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EDITED BY
Yan Li,
China University of Geosciences, China

REVIEWED BY
Miguel Caetano,
Portuguese Institute for Sea and
Atmosphere (IPMA), Portugal
Elena Badetti,
Ca' Foscari University of Venice, Italy

*CORRESPONDENCE
Yujia Liu
✉ yujia_liu@nuist.edu.cn
Hailong Lu
✉ hlu@pku.edu.cn

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Colloids and particulate matters in natural aquatic environments: dynamics and geochemical impact

Xinxin Fan^{1,2}, Yujia Liu^{3*} and Hailong Lu^{1*}

¹Beijing International Center for Gas Hydrate and School of Earth and Space Sciences, Peking University, Beijing, China, ²School of Marine Sciences, Peking University Shenzhen Graduate School, Shenzhen, China, ³School of Marine Sciences, Nanjing University of Information Science and Technology, Nanjing, China

Particulate materials, from macroparticles to colloids and nanoparticles, might be critical regulators of geochemical cycles in aquatic environments. However, their behaviors are profoundly dictated by surrounding physicochemical conditions in freshwater or marine systems. This review systematically synthesizes current knowledge by providing a comparative analysis of particle dynamics across this environmental boundary, with a specific emphasis on the distinct roles of nanoparticles (1–100 nm). We first compare the sources and composition of particles, highlighting the dominance of terrigenous inputs in freshwater versus biogenic sources in marine environment. Subsequently, we critically evaluate analytical methods, revealing how matrix-specific properties (e.g., salinity) create distinct challenges for accurate characterization. The review demonstrates that nanoparticles, due to their high reactivity, act as dynamic drivers of elemental cycling and contaminant fate. A case study on deep-sea hydrothermal vents illustrates this, revealing how nanoparticles facilitate the long-range transport of micronutrients like iron, overturning previous paradigms of localized impact. By highlighting these freshwater-marine disparities and trying to identify critical knowledge gaps in analytical methods and transformation mechanisms, this review provides an integrated framework and outlines priority directions for future research.

KEYWORDS

characterization, colloid, nanoparticle, natural aquatic environment, particles, geochemical impact

1 Introduction

Natural aquatic ecosystems, including oceans, rivers, lakes, and groundwaters, are critical components for sustaining global ecological balance and biological processes. In these systems, particulate materials, ranging from macroscopic sediments to nanoscale particles, serves as critical carriers for material cycling and energy transfer, greatly affecting pollutant migration and geochemical cycles. Among them, natural colloids (1–1000 nm) and nanoparticles (1–100 nm) have become major research themes in environmental science and geochemistry due to their unique physico-chemical properties and ecological impacts (Lead and Wilkinson, 2006b, LeadWilkinson, 2006a; Wigginton et al., 2007).

While studies on colloidal behavior are extensive, recent focus has shifted towards nanoparticles. These particles represent a size-defined subset of colloids with unique environmental behaviors which are driven by properties such as ultrahigh specific surface area, quantum size effects, and enhanced reactivity, distinguishing them from larger colloids (Tsao et al., 2011; Delay and Frimmel, 2012; Flores et al., 2025). It is also found that, the environmental fates of these particles are profoundly affected by their surrounding conditions. Key environmental factors, such as ionic strength, the composition of natural organic matter, and hydrodynamic conditions, differ substantially between freshwater and marine systems, leading to different particle behaviors (Zhuang and Yang, 2017). In this review particle dynamics will be discussed in different environments, to provide a more comprehensive understanding of the behaviors of these materials.

The structure of this review is as follows: 1), the classification, sources, and fundamental characteristics of aquatic particles are stated; 2), the analytical methods for particle separation and characterization are evaluated, focusing on their limitations and analytical artifacts; 3), the environmental behaviors and geochemical effects of the particles, especially nanoparticles, are summarized; 4), through a case study on nanoparticles from deep-sea hydrothermal vents, an example of their long-range transport mechanisms and influence over global-scale elemental cycles is given.

2 Classification of particulate materials

In aquatic environments, dissolved substances are generally with the sizes of < 1 nm, occurring as ionic or molecular species (e.g., simple ions such as Na^+ , Ca^{2+} , Cu^{2+} and small organic molecules) (Jacques, 1992), which are classified as the dissolved fraction. According to the definition of IUPAC, colloids are typically referred to the materials with at least one dimension between 1 nm and 1 μm , while particles are those larger than 1 μm (Lead and Wilkinson, 2006b, LeadWilkinson, 2006a).

In actual studies, these classifications are “operationally defined,” based on the pore size of the filter used for separation. Material passing through such filter is labeled “dissolved”, a fraction that includes both the truly dissolved species and colloids while material retained on the filter is termed as “particulate.” However, definitions are inconsistently applied by researchers both between and within various fields. For example, water engineers often use membrane filters with nominal pore sizes of around 5–10 μm , while aquatic chemists more frequently use those with pore sizes of 0.2 or 0.45 μm for their work. As a result, the definition of colloid can vary across studies (Wells, 2002; Aiken et al., 2011).

Even without an official universal definition, a useful conceptual framework distinguishes the dominant processes governing each phase. The mobility of the truly dissolved phase is largely governed by molecular diffusion. For the colloidal phase, a combination of diffusion and aggregation dictates their stability and transport. Conversely, the fate of the particulate phase is primarily

controlled by gravitational settling (sedimentation). However, it is critical to recognize that this is a simplified model. In many dynamic natural systems, such as rivers or coastal zones, other processes can be equally or even more significant. These processes include advection (bulk fluid motion), which influences all phases; heteroaggregation, which is crucial for scavenging processes; and the resuspension of settled particles from the sediment bed. In this review, the size-based classification is adopted as outlined above, after critically examining the distinct characteristics of each category in freshwater versus marine environments. The size ranges and chemical types of the key species are illustrated in Figure 1.

