

Marine colloids, agents of the self-cleansing capacity of aquatic systems: Historical perspective and new discoveries

Peter H. Santschi

Department of Marine Sciences, Texas A&M University – Galveston, Galveston, TX 77554, USA



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ABSTRACT

Colloids in the ocean are mainly composed of natural organic matter (NOM), with trace amounts of metals, metalloids, radionuclides, pollutants, and variable amounts of anthropogenically produced engineered nanoparticles and nanoplastics. State-of-the-art sampling and instrumental techniques were required to unravel both size spectra and chemical composition.

Chemical components of colloidal macromolecular organic matter (COM) include aquagenic substances (composed of microbially produced Exopolymeric Substances (EPS), gels, transparent exopolymer particles (TEP) and TEP precursors), and pedogenic substances (mostly humic and fulvic matter). COM can be bioavailable and biodegradable. EPS in aquatic systems can form flocs of Marine Snow (MS) or Marine Oil Snow (MOS). EPS is thus important in initiating and maintaining aggregation, flocculation, and sedimentation processes of particles and microorganisms that act also as sorbents of pollutants, a process that contributes in a major way to the 'self-cleansing capacity' of aquatic systems.

COM contains a diverse array of functionalities which can make them good metal chelating agents, amphiphilic and surface active pH-sensitive and redox-active. Due to numerous electrostatic and hydrophobic interactions between different moieties and ligand groups within a macromolecule, equilibrium constants, K_i , will become distribution functions for most reactions rather than fixed constants, as is common for low molecular weight organic molecules.

Colloidal pumping of trace substances bound to EPS and other reactive macromolecular NOM compounds is counteracting the prevailing pathway of degradation of the bulk macromolecular NOM. Due to strong sorption capabilities for stable and radioactive metal ions, particle- and colloid-reactive radionuclides are useful to trace particle and organic carbon fluxes in the ocean.

Open research questions include the role of different mechanisms that affect size spectra and composition of EPS in response to changing conditions, the role of macromolecular organic carrier molecules of radioactive and other trace substances that are used as oceanographic tracers; the potential use of the protein/carbohydrate ratio as a predictor of colloid or particle stickiness, aggregation or emulsification processes, and the importance of reactive oxygen species (ROS) mediated polymerization reactions of proteins and other molecules, which are part of EPS, for MS and MOS formation.

1. Introduction

1.1. Chemical composition of marine colloids is that of colloidal natural organic matter (NOM)

Aquatic colloids are nanoparticles and macromolecules in the 1 nm to 1 μ m size range, with at least one dimension less than 100 nm in size, and have the ability to scatter light (IUPAC, 2001). Colloids Science dates back almost 200 years when the term 'colloid' (Greek, "kolla" for glue) was coined by [Thomas Graham, 1805–1869]. During most of the next 150–200 years, it was understood that aquatic colloids were

mostly inorganic in origin, i.e., composed of metal oxides and clay minerals. Various organic resin-based extraction methods applied in the 1970's yielded great insights into the chemical composition and properties of pedogenic, humic and fulvic substances originating from decaying terrestrial plant matter. In the mid-1980's, aquatic colloid science experienced another great advance through the application of large-volume cross-flow ultrafiltration systems, which allowed the extraction of mg-g quantities of aquatic colloids and their molecular level chemical and physical characterization. It gave rise to the realization that aquatic colloids are mostly organic in nature, rather than inorganic, and that aquatic organic macromolecules contained not only

E-mail address: santschi@tamug.edu.

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humic substances, but also freshly produced aquagenic exopolymeric substances (EPS) originating from exudates of aquatic plant matter, i.e., phytoplankton and bacteria. The aim of this article is to not only give a historical perspective, but also to point to new insights into the composition, physical and chemical properties, as well as a more mechanistic understanding of colloids formation.

Aquatic colloids are not only defined by size, but also defined by their chemical, physical, and biological properties. They differ fundamentally from bulk solutions. In a solution, all the relevant interactions are comparable to the thermal energy, kT . Thus, even if water ‘prefers’ water, the tendency toward disorder-entropy is dominant. In contrast, the colloidal state is unstable because of large interfacial energies and thus the particle-particle interactions are stronger than kT . In aquatic systems, physical techniques based on diffusion and permeation (e.g., ultrafiltration, flow field-flow fractionation), light scattering (e.g., Dynamic Light Scattering, DLS), viscosity, Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM) can be used to separate and characterize colloidal systems, chemical techniques such as Mass Spectrometry and Nuclear Magnetic Resonance Spectroscopy can help to unravel their compositional complexities, and biological techniques such as enzymatic and genetic (molecular) techniques can give insights into degradability, bioavailability, and stability.

New insights into colloids in marine systems have always benefitted from the use of the newest instrumental techniques and new experimental or conceptual approaches coming from Health, Chemical and Biological Sciences, as well as industry, which, at times, have caused paradigm shifts in environmental and aquatic sciences. This is the case for large-volume cross-flow ultrafiltration.

Much of what we know about marine colloids has been gained through the applications of cross-flow ultrafiltration of large volumes of seawater, an industrial technique adapted to high salt conditions such as seawater. Ultrafiltration works for both characterization and pollutant partitioning purposes. Recent applications of large-volume cross-flow ultrafiltration methods (Guo and Santschi, 2007; Doucet et al., 2007, and references therein) to the sampling of sufficient amounts of aquatic colloids for most state-of-the-art instrumental methods have greatly advanced our understanding of the abundance, distribution, physical conformation, chemical composition, and environmental behavior of colloids in aquatic systems, including freshwater, seawater, and groundwater. Applications of ultrafiltration to marine systems date back to the 1970s and 1980s, when mostly stirred cell ultrafiltration units with membrane disks were used. Applications of large volume cross-flow ultrafiltration systems to sampling marine colloids started in the early 1990s, and they are now commonly used in marine science (Guo and Santschi, 1996, 1997; reviewed in Guo and Santschi, 2007, and references therein). More recently, a newer technique, ultrafiltration coupled to electrodialysis has occasionally been applied that can sample colloids more quantitatively (Vetter et al., 2007). This then allowed a more quantitative characterization of the major chemical composition of colloids by NMR and mass spectrometry techniques (Mao et al., 2012).

Small samples of colloids can also be size fractionated and characterized simultaneously using flow field-flow fractionation (FIFFF) techniques coupled with online or offline detectors (Lyven et al., 2003; Stolpe et al., 2014; Zhou et al., 2016). Besides flow field-flow fractionation (e.g., reviewed in Baalousha et al., 2011; Stolpe et al., 2014; Zhou et al., 2016), also Dynamic Light Scattering (e.g., Chin et al., 1998; Chen et al., 2011, 2015; Ding et al., 2008, 2009) analysis and flow cytometry (Verdugo et al., 2008) have been applied on small sample sizes to evaluate equilibrium or dynamic size distributions of colloids and/or gels.

The coupling of FIFFF with online UV-absorbance and fluorescence can provide simultaneous separation and characterization of colloidal organic matter, elucidating continuous molecular-size distribution, size-dependent composition, and the heterogeneity of bulk COM in seawater (e.g., Stolpe et al., 2014; Zhou et al., 2016; Xu and Guo, 2017).

