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Unraveling the impact of phytoplankton secretions on the behavior of metal-containing engineered nanoparticles in aquatic environment

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Based on the up-to-date knowledge we critically discuss the current understanding of the influence of the compounds secreted by phytoplankton species on the fate of metal-containing engineered nanoparticles (ENPs) in aquatic settings. Different biomolecules, such as extracellular polymeric substances (EPS) and exometabolites play important, yet to elucidate, role in the dissolution, colloidal stability, transformations and biouptake of the ENPs and thus shape their behavior within the phycosphere. Phytoplankton secretions can also mediate the synthesis of ENPs from dissolved ions by reducing the metals ions and capping the newly formed ENPs. However, the environmental significance of this process remains to be demonstrated. Exposure to ENPs triggers changes in the secretion of the biomolecules. An improved understanding of the regulatory mechanism and exometabolite changes due to ENP exposure is essential for deciphering the ENPs-phytoplankton interactions. Unveiling the significance of secreted biomolecules in modulating the behavior of the metal-containing ENPs is central for understudying the phytoplankton-ENPs feedbacks, drivers of transformations of ENPs and their mechanisms in the aquatic environment.

KEYWORDS

nanoparticles, phytoplankton, secretome, exudates, EPS, eco-corona, dissolution, aggregation

1 Introduction

Engineered nanoparticles (ENPs) have dimensions ranging from 1 to 100 nm (Vert et al., 2012), and possess unique properties which make them highly valuable for various applications in technology, medicine, environment and consumer products (Zhang et al., 2016; Mitchell et al., 2021; Keller et al., 2023). When released into freshwater environment, ENPs can undergo a variety of physical and chemical transformations (Levard et al., 2012; Batley et al., 2013; Yu et al., 2018; Wheeler et al., 2021; Liu et al., 2022; Rex M et al., 2023). The interconnected transformation processes determine collectively the environmental behavior and effects of ENPs on aquatic biota (French et al., 2009; Fernando and Zhou, 2019; Khort et al., 2022).

In the present review paper, we focus on the role of the phytoplankton secretions in the fate of the metal-containing ENPs in the freshwater environment. Phytoplankton play a central role in the global biogeochemical cycles of various nutrients (C, O, N, P, and Si) (Falkowski, 1994; Litchman et al., 2015), essential (Sunda, 2012) and toxic (Gregoire and

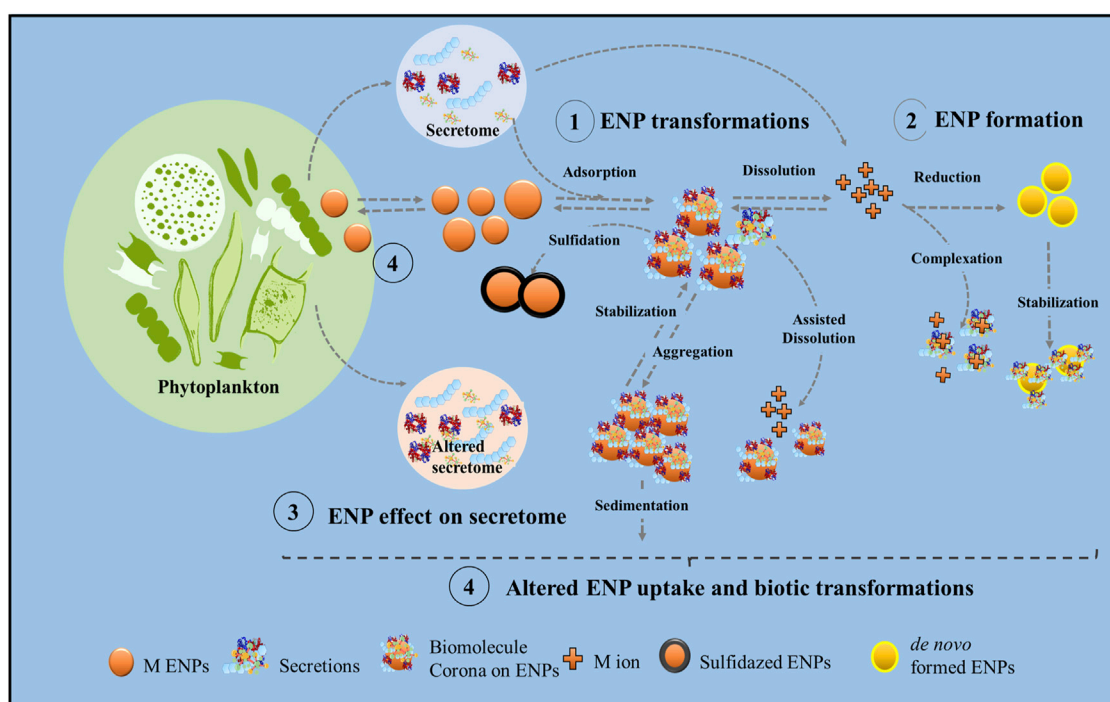


FIGURE 1

Conceptual view of the main physical and chemical processes involved in the interactions between phytoplankton secretions and metal-containing ENPs in the aquatic ecosystems, subject of this review paper.

Poulain, 2014; Cossart et al., 2022) trace metals and ENPs (Slaveykova, 2023). For example, the phytoplankton species have been shown to influence the fate of the ENPs by i) secreting various exometabolites and extracellular polymeric substances (EPS); ii) accumulating the ENPs and transforming them via different cellular processes; iii) synthesizing the ENPs inside the cells and/or on cell surfaces from dissolved metal species (Slaveykova, 2023).

The phytoplankton secretions contain various exometabolites and EPS, which form its “secretome” and play a key role for the processes in the phycosphere (Seymour et al., 2017; Mühlenbruch et al., 2018). The EPS are known to represent up to 25% of natural organic matter (NOM) in freshwaters, especially during algal blooms (Wilkinson et al., 1997) and to be predominant fraction of marine NOM (Corsi et al., 2020). The composition, types, and properties of microalgal and cyanobacterial EPS vary with the phytoplankton species and environmental conditions, and most often are dominated by polysaccharides and proteins as reviewed (Naveed et al., 2019).