2.1 Macroparticles (>1 μm)

In natural aquatic systems, the transport of macroparticles is significantly affected by gravitational force and can often be described by Stokes' law. Their sources, compositions, and ecological roles differ greatly between freshwater and marine system.

In freshwater systems, macroparticles are often dominated by externally derived materials, including inorganic mineral grains (e.g. sands, clays) derived from watershed erosion and transported as suspended load or bedload and being the main factor shaping river morphology and creating turbidity (Wohl et al., 2015; Mukhopadhyay et al., 2021). The organic fraction consists largely of terrestrial plant detritus (e.g., leaves, wood fragments) and soil aggregates (Sadchikov and Ostroumov, 2018), the role of which is often physical (e.g., habitat structuring, sediment transport) rather than biogeochemically reactive on short timescales.

In marine systems, macroparticles are predominantly internally produced and biogenic. These include sediment and biogenic detritus, such as decomposing aquatic vegetation, algal matter, and animal-derived residues. Among them, marine snow is well known, which are amorphous aggregates of dead phytoplankton, zooplankton fecal pellets, and microbial debris (Chajwa et al., 2024). The formation of these aggregates is often mediated by transparent exopolymer particles (TEPs), sticky, polysaccharide-rich gels excreted by phytoplankton, which act as a glue to bind smaller particles together (Radić et al., 2011). These marine macroparticles are central to the biological carbon pump, the critical process that transports vast amounts of organic carbon from the surface ocean to the deep sea, playing a vital role in regulating global climate (Turner, 2015).

2.2 Colloids (1–1000 nm)

Colloids represent a highly reactive and mobile fraction that bridges the truly dissolved and particulate materials. They are not simple, discrete particles but rather complex, heterogeneous assemblages with the properties resulted from their composite nature and their surrounding environment. The composition and origin of colloids differ significantly between freshwater and marine environments, largely reflecting their sources.

In freshwater systems, colloids are predominantly terrigenous, indicative of their originating from the surrounding land. Runoff

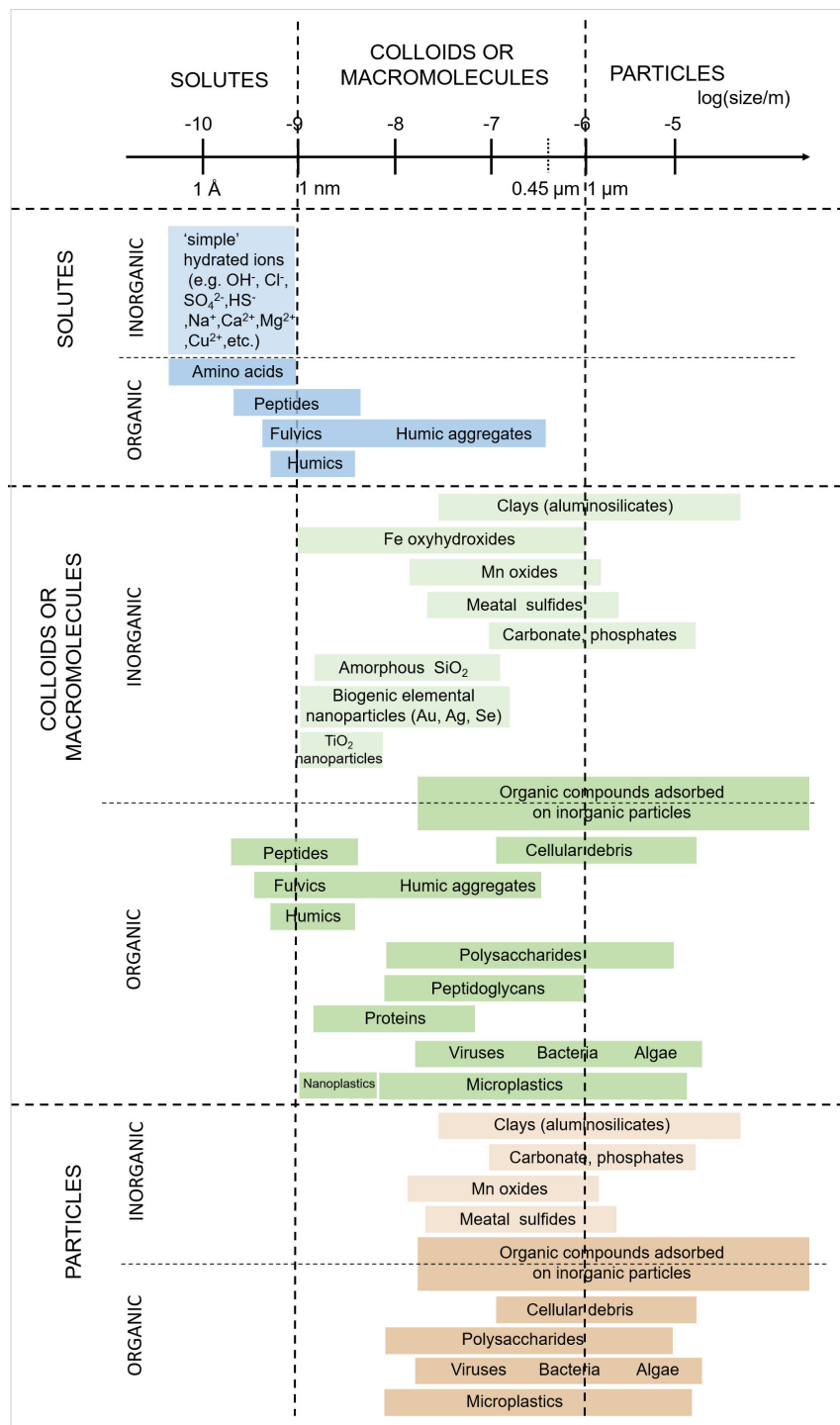


FIGURE 1 Size distributions of environmental colloids and particles (updated from Lead and Wilkinson (Lead and Wilkinson, 2006b)).

and weathering processes carry large amount of inorganic materials like clays (such as aluminosilicates) and iron or manganese oxyhydroxides into rivers and lakes (Hirst et al., 2017). These systems also receive substantial organic inputs from land, including humic and fulvic substances derived from soil and plant decomposition (Kawahigashi et al., 2005). While land-derived materials are dominant, there is also a significant contribution from autochthonous sources, e.g. microbial exudates,

polysaccharides, and biogenic particles like bacterial cells and viruses (Gargiulo et al., 2007).