As was true for ultrafiltration, FIFFF greatly benefitted also from using molecular probes (e.g., alginates; Alasonati et al., 2007; Van de Ven et al., 2009). In addition to online coupling, FIFFF coupled offline with other analytical techniques such as fluorescence excitation-emission matrix, can be used to reveal detailed changes in chemical composition with molecular size of colloids in a size continuum mode (Stolpe et al., 2013; Zhou and Guo, 2015). The heterogeneous nature of NOM in molecular size, composition, and environmental fate can be clearly revealed by the application of FIFFF technique.

While size and shape of colloids is clearly important, and can constrain molecular weights and other physical properties, information on chemical composition is mainly gained from instrumental techniques applied in organic chemistry such as mass spectrometry and nuclear magnetic resonance. What has been learned in the past several decades from research in marine chemistry, colloids are mainly made up by macromolecular organic matter (Guo et al., 1994; Guo and Santschi, 1997, 2007), contrary to some freshwater systems where inorganic forms (e.g., glacial waters; e.g., Chanudet and Filella, 2006) can be abundant as well. The organic colloiddally sized macromolecules, along with particles, are introduced in-situ mostly by the microbial community as exopolymeric substances (EPS), but also as humic substances by rivers, the atmosphere, or subterranean groundwater outflows. Colloidal macromolecular organic matter (COM) in the ocean thus contains both pedogenic (e.g., humic), and aquagenic (e.g., EPS) substances (Buffle, 1990), with a diverse array of different functionalities. COM can become surface active through the presence of amphiphilic groups, which can be pH-sensitive through protonation/deprotonation reactions, redox-active through hydroquinone/quinone and other redox active functionalities, and containing chelating properties through strongly (and often clustered) metal binding groups (e.g., Buffle, 1990).

Macromolecules have colloidal properties but are usually called by their chemical names. Because macromolecules are flexible entities that can organize themselves in space depending on electrical forces of charged moieties and the water, as well as the compatibility with water (hydrophobic forces), equilibrium constants, K_i , for most reactions will become distribution functions because of charge interactions between different moieties and ligand groups. These diverse functionalities allow colloids to get involved in aggregation reactions as well as hydrophilic (e.g., metal ions) and hydrophobic (e.g., oil and other hydrophobic pollutants) binding interactions. Sorption and aggregation reactions of NOM can increase with molecular weight and amphiphilicity. The presence of reactive oxygen species (ROS) that have the potential of inducing chemical crosslinking reactions between macromolecules (see below). Therefore, anthropogenic and natural substances that enter the ocean (e.g., metalloids, trace elements, radioactive substances, trace organics, engineered nanoparticles, nanoplastics, oil, etc.), can be removed by ‘scavenging’ (i.e., sorption, surface precipitation, encapsulation, etc) to aggregating colloids and particles entering the ocean in estuaries and other near-shore areas. Due to these diverse properties, the COM can become not only an agent of the self-cleansing capacity of marine and freshwater systems, but also involved in the organic carbon cycle of the ocean. In both cases, colloids are acting as glues and soaps, as well as gels, helping in this capacity to aggregate carbon containing particles. Thus, colloids become involved in a major way in the scavenging from the ocean waters of nutrients and pollutants, metals, radioisotopes, in short, any element in the periodic system. This scavenging action produces sinking particle aggregates that are all the while being degraded by bacteria and/or grazed and ‘repackaged’ by zooplankton. This overall scavenging process forms the basis for using particle-reactive radioisotopes as tracers of this multi-reaction process (Fig. 1).

COM can make up about 10–50% of the marine NOM pool, depending on the specific size fraction (Guo et al., 1994, 1997; Guo and Santschi, 2007). Humic substances consist of (higher molecular weight) humic and (lower molecular weight) fulvic acids, containing residues of decaying plant matter, and are, on their way to the ocean,

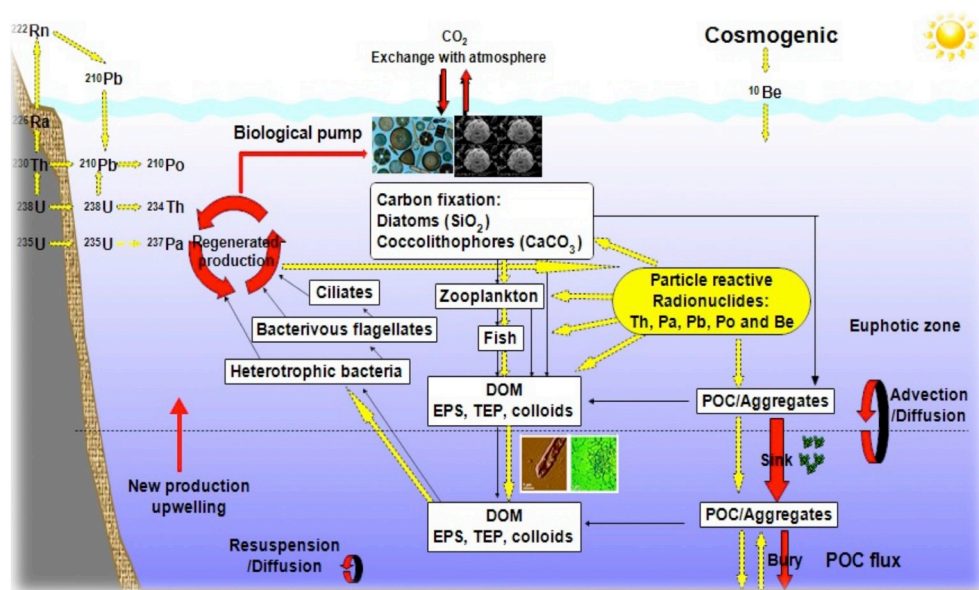


Fig. 1. Scavenging processes (the combined process of sorption, uptake, coagulation, flocculation) as traced by natural radioisotopes, that contribute to the self-cleansing capacity of aquatic systems, as well as the marine carbon cycle.

depolymerized through microbial enzymatic reactions and very likely re-polymerized through ROS mediated chemical crosslinking reactions (Chen et al., 2014; Sun et al., 2017).

While humic substances are mostly flexible and spherical in shape, with molecular weights of several thousands, present as aggregates that are held together by metal complexation and electrostatic interactions, exopolymeric substances (EPS) are rigid and fibrillar, with molecular weights of 10s to 1000s of kDa (Buffle et al., 1998; later confirmed by Loh et al., 2004). Those fibrils are 1 to few nanometer in diameter and a few micrometers in length (Fig. 2), and have a modern radiocarbon age when made up of mostly polysaccharides (Santschi et al., 1998). These fibrils are, however, only visible on TEM when a heavy metal stain is used during the sample preparation, and best, imbedded in a hydrophilic resin (Santschi et al., 1998). Earlier attempts to use TEM were not always successful because of the lack of stain, and only resulted in what one could call artifacts (e.g., Wells and Goldberg, 1991). Besides acidic and neutral polysaccharides, fibrillar EPS also contain proteins and other macromolecules (Benner et al., 1992; Hung et al., 2005; Quigg et al., 2016; Decho and Gutierrez, 2017).

EPS, in the form of 0.4 μm filter-retainable transparent exopolymeric particles (TEP), are forming flocs (marine or lake snow), which in turn can also provide the organic 'glue' for mineral aggregate buildup,

thus providing a vehicle for transport to the seafloor. COM also contains numerous trace elements (Benoit et al., 1994; Wen et al., 1996, 1997a, 1999; Stordal et al., 1996a; Guo et al., 2000), radionuclides (e.g., Baskaran et al., 1992, 1996; Baskaran and Santschi, 1993; Guo et al., 1997; Oktay et al., 2001), and biochemicals such as chl.a (Bianchi et al., 1995), lignin phenols (Bianchi et al., 1997; Mitra et al., 2000), hydroxamate siderophores (Chuang et al., 2013, 2015a; Xu et al., 2008), and extracellular DNA (Jiang and Paul, 1995).