The phytoplankton are source of exometabolites, such as carbohydrates, amino- and carboxylic acids, thiols, fatty acids etc. However, up to now, these exudate components have received limited attention in the research literature. The exudates of different strains of green algae, diatoms, red algae and cyanobacteria have been shown to contain multiples monosaccharides, uronic acid, pyruvate, glucosamine, glucuronic and galacturonic acids (Xiao and Zheng, 2016; Babiak and Krzemińska, 2021; Laroche, 2022). Amino acids have been measured in the secretions of the diatom *Skeletonema costatum* (Hosny et al., 2022), thiols in the secretions of green algae and

diatoms (Mangal and Guéguen, 2015; Mangal et al., 2020), as well as different marine microalgae (Yang et al., 2022). They are present in nanomolar concentration in freshwater environment (Mangal and Guéguen, 2015; Rasheduzzaman et al., 2018). Moreover, it has been demonstrated that various microalgae and cyanobacteria release various allelochemicals, serving for communication, defense, and adaptation purposes (Śliwińska-Wilczewska et al., 2021). Microalgal allelochemicals contain alkaloids, fatty acids and derivatives, polyketides, peptides, phenolics, terpenoids and other volatile organic compounds (Chaïb et al., 2021; Casanova et al., 2023). Lipids have also been found in the exudate (Tambiev et al., 1989), together with other non-polar exometabolites, such as di-tri peptides, lumichrome and prostaglandin-like substances (Brisson et al., 2021). Different constituents of secretome contain divers cationic (e.g., $-\text{NH}_4^+$, $-\text{RNH}_2^+$) or anionic (e.g., $-\text{SH}$, $-\text{NH}_2$, $-\text{COOH}$, $-\text{PO}_4^{3-}$) functional groups, which confer them metal binding properties (Xu et al., 2013), and play key role in the biomolecule adsorption to ENPs (Chetwynd and Lynch, 2020; Liu et al., 2022).

Drawing upon the latest advancements in current state of the research, the aim of the present review paper is to thoroughly discuss the impact of biomolecules produced by phytoplankton species on the fate of the ENPs in the aquatic environment. Our critical analysis delves into how phytoplankton secretions influence: i) the colloidal stability of the ENPs, the formation of biomolecular corona around them; ii) the chemical transformations, such as dissolution and sulfidation, and iii) the formation of the ENPs from dissolved ions (Figure 1). Furthermore, the influence of the ENP exposure on the secretion of exometabolites and EPS by different phytoplankton

TABLE 1 Selected examples illustrating the interaction between biomolecules and metal-containing ENPs.

Biomolecules	Phytoplanktonic species	ENPs type (size, type, and coating)	Type of transformation	Comment	References
Biomolecules released by phytoplankton species					
EPS	<i>Chlorella pyrenoidosa</i>	20 nm citrate and PVP-coated AgNPs	Aggregation, eco-corona formation, dissolution, influence on toxicity	Adsorption of EPS on both AgNPs prevented the dissolution, favored the aggregation, decreased the toxicity and the internalization in the cells	Zhou et al. (2016)
		40 nm CuONPs	Heteroaggregation, EPS production, influence on toxicity	Adsorption of EPS on CuONPs, favored the heteroaggregation, reduced the dissolution of ENPs. S-EPS and B-EPS increased the EPS production as a possible cellular protective mechanism	Zhao et al. (2016)
		5, 10, and 40 nm (anatase) and 25 nm (rutile) TiO ₂ NPs	Adsorption, aggregation and stabilization	Adsorption increased with specific surface area of TiO ₂ NPs. It depended on the composition of EPS, the size and type of TiO ₂ NPs. EPS stabilized the NPs	Gao et al. (2019)
		25 nm anatase and rutile TiO ₂ NPs	EPS and metabolite release	Increase of EPS and exometabolites production during TiO ₂ NPs exposure. Effect of anatase was higher	Gao et al. (2020)
		25 nm anatase and rutile TiO ₂ NPs	EPS and ENPs uptake	EPS favored the accumulation of ENPs on algal surface, but reduced TiO ₂ NPs internalization by cells. The removal of EPS activated the associated endocytosis pathways	Gao et al. (2021)
	<i>Chlamydomonas reinhardtii</i> and <i>Phaeodactylum tricornutum</i>	38 nm TiO ₂ NPs and 423 nm bulk TiO ₂	EPS production and aggregation	EPS induced ENPs heteroaggregations. Exposure to higher concentration of ENPs resulted in higher exopolysaccharides production	Sendra et al. (2017)
	<i>Scenedesmus obliquus</i>	Functionalized QDs CdSe/ZnS PEG-COOH and QDs CdSe/ZnS PEG-NH ₂	Aggregation, ecocorona formation and toxicity	EPS formed an eco-corona that induced aggregation and altered the surface charge of the QDs. EPS reduced the cellular uptake and toxicity of CdSe/ZnS QDs. Change in surface charge of QDs	Chakraborty et al. (2021)
<i>Chlorella vulgaris</i>	15 nm PVP-coated AgNPs	Bioaccumulation and toxicity	EPS complexed Ag ions and reduced their bioaccumulation and toxicity	Zheng et al. (2019)	

(Continued on following page)

TABLE 1 (Continued) Selected examples illustrating the interaction between biomolecules and metal-containing ENPs.

