, M., Schlegel, A., Spuriene, R., Egerton, T., Vaiciute, D., 2019. Composition and settling properties of suspended particulate matter in estuaries of the Chesapeake Bay and Baltic Sea regions. J. Soils Sediments 19, 2580–2593. doi:10.1007/s11368-018-02224-z

Bullen, T.D., White, A.F., Childs, C.W., Vivit, D. V., Schulz, M.S., 2001. Demonstration of significant abiotic iron isotope fractionation in nature. Geology 29, 699. doi:10.1130/0091-7613(2001)029<0699:DOSAII>2.0.CO;2

Cameron, A.J., Liss, P.S., 1984. The stabilization of "dissolved" iron in freshwaters. Water Res. 18, 179–185. doi:10.1016/0043-1354(84)90067-8

Cao, Y., Wei, X., Cai, P., Huang, Q., Rong, X., Liang, W., 2011. Preferential adsorption of extracellular polymeric substances from bacteria on clay minerals and iron oxide. Colloids Surfaces B Biointerfaces 83, 122–127. doi:10.1016/j.colsurfb.2010.11.018

Chanudet, V., Filella, M., 2008. Size and composition of inorganic colloids in a peri-alpine, glacial flour-rich lake. Geochim. Cosmochim. Acta 72, 1466–1479. doi:10.1016/j.gca.2008.01.002

Chanudet, V., Filella, M., 2007. Submicron organic matter in a peri-alpine, ultra-oligotrophic lake. Org. Geochem. 38, 1146–1160. doi:10.1016/j.orggeochem.2007.02.011

Cismasu, A.C., Michel, F.M., Tcaciuc, A.P., Tyliszczak, T., Brown, Jr, G.E., 2011. Composition and structural aspects of naturally occurring ferrihydrite. Comptes Rendus Geosci. 343, 210–218. doi:10.1016/j.crte.2010.11.001

Crump, B., Baross, J., 2000. Characterization of the bacterially-active particle fraction in the Columbia River estuary. Mar. Ecol. Prog. Ser. 206, 13–22. doi:10.3354/meps206013

Crump, B.C., Fine, L.M., Fortunato, C.S., Herfort, L., Needoba, J.A., Murdock, S., Prahl, F.G., 2017. Quantity and quality of particulate organic matter controls bacterial production in the Columbia River estuary. Limnol. Oceanogr. 62, 2713–2731. doi:10.1002/lno.10601

Cuadros, J., 2017. Clay minerals interaction with microorganisms: a review. Clay Miner. 52, 235–261. doi:10.1180/claymin.2017.052.2.05

Daugherty, E.E., Gilbert, B., Nico, P.S., Borch, T., 2017. Complexation and Redox Buffering of Iron(II) by Dissolved Organic Matter. Environ. Sci. Technol. 51, 11096–11104. doi:10.1021/acs.est.7b03152

Davison, W., De Vitre, R., 2019. Iron Particles in Freshwater, in: Environmental Particles. CRC Press, pp. 315–355. doi:10.1201/9780429286223-8

Ding, T., Wan, D., Wang, C., Zhang, F., 2004. Silicon isotope compositions of dissolved silicon and suspended matter in the Yangtze River, China. Geochim. Cosmochim. Acta 68, 205–216. doi:10.1016/S0016-7037(03)00264-3

Ding, T.P., Gao, J.F., Tian, S.H., Wang, H.B., Li, M., 2011. Silicon isotopic composition of dissolved silicon and suspended particulate matter in the Yellow River, China, with implications for the global silicon cycle. Geochim. Cosmochim. Acta 75, 6672–6689. doi:10.1016/j.gca.2011.07.040

Droppo, I.G., 2001. Rethinking what constitutes suspended sediment. Hydrol. Process. 15, 1551–1564. doi:10.1002/hyp.228

Droppo, I.G., Leppard, G.G., Flannigan, D.T., Liss, S.N., 1997. The Freshwater Floc: A Functional Relationship of Water and Organic and Inorganic Floc Constituents Affecting Suspended Sediment Properties, in: The Interactions Between Sediments and Water. Springer Netherlands, Dordrecht, pp. 43–53. doi:10.1007/978-94-011-5552-6_5

Droppo, I.G., Leppard, G.G., Liss, S.N., Milligan, T.G., 2004. Flocculation in Natural and Engineered Environmental Systems, Flocculation in Natural and Engineered Environmental Systems. CRC Press. doi:10.1201/9780203485330

Droppo, I.G., Nackaerts, K., Walling, D.E., Williams, N., 2005. Can flocs and water stable soil aggregates be differentiated within fluvial systems? CATENA 60, 1–18. doi:10.1016/j.catena.2004.11.002

Droppo, I.G., Ongley, E.D., 1994. Flocculation of suspended sediment in rivers of southeastern Canada. Water Res. 28, 1799–1809. doi:10.1016/0043-1354(94)90253-4

Droppo, I.G., Stone, M., 1994. In-channel surficial fine-grained sediment laminae. Part I: Physical characteristics and formational processes. Hydrol. Process. 8, 101–111. doi:10.1002/hyp.3360080202

Droppo, I.G., Walling, D.E., Ongley, E.D., 1998. Suspended sediment structure: Implications for sediment and contaminant transport modelling, in: Summer, W., Klaghofer, E., Zhang, W. (Eds.), Modelling Soil Erosion, Sediment Transport and Closely Related Hydrological Processes (Proceedings of a Symposium Held at Vienna, July 1998). IAHS, Wallingford, pp. 437–444.

Edwards, R.T., 1987. Sestonic bacteria as a food source for filtering invertebrates in two southeastern blackwater rivers1. Limnol. Oceanogr. 32, 221–234. doi:10.4319/lo.1987.32.1.0221

Eidam, J., Lehmann, J., Puff, T., 1997. Greifswalder Bodden und Oderästuar – Austauschprozesse (GOAP): Einfluß des Phasenbestandes von Schwebstoffen und Sedimenten des Odermündungsgebietes auf die Bindung und Mobilisierung von Schwermetallen – Beitrag zur Bilanzierung von Stoffaustauschprozess. Greifswald.

Eisma, D., 1993. Suspended Matter in the Aquatic Environment. Springer Berlin Heidelberg, Berlin, Heidelberg. doi:10.1007/978-3-642-77722-6

Elimelech, M., Gregory, J., Jia, X., Williams, R.A., 1995. Copyright, in: Particle Deposition & Aggregation. Elsevier, Woburn, p. iv. doi:10.1016/B978-0-7506-7024-1.50020-0

Elimelech, M., Nagai, M., Ko, C.-H., Ryan, J.N., 2000. Relative Insignificance of Mineral Grain Zeta Potential to Colloid Transport in Geochemically Heterogeneous Porous Media. Environ. Sci. Technol. 34, 2143–2148. doi:10.1021/es9910309

Filella, M., 2007. Colloidal Properties of Submicron Particles in Natural Waters, in: Wilkinson, K.J., Lead, J.R. (Eds.), Environmental Colloids and Particles: Behaviour, Separation and Characterisation Edited. Wiley & Sons, West Sussex, pp. 17–63.