Studies on the composition of colloidal macromolecular organic matter pointing to specific functionalities and carrier molecules for selected radionuclides include those of Alvarado Quiroz et al. (2006), and Chuang et al. (2015a, 2015b). Quigley et al. (2001) attributed potential radionuclide binding ligands in colloidal EPS from the Gulf of Mexico using radiotracers to acidic functional groups. In addition, Chuang et al. (2015a), when comparing the chemical composition of colloids from oligotrophic ocean basins such as the Gulf of Mexico and the North Pacific Ocean, found a close relationship between ²³⁴Th binding (i.e., particle/water partition coefficients) and the presence of hydroxamate siderophores. This built on earlier accounts of Th-binding colloidal ligands that have been summarized by Santschi et al. (2006).

Besides playing roles in colloid and of trace metal and radionuclide scavenging from the water, organic macromolecules such as EPS can

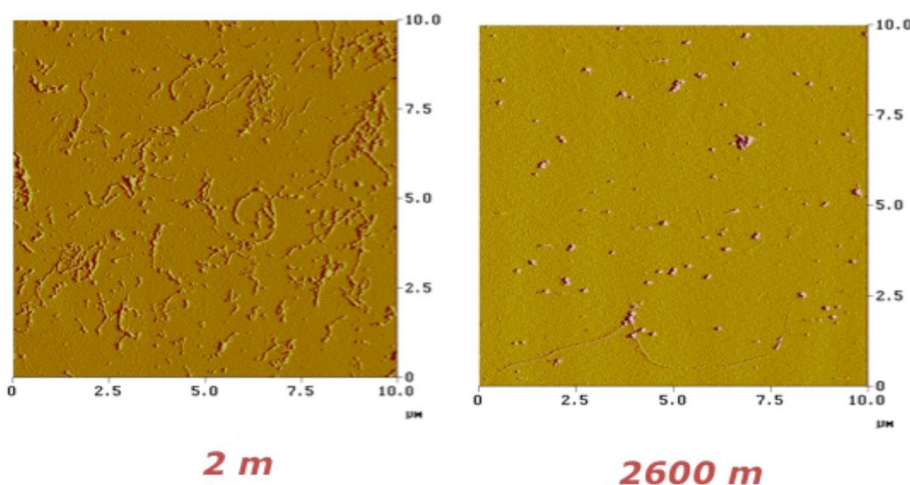


Fig. 2. First Atomic Force Microscopy pictures showing forms and shapes of colloids from the Middle Atlantic Bight (2 m and 2600 m) water depth, showing pearls on necklace, the most common colloidal form, with fibrillar macromolecules (1–2 nm (nm) thickness and several microns in lengths) arranged in a 'spiderweb' form (left), and mostly small, globular forms with the exception of a close to 10 μm long fibril near the bottom (right). No fibrils were visible at mid-depth. When these fibrils were subjected to polysaccharide enriching procedures using alcohol precipitation, pure fibrils showed modern radiocarbon ages, much younger than for the mixture of colloids (from Santschi et al., 1998, open access).

also provide a matrix for FeOOH, MnO₂, CaCO₃ and SiO₂ growth, and can alter the surface characteristics of suspended particles. EPS can also facilitate microbial adhesion to surfaces, and thus, provide the matrix components of biofilms and bind extracellular enzymes in their active forms, and are thus the first-line of defense against toxic substances by immobilizing toxicants.

EPS production is occurring from both prokaryotic and eukaryotic organisms, and is thus of great ecological importance (Passow, 2002). The microbial release of EPS in aquatic environments may be thought of as part of an autopoietic system, that is, a self-sustaining community response (Maturana and Varela, 1980; Santschi et al., 2003). The self-sustaining processes, mechanisms, and participants in the cycling of EPS in the aquatic environment can, however, still bring great surprises. For example, while searching for the main producers of EPS in the Gulf of Mexico, it was found that at different times, different phytoplankton species were present producing similar amounts of EPS over time. Furthermore, while the focus of the study by Santschi et al. (2003) was on relationships between Th-234 scavenging, phytoplankton and compositional variables of EPS, the role bacteria in the phycosphere, which can be the primary producers of protein-rich EPS (Decho and Gutierrez, 2017), were not directly assessed.

Among environmental colloids, engineered nanoparticles (ENPs) in the aquatic environment have to be mentioned, too, as they have become an emerging research field in their own right (e.g., see recent reviews by Lead and Wilkinson, 2006; Navarro et al., 2008; Klaine et al., 2008; Ray et al., 2009; Andradý, 2011; Quigg et al., 2013). Man-made nanoparticles, such as oxides of Zn or Ti, nanosilver, buckyballs, carbon fibers, and nanotubes, which are potentially toxic to humans and organisms in the environment, are making their way into the aquatic environment, and ultimately into the ocean, where they can temporarily exert potentially toxic behavior (e.g., Navarro et al., 2008) before they become eliminated by the self-cleansing capacity of the water. Engineered nanoparticles, i.e., ENPs (Navarro et al., 2008; Quigg et al., 2013; Ray et al., 2009), and microplastics and nanoplastics (e.g., Andradý, 2011), have become important colloidal pollutants in the Ocean.

1.2. Metal complexation to colloidal macromolecular organic matter

Understanding metal binding to macromolecular ligands requires different concepts than for low molecular weight organic ligands. For example, while one is used to have thermodynamic constants of metal ion interactions with crystalline solids and low molecular weight compounds as more rigorously defined constants, this is not the case for macromolecular COM, where all these so-called ‘constants’ become distribution functions around a mean, due to the various interactions between different functional groups. Furthermore, there is a continuum of sites, with the strongest ligands usually being also the rarest sites (Buffle, 1990).

In the 1970's and 1980's, concepts of metal complexation were considering only low molecular weight ligand molecules, while still valid today, then became dogmas and prevented progress for decades. It took until the 1990's that it became evident that metals bound to macromolecules need to be seriously considered as well. As is often the case, the application of more rigorous analytical approaches (such as electrochemical techniques) provided evidence for the importance of macromolecules (e.g., Wen et al., 1999a,b; Tang et al., 2001). By the end of the 1990's, selected thermodynamic metal complexation constants to fulvic substances, parts of the lower molecular weight NOM continuum, were incorporated into metal speciation models (e.g., WHAM, Tipping, 1998, 2002; Tipping et al., 2011; Town and Fillela, 2000, 2002). These models are most useful for assessing bioavailability of toxic metals to aquatic organisms considering that only molecular entities with molecular weights smaller than about 600 Da can pass membranes. Though there are exceptions (see below), the free-ion bioavailability models have been proven to be most useful. However,

thermodynamic stability constants for COM moieties are still not readily available, but such ligands can be equally strong or stronger than those of low molecular weight ligands. The fact that COM can act as a powerful ligand for many trace metals was shown in coastal and open ocean environments. (e.g., Wen et al., 1996, 1997a, 1999, 2006, 2008, 2011; Guo et al., 2000; Wells, 2002; Guo and Santschi, 2007, and Doucet et al., 2007). There are even indications that such macromolecular ligands are stronger than low molecular weight dissolved ligands, e.g., Cu (Tang et al., 2001), and other soft metals (Tang et al., 2002).