Biomolecules	Phytoplanktonic species	ENPs type (size, type, and coating)	Type of transformation	Comment	References
	<i>Microcystis aeruginosa</i>	50 nm CeO ₂ NPs, 50 nm CuONPs, 30–50 nm ZnONPs	EPS production	Increase in the EPS production as a response to ENPs exposure	Hou et al. (2017)
	<i>Synechocystis</i> sp.	20 nm and 50 nm citrate, PVP- and lipoic acid coated-AgNPs	Aggregation, stabilization, dissolution	The effect was dependent on the surface coating and primary size of the AgNPs. PVP-coated AgNPs agglomerated to a lesser extent as compared with the citrate- and lipoic acid coated-AgNPs	Jiménez-Lamana and Slaveykova (2016)
	Cyanobacterial bloom	ZnONPs	Aggregation, stabilization, and adsorption	Electrostatic attraction and surface complexation contribute to the adsorption of EPS to ZnONPs. EPS-favored stability and dissolution of NPs	Xu and Jiang (2015)
	Cyanobacterial biomass	TiO ₂ NPs	Adsorption	Adsorption of EPS on TiO ₂ NPs depended on the molecular weight of the proteins and polysaccharides	Xu et al. (2020)
	<i>Skeletonema costatum</i> and <i>Nitzschia closterium</i>	10–30 nm CuNPs and 40 nm CuONPs	Heteroaggregation and toxicity	EPS induced collisions between microalgae and the EPS and alleviated CuONPs toxicity	Huang et al. (2022)
	<i>Cylindrotheca closterium</i>	12 nm SiO ₂ NPs	Aggregation	EPS prevented aggregation of SiO ₂ NPs	Vukosav et al. (2023)
12 nm SiO ₂ NPs, and 15–30 nm CeO ₂ NPs	<i>Odontella mobiliensis</i> , <i>Skeletonema grethae</i> , <i>Phaeodactylum tricornutum</i> , <i>Thalassiosira pseudonana</i> , and <i>Dunaliella tertiolecta</i>	25 nm TiO ₂ NPs, 10–20 nm	EPS production and toxicity	Exposure to TiO ₂ NPs decreased EPS production. CeO ₂ NPs had a concentration dependent effect on the EPS production. SiO ₂ NPs increased significantly the EPS production	Chiu et al. (2017)
EPS	<i>Amphora</i> sp., <i>Dunaliella tertiolecta</i> , <i>Phaeocystis globosa</i> , and <i>Thalassiosira pseudonana</i>	Coated (carboxyl- and amine-) or uncoated QDs	Stabilization	Decrease in the stability of both nonfunctionalized and functionalized (carboxyl- and amine-) QDs in artificial seawater. The degradation rate of the QDs was positively correlated to the protein content in the EPS	Zhang et al. (2012)
EPS	<i>Dunaliella tertiolecta</i>	Aeroxide [®] P25 TiO ₂ NPs	Aggregation, sedimentation and ecocorona formation	Stabilization and hindering of aggregation, 20–80 kDa exoproteins involved. No changes in carbohydrate/protein proportion and quantities over 24 h exposure	Morelli et al. (2018)
EPS	<i>Chlamydomonas reinhardtii</i> and <i>Dunaliella tertiolecta</i>	3.6 nm (anatase) and 23 and 24 nm (rutile) TiO ₂ NPs	Aggregation, ecocorona formation and stabilization	Electrostatic interactions and chemical bonding (bridge-coordination) between the COO ⁻ group of EPS and TiO ₂ NPs. Change in surface charge of TiO ₂ NPs in presence of EPS	Adeleye and Keller (2016)

(Continued on following page)

TABLE 1 (Continued) Selected examples illustrating the interaction between biomolecules and metal-containing ENPs.

Biomolecules	Phytoplanktonic species	ENPs type (size, type, and coating)	Type of transformation	Comment	References
EPS	<i>Raphidocelis subcapitata</i> and freshwater NOM	Citrate and PVP-coated AgNPs	Dissolution	EPS prevented dissolution	Watanabe et al. (2023)
EPS and biomolecules	<i>Scenedesmus</i> sp.	40–80 nm cemented tungsten carbide cobalt (WC-Co) NPs and CoNPs	Ecocorona formation and toxicity	Biomolecules from green algae culture decreased the toxicity to <i>Daphnia magna</i> due to eco-corona formation	Ekvall et al. (2021)
S-EPS and B-EPS	<i>Microcystis</i> sp. and <i>Chlorella vulgaris</i>	50 nm ZnONPs	Aggregation and deposition under different ionic strength	Hindering of aggregation and influence on the deposition of the ZnONPs	Huang et al. (2023)
S-EPS and B-EPS	<i>Microcystis aeruginosa</i>	50 nm CeO ₂ NPs	Aggregation and toxicity	S-EPS induced heteroaggregation by forming EPS-NPs aggregates with cells and B-EPS buffered the toxicity of the nCeO ₂	Yang et al. (2018)
B-EPS	<i>Chlamydomonas reinhardtii</i>	60–120 nm spherical AgNPs	Bioaccumulation and toxicity	Exopolysaccharide and protein in bound-EPS increased under AgNPs stress, providing a first barrier against AgNPs toxicity	Xu et al. (2022)
	<i>Chlorella</i> sp.	P25 TiO ₂ NPs	Aggregation/agglomeration, sedimentation, and toxicity	Exudate increased the sedimentation of nTiO ₂ forming aggregates and reduced the toxicity on <i>Chlorella</i> sp.	Natarajan et al. (2023)
	<i>Chlorella vulgaris</i>	30 nm ZnONPs	Increasing EPS production	Exposure to ZnONPs increased S-EPS and B-EPS production as a protective mechanism	Zhao et al. (2019)
Model biomolecules					
Thiols		100 nm AgNPs	Aggregation and toxicity	N-acetyl-L-Cysteine, L-Cysteine, and glutathione promoted aggregation and lower the cytotoxicity of AgNPs	Ferreira et al. (2020)
		13 metal oxide NPs	Adsorption	2-naphthalenethiol (2-NPT) and methanethiol (MT) adsorbed on ZnO, TiO ₂ , and In ₂ O ₃ NPs and not on the others, suggesting an adsorption of a range of thiols to these three NPs	Grimm et al. (2021)
		5–13 nm citrate-coated AgNPs	Stabilization, chemical interaction, and coating replacement	Mercaptohexanol formed an Ag (I) thiolate complex; Cysteine replaced the citrate coating of AgNPs	Toh et al. (2014)
		18 nm citrate-coated AgNPs	Stabilization and dissolution	L-Cysteine and N-acetyl L-cysteine decreased AgNPs dissolution, having an impact on the stability based on the functional group on the molecules	Afshinnia et al. (2018)

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TABLE 1 (Continued) Selected examples illustrating the interaction between biomolecules and metal-containing ENPs.