Filella, M., Buffle, J., Leppard, G.G., 1993. Characterization of Submicrometre Colloids in Freshwaters: Evidence for Their Bridging by Organic Structures. Water Sci. Technol. 27, 91–102. doi:10.2166/wst.1993.0268

Fleming, E.J., Cetinić, I., Chan, C.S., Whitney King, D., Emerson, D., 2014. Ecological succession among iron-oxidizing bacteria. ISME J. 8, 804–815. doi:10.1038/ismej.2013.197

Flemming, H.-C., Wingender, J., 2010. The biofilm matrix. Nat. Rev. Microbiol. 8, 623–633. doi:10.1038/nrmicro2415

Flemming, H.-C., Wingender, J., 2001. Relevance of microbial extracellular polymeric substances (EPSs) - Part I: Structural and ecological aspects. Water Sci. Technol. 43, 1–8. doi:10.2166/wst.2001.0326

Fortin, D., Leppard, G.G., Tessier, A., 1993. Characteristics of lacustrine diagenetic iron oxyhydroxides. Geochim. Cosmochim. Acta 57, 4391–4404. doi:10.1016/0016-7037(93)90490-N

Garcia-Aragon, J., Droppo, I.G., Krishnappan, B.G., Trapp, B., Jaskot, C., 2011. Erosion characteristics and floc strength of Athabasca River cohesive sediments: towards managing sediment-related issues. J. Soils Sediments 11, 679–689. doi:10.1007/s11368-011-0345-4

Géhin, A., Grenèche, J.-M., Tournassat, C., Brendlé, J., Rancourt, D.G., Charlet, L., 2007. Reversible surface-sorption-induced electron-transfer oxidation of Fe(II) at reactive sites on a synthetic clay mineral. Geochim. Cosmochim. Acta 71, 863–876. doi:10.1016/j.gca.2006.10.019

Gerhardt, S., Schink, B., 2005. Redox Changes of Iron Caused by Erosion, Resuspension and Sedimentation in Littoral Sediment of a Freshwater Lake. Biogeochemistry 74, 341–356. doi:10.1007/s10533-004-4725-3

Gordon, B.A., Dorothy, O., Lenhart, C.F., 2020. Nutrient Retention in Ecologically Functional

Floodplains: A Review. Water 12, 2762. doi:10.3390/w12102762

Grangeon, T., Droppo, I.G., Legout, C., Esteves, M., 2014. From soil aggregates to riverine flocs: a laboratory experiment assessing the respective effects of soil type and flow shear stress on particles characteristics. Hydrol. Process. 28, 4141–4155. doi:10.1002/hyp.9929

Gregory, J., 2005. Particles in Water. CRC Press, Boca Raton. doi:10.1201/9780203508459

Greiser, N., 1988. Zur Dynamik von Schwebstoffen und ihren biologischen Komponenten in der Elbe bei Hamburg. Hamb. Küstengorsch. 45, 1–170.

Grimm, C., 2017. The Effect of Riverine Particulate Material on Primary Productivity and the Global Organic Carbon Cycle. Université Fédérale Toulouse Midi-Pyrénées.

Grossart, H.-P., Ploug, H., 2000. Bacterial production and growth efficiencies: Direct measurements on riverine aggregates. Limnol. Oceanogr. 45, 436–445. doi:10.4319/lo.2000.45.2.0436

Grossart, H., Simon, M., 1998. Bacterial colonization and microbial decomposition of limnetic organic aggregates (lake snow). Aquat. Microb. Ecol. 15, 127–140. doi:10.3354/ame015127

Gu, B., 1992. The Interaction of Polysaccharides with Silver Hill Illite. Clays Clay Miner. 40, 151–156. doi:10.1346/CCMN.1992.0400203

Gu, B., Schmitt, J., Chen, Z., Liang, L., McCarthy, J.F., 1995. Adsorption and desorption of different organic matter fractions on iron oxide. Geochim. Cosmochim. Acta 59, 219–229. doi:10.1016/0016-7037(94)00282-Q

Guan, J., Yan, B., Zhu, H., Wang, L., Lu, D., Cheng, L., 2015. Flux characteristics of total dissolved iron and its species during extreme rainfall event in the midstream of the Heilongjiang River. J. Environ. Sci. 30, 74–80. doi:10.1016/j.jes.2014.10.009

Guénet, H., Davranche, M., Vantelon, D., Gigault, J., Prévost, S., Taché, O., Jaksch, S., Pédrot, M., Dorcet, V., Boutier, A., Jestin, J., 2017. Characterization of iron–organic matter nano-aggregate networks through a combination of SAXS/SANS and XAS analyses: impact on As binding. Environ. Sci. Nano 4, 938–954. doi:10.1039/C6EN00589F

Guo, H., Barnard, A.S., 2013. Naturally occurring iron oxide nanoparticles: morphology, surface chemistry and environmental stability. J. Mater. Chem. A 1, 27–42. doi:10.1039/C2TA00523A

Guo, L., Lehner, J.K., White, D.M., Garland, D.S., 2003. Heterogeneity of natural organic matter from the Chena River, Alaska. Water Res. 37, 1015–1022. doi:10.1016/S0043-1354(02)00443-8

Guo, L., Macdonald, R.W., 2006. Source and transport of terrigenous organic matter in the upper Yukon River: Evidence from isotope (δ 13 C, Δ 14 C, and δ 15 N) composition of dissolved, colloidal, and particulate phases. Global Biogeochem. Cycles 20.

doi:10.1029/2005GB002593

Guo, L., Zhang, J.-Z., Guéguen, C., 2004. Speciation and fluxes of nutrients (N, P, Si) from the upper Yukon River. Global Biogeochem. Cycles 18. doi:10.1029/2003GB002152

Guo, W., He, M., Yang, Z., Lin, C., Quan, X., Wang, H., 2007. Distribution of polycyclic aromatic hydrocarbons in water, suspended particulate matter and sediment from Daliao River watershed, China. Chemosphere 68, 93–104. doi:10.1016/j.chemosphere.2006.12.072

Håkanson, L., Mikrenska, M., Petrov, K., Foster, I., 2005. Suspended particulate matter (SPM) in rivers: empirical data and models. Ecol. Modell. 183, 251–267. doi:10.1016/j.ecolmodel.2004.07.030

Hatten, J.A., Goñi, M.A., Wheatcroft, R.A., 2012. Chemical characteristics of particulate organic matter from a small, mountainous river system in the Oregon Coast Range, USA. Biogeochemistry 107, 43–66. doi:10.1007/s10533-010-9529-z