1.3. Coagulation/aggregation of colloids

Colloidal macromolecular organic matter contains a diverse array of functionalities which can make them, in addition to being good metal chelating sites, also surface active through the presence of amphiphilic groups, pH-sensitive through protonation/deprotonation reactions, and redox-active through having hydroquinone/quinone and other redox active functionalities, and chelating properties through strongly (and often clustered) metal binding groups (e.g., Buffle, 1990). This allows them to get involved in multiple and closely linked processes of metal complexation, redox reactions, and aggregation reactions as well as hydrophilic (e.g., metal ion) and hydrophobic (e.g., oil and other hydrophobic pollutant) binding reactions. Sorption and aggregation reactions of NOM then become dependent on molecular weight, amphiphilicity and presence of ROS to induce chemical crosslinking reactions (Chen et al., 2014; Sun et al., 2017, 2018a, 2018b).

Macromolecules of colloidal size also act as templates for building silica and carbonate shells of phytoplankton, i.e., biopolymers. and can contain important binding sites for radioactive and stable trace elements. Biopolymers control the scavenging of metals and radionuclides and the coagulation/flocculation of particles in marine systems (Santschi et al., 2005, and references therein) and also the early development of biofilms (Leppard et al., 1997), which is largely due to their surface-active nature. These biopolymers can also initiate or modify precipitation of MnO₂ and FeOOH (Cowen and Bruland, 1985; Taillefert et al., 2000), SiO₂ (Kinrade et al., 2002), and CaCO₃ (Leveille et al., 2000). Moreover, EPS-rich polymers in the extracellular milieu form flocs (Mopper et al., 1995; Alldredge et al., 1993) and also bind extracellular enzymes in their active forms. The physicochemical properties of EPS molecules can also provide chelating sites for micronutrients such as trace metals (Quigley et al., 2002; Guo et al., 2000). EPS can also modify the solubility and mobility of associated molecules (Leppard et al., 1997). Other important chelating compounds are contained in microbially derived EPS that make up the bulk of what is called ‘marine snow’ or ‘lake snow’, and which in turn can also provide the organic ‘glue’ for mineral aggregate buildup, thus providing a vehicle for transport to the seafloor.

Also, a major fraction of COM is forming 4–6 μm sized gels that provide microhabitats for microbial degradation of NOM (Verdugo et al., 2004; Verdugo and Santschi, 2010). While gels form reversibly via electrostatic interactions, EPS with more hydrophobic domains (such as nanoplastics) can greatly accelerate the process, and make it irreversible (Ding et al., 2008, 2009; Chen et al., 2011).

While the colloid/particle partitioning is dynamic, as parts of colloids are continuously aggregating to particles (e.g., ‘colloidal pumping’, Honeyman and Santschi, 1989), while others are disintegrating or decomposing into smaller molecules through enzymatic and/or photochemical reactions (Fig. 3), most of the attention by aquatic scientists has been focused on the size continuum model (Amon and Benner, 1994; Santschi et al., 1995), where it was shown that the main pathway is from high molecular weight to low molecular weight through biodegradation and disaggregation (Wang and Guo, 2001; Santschi et al., 2006).

There are, however, opposing pathways, including colloidal pumping (Honeyman and Santschi, 1989, 1991) and self-assembly (e.g.,

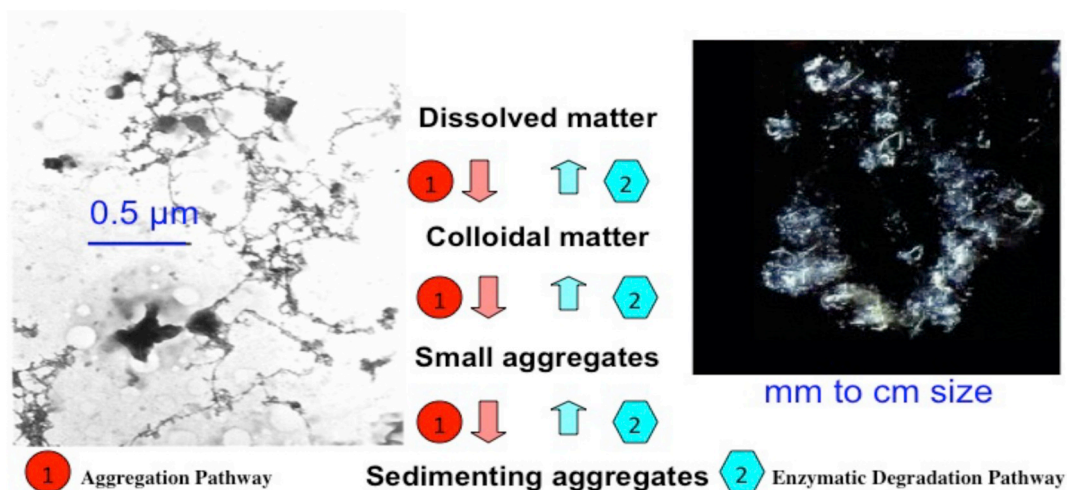


Fig. 3. Due to its sticky qualities, colloid aggregation (red) is a pathway that is opposite to the prevailing degradation pathway (blue) going from large to small molecules (Amon and Benner, 1994; Santschi et al., 1995). This is illustrated by the (nm to μm sized) colloid spiderweb-like fibrils acting as ‘colloid-traps’ (by Transmission Electron Microscopy (TEM), after staining with a heavy metal dye; Santschi et al., 1998, with permission from the publisher) on left, and cm sized Marine Snow on the right (Aldredge and Gotschalk, 1989, with permission from the publisher). Marine Snow aggregates have fractal properties, i.e., showing similarities across scales, i.e., self-similarity and scaling invariance. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

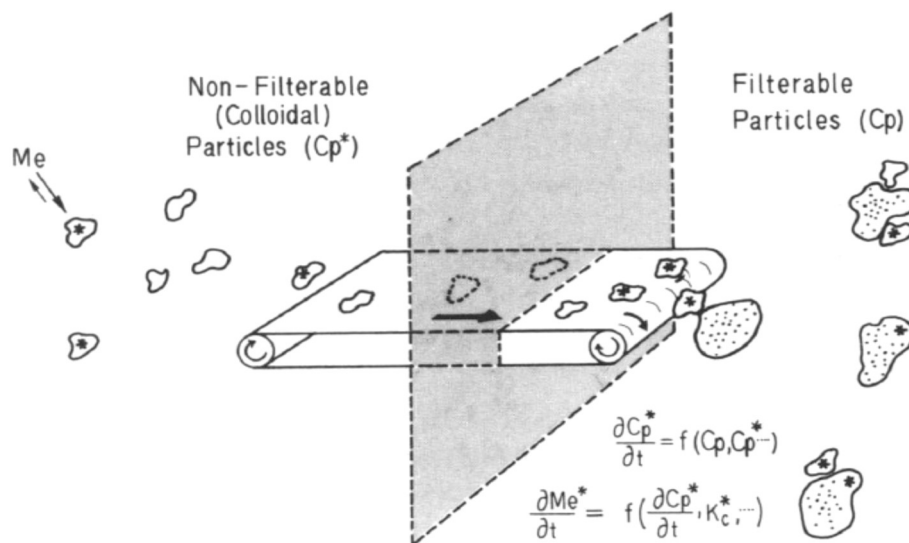


Fig. 4. Brownian-pumping: the transfer of dissolved metal to filterable particles via a colloidal intermediate. The rate of coagulation of colloidal particles with filterable particles is a function of particle concentration, C_p . The rate of transfer of a metal, Me , from the truly dissolved state to the filterable-particle fraction is a function of the solution/colloid distribution coefficient, K_c , in addition to the colloids coagulation rate * on particles represents those “tagged” with radioactive metal species (Honeyman and Santschi, 1989).