Biomolecules	Phytoplanktonic species	ENPs type (size, type, and coating)	Type of transformation	Comment	References
		20 nm citrate-coated AgNPs citrate coated	Dissolution	Glutathione, phytochelatin with 2,3 and 6 thiols, and copper chaperone Atx1 (protein with thiol site exposed) favored AgNP dissolution; The dissolution rate increased with the number of thiols per molecule	Marchioni et al. (2018)
		20 nm citrate-coated AgNPs	Dissolution, aggregation, and toxicity	Cysteine changed the diameter, zeta potential, and Ag ⁺ dissolution of AgNPs, increasing the stability and decreasing the toxicity	Yi et al. (2016)
Amines		10 nm citrate-coated AuNPs	Adsorption	13 amines (primary, secondary, and tertiary) showed a replacement in the coating of AuNPs. The replacement yield was influenced by steric factor. The mechanism involved the reduction of surface Au(I) in ENPs	Lyu et al. (2023)
Amino acids, monosaccharides		22 nm SiO ₂ NPs, 13 nm TiO ₂ NPs (uncapped, polyvinylpyrrolidone capped, and Dispex AA4040 capped)	Metabolite corona	Presence of proteins facilitated the complete biomolecular corona formation with metabolites. Metabolite corona formation, highly specific to the isomeric nature, was confirmed with two categories of metabolites (30 cations and 12 anions)	Chetwynd et al. (2020)
		12 nm PVP-coated AgNPs	Adsorption (biocorona formation) and aggregation	Glucose and glutamine reduced nAg aggregation improving colloidal and chemical stability of ENPs	Rónavári et al. (2021)
		4–130 nm ZnONPs	Dissolution	Citric acid promoted ligand-dependent dissolution	Mudunkotuwa et al. (2012)
		50 nm CuONPs	Dissolution	Eleven amino acids promoted the dissolution of the CuONPs depending on the nature of the amino acids	Wang et al. (2013)
		6 nm CuONPs	Adsorption	Negative ENPs interact with arginine, a positively charged amino acid, through an electrostatic mode, but they do not interact with aspartic acid, a negatively charged amino acid	El-Trass et al. (2012)
Lipids		TiO ₂ NPs	Adsorption	Adsorption of lipids on the particle was driven by affinity to different class of lipids	Lee et al. (2018)

species is also considered. The role of the secreted biomolecules on the uptake of ENPs to phytoplankton species and thus their cellular transformations is also briefly discussed. The discussion is illustrated by selected recent examples (Tables 1, 2) and sheds light on the complex interplay between phytoplankton, their secretions, and the behavior of ENPs in aquatic ecosystems.

2 Phytoplankton secretions and colloidal stability of ENPs

Most of the available knowledge has been obtained from the studies with EPS produced by cultures of marine and freshwater phytoplankton. It reveals that EPS are able to form biomolecular corona on different ENPs which alters the colloidal stability, transformations (Zheng et al., 2019; Zhang et al., 2020b; Junaid and Wang, 2021; Liu et al., 2022; Slaveykova, 2023) and the uptake (and toxicity) of the ENPs by phytoplankton (Zhou et al., 2016; Natarajan et al., 2023). Key transformations involving ENPs in freshwaters, the role of the NOM in these transformation (Hedberg et al., 2019; Abbas et al., 2020; Milosevic et al., 2020; Spurgeon et al., 2020) and the uptake and biological effects have been comprehensively reviewed (Xu et al., 2020). The EPS released by the major phytoplankton groups, such as cyanobacteria, green algae and diatoms were shown to increase the stability of the ENPs, although examples of enhanced aggregation exist too (Table 1; Figure 1. ①).

The EPS isolated from bloom-forming cyanobacteria has been demonstrated to stabilize the ZnONPs via *electrostatic attraction* and *surface complexation* (Xu and Jiang, 2015). Interestingly, the binding affinity of EPS to ZnONPs differs for the fluorophore families identified in the EPS and decreased in the order humic-like > tryptophan-like > fulvic-like components (Xu and Jiang, 2015). Rich in proteins soluble and bound EPS extracted from cyanobacterium *Microcystis* sp. have been shown to hinder the aggregation of 50 nm ZnONPs in NaCl and low CaCl₂ media due to the adsorption of the proteins to the surface of the ENPs for the soluble EPS and through *steric repulsion* for the bound EPS. However, at higher Ca²⁺ concentration, soluble EPS promoted the aggregation, whereas the bound EPS stabilized ZnONPs through steric repulsion (Huang et al., 2023). The EPS from *C. vulgaris* prevented the aggregation of ZnONPs likely due to the *electrostatic interactions* (Huang et al., 2023). Hydroxyl, carboxyl and amide groups in the EPS have been shown to participate in the adsorption of dissolved and bound EPS of *C. vulgaris* on the ZnONPs in addition to the interaction of the tryptophan-like components in the soluble EPS with ZnONPs (Zhao et al., 2019). *Hydrogen bonding* involving the hydroxyl, carboxyl and the amine groups of the EPS have also been shown to play a role in the EPS interaction with ZnONPs (Chen et al., 2012).