He, M., Sun, Y., Li, X., Yang, Z., 2006. Distribution patterns of nitrobenzenes and polychlorinated biphenyls in water, suspended particulate matter and sediment from mid- and down-stream of the Yellow River (China). Chemosphere 65, 365–374. doi:10.1016/j.chemosphere.2006.02.033

He, Q., Qiu, Y., Liu, H., Sun, X., Kang, L., Cao, L., Li, H., Ai, H., 2017. New insights into the impacts of suspended particulate matter on phytoplankton density in a tributary of the Three Gorges Reservoir, China. Sci. Rep. 7, 13518. doi:10.1038/s41598-017-13235-0

Hedges, J.I., Hare, P.E., 1987. Amino acid adsorption by clay minerals in distilled water. Geochim. Cosmochim. Acta 51, 255–259. doi:10.1016/0016-7037(87)90237-7

Henao, L., Mazeau, K., 2008. The molecular basis of the adsorption of bacterial exopolysaccharides on montmorillonite mineral surface. Mol. Simul. 34, 1185–1195. doi:10.1080/08927020802235714

Henning, K.-H., Damke, H., Kasbohm, J., Puff, T., Breitenbach, E., Theel, O., Kießling, A., 2001. Schwebstoffbeschaffenheit im Odersystem. Greifswald.

Henning, K.-H., Lehmann, J., Kasbohm, J., Damke, H., 2000. CD-ROM “Interaktiver Schwebstoff-Atlas” : Bestandteile von fluviatilen Schwebstoffen und Sedimenten von Elbe, Saale und Havel. ZEITSCHRIFT FUR Geol. WISSENSCHAFTEN 28, 469–500.

Herzog, S.D., Gentile, L., Olsson, U., Persson, P., Kritzberg, E.S., 2020. Characterization of Iron and Organic Carbon Colloids in Boreal Rivers and Their Fate at High Salinity. J. Geophys. Res. Biogeosciences 125, 1–14. doi:10.1029/2019JG005517

Hillier, S., 2001. Particulate composition and origin of suspended sediment in the R. Don, Aberdeenshire, UK. Sci. Total Environ. 265, 281–293. doi:10.1016/S0048-9697(00)00664-1

Hiraide, M., Arima, Y., Mizuike, A., 1988a. Selective desorption and analysis of humic substances on suspended particles in river water. Mikrochim. Acta 96, 231–238. doi:10.1007/BF01236107

Hiraide, M., Ishii, M., Mizuike, A., 1988b. Speciation of iron in river water. Anal. Sci. 4, 605–609. doi:10.2116/analsci.4.605

Hirst, C., Andersson, P.S., Shaw, S., Burke, I.T., Kutscher, L., Murphy, M.J., Maximov, T., Pokrovsky, O.S., Mörth, C.-M., Porcelli, D., 2017. Characterisation of Fe-bearing particles and colloids in the Lena River basin, NE Russia. Geochim. Cosmochim. Acta 213, 553–573. doi:10.1016/j.gca.2017.07.012

Hong, P.-N., Taing, C., Phan, P.-T., Honda, R., 2018. Polarity-Molecular Weight Profile of Extracellular Polymeric Substances in a Membrane Bioreactor: Comparison between Bulk Sludge and Cake Layers. J. Water Environ. Technol. 16, 40–53. doi:10.2965/jwet.17-020

Hoppe, H.-G., 1984. Attachment of Bacteria: Advantage or Disadvantage for Survival in the Aquatic Environment, in: Microbial Adhesion and Aggregation. Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 283–301. doi:10.1007/978-3-642-70137-5_19

Ingri, J., Malinovsky, D., Rodushkin, I., Baxter, D.C., Widerlund, A., Andersson, P., Gustafsson, Ö., Forsling, W., Öhlander, B., 2006. Iron isotope fractionation in river colloidal matter. Earth Planet. Sci. Lett. 245, 792–798. doi:10.1016/j.epsl.2006.03.031

Ittekkot, V., 1988. Global trends in the nature of organic matter in river suspensions. Nature 332, 436–438. doi:10.1038/332436a0

Ittekkot, V., Laane, R.W.P.M., 1991. Fate of riverine particulate organic matter. SCOPE 42 - Biogeochem. Major World Rivers 233–243.

Jeandel, C., Oelkers, E.H., 2015. The influence of terrigenous particulate material dissolution on ocean chemistry and global element cycles. Chem. Geol. 395, 50–66. doi:10.1016/j.chemgeo.2014.12.001

Jilbert, T., Asmala, E., Schröder, C., Tiihonen, R., Myllykangas, J., Virtasalo, J.J., Kotilainen, A., Peltola, P., Ekholm, P., Hietanen, S., 2018. Impacts of flocculation on the distribution and diagenesis of iron in boreal estuarine sediments. Biogeosciences 15, 1243–1271. doi:10.5194/bg-15-1243-2018

Johnson, E.R., Inamdar, S., Kan, J., Vargas, R., 2018. Particulate Organic Matter Composition in Stream Runoff Following Large Storms: Role of POM Sources, Particle Size, and Event Characteristics. J. Geophys. Res. Biogeosciences 123, 660–675. doi:10.1002/2017JG004249

Jones, A.A., Saleh, A.M., 1987. A study of the thickness of ferrihydrite coatings on kaolinite. Mineral. Mag. 51, 87–92. doi:10.1180/minmag.1987.051.359.08

Juracic, M., Menegazzo Vitturi, L., Rabitti, S., Rampazzo, G., 1986. Suspended matter properties and its role in pollutant transfer from the river to the sea. Case study: Adige river-adriatic sea. Sci. Total Environ. 55, 243–249. doi:10.1016/0048-9697(86)90183-X

Karlsson, T., Persson, P., 2012. Complexes with aquatic organic matter suppress hydrolysis and precipitation of Fe(III). Chem. Geol. 322–323, 19–27. doi:10.1016/j.chemgeo.2012.06.003

Kernegger, L., Zweimüller, I., Peduzzi, P., 2009. Effects of suspended matter quality and virus abundance on microbial parameters: experimental evidence from a large European river. Aquat. Microb. Ecol. 57, 161–173. doi:10.3354/ame01341

Kondratieff, P.F., Simmons, G.M., 1985. Microbial colonization of seston and free bacteria in an impounded river. Hydrobiologia 128, 127–133. doi:10.1007/BF00008732

Kosmulski, M., 2014. The pH dependent surface charging and points of zero charge. VI. Update. J. Colloid Interface Sci. 426, 209–212. doi:10.1016/j.jcis.2014.02.036

Kosmulski, M., 2001. Chemical properties of material surfaces. Marcel Dekker, New York.