Chin et al., 1998; Xu and Guo, 2018), that have received less attention. This involves various mechanisms that can be responsible for the formation of aggregates of higher molecular weight material that also can contribute to the removal of radioactive tracers in the ocean. This mechanism is related to the presence, chemical composition and concentration of colloidal, nano-particulate substances. However, the presence of colloidal forms of these metal radionuclides in the filter-passing fraction is often ignored. When observing the kinetics of aggregation of colloids into particles (termed ‘colloidal pumping’; Honeyman and Santschi, 1989), colloids and particle concentration effects on kinetic constants and pseudo-equilibrium particle-water partition coefficients are often observed. (Fig. 4). This colloidal pumping mechanism involves colloidal ligands in the filter-passing fraction that can aggregate, mainly through Brownian motion, but also through differential settling and fluid shear. This model was able to closely reproduce observations of dependencies of values of both kinetic rate constants and (non-thermodynamic) particle-solution concentration ratios (K_d) of the radioisotope ^{234}Th (half-life of 24 days), and other radionuclides, on particle concentration. This ‘Brownian

Pumping model’ of Honeyman and Santschi (1988, 1989, 1991) also explain well the observations that Th-234 /organic carbon ratios in different sized colloids and particles in the ocean are lowest in the smaller size fractions, opposite to what would be expected from their relative specific surface areas and surface sites concentrations (Santschi et al., 2006). It was also shown to be a predictor for colloidal trace metal coagulation rates (Stordal et al., 1996b; Wen et al., 1997b). A parameter that represents the collision efficiency in this simplified ‘Brownian Colloidal Pumping Model’, as well as more sophisticated coagulation models (e.g., Burd et al., 2000), is a physical (fudge) factor, a “sticky factor”, which is often observed to be between 0.1 and 1. For example, Quigley et al. (2001) found that the sticky factor for COM, when mainly composed of EPS, increased from 0.7 to 0.9 after polysaccharide enrichment to close to 100% through ethanol precipitation of bulk colloids (COM). Engel (2000) found that this sticky factor of the combined ensemble of TEP (transparent exopolymeric particles) and Coulter Counter detectable particles increased during a diatom bloom from about 0.2 to about 1, i.e., every collision would be successful at the end of the bloom. Clearly, this empirical sticky factor contains both

biology and chemistry. However, the molecular significance of this factor requires further study.

Owing to their strong particle-reactive nature, many radionuclides, such as thorium (Th), protactinium (Pa), lead (Pb), polonium (Po), and beryllium (Be), are used as tracers for oceanic particle cycling or for soil erosion and transport. Many of them are continuously removed from the water aided by this colloidal pumping mechanisms, after they are introduced to the water by parent decay of atmospheric deposition. The ‘scavenging’ of these radionuclides can then be modeled by incorporating the kinetics of tracer adsorption to colloids and particles. Based on the differences in particle reactivity and disequilibria between parent and daughter radionuclides, various biogeochemical and physical processes in the ocean can then be explored (Santschi and Honeyman, 1989). Examples include export fluxes of different chemical species, boundary scavenging, oceanic circulation, and paleoproductivity. However, most of these applications are generally resting on inferences from correlations of isotopic ratios with bulk particle properties, with little knowledge on the exact chemical reactions or knowing what carrier phase(s) transport the radionuclides Xu et al., 2011a,b.

1.4. Macromolecular carrier molecules for radioactive and stable metal ions

Radionuclides will only become tracers for any particle cycling process if we know what they are attached to. Thus, it is important to decipher the exact compound and binding site, be they of inorganic or organic nature. For the study of radionuclides bound to organic compounds, it is then necessary to use molecular-level techniques, in conjunction with radiochemical techniques. Using a combination of such techniques, it was shown that, at environmental levels, many radionuclides, such as those of Pu, Th, Pa, and Po, are found at significant levels in the colloidal, macromolecular fraction in soil and marine particles, tightly bound to specific chelating molecules such as hydroxamate siderophores for Pu bound to soils (Xu et al., 2015), and Th, Po, Pa (Chuang et al., 2013) in sinking particles in the North Atlantic. As a matter of fact, Chuang et al. (2013) found that hydroxamate siderophore (HS) compounds constitute a considerable fraction of the sinking particles collected from the Bermuda Oceanic Flux Program (OFP) time-series site. In contrast, HS occur as a minor fraction in the 1 kDa–0.4 μm COM collected from the Gulf of Mexico and the North-western Pacific Ocean (Chuang et al., 2015a). Interestingly, hydroxamate siderophores bind other metal ions with similar ionic potential (i.e., ionic charge to radius ratio) to similar or greater extent than Fe³⁺ (Fig. 5).

To find HS molecules in the colloidal and particulate fraction is surprising, as they are produced to solubilize iron from solids. Hypothetically, as hydroxamates have antioxidant properties susceptible to interacting with ROS, ROS mediated chemical crosslinking could incorporate HS molecules into colloids and particles. Such a polymerization process is novel, and if confirmed, indicates that the excess of ROS in the water overwhelms the hydroxamate concentration in the water leading to crosslinking polymerization with other NOM. To find them in a colloidal or particulate form is also unexpected since siderophores are produced by microorganisms to solubilize iron and make it available as a micronutrient. If confirmed, it might indicate that the ecosystem as a whole might benefit by transporting iron chelates to the bottom of the ocean, where they might be made accessible to benthic macro- and microflora.

Not only metal ions were found to become covalently bound to COM, but other trace elements, such as iodine, which was identified as covalently bound to specific binding sites in aromatic moieties of macromolecules (Xu et al., 2012), moieties broadly similar to those of thyroxine in the human body. For example, Oktay et al. (2001) determined that a major (72%) fraction of stable ¹²⁷I and radioactive ¹²⁹I associated with the colloidal fraction.

By studying the sorption of selected natural radionuclides (²³⁴Th, ²³³Pa, ²¹⁰Po, ²¹⁰Pb, and ⁷Be) onto inorganic (pure silica and acid-

cleaned diatom frustules) and organic (whole diatom cells of *Phaeodactylum tricornutum*, with or without silica frustules) particles in natural seawater, it was revealed that the sorption of these radionuclides was much higher than to inorganic silica or cleaned frustules when in the presence of templating or surrounding organic matter molecules associated with the diatoms (Chuang et al., 2015b). Thus, templating biomolecules and exopolymeric substances (EPS) associated with the same species of diatom, are more important for the uptake of these radionuclides and strongly indicate that these biomolecules in diatom cells are responsible for the sorption enhancement rather than the bare silica shell itself. Isoelectric focusing results furthermore suggested that each radionuclide binds to specific biopolymeric functional groups, with the most efficient binding sites likely occurring in acid polysaccharides, iron hydroxides, and proteins. It was also shown that Coccolithophore-associated organic biopolymers rather than biogenic calcite serve as the main carrier phases for Th and Pa, while Po, Pb and Be are also incorporated into biogenic calcite by Ca²⁺ substitution during coccolith formation (Lin et al., 2017), and that different patterns of fractionation between radionuclides occur for coccolithophores versus diatom-dominated systems. Thus, the carrier-phase approach using organic moieties is more complicated, and provides new challenges when attempting to identify radionuclide carrier phases.