The adsorption of the EPS with high *molecular weight* (HMW, 1 kDa–0.45 μm) isolated from lake cyanobacteria on the TiO₂NPs has been found to be more important than that of low MW EPS (LMW, <1 kDa) (Xu et al., 2020). The EPS secreted by green alga *Chlorella pyrenoidosa* decreased significantly the aggregation rate of TiO₂NPs (Lin et al., 2016). Interestingly, a selective adsorption of aromatic components of the EPS from the same alga onto four types of TiO₂NPs (5, 10, and 40 nm anatase and 25 nm rutile) and an

increase of the adsorption (and stabilization effect) with the specific surface area of the ENPs have been observed (Gao et al., 2019). Comparative study of the soluble EPS from *C. reinhardtii* and *D. tertiolecta* has revealed that the EPS adsorption to three commercial TiO₂NPs with different coatings depends on the *particle surface area*, *surface charge* and *hydrophobicity*. The interactions between EPS and TiO₂NPs have been shown to be driven by electrostatic interactions and chemical bonding between the COO⁻ group of EPS and TiO₂NPs (Adeleye and Keller, 2016). The exoproteins (MW of 20–80 kDa) produced by green alga *Dunaliella tertiolecta* prevent the aggregation of the TiO₂NPs in marine water by forming an eco-corona (Morelli et al., 2018; Corsi et al., 2020).

The EPS produced by diatom *Cylindrotheca closterium* stabilized 12 nm SiO₂NPs in marine environment due to molecular and nanoscale interactions (Vukosav et al., 2023). However, the EPS isolated from four other diatoms *Amphora* sp., *D. tertiolecta*, *Phaeocystis globosa*, and *Thalassiosira pseudonana* decrease the stability of both nonfunctionalized and functionalized (carboxyl- and amine-) quantum dots (QDs) in artificial seawater with a rate positively correlated to the protein fraction of the EPS (Zhang et al., 2012). Similarly the EPS from green alga *Scenedesmus obliquus* induced the aggregation of both PEG-COOH and PEG-NH₂ functionalized QDs, forming an eco-corona that changes the surface charge of the ENPs (Chakraborty et al., 2021). A steric stabilization of sulfide/silica-modified zero valent iron (ZVI) NPs by organic matter released from *C. reinhardtii* at different growth stages, demonstrating that the feedback from algae may play important roles in the environmental implications of ENPs (Adeleye et al., 2016).

The EPS (<1 kDa MW) released by cyanobacterium *Synechocystis* sp. stabilized AgNPs with primary size of 20 nm and 50 nm, and three different coatings (Jiménez-Lamana and Slaveykova, 2016). However the stabilization was dependent on the primary surface coating as the effect was significant for citrate-, and lipoic acid-coated AgNPs, but minor on the PVP-coated AgNPs (Jiménez-Lamana and Slaveykova, 2016). EPS from green alga *C. vulgaris* stabilized both PVP and citrate coated AgNPs (Zhou et al., 2016).

Opposite to the studies with the EPS, very limited knowledge is available concerning the effect of the exometabolites on the stability of the ENPs. Some examples from rather scarce literature are provided below. The adsorption of glucose and glutamine on PVP-coated AgNPs resulted in a formation of biomolecular corona, decreasing their zeta potential and aggregation (Rónavári et al., 2021). A recent study on the interaction between citrate-coated AuNPs and 13 different primary, secondary, and tertiary amines has revealed that the exchange of coating is influenced by steric factors and by the presence of oxidized Au (I) on the surface of ENPs allowing the reduction of Au (I) by amines involved also in the protein corona formation (Lyu et al., 2023). Positively charged arginine adsorbs on the negatively charged CuONPs, but this was not the case of negative charged aspartic acid, demonstrating the importance of the electrostatic interactions (El-Trass et al., 2012). A pilot study has shown the formation of a metabolite corona on SiO₂NPs and three different TiO₂NPs by 28 cationic metabolites and 12 anionic metabolites, which was highly specific to the isomeric nature of the metabolites (Chetwynd et al., 2020). *Thiols* such as 2-naphthalenethiol and methanethiol have been also demonstrated to

form a corona on the ZnONPs, TiO₂NPs, and In₂O₃NPs (Grimm et al., 2021). Cysteine, but not serine, stabilized ZnS- and HgSNPs, showing the importance of the chemical nature of the exometabolites in the interactions with ENPs (Gondikas et al., 2010). By contrast, the presence of cysteine destabilized the citrate-coated AgNPs, whereas the addition of N-acetyl L-cysteine stabilized the same NPs. This contrasting effect has been attributed to the different functional groups in these two molecules: negatively charged carboxylic groups and positively charged amine group in the cysteine favor bridging interactions (Afshinnia et al., 2018). The addition of small thiols (e.g., cysteine) mitigated the aggregation kinetics of AgNPs in the presence of Suwannee River fulvic acid (Afshinnia et al., 2018), pointing out the complexity in determining the ENPs stability in complex environmental settings. Different classes of lipids formed corona on the TiO₂NPs, with LysoPL exhibited higher affinity to TiO₂NPs than other lipid categories (Lee et al., 2018).

3 Phytoplankton secretion and ENPs dissolution and transformations

Studies have demonstrated both increase and decrease of the dissolution of metal-containing ENPs in the presence of phytoplankton secretions (Table 1; Figure 1. ①). The EPS from haptophyta *Isochrysis galbana* increase the dissolution of CuONPs, CuNPs and Cu (OH)₂NPs (Kocide) (Adeleye et al., 2014). This is in agreement with early literature showing that the EPS released by various phytoplankton species, including *D. tertiolecta* (Gonzalez-Davila et al., 1995), *Chlorella* sp. (Kaplan et al., 1987), *C. reinhardtii* (Xue et al., 1988), *Phaeodactylum tricornutum*, and *T. weissflogii* (Gonzalez-Davila et al., 2000) complexed different ions that can be released from the ENPs, such as Cu (II).

The EPS from *Chlorella* sp. (Chen et al., 2012) and lake cyanobacteria (Xu and Jiang, 2015) decreased the dissolution of the ZnONPs. Moreover, EPS isolated from *C. pyrenoidosa* reduced the dissolution of citrate- or PVP-coated 20 nm AgNPs by complexing the Ag (I) ions (Zhou et al., 2016). Similarly the EPS from *Raphidocelis subcapitata* prevented the dissolution of both citrate- and PVP-coated AgNPs (Watanabe et al., 2023). High concentrations of the alginate, an extracellular polysaccharide released from cyanobacterium *M. aeruginosa*, adsorbed to 20 nm citrate-coated AgNPs and reduced their dissolution rate (Ostermeyer et al., 2013).