Kravchishina, M.D., Dara, O.M., 2014. Mineral composition of the suspended particulate matter in the White Sea. Oceanology 54, 327–337. doi:10.1134/S000143701402012X

Kravchishina, M.D., Shevchenko, V.P., Filippov, A.S., Novigatskii, A.N., Dara, O.M., Alekseeva, T.N., Bobrov, V.A., 2010. Composition of the suspended particulate matter at the Severnaya Dvina River mouth (White Sea) during the spring flood period. Oceanology 50, 365–385. doi:10.1134/S0001437010030070

Kretzschmar, R., Holthoff, H., Sticher, H., 1998. Influence of pH and Humic Acid on Coagulation Kinetics of Kaolinite: A Dynamic Light Scattering Study. J. Colloid Interface Sci. 202, 95–103. doi:10.1006/jcis.1998.5440

Kunhi Mouvenchery, Y., Kučerík, J., Diehl, D., Schaumann, G.E., 2012. Cation-mediated cross-linking in natural organic matter: a review. Rev. Environ. Sci. Bio/Technology 11, 41–54. doi:10.1007/s11157-011-9258-3

Labille, J., Thomas, F., Milas, M., Vanhaverbeke, C., 2005. Flocculation of colloidal clay by bacterial polysaccharides: effect of macromolecule charge and structure. J. Colloid Interface Sci. 284, 149–156. doi:10.1016/j.jcis.2004.10.001

Lartiges, B.S., Deneux-Mustin, S., Villemin, G., Mustin, C., Barrès, O., Chamerois, M., Gerard, B., Babut, M., 2001. Composition, structure and size distribution of suspended particulates from the Rhine River. Water Res. 35, 808–816. doi:10.1016/S0043-1354(00)00293-1

Laspidou, C., 2002. A unified theory for extracellular polymeric substances, soluble microbial products, and active and inert biomass. Water Res. 36, 2711–2720. doi:10.1016/S0043-1354(01)00413-4

Le Meur, M., Mansuy-Huault, L., Lorgeoux, C., Bauer, A., Gley, R., Vantelon, D., Montargès-Pelletier, E., 2017. Spatial and temporal variations of particulate organic matter from Moselle River and tributaries: A multimolecular investigation. Org. Geochem. 110, 45–56. doi:10.1016/j.orggeochem.2017.04.003

Le Meur, M., Montargès-Pelletier, E., Bauer, A., Gley, R., Migot, S., Barres, O., Delus, C., Villiéras, F., 2016. Characterization of suspended particulate matter in the Moselle River (Lorraine, France): evolution along the course of the river and in different hydrologic regimes. J. Soils Sediments 16, 1625–1642. doi:10.1007/s11368-015-1335-8

Lee, B., Hur, J., Toorman, E., 2017. Seasonal Variation in Flocculation Potential of River Water: Roles of the Organic Matter Pool. Water 9, 335. doi:10.3390/w9050335

Lee, B.J., Kim, J., Hur, J., Choi, I.H., Toorman, E.A., Fettweis, M., Choi, J.W., 2019. Seasonal Dynamics of Organic Matter Composition and Its Effects on Suspended Sediment Flocculation in River Water. Water Resour. Res. 55, 6968–6985. doi:10.1029/2018WR024486

Lee, D.J., Gang, J.G., Lee, S.Y., Choi, I.W., Chun, K.M., Cho, J.S., Seo, D.C., 2015. Characterization of River Natural Organic Matter by High-Performance Size Exclusion Chromatography. Anal. Lett. 48, 2936–2946. doi:10.1080/00032719.2015.1060601

Leithold, E.L., Blair, N.E., Wegmann, K.W., 2016. Source-to-sink sedimentary systems and global carbon burial: A river runs through it. Earth-Science Rev. 153, 30–42. doi:10.1016/j.earscirev.2015.10.011

Leppard, G.G., 1997. Colloidal organic fibrils of acid polysaccharides in surface waters: electron-optical characteristics, activities and chemical estimates of abundance. Colloids Surfaces A Physicochem. Eng. Asp. 120, 1–15. doi:10.1016/S0927-7757(96)03676-X

Li, Y., Wang, X., Fu, W., Xia, X., Liu, C., Min, J., Zhang, W., Crittenden, J.C., 2019. Interactions between nano/micro plastics and suspended sediment in water: Implications on aggregation and settling. Water Res. 161, 486–495. doi:10.1016/j.watres.2019.06.018

Liao, P., Li, W., Jiang, Y., Wu, J., Yuan, S., Fortner, J.D., Giammar, D.E., 2017. Formation, Aggregation, and Deposition Dynamics of NOM-Iron Colloids at Anoxic–Oxic Interfaces. Environ. Sci. Technol. 51, 12235–12245. doi:10.1021/acs.est.7b02356

Lin, D., Ma, W., Jin, Z., Wang, Y., Huang, Q., Cai, P., 2016. Interactions of EPS with soil minerals: A combination study by ITC and CLSM. Colloids Surfaces B Biointerfaces 138, 10–16. doi:10.1016/j.colsurfb.2015.11.026

Liss, S.N., Droppo, I.G., Flannigan, D.T., Leppard, G.G., 1996. Floc Architecture in Wastewater and Natural Riverine Systems. Environ. Sci. Technol. 30, 680–686. doi:10.1021/es950426r

Liu, Xinran, Eusterhues, K., Thieme, J., Ciobota, V., Höschen, C., Mueller, C.W., Küsel, K., Kögel-Knabner, I., Rösch, P., Popp, J., Totsche, K.U., 2013. STXM and NanoSIMS Investigations on EPS Fractions before and after Adsorption to Goethite. Environ. Sci. Technol. 47, 3158–3166. doi:10.1021/es3039505

Liu, Xiandong, Lu, X., Sprik, M., Cheng, J., Meijer, E.J., Wang, R., 2013. Acidity of edge surface sites of montmorillonite and kaolinite. Geochim. Cosmochim. Acta 117, 180–190. doi:10.1016/j.gca.2013.04.008

Lučić, M., Jurina, I., Ščančar, J., Mikac, N., Vdović, N., 2019. Sedimentological and geochemical characterization of river suspended particulate matter (SPM) sampled by time-integrated mass flux sampler (TIMS) in the Sava River (Croatia). J. Soils Sediments 19, 989–1004. doi:10.1007/s11368-018-2104-2

Lučić, M., Mikac, N., Bačić, N., Vdović, N., 2021. Appraisal of geochemical composition and hydrodynamic sorting of the river suspended material: Application of time-integrated suspended sediment sampler in a medium-sized river (the Sava River catchment). J. Hydrol. 597, 125768. doi:10.1016/j.jhydrol.2020.125768

Luef, B., Neu, T.R., Peduzzi, P., 2009. Imaging and quantifying virus fluorescence signals on aquatic aggregates: a new method and its implication for aquatic microbial ecology. FEMS Microbiol. Ecol. 68, 372–380. doi:10.1111/j.1574-6941.2009.00675.x

Lunsdorf, Erb, Abraham, Timmis, 2000. "Clay hutches": a novel interaction between bacteria and clay minerals. Environ. Microbiol. 2, 161–168. doi:10.1046/j.1462-2920.2000.00086.x