Through both field and laboratory studies, considerable evidence has now accumulated showing compound-specific scavenging and partitioning for different radionuclides, either from an inorganic or from an organic compound prospective (Lin et al., 2017). While many oceanographers consider only inorganic carrier compounds because they observe correlations between different radionuclides and inorganic compounds, organic macromolecular carrier compounds have largely been ignored so far. Organic chelating compounds can originate intracellularly (e.g., as organic templates for phytoplankton CaCO₃ or SiO₂ shell formation), or extracellularly (as EPS that can form marine snow), or from land (e.g., as humic acid compounds). Inorganic carrier compounds that had been suggested include CaCO₃, SiO₂, MnO₂, and Fe₂O₃. This is important if we want to predict their behavior under changing conditions, and to help the data interpretation of oceanographic surveys such as GEOTRACES.

1.5. Bioavailability of colloidal macromolecular organic matter

While the ‘biotic ligand model’ for metal ion uptake can explain many of the observations, there is also good evidence that larger macromolecules of COM and their associated pollutants can be incorporated into plankton also through ternary metal complexes (Zhao and Wilkinson, 2015; Zhao et al., 2016; Slaveykova and Wilkinson, 2005) or phagocytosis (Miao et al., 2010). However, for general predictions of metal bioavailability to aquatic organisms, low molecular weight ligands are likely more important.

The important question remains if COM larger than 600 Da, with associated pollutants, is able to be incorporated by aquatic organisms. It was found that this is indeed the case. Colloidal-sized particles were shown to be taken up by some plankton species as well as some higher organisms. For example, it was shown that radiolabeled COM can be taken up by shrimp, clams and oysters (Haye et al., 2006; Carvalho et al., 1999), and engineered nanoparticles (ENPs) can be taken up by phytoplankton (Miao et al., 2010). While uptake of colloidal radiotracers by plankton is aided by phagocytosis or endocytosis (Miao et al., 2010) colloidal uptake by filter-feeding animals was through gills, and accumulated in the carapas (Haye et al., 2006; Carvalho et al., 1999). Gill uptake of dioxin associated COM by fish and other filter feeders from a superfund site in the Houston Ship Channel (Suarez et al., 2005) could also be the cause for their high concentrations, as dioxins in pore waters at the site were shown to be very low, even lower than predicted from theoretical considerations (Louchouart et al., 2018). Reviews of bioavailability, including colloidal metals and ENPs can be found in Lead and Wilkinson (2006), Klaine et al. (2008),

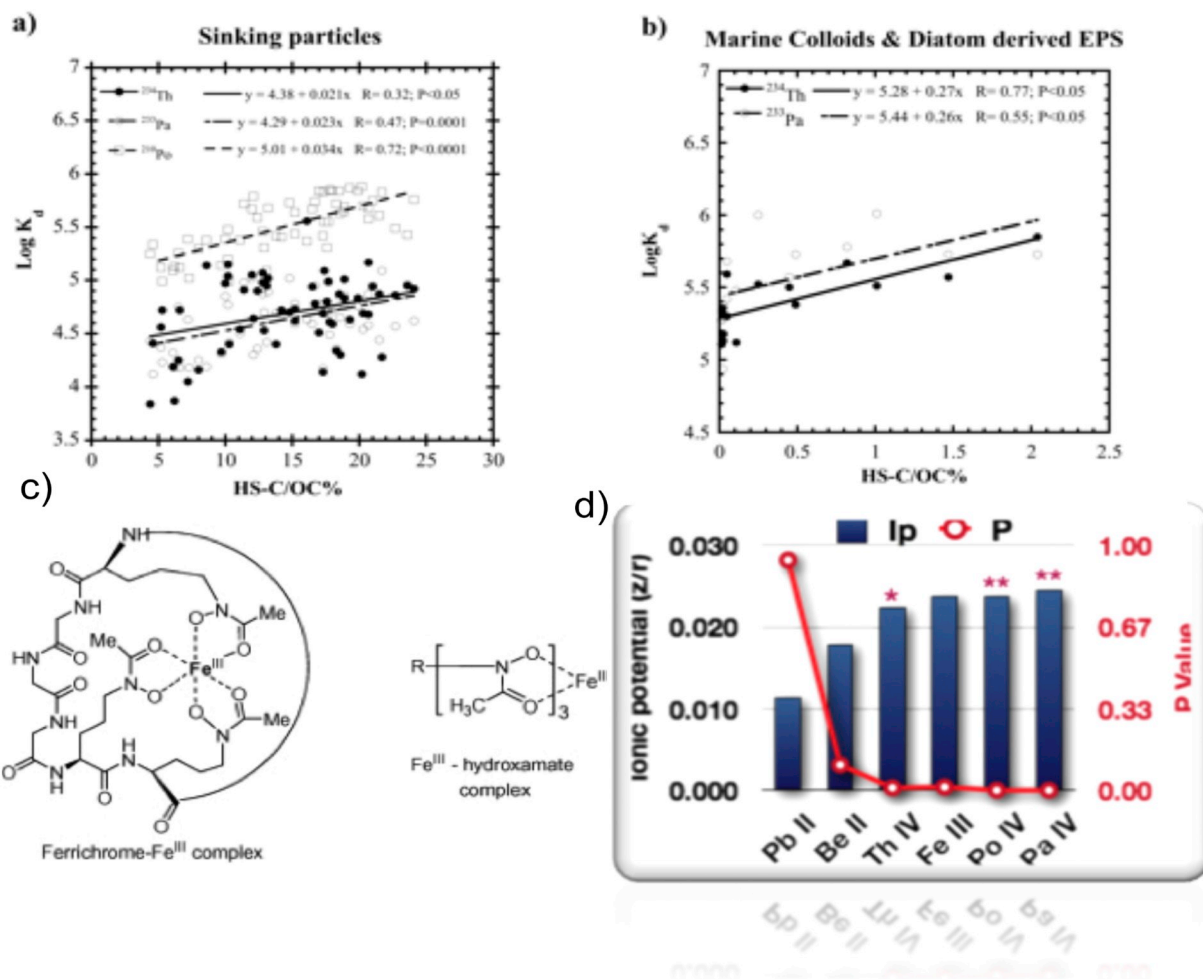


Fig. 5. a) Correlations between the $\text{Log}K_d$ values of ^{234}Th , ^{233}Pa , ^{210}Po with particles from Bermuda Oceanic Flux Program (OFP) time-series site (data from Chuang et al., 2013); b) ^{234}Th and ^{233}Pa with colloids from Northwestern Pacific Ocean and diatom derived EPS vs concentrations of hydroxamate siderophores (HS) normalized to OC (Chuang et al., 2015a, with permission from Elsevier); c) Ferrichrome Fe^{III} complex; d) a) Ionic potentials (I_p = Ionic Charge/radius ratio) of Fe^{III} , Po^{IV} , Th^{IV} and Pa^{IV} are very similar (p values from Chuang et al., 2013).