In contrast, marine colloids are primarily autochthonous, originating from the high biological productivity of the oceans. The vast majority of these colloids are organic and biogenic, created by phytoplankton and bacteria. Key examples include TEPs, microbial debris, and polysaccharides derived from phytoplankton (Decho and Gutierrez, 2017). The influence from

land is much weaker, so terrigenous inputs and the associated inorganic colloids (like carbonates and iron oxyhydroxides) are far less abundant, though they can still be critically important in coastal zones where the connection to land is stronger (Stolpe and Hassellöv, 2007).

Freshwater colloids are stabilized by low ionic strength, which enhances electrostatic repulsion between particles, leading to long residence times in rivers and lakes. Marine colloids, in high ionic strength seawater, experience compressed double layers that reduce stability, promoting aggregation into larger flocs like marine snow.

2.3 Nanoscale materials (1–100 nm)

Nanomaterials are defined as materials with at least one external dimension in the size range 1–100 nm (Commission, 2011). In aquatic environments, these encompass nanoparticles and nanocolloids and the boundary between nanoparticles and nanocolloids is not always clear, so we collectively refer to them as nanoscale materials. Nanoparticles can be divided into three main types: natural, incidental, and engineered, while nanocolloids potentially include aggregates of nanoparticles, macromolecules, and humic substances, and show more stable behavior than nanoparticles in the aquatic environment. Both possess unique surface properties, high reactivity, and colloidal stability that enable them to play significant roles in the chemical and biogeochemical processes in aquatic systems.

In terms of sources, naturally occurring nanoscale materials originate from mineral weathering, volcanoes, dust and biogenic microbial processes contain crustal earth abundant elements, and minerals which may be transported into surface waters (Nowack and Bucheli, 2007; Toner et al., 2009b; Kadar et al., 2012; Von Der Heyden et al., 2019). Incidental ones are derived from human activities such as combustion and industrial processes, entering water bodies via stormwater runoff, atmospheric transport, and wastewater discharge. Engineered nanoscale materials come from industrial production (e.g., TiO₂ in sunscreens), medical applications (e.g., Au nanoparticles), and consumer products, released through direct disposal during use, wastewater effluents, and urban runoff (Weinberg et al., 2011; Abbas et al., 2020). Globally, for nanoscale materials which permeate into surface waters, the natural ones dominate with a flux exceeding 300 Tg/yr, followed by incidental ones (1–10 Tg/yr) and engineered ones (0.3 Tg/yr) (Hochella et al., 2019).

Figure 2 illustrates the morphological diversity of particles across different aquatic settings. The images highlight the stark contrast between particles from different origins. For example, panels (A) and (B) showcase particles typical of marine systems: large, amorphous aggregates of “marine snow” (Chajwa et al., 2024) and the underlying gel networks that drive their formation (Radić et al., 2011). In contrast, panel (C) depicts particles characteristic of freshwater environments, where terrestrial influence is stronger, showing inorganic mineral cores (clay, iron oxyhydroxides) bound together by a mesh of organic filaments in a eutrophic lake (Buffle and Leppard, 1995).

Collectively, natural aquatic particles often exist as complex, composite structures—including fibrils, globules, and amorphous

aggregates—as observed through various microscopy techniques. This inherent complexity in shape and composition directly influences their environmental dynamics and presents significant challenges for characterization, necessitating the advanced analytical approaches discussed in the following section.

3 Analytical methods

For natural colloids, including nanoscale materials, analytical workflows revolve around two core stages: physical separation and subsequent characterization. While most materials science characterization methods can be adapted to environmental samples, below we focus on key separation techniques, summarize core characterization tools, and highlight matrix-specific challenges in freshwater and marine systems.

Core separation methods are led by two widely used techniques. The first techniques are filtration and ultrafiltration, which are widely used for freshwater samples, with ultrafiltration (UF) membranes (1 kDa–10 kDa) separating colloids and nanoparticles. Cross-flow ultrafiltration (CFF) is preferred for marine samples, as it could handle high-salt conditions and large volumes without colloidal alteration. However, marine samples are prone to membrane fouling by salt crystals and organic gels, requiring pre-rinsing with low-salinity buffers (Wang and Tarabara, 2008; Xiang et al., 2022). The second is Field-flow fractionation (FFF, especially Flow FFF) which is ideal for freshwater colloids and nanoparticles, enabling high-resolution size separation (Baalousha et al., 2011). When coupled with online detectors like light scattering and ICP-MS, FIFFF can provide multi-dimensional information on particle properties (e.g., size, composition). Subsequent off-line characterization of collected fractions by techniques such as electron microscopy can further reveal details about particle morphology and structure (Lyvén et al., 2003; Plathe et al., 2013). However, it requires specialized instrumentation and expertise, has relatively low throughput with resolving power compromised by complex matrices (e.g., high salinity) (Vaillancourt and Balch, 2000). It is particularly challenging to match the FIFFF carrier to the sample when analyzing seawater—given its high ionic strength (up to 0.7 M) and elevated concentrations of Ca²⁺ and Mg²⁺. Notably, seawater cannot serve as the carrier in FIFFF-ICP-MS hyphenation, as even low levels of salt can drastically impair the ICP-MS performance. Additionally, high salinity triggers particle aggregation, leads to much lower sample recovery, and increases membrane adsorption and permeation issues that affect analytical accuracy. Apart from the aforementioned two separation approaches, complementary separation tools include centrifugation/ultracentrifugation (Oshima et al., 2022) and size-exclusion chromatography (Nordin et al., 2015).