Mannino, A., Harvey, H.R., 2000. Biochemical composition of particles and dissolved organic matter along an estuarine gradient: Sources and implications for DOM reactivity. Limnol. Oceanogr. 45, 775–788. doi:10.4319/lo.2000.45.4.0775

Mao, C., Chen, J., Yuan, X., Yang, Z., Balsam, W., Ji, J., 2010. Seasonal variation in the mineralogy of the suspended particulate matter of the lower Changjiang River at Nanjing, China. Clays Clay Miner. 58, 691–706. doi:10.1346/CCMN.2010.0580508

Markussen, T.N., Elberling, B., Winter, C., Andersen, T.J., 2016. Flocculated meltwater particles control Arctic land-sea fluxes of labile iron. Sci. Rep. 6, 24033. doi:10.1038/srep24033

Martin, J.-M., Meybeck, M., 1979. Elemental mass-balance of material carried by major world rivers. Mar. Chem. 7, 173–206. doi:10.1016/0304-4203(79)90039-2

Mavrocordatos, D., Mondi-Couture, C., Atteia, O., Leppard, G.., Perret, D., 2000. Formation of a distinct class of Fe–Ca(–Corg)-rich particles in a complex peat–karst system. J. Hydrol. 237, 234–247. doi:10.1016/S0022-1694(00)00309-7

McConnachie, J.L., Petticrew, E.L., 2006. Tracing organic matter sources in riverine suspended sediment: Implications for fine sediment transfers. Geomorphology 79, 13–26. doi:10.1016/j.geomorph.2005.09.011

McGuire, M.M., Herman, E.K., 2015. A novel ATR-FTIR technique for identifying colloid composition in natural waters. Hydrol. Process. 29, 1314–1323. doi:10.1002/hyp.10261

Meier, M., Namjesnik-Dejanovic, K., Maurice, P.A., Chin, Y.-P., Aiken, G.R., 1999. Fractionation of aquatic natural organic matter upon sorption to goethite and kaolinite. Chem. Geol. 157, 275–284. doi:10.1016/S0009-2541(99)00006-6

Meybeck, M., 1982. Carbon, nitrogen, and phosphorus transport by world rivers. Am. J. Sci. 282, 401–450. doi:10.2475/ajs.282.4.401

Meybeck, M., 1981. Flux of Organic Carbon by Rivers to the Oceans, Flux of Organic Carbon by Rivers to the Oceans. National Academies Press, Washington, D.C. doi:10.17226/19737

Meybeck, M., 1976. Total mineral dissolved transport by world major rivers. Hydrol. Sci. Bull. 21, 265–284. doi:10.1080/02626667609491631

Mikutta, C., Wiederhold, J.G., Cirpka, O.A., Hofstetter, T.B., Bourdon, B., Gunten, U. Von, 2009. Iron isotope fractionation and atom exchange during sorption of ferrous iron to mineral surfaces. Geochim. Cosmochim. Acta 73, 1795–1812. doi:10.1016/j.gca.2009.01.014

Mikutta, R., Lorenz, D., Guggenberger, G., Haumaier, L., Freund, A., 2014. Properties and reactivity of Fe-organic matter associations formed by coprecipitation versus adsorption: Clues from arsenate batch adsorption. Geochim. Cosmochim. Acta 144, 258–276. doi:10.1016/j.gca.2014.08.026

Mylon, S.E., Chen, K.L., Elimelech, M., 2004. Influence of Natural Organic Matter and Ionic Composition on the Kinetics and Structure of Hematite Colloid Aggregation: Implications to Iron Depletion in Estuaries. Langmuir 20, 9000–9006. doi:10.1021/la049153g

Nachtnebel, H.P., Seidelman, R., Müller, H.W., Schwaighofer, B., 1998. Schwebstoffe in der Donau, Forschung im Verbund Schriftenreihe Band 45. Vienna.

Neu, T., 2000. In situ cell and glycoconjugate distribution in river snow studied by confocal laser scanning microscopy. Aquat. Microb. Ecol. 21, 85–95. doi:10.3354/ame021085

Neu, T.R., 1996. Significance of bacterial surface-active compounds in interaction of bacteria with interfaces. Microbiol. Rev. 60, 151–166. doi:10.1128/MMBR.60.1.151-166.1996

Neubauer, E., Köhler, S.J., von der Kammer, F., Laudon, H., Hofmann, T., 2013a. Effect of pH and Stream Order on Iron and Arsenic Speciation in Boreal Catchments. Environ. Sci. Technol. 47, 7120–7128. doi:10.1021/es401193j

Neubauer, E., Schenkeveld, W.D.C., Plathe, K.L., Rentenberger, C., von der Kammer, F., Kraemer, S.M., Hofmann, T., 2013b. The influence of pH on iron speciation in podzol extracts: Iron complexes with natural organic matter, and iron mineral nanoparticles. Sci. Total Environ. 461–462, 108–116. doi:10.1016/j.scitotenv.2013.04.076

Nomizu, T., Nozue, T., Mizuike, A., 1987. Electron microscopy of submicron particles in natural waters?Morphology and elemental analysis of particles in fresh waters. Mikrochim. Acta 92, 99–106. doi:10.1007/BF01201722

Omoike, A., Chorover, J., Kwon, K.D., Kubicki, J.D., 2004. Adhesion of bacterial exopolymers to alpha-FeOOH: inner-sphere complexation of phosphodiester groups. Langmuir 20, 11108–14. doi:10.1021/la048597+

Onstad, G.D., Canfield, D.E., Quay, P.D., Hedges, J.I., 2000. Sources of particulate organic matter in rivers from the continental usa: lignin phenol and stable carbon isotope compositions. Geochim. Cosmochim. Acta 64, 3539–3546. doi:10.1016/S0016-7037(00)00451-8

Oriekhova, O., Stoll, S., 2018. Heteroaggregation of nanoplastic particles in the presence of inorganic colloids and natural organic matter. Environ. Sci. Nano 5, 792–799. doi:10.1039/c7en01119a

Panagiotopoulos, C., Sempéré, R., Para, J., Raimbault, P., Rabouille, C., Charrière, B., 2012. The composition and flux of particulate and dissolved carbohydrates from the Rhone River into the Mediterranean Sea. Biogeosciences 9, 1827–1844. doi:10.5194/bg-9-1827-2012

Patrolecco, L., Ademollo, N., Capri, S., Pagnotta, R., Polesello, S., 2010. Occurrence of priority hazardous PAHs in water, suspended particulate matter, sediment and common eels (Anguilla anguilla) in the urban stretch of the River Tiber (Italy). Chemosphere 81, 1386–1392. doi:10.1016/j.chemosphere.2010.09.027

Peduzzi, P., Luef, B., 2008. Viruses, bacteria and suspended particles in a backwater and main channel site of the Danube (Austria). Aquat. Sci. 70, 186–194. doi:10.1007/s00027-008-8068-3