Studies on model exometabolites have shown an increase, decrease or no effect on the dissolution of the ENPs. For example, cysteine adsorbed to the surface of AgNPs via SH-group and increased the release of Ag (I) (Gondikas et al., 2012; Wang et al., 2013), however decreased the dissolution and reduced the toxicity of AgNPs to *Phanerochaete chrysosporium* (Yi et al., 2016). Cysteine has been reported to replace the citrate coating in AgNPs and to increase their stability, however mercaptohexanol formed a silver (I) thiolate complex and favored the AgNPs dissolution (Toh et al., 2014). Cysteine and N-acetyl L-cysteine (NAL-cys) decreased citrate-coated AgNPs dissolution at high cysteine and NAL-cys concentrations (Afshinnia et al., 2018). Given the high affinity of Ag to sulfur and nitrogen groups, it is expected that sulfur- and nitrogen-rich molecules will adsorb more

strongly on AgNPs and result in a decrease in the dissolution rate of AgNPs and in an increase of stability (Gunsolus et al., 2015). Glutathione and phytochelatins with 2, 3 or 6 thiols favored AgNPs dissolution into Ag (I) with a rate that increases with the number of thiols per molecule (Marchioni et al., 2018). Citrate enhanced the dissolution of the ZnONPs by ligand-induced dissolution (Mudunkotuwa et al., 2012). Eleven amino-acids Cys, Met, Arg, Glu, Lys, Val, GSH, Thr, Asp, Gln, and His significantly promoted the dissolution of the CuONPs, but the effect was dependent on the nature of the amino acids (Wang et al., 2013).

Much less studies dealt with the role of phytoplankton secretions in other transformation processes, for example, sulfidation. AgNPs, CdNPs, CuNPs, and ZnNPs have been shown to undergo sulfidation with reduced sulfur species of different biomolecules (Levard et al., 2012; Liu et al., 2012). The formation of Ag₂SNPs under various environmental scenarios have been reviewed from thermodynamic and kinetic perspectives (He et al., 2019). Dissolution-precipitation mechanism for the sulfidation of ZnONPs (Ma et al., 2013; Banerjee and Jain, 2018) and CuONPs (Wang et al., 2013) was proposed. Sulfidation of metallic ENPs is considered as a major transformation process in urban water sewage systems (Kaegi et al., 2013) and sulphur-rich environment (Thalmann et al., 2014; Liu et al., 2018; He et al., 2019; Zhang et al., 2019).

4 Phytoplankton secretions and ENP formation from dissolved metals

Phytoplankton secretions have been found to mediate the formation of the metal-containing ENPs via reduction of dissolved metal ions (Figure 1. ②; Table 2). Indeed, different EPS components contain reducing functional groups, such as aldehydes, hydroxyls, and phenolic groups (Sheng et al., 2010), tyrosine and tryptophan (Si and Mandal, 2007). Indeed, proteins, peptides, amino acids, polysaccharides, lipids, and nucleic acids and some aromatic compounds are among the compounds reported to guide the formation from dissolved ions, crystal growth and stabilization of metal and metal oxide ENPs (Siddiqi and Husen, 2016). Selected recent examples (Table 2) illustrated the major interested for the synthesis of AgNPs from Ag (I). For example, the carbohydrates from green alga *Scenedesmus* sp. have been used to synthesize and stabilize the AgNPs (Patel et al., 2015). The proteases, β-D-glucosidases, chitinases, alkaline phosphatases have been also shown to participate in the reduction of Ag (I) to AgNPs (Naveed et al., 2019). In addition, several oxidoreductive proteins produced by *C. reinhardtii*, including histone H4, superoxide dismutase, and carbonic anhydrase, have been demonstrated to be involved in biosynthesis and stabilization of AgNPs (Barwal et al., 2011). The exopolysaccharides isolated from two green microalgae *Botryococcus braunii* and *C. pyrenoidosa* were used to synthesize AgNPs with antibacterial capacity (Navarro Gallón et al., 2019). Similarly the exudates from another green alga *Desmodesmus abundans*, have been found to synthesize AgNPs under different condition of CO₂ and pH (Mora-Godínez et al., 2022). The exoproteins and exopolysaccharides extracted from *C. vulgaris*, have been shown to be responsible for the reduction of Ag (I) and the consecutive formation and stabilization of AgNPs (Da Silva Ferreira et al., 2017), as it was the case for the exoproteins of the

cyanobacterium *Oscillatoria willei* (Ali et al., 2011) and the phycobiliproteins produced by *Spirulina platensis* and *Nostoc linckia*, (Ismail et al., 2021). A three-step mechanism for photo-induced synthesis of AgNPs by EPS released from green alga *C. reinhardtii* has been proposed including: i) adsorption of Ag(I) to EPS biomolecules, ii) a light-dependent reaction that reduce the Ag (I) for the formation of AgNPs involving functional group like -COOH, -OH and phenols and iii) capping by biomolecules that provide the colloidal stabilization of NPs (Rahman et al., 2019b). Moreover, the polyphenols, polysaccharides and proteins and their nanoparticle-capping capacity determined the different stability, size, and shape of AgNPs produced by *C. reinhardtii* (Rahman et al., 2019a). A recent study with EPS from *Chlorella sp.* isolated from a brackish water high-altitude lake of the Northern-Western Himalayas demonstrated that exopolysaccharides synthesized polysaccharide-capped AuNPs that are stable in extended range of pH and salinity (Jakhu et al., 2021). The EPS from chlorophyceae *Cosmarium impressulum* (Dahoumane et al., 2014), diatoms *Navicula atomus* and *Diadmesmis gallica* (Schröfel et al., 2011) favored the formation and controlled the shape and size of the AuNPs. Alginate has also reduced Ag (I) forming hetero-shaped AgNPs (Sharma et al., 2012; Bhagyaraj and Krupa, 2020) and Au (I) into AuNPs (Zhao et al., 2017). Similar results have been obtained for the synthesis of AuNPs by *C. vulgaris* cell extract: peptides, proteins, phenols, and flavonoid carried out the reduction and the capping of AuNPs from Au ions (Annamalai and Nallamuthu, 2015).