For the purpose of characterization, most materials science methods can be adapted for environmental samples. Below, we summarize several key characterization techniques in this research field in Table 1, including their applicable size ranges and limitations. Size and morphology were analyzed using transmission/scanning

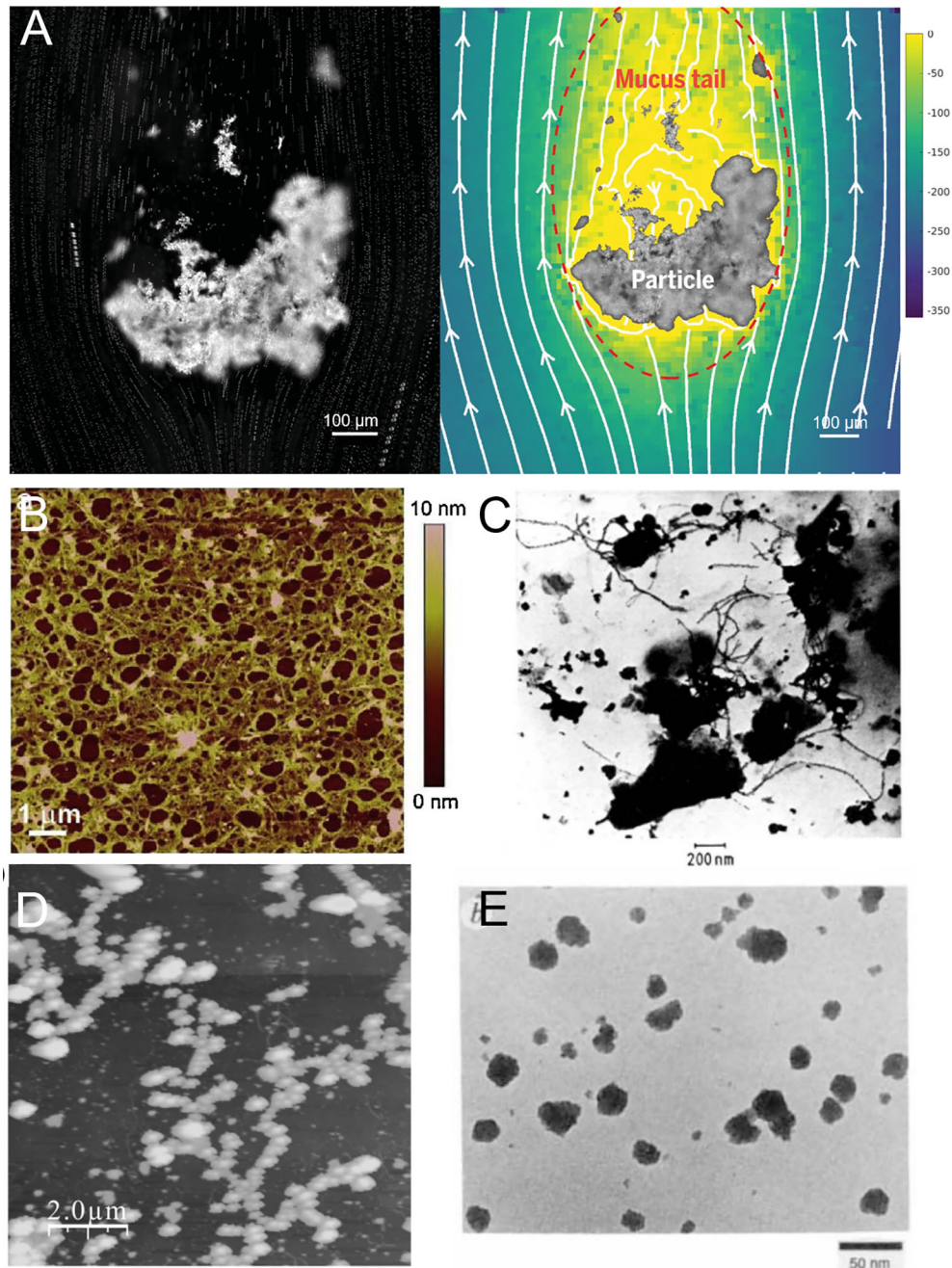


FIGURE 2

(A) (Left) Flow-trace image of sinking marine snow visualized with tracer beads in the background and (right) fluid flow corresponding to the same particle showing the invisible mucus tail (yellow region) that falls along with the particle, greatly increasing the particle's effective size (Chajwa et al., 2024). (B) Gel network as imaged at the edge of a native marine gel particle (Radić et al., 2011). (C) Typical examples of colloidal materials in a eutrophic lake [Bret/VD, Switzerland] observed by transmission electron microscopy (TEM), inorganic colloids, in particular clay (large angular particles) and iron oxyhydroxide globules, aggregated together by a mesh of organic filaments (Buffle and Leppard, 1995). (D) AFM images from samples taken from tributaries of the River Tame in the West Midlands, U.K. site 1 (Lead et al., 2005). (E) TEM images of small colloids occurred in sea water (Wells and Goldberg, 1991).

electron microscopy (TEM/SEM) (Qian et al., 2015; Xing et al., 2023), atomic force microscopy (AFM) (Lead et al., 2005), dynamic light scattering (DLS), and laser-induced breakdown detection (LIBD) (Bundschuh et al., 2001); chemical composition and structure were characterized via X-ray absorption spectroscopy (XAS/XANES/EXAFS) (Newville, 2014; Terzano et al., 2019), Fourier-transform infrared spectroscopy (FTIR) (Fomina et al., 2022), inductively coupled plasma-mass spectrometry (ICP-MS, including single-

particle SP-ICP-MS) (Bever et al., 2020; Montaña et al., 2022), and nano secondary ion mass spectrometry (NanoSIMS) (Huang et al., 2017); and surface properties were evaluated through zeta potential measurements (for charge) (Gopmandal and Duval, 2022) and BET analysis (for specific surface area) (Edinger and Gernand, 2018).