Perret, D., Gaillard, J.-F., Dominik, J., Atteia, O., 2000. The Diversity of Natural Hydrous Iron Oxides. Environ. Sci. Technol. 34, 3540–3546. doi:10.1021/es0000089

Perret, D., Newman, M.E., Nègre, J.-C., Chen, Y., Buffle, J., 1994. Submicron particles in the rhine river—I. Physico-chemical characterization. Water Res. 28, 91–106. doi:10.1016/0043-1354(94)90123-6

Philippe, A., Schaumann, G.E., 2014. Interactions of Dissolved Organic Matter with Natural and Engineered Inorganic Colloids: A Review. Environ. Sci. Technol. 48, 8946–8962. doi:10.1021/es502342r

Pohlert, T., Hillebrand, G., Breitung, V., 2011. Trends of persistent organic pollutants in the suspended matter of the River Rhine. Hydrol. Process. 25, 3803–3817. doi:10.1002/hyp.8110

Pont, D., Simonnet, J.-P., Walter, A.V., 2002. Medium-term Changes in Suspended Sediment Delivery to the Ocean: Consequences of Catchment Heterogeneity and River Management (Rhône River, France). Estuar. Coast. Shelf Sci. 54, 1–18. doi:10.1006/ecss.2001.0829

Poulton, S.W., Raiswell, R., 2005. Chemical and physical characteristics of iron oxides in riverine and glacial meltwater sediments. Chem. Geol. 218, 203–221. doi:10.1016/j.chemgeo.2005.01.007

Praetorius, A., Badetti, E., Brunelli, A., Clavier, A., Gallego-Urrea, J.A., Gondikas, A., Hassellöv, M., Hofmann, T., Mackevica, A., Marcomini, A., Peijnenburg, W., Quik, J.T.K., Seijo, M., Stoll, S., Tepe, N., Walch, H., von der Kammer, F., 2020. Strategies for determining heteroaggregation attachment efficiencies of engineered nanoparticles in aquatic environments. Environ. Sci. Nano 7, 351–367. doi:10.1039/C9EN01016E

Praetorius, A., Labille, J., Scheringer, M., Thill, A., Hungerbühler, K., Bottero, J.-Y., 2014. Heteroaggregation of Titanium Dioxide Nanoparticles with Model Natural Colloids under Environmentally Relevant Conditions. Environ. Sci. Technol. 48, 10690–10698.

doi:10.1021/es501655v

Preocanin, T., Abdelmonem, A., Montavon, G., Luetzenkirchen, J., 2016. Charging Behavior of Clays and Clay Minerals in Aqueous Electrolyte Solutions — Experimental Methods for Measuring the Charge and Interpreting the Results, in: Clays, Clay Minerals and Ceramic Materials Based on Clay Minerals. InTech, pp. 137–144. doi:10.5772/62082

Ran, Y., Fu, J.M., Sheng, G.Y., Beckett, R., Hart, B.T., 2000. Fractionation and composition of colloidal and suspended particulate materials in rivers. Chemosphere 41, 33–43. doi:10.1016/S0045-6535(99)00387-2

Reinhardt, A., Wilkinson, K., 2004. Contrasting Roles Of Natural Organic Matter On Colloidal Stabilization And Flocculation In Freshwaters, in: Flocculation in Natural and Engineered Environmental Systems. CRC Press, pp. 143–170. doi:10.1201/9780203485330.ch7

Rosi-Marshall, E.J., Meyer, J.L., 2004. Quality of suspended fine particulate matter in the Little Tennessee River. Hydrobiologia 519, 29–37. doi:10.1023/B:HYDR.0000026482.10915.15

Rowland, R., Inamdar, S., Parr, T., 2017. Evolution of particulate organic matter (POM) along a headwater drainage: role of sources, particle size class, and storm magnitude. Biogeochemistry 133, 181–200. doi:10.1007/s10533-017-0325-x

Saleh, A.M., Jones, A.A., 1984. The crystallinity and surface characteristics of synthetic ferrihydrite and its relationship to kaolinite surfaces. Clay Miner. 19, 745–755. doi:10.1180/claymin.1984.019.5.05

Salminen, R., Batista, M.J., Bidovec, M., Demetriades, A., De Vivo, B., De Vos, W., Duris, M., Gilucis, A., Gregorauskiene, V., Halamic, J., Heitzmann, P., Lima, A., Jordan, G., Klaver, G., Klein, P., Lis, J., Locutura, J., Marsina, K., Mazreku, A., O'Connor, P.J., Olsson, S.Å., Ottesen, R.-T., Petersell, V., Plant, J.A., Reeder, S., Salpeteur, I., Sandström, H., Siewers, U., Steenfelt, A., Tarvainen, T., 2005. Geochemical Atlas of Europe. Part 1: Background Information, Methodology and Maps. Geological Survey of Finland, Espoo.

Schwertmann, U., 1988. Goethite and Hematite Formation in the Presence of Clay Minerals and Gibbsite at 25°C. Soil Sci. Soc. Am. J. 52, 288–291. doi:10.2136/sssaj1988.03615995005200010052x

Servais, P., Garnier, J., 2006. Organic carbon and bacterial heterotrophic activity in the maximum turbidity zone of the Seine estuary (France). Aquat. Sci. 68, 78–85. doi:10.1007/s00027-005-0809-y

Shin, H., Son, M., Lee, G., 2015. Stochastic Flocculation Model for Cohesive Sediment Suspended in Water. Water 7, 2527–2541. doi:10.3390/w7052527

Sigleo, A.C., Helz, G.R., 1981. Composition of estuarine colloidal material: major and trace elements. Geochim. Cosmochim. Acta 45, 2501–2509. doi:10.1016/0016-7037(81)90101-0

Sigmund, G., Jiang, C., Hofmann, T., Chen, W., 2018. Environmental transformation of natural and engineered carbon nanoparticles and implications for the fate of organic contaminants. Environ. Sci. Nano 5, 2500–2518. doi:10.1039/C8EN00676H

Simon, M., Grossart, H., Schweitzer, B., Ploug, H., 2002. Microbial ecology of organic aggregates in aquatic ecosystems. Aquat. Microb. Ecol. 28, 175–211. doi:10.3354/ame028175

Sinawi, G., Walling, D.., 1996. The characteristics of composite suspended sediment particles transported during storm events in the river Exe, Devon, U.K. Géomorphologie Reli. Process. Environ. 2, 29–40. doi:10.3406/morfo.1996.876

Sletmoen, M., Maurstad, G., Sikorski, P., Paulsen, B.S., Stokke, B.T., 2003. Characterisation of bacterial polysaccharides: steps towards single-molecular studies. Carbohydr. Res. 338, 2459–2475. doi:10.1016/j.carres.2003.07.007