The exoproteins, exopolysaccharides, and carotenoids from diatom *P. tricornutum* have been identified as the agent responsible for the synthesis of TiO₂NPs (Caliskan et al., 2022). Similarly, the exoproteins and exopolysaccharides produced by *C. reinhardtii* played a role in reduction of Zn (II), consecutive formation and stabilization of ZnO nanoflowers (Rao and Gautam, 2016). The proteins, peptides, carbohydrates, vitamins, and fibers of *Chlorella sp.* have been found to play a role in both reduction of Zn (II) and effective stabilization of ZnONPs in a three steps process: (i) initial activation step involving Zn (II) dissolution from zinc nitrate salt in water, (ii) Zn (II) reduction to metallic form by algal derived biomolecules and (iii) immediate oxidation to ZnONPs during air-drying process by hydroxyl groups present in the biomolecules (Khalafi et al., 2019). Secretions containing polyphenols, alkaloids, proteins, flavonoids, sugars, vitamins terpenoids, steroids, tannins, carboxylic acids and amines, have been demonstrated to synthesize CuONPs (Mallakpour et al., 2020). The proposed reaction mechanism an ininitial interaction between Cu (II) polyphenols, leading to a sequential reduction to Cu (I) and to Cu (0), which is further converted to CuONPs.

Glucose was used as reducing and capping reagent in the synthesis of AgNPs (Pattnaik et al., 2023), AuNPs (Suvarna et al., 2017), and CuNPs (Granata et al., 2019). Amino acids, tyrosine and tryptophan, have been shown to be involved in the formation and capping process of AgNPs (Shankar and Rhim, 2015). Similarly twenty amino acids contributed to the formation of the AuNPs (Maruyama et al., 2015). Furthermore, the structural diversity of amino acids enabled a preparation of Cu nanomaterials with variety of structure as nanoparticles, nanorods and nanocrystals (Yu et al., 2015).

5 Influence of ENPs on the release of phytoplankton secretions

Different ENPs have been shown to alter the concentration and composition of the secreted biomolecules by various phytoplankton species (Figure 1. ③). For example, the exposure of the green alga *C. pyrenoidosa* to anatase and rutile TiO₂NPs resulted in an increase of the EPS secretion, which was more pronounced in the case of anatase (Gao et al., 2020). The authors have demonstrated that the effect of anatase on EPS secretion depended mainly on the cellular ROS production, whereas the rutile altered the Ca²⁺ signaling pathway (Gao et al., 2020). Exposure to CeO₂NPs induced ENPs-concentration dependent increase in the production of the EPS by *O. mobiliensis*, *P. tricornutum*, *D. tertiolecta* (Chiu et al., 2017). SiO₂NPs significantly increased the secretion of the EPS by *T. pseudonana* (around 600%) and *S. grethae* (around 1,000%–1,500%) but not by the *O. mobiliensis*, *P. tricornutum*, *D. tertiolecta* (Chiu et al., 2017). By contrast, the exposure of four different diatom species *Odontella mobiliensis*, *Skeletonema grethae*, *P. tricornutum*, *T. pseudonana* and green alga *D. tertiolecta* to TiO₂NPs of comparable size demonstrated a decrease of the amount of the released biomolecules (Chiu et al., 2017). AgNPs enhanced the exopolysaccharides and proteins production in bound EPS of *C. reinhardtii* (Xu et al., 2022). The exposure to TiO₂NPs increased in the protein content in the EPS of both *C. reinhardtii* and marine diatom *P. tricornutum* (Sendra et al., 2017) Likewise, the exposure to 30 nm ZnONPs resulted in an increase of the protein fraction of the EPS as a protective response of *C. vulgaris* (Zhao et al., 2019). These findings pointed out that the effect of the ENPs on the release of the EPS by phytoplankton species was dependent on both the type of the phytoplankton species and the type and primary size of the ENPs.

Exposure to 50 nm CeO₂NPs, 50 nm CuONPs or 30–50 nm ZnONPs has led to an increase of both tightly and loosely bound EPS of cyanobacterium *M. aeruginosa* (Hou et al., 2017). It has been suggested that the enhanced EPS production by phytoplankton species when exposed to ENPs lowered collisions between microalgae and the ENPs by decreasing the specific contact area, and thus alleviated CuONPs toxicity in two diatoms *S. costatum* and *N. closterium* (Huang et al., 2022). CuONPs enhanced the production of both soluble and cell bounded EPS of *C. pyrenoidosa*, that consequentially enhance the hetero-aggregation of the ENPs (Zhao et al., 2016).

Most of the published literature has demonstrated that the exposure to ENPs resulted in an increase of the EPS produced by the phytoplankton species, which can be considered as a cellular defense mechanism (Hou et al., 2017). To date no studies have explored the effect of ENPs on the release of exometabolites. However, a recent study revealed an increase in intracellular microcystin concentrations, which was subsequently released in the extracellular environment due to cell death triggered by either ENPs exposure or environmental factors (Zhang et al., 2020a). Despite the current advancements, the underlying regulatory mechanisms of the EPS and exometabolite secretion and ENPs-induced effects are not well known and need to be further explored. In addition to the direct exposure of phytoplankton species to ENPs, the secretion of biomolecules

TABLE 2 Selected examples illustrating the involvement of phytoplankton secretions in metal-containing ENPs formation from dissolved metals.