Analytical challenges are significantly amplified by the fundamental chemical differences between freshwater and marine systems. Marine analysis requires methods that can overcome

TABLE 1 . Separation and characterization methods for aquatic colloids and nanoscale materials. See text for abbreviations and citations.

Categories	Analytical methods	Key principles	Typical application	Applicable size range	Limitation
Separation Methods	Filtration and Ultrafiltration	Uses porous membranes to retain particles larger than the pore size.	Pre-concentration of large-volume samples, operational size fractionation	Determined by membrane pore size (e.g., ultrafiltration: ~1–100 nm; microfiltration: ~0.1–5 µm)	High risk of particle loss via membrane adsorption, pore blocking, aggregation artifacts
	FFF	Separates particles in a channel based on their diffusion coefficients under a perpendicular flow field	High-resolution sizing of complex natural colloids and engineered nanoparticles.	~1 nm - 100 µm	Low throughput, complex instrumentation, sensitive to matrix effects (e.g., salinity)
	Centrifugation and Ultracentrifugation	Separates based on differential sedimentation in a strong centrifugal field	Isolating high-density nanoparticles (e.g., metal oxides, sulfides).	> ~5 nm (ultracentrifugation)	Can cause irreversible aggregation, ineffective for low-density organic colloids.
Size and Morphology	SEC	Separates molecules/particles based on their hydrodynamic volume as they pass through a porous column.	Fractionating organic macromolecules (e.g., humic substances).	~1 nm - 100 nm (specific range depends on the column)	Prone to adsorption artifacts on the stationary phase, limited resolution.
	TEM/SEM	Uses an electron beam to generate high-magnification images.	Direct visualization of particle morphology, size, and crystal structure (TEM).	~1 nm - >100 µm	Requires high vacuum (sample dehydration artifacts), limited sample representativeness.
	AFM	Scans a sharp tip over a surface to generate a 3D topographical map	Imaging particle height and surface features in liquid or air.	~1 nm - <100 µm	Slow scan for large areas, potential for tip-sample interaction artifacts.
	DLS	Measures temporal fluctuations in scattered light intensity caused by Brownian motion.	Rapid determination of hydrodynamic diameter in suspensions.	~1 nm - 5 µm	Highly biased by larger particles in polydisperse samples, requires low concentrations
	LIBD	Detects plasma generated from single particles hit by a pulsed laser.	Ultra-sensitive detection of low concentrations of nanoparticles.	~10 nm - 1 µm	Provides little morphological information, requires calibration.
	Chemical Composition and Structural Analysis	XAS/XANES/EXAFS	Analyzes X-ray absorption fine structure to determine elemental speciation and local coordination.	Determining the oxidation state of metals (e.g., Fe, Mn) in nanoparticles.	N/A (Bulk analysis method)
FTIR		Measures absorption of infrared radiation to identify functional groups	Characterizing organic matter (e.g., humic acids, EPS).	N/A (Bulk analysis method)	Complex spectra can be difficult to interpret in mixed samples.
ICP-MS/SP-ICP-MS		Measures elemental composition (ICP-MS) or single particle events (sp-ICP-MS).	Quantifying trace metal content; determining particle size distribution and number concentration	~10 nm - 200 nm for sp-ICP-MS	sp-ICP-MS has size detection limits (~10–200 nm), matrix can interfere with detection.
Surface Property Characterization	Nano Secondary Ion Mass Spectrometry	High-resolution mass spectrometry imaging.	Mapping elemental distribution on the surface of individual particles.	> ~50 nm (depends on instrument resolution)	dynamic SIMS is destructive; NanoSIMS requires conductive coating and specialized sample preparation.
	Zeta Potential Measurement	Measures electrophoretic mobility of particles in an electric field to infer surface charge.	Assessing colloidal stability and aggregation propensity	~1 nm - 100 µm	Highly sensitive to solution chemistry (pH, ionic strength), model-dependent interpretation.
	BET analysis	Measures the amount of inert gas adsorbed onto a solid surface.	Determining the specific surface area of dried particle powders.	N/A (Bulk analysis method)	Requires dry samples, which may not reflect <i>in-situ</i> surface area in aqueous solution.

FFF, field-flow fractionation; SEC, size-exclusion chromatography; TEM, transmission electron microscopy; SEM, scanning electron microscopy; AFM, atomic force microscopy; DLS, dynamic light scattering; LIBD, laser-induced breakdown detection; XAS/XANES/EXAFS, X-ray absorption spectroscopy/X-ray Absorption Near-Edge Structure/Extended X-ray Absorption Fine Structure; FTIR, Fourier-transform infrared spectroscopy; ICP-MS/SP-ICP-MS, inductively coupled plasma-mass spectrometry/single-particle inductively coupled plasma-mass spectrometry; BET, Brunauer-Emmett-Teller analysis.

interference from a high-salinity matrix and gel-like organic matter, whereas freshwater techniques must navigate the complexity of humic substances. This leads to several critical limitations: it is difficult to distinguish between natural and engineered nanoparticles (e.g., Fe₃O₄ nanoparticles) in either setting, and the

high ionic strength of seawater severely complicates the detection of trace nanoparticles. Future progress depends on developing *in-situ* monitoring technologies, such as underwater AFM for marine systems, alongside standardized methods like unified colloid size definitions to enable meaningful cross-environment comparisons.