Slomberg, D.L., Ollivier, P., Radakovitch, O., Baran, N., Sani-Kast, N., Miche, H., Borschneck, D., Grauby, O., Bruchet, A., Scheringer, M., Labille, J., 2016. Characterisation of suspended particulate matter in the Rhone River: insights into analogue selection. Environ. Chem. 13, 804. doi:10.1071/EN15065

Smith, B.M., Pike, D.J., Kelly, M.O., Nason, J.A., 2015. Quantification of Heteroaggregation between Citrate-Stabilized Gold Nanoparticles and Hematite Colloids. Environ. Sci. Technol. 49, 12789–12797. doi:10.1021/acs.est.5b03486

Spencer, R.G.M., Hernes, P.J., Dinga, B., Wabakanghanzi, J.N., Drake, T.W., Six, J., 2016. Origins, seasonality, and fluxes of organic matter in the Congo River. Global Biogeochem. Cycles 30, 1105–1121. doi:10.1002/2016GB005427

Srivastava, A., Seo, S.H., Ko, S.R., Ahn, C.Y., Oh, H.M., 2018. Bioflocculation in natural and engineered systems: current perspectives. Crit. Rev. Biotechnol. 38, 1176–1194. doi:10.1080/07388551.2018.1451984

Stehr, G., Zörner, S., Böttcher, B., Koops, H.P., 1995. Exopolymers: An ecological characteristic of a floc-attached, ammonia-oxidizing bacterium. Microb. Ecol. 30, 115–126. doi:10.1007/BF00172568

Stone, M., Droppo, I.G., 1994. In-channel surficial fine-grained sediment laminae. Part II: Chemical characteristics and implications for contaminant transport in fluvial systems. Hydrol. Process. 8, 113–124. doi:10.1002/hyp.3360080203

Subramanian, V., 1979. Chemical and suspended-sediment characteristics of rivers of India. J. Hydrol. 44, 37–55. doi:10.1016/0022-1694(79)90145-8

Surette, M.C., Nason, J.A., 2019. Nanoparticle aggregation in a freshwater river: the role of engineered surface coatings. Environ. Sci. Nano 6, 540–553. doi:10.1039/C8EN01021H

Sutherland, I.W., 2001. Biofilm exopolysaccharides: a strong and sticky framework. Microbiology 147, 3–9. doi:10.1099/00221287-147-1-3

Sutherland, I.W., 1990. Exopolysaccharide structure, in: Biotechnology of Microbial Exopolysaccharides. Cambridge University Press, pp. 20–37. doi:10.1017/CBO9780511525384.004

Tarchitzky, J., Chen, Y., Banin, A., 1993. Humic Substances and pH Effects on Sodium- and Calcium-Montmorillonite Flocculation and Dispersion. Soil Sci. Soc. Am. J. 57, 367–372. doi:10.2136/sssaj1993.03615995005700020014x

Teutsch, N., von Gunten, U., Porcelli, D., Cirpka, O.A., Halliday, A.N., 2005. Adsorption as a cause for iron isotope fractionation in reduced groundwater. Geochim. Cosmochim. Acta 69, 4175–4185. doi:10.1016/j.gca.2005.04.007

Thomas, R., Meybeck, M., 1996. The use of particulate material, in: Chapman, D. (Ed.), Water Quality Assessments - a Guide to Use of Biota, Sediments and Water in Environmental Monitoring - Second Edition. E & FN Spon, pp. 127–174.

Tipping, E., Heaton, M.J., 1983. The adsorption of aquatic humic substances by two oxides of manganese. Geochim. Cosmochim. Acta 47, 1393–1397. doi:10.1016/0016-7037(83)90297-1

Tipping, E., Woof, C., Cooke, D., 1981. Iron oxide from a seasonally anoxic lake. Geochim. Cosmochim. Acta 45, 1411–1419. doi:10.1016/0016-7037(81)90275-1

Tombácz, E., Libor, Z., Illés, E., Majzik, A., Klumpp, E., 2004. The role of reactive surface sites and complexation by humic acids in the interaction of clay mineral and iron oxide particles. Org. Geochem. 35, 257–267. doi:10.1016/j.orggeochem.2003.11.002

Tournassat, C., Davis, J.A., Chiaberge, C., Grangeon, S., Bourg, I.C., 2016. Modeling the Acid–Base Properties of Montmorillonite Edge Surfaces. Environ. Sci. Technol. 50, 13436–13445. doi:10.1021/acs.est.6b04677

van der Grift, B., Rozemeijer, J.C., Griffioen, J., van der Velde, Y., 2014. Iron oxidation kinetics and phosphate immobilization along the flow-path from groundwater into surface water. Hydrol. Earth Syst. Sci. 18, 4687–4702. doi:10.5194/hess-18-4687-2014

Van Groeningen, N., ThomasArrigo, L.K., Byrne, J.M., Kappler, A., Christl, I., Kretzschmar, R., 2020. Interactions of ferrous iron with clay mineral surfaces during sorption and subsequent oxidation. Environ. Sci. Process. Impacts 22, 1355–1367. doi:10.1039/D0EM00063A

Vázquez-Ortega, A., Hernandez-Ruiz, S., Amistadi, M.K., Rasmussen, C., Chorover, J., 2014. Fractionation of Dissolved Organic Matter by (Oxy)Hydroxide-Coated Sands: Competitive Sorbate Displacement during Reactive Transport. Vadose Zo. J. 13, 1–13. doi:10.2136/vzj2013.10.0179

Vidmar, J., Zuliani, T., Novak, P., Drinčić, A., Ščančar, J., Milačič, R., 2017. Elements in water, suspended particulate matter and sediments of the Sava River. J. Soils Sediments 17, 1917–1927. doi:10.1007/s11368-016-1512-4

Viers, J., Dupré, B., Gaillardet, J., 2009. Chemical composition of suspended sediments in World Rivers: New insights from a new database. Sci. Total Environ. 407, 853–868. doi:10.1016/j.scitotenv.2008.09.053

Vindedahl, A.M., Strehlau, J.H., Arnold, W.A., Penn, R.L., 2016. Organic matter and iron oxide nanoparticles: aggregation, interactions, and reactivity. Environ. Sci. Nano 3, 494–505. doi:10.1039/C5EN00215J

von Gunten, U., Schneider, W., 1991. Primary products of the oxygenation of iron(II) at an oxic—anoxic boundary: Nucleation, aggregation, and aging. J. Colloid Interface Sci. 145, 127–139. doi:10.1016/0021-9797(91)90106-I

Vu, B., Chen, M., Crawford, R., Ivanova, E., 2009. Bacterial Extracellular Polysaccharides Involved in Biofilm Formation. Molecules 14, 2535–2554. doi:10.3390/molecules14072535

Wagner, S., Hüffer, T., Klöckner, P., Wehrhahn, M., Hofmann, T., Reemtsma, T., 2018. Tire wear particles in the aquatic environment - A review on generation, analysis, occurrence, fate and effects. Water Res. 139, 83–100. doi:10.1016/j.watres.2018.03.051

Wall, G.J., Wilding, L.P., 1976. Mineralogy and Related Parameters of Fluvial Suspended Sediments in Northwestern Ohio. J. Environ. Qual. 5, 168–173. doi:10.2134/jeq1976.00472425000500020012x

Walling, D., Phillips, J., 2004. Intra- Storm And Seasonal Variations In The Effective Particle Size Characteristics And Effective Particle Density Of Fluvial Suspended Sediment In The Exe Basin, Devon, United Kingdom, in: Flocculation in Natural and Engineered Environmental Systems. CRC Press, pp. 47–70. doi:10.1201/9780203485330.ch3

Walling, D.E., Webb, B.W., 1987. Material transport by the world's rivers: evolving perspectives, in: Rodda, J.C., Matalas, N.C. (Eds.), Water for the Future: Hydrology in Perspective. Proceedings of the Rome International Symposium, April 1987. IAHS Publ no. 164, Rome, pp. 313–329.