Navarro et al. (2008), and Quigg et al. (2013). Furthermore, colloidal macromolecular organic matter can also form interfacial corona on ENPs' surfaces (Baalousha et al. 2018), altering ENPs' toxicity to aquatic organisms (e.g., Kteeba et al., 2017).

In addition, direct uptake of ENPs by biota (Navarro et al., 2008; Zhang et al., 2013; Quigg et al., 2013; Ray et al., 2009), and microplastics and nanoplastics in aquatic environments (e.g., Andradý, 2011), have become important colloidal pollutants in the ocean that greatly affect aquatic biota, and deserve further study.

A better knowledge of the role of colloidal macromolecular organic matter, as well as ENPs, is essential for understanding the health of marine ecosystems, as both colloidal macromolecular organic matter can greatly modify the fate of dissolved and ENP pollutants and nutrients through complexation, aggregation and/or emulsification reactions.

1.6. Significance of exopolymeric substances for pollutant (e.g., oil) binding and removal

Hydrophobic moieties make COM amphiphilic and thus, suitable as a surfactant and/or emulsifier to help solubilize hydrophobic pollutants via hydrophobic interactions (Daly et al., 2016). For example, studies of oil removal through 'marine oil snow' formation and particle aggregation showed in mesocosms that simulate critical processes in the water, that oil removal from the water is facilitated by microbial EPS

production (Quigg et al., 2016; Daly et al., 2016), but is greatly decreased when Corexit, a surfactant and emulsifier, is used. Because oil incorporation into aggregates decreases their buoyancy, ballasting minerals of terrestrial or marine origin need to be present for the removal to the bottom. This finding is consistent with the fact that significant amounts of oil were subsequently found at the bottom of the Gulf of Mexico, during the Deep Water Horizon oil spill in 2010, which released "live oil" that is, a mixture of oil and natural gas with very high vapor pressures, into the Gulf of Mexico,

Based on radiocarbon and ^{13}C NMR results, it was also shown that the presence of dispersants drastically decreased petrocarbon incorporation into sinking MOS, but increased oil in dispersed, non-sinking colloidal EPS containing a relatively low mineral content. Formation of Marine Oil Snow, or MOS, and subsequent sinking proceeded in two stages: first a faster removal via terrestrial-derived detritus containing humics, and subsequently, slower removal via freshly produced material, such as EPS sequestering the oil greatly reducing the buoyancy of the MOS (Xu et al., 2018a).

Furthermore, the presence of the water-accommodated fraction of oil was observed to stimulate extracellular polysaccharide production by phytoplankton, whereas Corexit, an emulsifier and detergent, promoted protein production by bacteria. Corexit also promoted the association between oil and EPS, thus retaining both more oil and EPS in colloids and suspended particles. Likely, microbially-mediated EPS are the key compound class that anchors mineral ballast until the

aggregates can sink. Therefore, it is the interactions between Corexit, EPS and mineral particles that partially regulate the partitioning of petroleum hydrocarbon between the water column and the sinking of MOS out of the water column. (Xu et al., 2018b).

1.7. Importance of ROS mediated protein polymerization reactions of EPS for MS and MOS formation

While microorganisms are mostly responsible for forming aggregates in the water column, there is a mostly abiotic process that was recently discovered called photo-flocculation in the surface ocean (Helms et al., 2013). Sunlight is known to inhibit or disrupt the aggregation process of marine colloids via cleavage of high molecular weight compounds into smaller, less stable fragments. In contrast, what has not been known and is novel, is that some biomolecules, such as proteins excreted from bacteria, can form aggregates via chemical cross-linking due to photo-oxidation, as was recently shown by Sun et al. (2017), and previously termed ‘photoflocculation’ (Helms et al., 2013; Shammii et al., 2017; Waggoner and Hatcher, 2017) for freshwater systems that produces N-enriched compounds. This process was shown by Sun et al. (2017, 2018a,b) to be mediated by ROS, i.e., hydroxyl radicals and peroxide. When irradiation experiments were conducted on a well-characterized protein-containing EPS from the marine bacterium *Sagittula stellata*, after 1 h sunlight irradiation, more aggregates formed, as shown by turbidity levels, aggregates mass and flow cytometry, in contrast to a non-protein containing EPS (Fig. 6). This new light-induced aggregation process provides new insights into polymer assembly, marine snow formation, and the fate/transport of organic carbon and nitrogen in the ocean Sun et al., 2017.

The importance of ROS mediated reactions as a novel chemical, rather than physical, aggregation mechanisms that acts by forming larger aggregates through chemical crosslinking requires further studies. Subsequent work by Sun et al. (2018a) elaborated further on this study, and showed that sunlight causes aggregation of various EPS and model biomolecules via ROS mediated chemical crosslinking of proteins leading to increased N/C ratios in aggregates and highly significant correlations between aggregate size and protein/carbohydrate ratio.

To test the effects of sunlight on marine oil snow (MOS) formation during the Deepwater Horizon oil spill, short-term irradiation experiments were conducted in three treatments, i.e., control (GOM coastal

seawater), water accommodated fraction of oil (WAF), and chemically-enhanced WAF (CEWAF) (Sun et al., 2018b). It observed formation of larger sized aggregates in the irradiated WAF treatments. The natural sunlight could stimulate polysaccharide secretion from microbes, coinciding with increased ROS production from oil. The results support the hypothesis that sunlight plays an important role in MOS formation during an oil spill.

The hydroxamate siderophore moieties that appear to be present in the particulate or colloidal organic matter phases at considerable concentrations (Chuang et al., 2013, 2015a) are likely present because they are stabilized by metal chelation (e.g., Fe (III)), and possibly have become part of biopolymers by chemical crosslinking mediated by ROS generated by photochemical or microbial reactions (Chen et al., 2014; Sun et al., 2017, 2018a, 2018b).

While more evidence has now accumulated for the relative importance of microbial vs. photo degradation in the ocean and on land, much more remains to be learned about their direct and indirect roles in the cycling and removal of trace substances. For example, Wozniak et al. (2018), as well as Das and Chandran (2011) demonstrated that oil compounds from WAF were mostly oxidized via microbial degradation within MOS, while data from Saeed et al. (2011) and Frena et al. (2014) indicated that photodegradation was more important for oil oxidation.

1.7.1. New discoveries and open questions

There are many things we still do not know yet about marine colloids. For example, even though major fractions of the extractable organic matter in this pool are now well characterized at the molecular level (Benner, 2002; Mao et al., 2012; Chen et al., 2014; Hatcher et al., 2018), and our knowledge about their tendency toward gel formation is increasing greatly (Chin et al., 1998; Ding et al., 2008, 2009; Orellana and Leck, 2015), we still do not have a quantitative assessment of the relative role of biodegradation (Verdugo and Santschi, 2010) vs. photo-degradation (Timko et al., 2015), vs. photo-flocculation (Helms et al., 2013) vs. colloid aggregation through electrostatic and hydrophobic interactions, vs. self-assembly (Chin et al., 1998; Xu and Guo, 2018), contributing to the observed size distribution and properties of marine colloids and particles (Santschi et al., 1995, 2003, 2006, Verdugo et al., 2004; Xu et al., 2011a,b; Xu and Guo, 2017). Furthermore, while analytical methods for EPS characterization have greatly improved, we still do not have quantitative comparisons of EPS, TEP, and gels, terms that are often used interchangeably in the literature.