4 Environmental behaviors and biogeochemical effects of aquatic colloids, with emphasis on nanoscale materials

Colloids are ubiquitous in natural aquatic systems and play pivotal roles in regulating chemical cycles and pollutant fate. Shaped by intrinsic properties (size, charge, composition) and external conditions (pH, ionic strength, natural organic matter content), their key behaviors include size-dependent transport, charge-governed stability, fractal aggregation structures, and reactive surface interactions (e.g., surface complexation, electrostatic adsorption) that mediate trace element binding and phase transitions. This size-dependency is particularly evident in their transport mechanisms: while Brownian motion largely governs the mobility of the smallest nanoscale colloids, aggregation processes become increasingly influential for their larger, submicron counterparts. These characteristics translate to profound biogeochemical impacts, such as facilitating long-distance transport of metals (e.g., in some river systems, over 80% of Pb can be colloid-bound (Benoit, 1995; Lyvén et al., 2003)), regulating carbon cycling via colloidal organic matter (which is estimated to constitute 25–40% of the total marine dissolved organic carbon pool (Benner et al., 1992; Hansell, 2013)), and modifying pollutant mobility and bioavailability (Lead and Wilkinson, 2006b). Colloid behavior varies across ecosystems due to distinct physicochemical conditions, and this topic has been comprehensively summarized in numerous prior reviews, providing a solid foundational understanding of fine-particle dynamics in natural waters (Petosa et al., 2010; Liu et al., 2019; Pontoni et al., 2021; Wang et al., 2021).

Given the broad scope of colloid, this review centers on nanoparticles that possess distinctive physicochemical properties—including ultrahigh specific surface area, quantum effects, and elevated reactivity—which set their environmental behavior and geochemical functions apart from those of larger colloids. Shifting away from early work centered on toxicology of engineered nanoparticles, recent research draws attention to the profound and often unrecognized influence they exert on fundamental biogeochemical processes (Flores et al., 2025).

4.1 DOM-nanoparticle interactions: a dominant control on the fate of nanoparticle

A central driver of behaviors of nanoparticles in aquatic systems is their interaction with dissolved organic matter (DOM)—a complex mixture of humic/fulvic acids and biomolecules derived from terrestrial and aquatic biomass decomposition. Once nanoparticles enter natural aquatic systems, nearly all of them rapidly develop a coating of DOM, known as a corona, which governs their environmental fate through diverse mechanisms.

Most commonly, this DOM corona imparts stability to nanoparticles. Negatively charged DOM molecules can adsorb to mineral-based nanoparticles, generating a strongly negative zeta potential that enhances electrostatic repulsion. This effect,

combined with steric hindrance from the bulky organic molecules, inhibits rapid aggregation and sedimentation, thereby keeping the nanoparticles suspended and mobile (Burns et al., 2013). However, this stabilizing effect is not universal and is highly dependent on the specific physicochemical conditions. For instance, in the presence of high concentrations of divalent cations like Ca^{2+} , humic acid can be cross-linked, forming bridges between fullerene nanoparticles that lead to enhanced aggregation rather than stabilization (Chen and Elimelech, 2007). Furthermore, the outcome can depend on both the concentration and chemical composition of the DOM itself; some studies have shown that low DOM concentrations can initially destabilize particles, while certain types of DOM, such as those rich in aromatic content, may promote the formation of larger aggregates (Millour et al., 2021).

The DOM corona can serve as a physical barrier that can minimize direct interaction between nanoparticles and biological membranes and complex with toxic metal ions released from nanoparticles (e.g., Ag^+ from Ag nanoparticles, Cd^{2+} from quantum dots), often decreasing bioavailability and mitigating acute toxicity. Moreover, DOM coatings can also affect the photochemical and redox behaviors and dissolution kinetics of nanoparticles, indirectly regulating their environmental persistence and reactivity (Aiken et al., 2011).

4.2 Biogeochemical roles of nanoparticles in aquatic systems

Nanoparticles are highly reactive in aquatic environments, and this reactivity enables them to contribute to or modulate biogeochemical processes as well as influence the fate and transport of pollutants. Thanks to their ultrahigh specific surface area, nanoparticles can efficiently scavenge diverse contaminants, but this efficiency is strongly dependent on nanoparticle composition, surface coatings, and environmental conditions (e.g., pH, ionic strength, presence of NOM). For instance, inorganic nanoparticles (such as iron oxides, manganese oxides) exhibit strong affinity for heavy metals (e.g., Pb, Cu, Zn) via surface complexation, ligand exchange, or cation bridging, thereby mediating their transport in aquatic systems (Xu et al., 2019). Hydrophobic organic compounds, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), readily partition onto organic-rich nanomaterials and carbonaceous nanomaterials like humic substances (Ouyang et al., 2018). pH is a critical regulator of colloidal adsorption, as it simultaneously modulates the competition between H^+ and metal ions for surface sites on colloids, alters colloidal surface charge, and reshapes the speciation of adsorbing species. For instance, natural iron oxides can carry either positive or negative surface charges, with this variability dependent on solution pH values and the presence of organic matter coatings. Furthermore, low pH conditions strengthen the affinity of dissolved phosphate for iron oxide colloids in both freshwater and seawater systems (Crosby et al., 1984). Additionally, the presence of NOM can either promote or hinder contaminant scavenging by modifying nanoparticle surface charge and colloidal stability. Nanoparticles also act as catalytically active surfaces: semiconductor nanoparticles (e.g.,