Wang, X., Bolan, N., Tsang, D.C.W., Sarkar, B., Bradney, L., Li, Y., 2021. A review of microplastics aggregation in aquatic environment: Influence factors, analytical methods, and environmental implications. J. Hazard. Mater. 402, 123496. doi:10.1016/j.jhazmat.2020.123496

Wang, Z., Feng, B., Zhang, D., Ghosh, S., Pan, B., Xing, B., 2021. Role of NOM–hematite nanoparticle complexes and organic and inorganic cations in the coherence of silica and clay particles: evaluation based on nanoscale forces and molecular self-assembly. Environ. Sci. Nano 8, 822–836. doi:10.1039/D0EN01182G

Wei, S.-Y., Liu, F., Feng, X.-H., Tan, W.-F., Koopal, L.K., 2011. Formation and Transformation of Iron Oxide-Kaolinite Associations in the Presence of Iron(II). Soil Sci. Soc. Am. J. 75, 45–55. doi:10.2136/sssaj2010.0175

Wheatland, J.A.T., Bushby, A.J., Spencer, K.L., 2017. Quantifying the Structure and Composition of Flocculated Suspended Particulate Matter Using Focused Ion Beam Nanotomography. Environ. Sci. Technol. 51, 8917–8925. doi:10.1021/acs.est.7b00770

Wilkinson, K.J., Joz-Roland, A., Buffle, J., 1997. Different roles of pedogenic fulvic acids and aquagenic biopolymers on colloid aggregation and stability in freshwaters. Limnol. Oceanogr. 42, 1714–1724. doi:10.4319/lo.1997.42.8.1714

Woodward, J.C., Porter, P.R., Lowe, A.T., Walling, D.E., Evans, A.J., 2002. Composite suspended sediment particles and flocculation in glacial meltwaters: preliminary evidence from Alpine and Himalayan basins. Hydrol. Process. 16, 1735–1744. doi:10.1002/hyp.361

Woodward, J.C., Walling, D.E., 2007. Composite suspended sediment particles in river systems: their incidence, dynamics and physical characteristics. Hydrol. Process. 21, 3601–3614. doi:10.1002/hyp.6586

Wörner, U., Zimmerman-Timm, H., Kausch, H., 2000. Succession of Protists on Estuarine Aggregates. Microb. Ecol. 40, 209–222. doi:10.1007/s002480000051

Wörner, U., Zimmermann-Timm, H., Kausch, H., 2002. Aggregate-Associated Bacteria and Heterotrophic Flagellates in the River Elbe - Their Relative Significance along the Longitudinal Profile from km 46 to km 583. Int. Rev. Hydrobiol. 87, 255–266. doi:10.1002/1522-2632(200205)87:2/3<255::AID-IROH255>3.0.CO;2-R

Wotton, R.S., 2011. EPS (Extracellular Polymeric Substances), silk, and chitin: vitally important exudates in aquatic ecosystems. J. North Am. Benthol. Soc. 30, 762–769. doi:10.1899/10-120.1

Wotton, R.S., 2007. Do benthic biologists pay enough attention to aggregates formed in the water column of streams and rivers? J. North Am. Benthol. Soc. 26, 1–11. doi:https://doi.org/10.1899/0887-3593(2007)26[1:dbbpea]2.0.co;2

Yan, L., Chen, Q., Yang, Y., Zhu, R., 2021. The significant role of montmorillonite on the formation of hematite nanoparticles from ferrihydrite under heat treatment. Appl. Clay Sci. 202, 105962. doi:10.1016/j.clay.2020.105962

Yates, P.D., Franks, G. V., Biggs, S., Jameson, G.J., 2005. Heteroaggregation with nanoparticles: effect of particle size ratio on optimum particle dose. Colloids Surfaces A Physicochem. Eng. Asp. 255, 85–90. doi:10.1016/j.colsurfa.2004.12.035

Yeasmin, S., Singh, B., Kookana, R.S., Farrell, M., Sparks, D.L., Johnston, C.T., 2014. Influence of mineral characteristics on the retention of low molecular weight organic compounds: A batch sorption–desorption and ATR-FTIR study. J. Colloid Interface Sci. 432, 246–257. doi:10.1016/j.jcis.2014.06.036

Yin, X., 2012. Anisotropic surface features of selected phyllosilicates. University of Utah.

Yin, X., Yan, L., Liu, J., Xu, Z., Miller, J.D., 2013. Anisotropic Surface Charging of Chlorite Surfaces. Clays Clay Miner. 61, 152–164. doi:10.1346/CCMN.2013.0610212

Yong, R.N., Ohtsubo, M., 1987. Interparticle action and rheology of kaolinite-amorphous iron hydroxide (ferrihydrite) complexes. Appl. Clay Sci. 2, 63–81. doi:10.1016/0169-1317(87)90014-7

Zhang, G., Yin, H., Lei, Z., Reed, A.H., Furukawa, Y., 2013. Effects of exopolymers on particle size distributions of suspended cohesive sediments. J. Geophys. Res. Ocean. 118, 3473–3489. doi:10.1002/jgrc.20263

Zhang, M., Peacock, C.L., Cai, P., Xiao, K.-Q., Qu, C., Wu, Y., Huang, Q., 2021. Selective retention of extracellular polymeric substances induced by adsorption to and coprecipitation with ferrihydrite. Geochim. Cosmochim. Acta 299, 15–34. doi:10.1016/j.gca.2021.02.015

Zimmermann-Timm, H., 2002. Characteristics, Dynamics and Importance of Aggregates in Rivers - An Invited Review. Int. Rev. Hydrobiol. 87, 197–240. doi:10.1002/1522-2632(200205)87:2/3<197::AID-IROH197>3.0.CO;2-7

Zimmermann, H., 1997. The microbial community on aggregates in the Elbe Estuary, Germany. Aquat. Microb. Ecol. 13, 37–46. doi:10.3354/ame013037