The relative hydrophobicity (Xu et al., 2011a,b) or protein/carbohydrate ratio in COM appears, in defined circumstances, to be a predictor of the ‘stickiness’ and aggregation potential of COM (Sun et al., 2017, 2018a,b; Schwehr et al., 2018; Xu et al., 2018a,b). Our current understanding of colloidal ‘stickiness’, however, suggests that the protein/carbohydrate ratio could be an effective predictor of the relative relative stickiness of EPS or COM and its propensity for aggregation. For example, preliminary results by White et al. (2018) suggest that the growth rate and growth rate constant of EPS aggregating on an oil droplet show a positive correlation with the Protein/Carbohydrate Ratio. Schwehr et al. (2018) found that surface tension showed a negative correlation with the Protein/Carbohydrate Ratio of colloids in 3 mesocosm tank experiments. Sun et al. (2017, 2018a, 2018b) suggested that sunlight causes aggregation of EPS as observed by an increase of aggregate size that was positively correlated to the protein/carbohydrate ratio. In addition, preliminary results by Chiu et al. (2018a,b) suggest that Corexit will completely disperse high and low protein/carbohydrate ratio EPS aggregates, but can only partially disperse medium protein/carbohydrate ratio EPS aggregates. They also found that CEWAF promotes interfacial EPS aggregation for different types of EPS, regardless of their protein/carbohydrate ratio. However, this ratio and especially the protein content and other hydrophobic materials in polymer networks were proposed to be responsible for the hydrophobic interactions that are critical factors in initiating the formation and keeping tangled networks together (Chiu et al., 2018a). Furthermore,

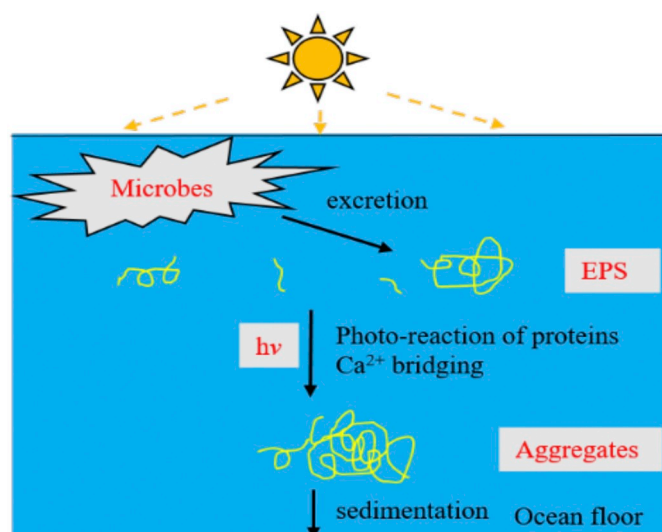


Fig. 6. Sunlight can induce aggregation of bacterial exopolymeric substances (Sun et al., 2017). Reactive oxygen species play critical roles in both photo-degradation (the prevailing view) and photo-flocculation. This study pinpoints proteins as likely components taking part in light-induced aggregation in the marine environment.

results by Xu et al. (2018a, 2018b) suggest that additional factors are also important. While the observations that protein/carbohydrate ratios in colloids increase in oil/corexit treatments in mesocosm experiments, sedimentation efficiency or carbon flux can be low due to a lack of ballasting minerals, and the high incorporation rate of oil into MOS aggregates can provide them with a net buoyancy. Conflicting observations, however, can also originate from filtration artifacts as many experiments rely on filtration to separate colloidal or particulate EPS from solution. Filtration through filters with different electrical and pore properties can retain fibrillar shaped EPS which should easily pass through these filters based on their smallest dimension, but are prevented from passing through by either electrical or hydrophobic forces, as well as shape factors, as documented by Buffle (1990) and Wilkinson and Lead (2007).

Since sorption and aggregation and uptake rates of COM onto particles are related to their molecular weight, the molecular weight distribution of DOC is not as certain as one would conclude from the application of just one single method. For example, results from the application of electrospray mass spectrometry techniques (Leenheer et al., 2001; Kujawinski et al., 2002; Chen et al., 2014) indicate average molecular weights of DOC, normalized to charge, of less than 1 kDa, likely due to fragmentation of carboxylic acid-rich compounds during ionization and acceleration in Mass Spectrometry. On the other hand, much higher average molecular weights (e.g., 10^5 to 10^6 Da, or higher) can be obtained from images of freshwater (Wilkinson et al., 1999) or marine colloids (Santschi et al., 1998) when using AFM techniques of the same specimens mounted by adsorption or centrifugation onto mica surfaces that are flat on the atomic scale, consisting of abundant fibrillar macromolecules 100's to 1000's of nm long (Fig. 2). Transmission electron microscopy (TEM) of heavy-metal stained specimens embedded in hydrophilic resins confirmed that these fibrils are arranged like marine spiderwebs that trap smaller colloids (Fig. 3).

The importance of radical oxygen species (ROS) mediated polymerization reactions as a novel chemical, rather than physical, aggregation mechanisms that acts by forming larger aggregates through chemical crosslinking, should be studied in greater detail. Sun et al. (2017, 2018a, 2018b) suggested that long-wavelength UV light (UVA) of sunlight causes aggregation of EPS, either as model EPS, or that was introduced into the water by natural consortia. This aggregation was attributed to the actions of OH· radicals that mediated a chemical crosslinking of proteins (similar to what's happening in the human body) a process that lead to increased N/C ratios in aggregates. Most importantly, aggregate size and protein/carbohydrate ratio correlated significantly. It thus appears that ROS act as 'randomizers', i.e., by randomly re-assembling organic molecules' bonds along newly formed radical and peroxy-species, making them less recognizable to enzymes and other biomolecules. As a matter of fact, peroxy-acids are also abundant in soil pore waters (Li et al., 2012, 2014), where similar radical mediated polymerization mechanisms have been shown to occur (Chen et al., 2014). It is thus also a potential mechanism that can lead to 'encapsulation' of molecules, especially proteins and other molecules.

Low molecular weight hydroxamate siderophore moieties have been identified in sinking particles (Chuang et al., 2013) and colloids (Chuang et al., 2015a,b). These moieties could be enmeshed in particles due to the same ROS polymerization mechanism mentioned above. The microbial synthesis is geared toward solubilizing Fe, not immobilizing it. Thus, there is a quandary. Since hydroxamates are also photolabile, there is a high likelihood that they are also present in colloids due to ROS mediated photochemical crosslinking reactions, similar to what Sun et al. (2017, 2018a, 2018b) observed for marine colloids, and to what Chen et al. (2014) and Waggoner and Hatcher (2017) reported for soil organic matter compounds leading to increases in N and Fe. Such a polymerization mechanism is intriguing, and clearly needs to be considered more seriously and explored in more detail.

There is also a need to better integrate colloidal/macromolecular

interactions into coupled physical-biogeochemical models, as the long-term dogma about the existence of colloids in particle/solution partitioning being an artifact of sample processing had been accepted for too long. What had been considered an artifact for aquatic chemists for some time (e.g., since the 1980's) has to become a worthy natural process in its own right. A unified and more thermodynamic description and parameterization for COM that incorporates properties of ligand-, proton-, electron-exchange, as well as photo-reactive and hydrophobic sites, to be used in particle and pollutant (including radionuclide) binding and cycling models, is still lacking, and would require more integrative work.

Thus, scientists interested in the properties of marine colloidal matter still have a long way to go until the different roles and properties of this abundant material in seawater can be modeled to be fully understood.

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