natural and engineered TiO₂, Fe₃O₄) can generate reactive oxygen species (ROS, e.g., hydroxyl radicals, singlet oxygen, and hydrogen peroxide) upon UV/visible light exposure. With environmentally relevant ROS concentrations (0.1–10 fM) comparable to excited-state DOM, these photocatalytic nanoparticles represent a potentially important, previously overlooked contributor to indirect photochemistry that mediates micropollutant degradation, though this reactivity is restricted to certain nanoparticle types and strongly dependent on environmental conditions (e.g., light availability, matrix composition) (Hanigan et al., 2018). Additionally, metal oxide nanoparticles surfaces (e.g., TiO₂, iron oxides) also capable of catalyzing hydrolysis reactions, such as converting organic phosphorus into bioavailable inorganic phosphate, which have the potential to act as an important pathway in phosphorus cycling (Li et al., 2020). Through these catalytic activities, nanoparticles can participate in biogeochemical cycles of key nutrients (nitrogen, phosphorus, and carbon) by acting as reactive surfaces or secondary contributors (Soares et al., 2014; Gora et al., 2018). They may expand bioavailable orthophosphate pools for primary producers, facilitate nitrate reduction under specific conditions, and break down high-molecular-weight DOM into labile organic compounds.

4.3 Ecotoxicological effects of nanoparticles across trophic levels

The unique properties of nanoparticles that make them biogeochemically active also underpin their potential for inducing ecotoxicological effects across all aquatic trophic levels (Brunelli et al., 2024; Suji et al., 2025). The primary mechanism of nanotoxicity is widely accepted to be the generation of excessive ROS, leading to oxidative stress (Ouyang et al., 2022; Singh et al., 2022).

At the base of the food web, microorganisms are particularly vulnerable. For instance, nanoparticles can physically envelop algal cells, reducing light and nutrient uptake, inhibiting photosynthesis (Tao et al., 2015), and causing direct cell wall damage through sharp edges or abrasive action (Ouyang et al., 2015). For bacteria, nanoparticles exhibit potent antimicrobial activity through several pathways, including direct cell membrane disruption (Brayner et al., 2006), overwhelming oxidative stress (Quinteros et al., 2018), and the release of toxic metal ions such as Ag⁺ from Ag nanoparticles or Cu²⁺ from CuO nanoparticles (Wang et al., 2016). These impacts are then propagated up the food chain. Filter-feeding and deposit-feeding invertebrates, like *Daphnia magna* or marine bivalves, readily ingest nanoparticles, leading to their accumulation in the gut (Barmo et al., 2013). There, the production of ROS can cause severe cellular damage, including lipid peroxidation, membrane disruption, and genotoxicity in the form of DNA strand breaks (Manke et al., 2013). Ultimately, these cellular-level impacts can interfere with critical organismal-level functions, such as reproduction (Suji et al., 2025). This susceptibility is also pronounced in vertebrates. Fish, such as zebrafish (*Danio rerio*), are particularly susceptible to nanoparticle uptake through their gills, and because animal cells lack the protective structure of a cell

wall, nanoparticles can cause more direct damage. In addition, exposure to environmentally relevant concentrations has been shown to induce developmental abnormalities in embryos, including pericardial/yolk sac edema and spinal curvature, which have been directly linked to oxidative stress-driven metabolic disorders affecting amino acid and fatty acid metabolism (Kang et al., 2019; Ouyang et al., 2022).

5 Natural case study: hydrothermal vent-derived nanoparticles

Deep-sea hydrothermal vents act as natural “nanofactories” in extreme marine environments, producing a diverse array of nanoparticles that exert a transformative influence on the geochemical processes of the global ocean. These systems serve as a striking example of naturally occurring nanoparticles, formed by the violent mixing of superheated, metal-rich hydrothermal fluids with cold, oxygenated seawater (Gartman et al., 2014).

For decades, it was widely believed that the metals released from these vents precipitated rapidly and remained confined to the immediate vicinity. However, this long-standing paradigm has been upended by recent discoveries—particularly from the GEOTRACES program—which demonstrate that these metals can be transported thousands of kilometers, exerting a significant impact on ocean chemistry across vast scales (Resing et al., 2015; Gartman and Findlay, 2020). The key factor of this long-range dispersal lies in the stabilization of these metals in the form of nanoparticles.

The primary geochemical significance of these particles rest on their role as transport vectors for essential elements, most notably iron. The process begins in the hot, buoyant plume rising from the vent, where rapid cooling and chemical gradients trigger the formation of metal sulfide nanoparticles such as pyrite (FeS₂) and zinc sulfide (ZnS) (Hsu-Kim et al., 2008). As the plume travels farther and mixes more extensively with oxygenated seawater, environmental conditions shift, leading to a transition in the dominant particle species to Fe(III) oxyhydroxide nanoparticles (Hoffman et al., 2020).

Characterizing these hydrothermal vent-derived nanoparticles relies on a set of advanced techniques. Field sampling is foundational, with pristine samples collected via remotely operated vehicles (ROVs) and stored in inert containers to avoid oxidation or contamination (Toner et al., 2016). For imaging and structural analysis, SEM and TEM are key tools (Figure 3)—SEM reveals the morphology of aggregated nanoparticle clusters, while TEM captures high-resolution details of individual particles (down to 4 nm) and their crystallinity (Gartman et al., 2014). X-ray diffraction (XRD) complements these by confirming the crystalline structure of minerals like pyrite and Fe(III) oxyhydroxides (Hoffman et al., 2020). For compositional and speciation analysis, energy-dispersive X-ray spectroscopy (EDS) identifies elemental components (e.g., Fe, Zn, S) and trace constituents (Pb, As), while synchrotron-based techniques like X-

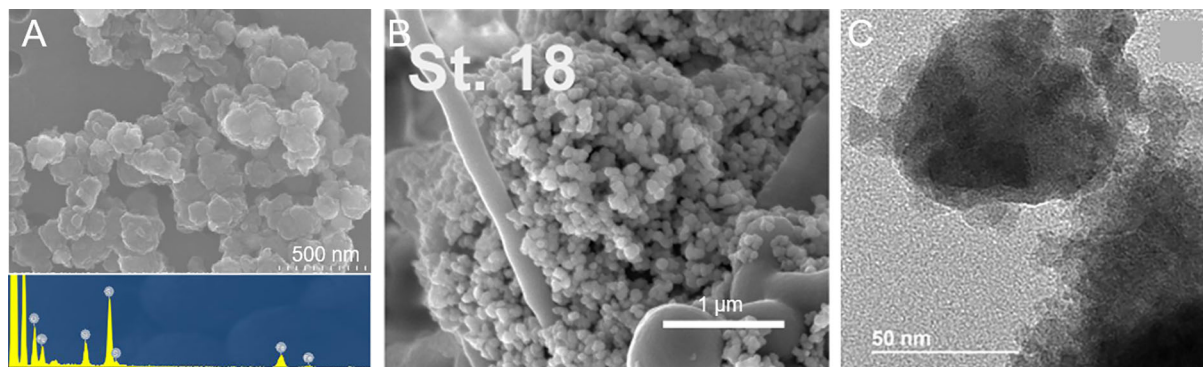


FIGURE 3
(A) SEM image and EDX spectra demonstrating clumps of nanoparticles that contain nanoparticulate pyrite from Kilo Moana at EPR 9°N (Gartman et al., 2014). **(B)** SEM image for midplume particles from the Southern East Pacific Rise hydrothermal plume, most of which were short-range ordered Fe(III) oxyhydroxides nanoparticles (Hoffman et al., 2020). **(C)** TEM image for nano-zinc sulfide collected from black smoker fluids from Niua South vent field (Gartman et al., 2019).

ray absorption near-edge structure (XANES) spectroscopy clarify metal speciation (Toner et al., 2016). Isotopic tracing (Fe, S isotopes) and size-fractionation methods (ultrafiltration, field-flow fractionation) further aid in tracking particle transport and distinguishing between soluble, colloidal, and particulate fractions (Resing et al., 2015).

The formation of organic-inorganic hybrids also play an important role in this process. Organic ligands, sourced either from the vent environment (e.g., low-temperature diffuse fluids) or ambient seawater (e.g., abiotically synthesized thiols), bind to dissolved metals and coat mineral nanoparticle surfaces. This organic coating serves to mitigate aggregation and rapid settling, thereby forming highly mobile hybrid colloids that enable metals to escape local sinks and persist in the water column across vast distances (Toner et al., 2009a; Sander and Koschinsky, 2011).

Thus, these hydrothermally derived nanoparticles serve as the critical link between the geology of the deep seafloor and the biology of the global ocean. By transporting iron—a vital yet often limiting nutrient for primary production in large oceanic regions—they directly influence marine ecosystems and play an important, previously underestimated role in the global carbon cycle. Despite advancements in analytical techniques, significant challenges persist, including the inability to capture ultrafast real-time nanoparticle transformations (e.g., sulfide-to-oxyhydroxide transitions), and insufficient understanding of organic-inorganic hybrid formation.

6 Conclusion

Particles in aquatic environments, spanning a vast scale from macro to nano in size, are not isolated entities but components of a dynamic continuum— with nanoscale materials (1–100 nm) representing a size-defined subset of colloids (1–1000 nm). This review has discussed the categories of macroparticles, colloids, and nanoparticles, emphasizing that their behavior is governed not only

by intrinsic properties like size, composition, and surface charge, but is also profoundly constrained by the physicochemical conditions of their environment—particularly the distinct settings of freshwater and marine systems. Our analysis indicates that while colloids provide a foundational framework for understanding fine-particle dynamics, nanoparticles exhibit unique environmental behaviors and geochemical effects driven by their ultra-small size, ultrahigh specific surface area and consequently enhanced reactivity, which distinguish them from larger colloidal particles.

In terms of analytical methods, the techniques such as Flow Field-Flow Fractionation coupled with ICP-MS (FIFFF-ICP-MS) have greatly advanced our ability to characterize particles with minimal perturbation. However, quantitative *in-situ* characterization in complex natural matrices remains a major bottleneck. The high-salinity and high-organic-matter matrices typical of seawater, pose severe challenges for particle separation and detection, often compounded by artifacts introduced during sample collection and preparation (e.g., aggregation, adsorptive losses).

The case study on nanoparticles from deep-sea hydrothermal vents illustrates the critical role these natural particles play, overturning the paradigm of localized metal precipitation. It reveals that nanoparticles can act as key vectors for transporting essential micronutrients like iron over thousands of kilometers, thereby influencing global marine productivity and carbon cycling.

Although significant progresses have been reached, critical knowledge gaps persist, and these challenges highlight clear directions for future research. A primary need is the establishment of standardized analytical protocols and classification thresholds to ensure cross-study comparability. This must be coupled with the development of novel techniques for real-time, high-resolution and *in-situ* monitoring of dynamic transformations like aggregation, dissolution, and speciation changes. Mechanistically, the formation and reactivity of organic-inorganic hybrids, which modulate nanoparticle transport and bioavailability, remain poorly understood. Furthermore, with the increasing environmental input of engineered nanomaterials,

effectively differentiating between natural, incidental, and engineered nanoparticles in complex backgrounds is a formidable yet urgent scientific challenge.

In summary, a better understanding of the sources, behaviors, and effects of aquatic particles (especially nanoparticles) is essential for assessing their roles in pollutant fate, global element cycling, and ecosystem health. As a result, future studies should be focused on these challenges, and interdisciplinary approaches should be employed.

Author contributions

XF: Conceptualization, Data curation, Writing – original draft. YL: Conceptualization, Data curation, Formal analysis, Funding acquisition, Writing – review & editing. HL: Conceptualization, Data curation, Formal analysis, Writing – review & editing.

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