Biomolecules	Phytoplankton species	ENPs	Comments	References
Biomolecules released by phytoplankton studies				
Extracellular biomolecules	Seven cyanobacteria and seven green algae strains	AgNPs	Light-induced synthesis; Nanoparticle formation mediated by exopolysaccharides; The shape and size of newly formed ENPs are strain dependent	(Patel et al., 2015)
	<i>Desmodesmus abundans</i> and <i>Spirulina platensis</i>	AgNPs	Exudate produced by microalgae in different condition of CO ₂ and pH can synthesize AgNPs	Mora-Godínez et al. (2022)
Exudate	<i>Phaeodactylum tricornutum</i>	TiO ₂ NPs	Biomolecules present in the exudate (exoproteins, exopolysaccharides and carotenoids) were responsible to the reduction and synthesis of TiO ₂ NPs	Caliskan et al. (2022)
	<i>C. reinhardtii</i>	ZnONPs (nanoflower)	Algal proteins and polysaccharides might play an important role in the synthesis and stabilization of ZnO nanoarchitectures	Rao and Gautam (2016)
	<i>Scenedesmus</i> sp.	AgNPs	Biomolecules, proteins, and peptides, were mainly responsible for the formation and stabilization of SNPs	Jena et al. (2014)
	<i>Chlorella vulgaris</i>	AgClNPs	Exoproteins and exopolysaccharides were responsible for the synthesis and stabilization of AgClNPs	Da Silva Ferreira et al. (2017)
Cells-extract	<i>Chlorella vulgaris</i>	AuNPs	Peptides, proteins, phenols, and flavonoid carried out the dual function of effective Au (III) reduction and capping of AuNPs	Annamalai and Nallamuthu (2015)
	<i>Spirulina platensis</i>	Fe ₃ O ₄ @AgNPs	The biomolecules contained in the cells-extract were used as reductant in the formation of the nanocomposites NPs	Shokoofeh et al. (2019)
	<i>Spirulina platensis</i>	TiO ₂ NPs	Cells-extract biomolecules were able to synthesize TiO ₂ NPs	Vasanth V et al. (2022)
	<i>Chlorella</i> sp.	ZnONPs	Proteins, peptides, carbohydrates, vitamins, and fibers were involved Zn (II) reduction and effective stabilization of ZnO NPs. Three step synthesis: (i) Zn (II) dissolution of zinc nitrate salt in water, (ii) Zn (II) reduction to metallic form by algal derived molecules and (iii) oxidation to ZnONPs by hydroxyl groups of the biomolecules	Khalafi et al. (2019)
Exopolysaccharides	<i>Chlorella</i> sp	AuNPs	Exopolysaccharides reduced Au(III) and capped AuNPs	Jakhu et al. (2021)
	<i>Botryococcus braunii</i> and <i>C. pyrenoidosa</i>	AgNPs	Exopolysaccharides reduced the Ag(I) and served as AgNPs capping agents	Navarro Gallón et al. (2019)
Protein	<i>Oscillatoria willei</i>	AgNPs	Proteins reduced Ag(I) and capped AgNPs	Ali et al. (2011)
EPS	<i>C. reinhardtii</i>	AgNPs	Three step photo-induced synthesis: (i) adsorption of Ag(I) to EPS biomolecules, (ii) a light-dependent reduction of Ag(I) to AgNPs involving functional group like -COOH, -OH and phenols of the EPS and (iii) capping of NPs by biomolecules that provide the colloidal stabilization	Rahman et al. (2019b)
EPS	<i>C. reinhardtii</i>	AgNPs	Polyphenols, polysaccharides, and proteins worked as reducing agent and determine stability, size, and shape of AgNPs through their coating capacity	Rahman et al. (2019a)
Phycobiliprotein extract	<i>Spirulina platensis</i> and <i>Nostoc linckia</i>	AgNPs	The proteins were responsible for stabilizing and capping the formed AgNPs	Ismail et al. (2021)
EPS	<i>Cosmarium impressulum</i>	AuNPs	EPS favored the formation and controlled the shape and size of the AuNPs	Dahoumane et al. (2014)
EPS	<i>Navicula atomus</i> and <i>Diademsis gallica</i>	Silica-AuNPs and AuNPs	EPS favored the formation and controlled the shape and size of the EPS-AuNPs, while frustule is related to the silica-AuNPs	Schröfel et al. (2011)
Model biomolecules				
Alginate		AgNPs	Alginate was employed as both reductant and stabilizer in the synthesis of AgNPs of different size and shape, and AuNPs	Sharma et al. (2012)
				Bhagyaraj and Krupa (2020)
		AuNPs		Zhao et al. (2017)
Glucose		AgNPs	Glucose was employed as both reductant and stabilizer in the synthesis of AgNPs of different size and shape, and AuNPs	Pattnaik et al. (2023)

(Continued on following page)

TABLE 2 (Continued) Selected examples illustrating the involvement of phytoplankton secretions in metal-containing ENPs formation from dissolved metals.

Biomolecules	Phytoplankton species	ENPs	Comments	References
		AuNPs		Suvarna et al. (2017)
		CuNPs		Granata et al. (2019)
Amino acids		AgNPs	Tyrosine and tryptophan were involved in the synthesis of AgNPs, as reductant and capping agent	Shankar and Rhim (2015)
		AuNPs	Twenty amino acids were involved in the synthesis of AuNPs, as reductant and capping agent, showing the possible role of different amino acids in new M NPs	Maruyama et al. (2015)
		CuNPs	The structural diversity of amino acids enabled a preparation of Cu nanomaterials with variety of structure as nanoparticles, nanorods and nanocrystals	Yu et al. (2015)

could be affected indirectly *via* the interaction of the released metal ions with cells (Naveed et al., 2019).

6 Phytoplankton secretions, ENPs uptake and biotic transformations

Both intracellular and cell surface-mediated physical and chemical transformations of ENPs by phytoplankton species have been reported (Chen et al., 2019; Spurgeon et al., 2020). They include heteroaggregation of ENPs and cells, cellular dissolution, sulfidation, redox transformations etc. However, the influence of the phytoplankton secretions on these processes is overlooked. Few examples found in the literature demonstrate that the EPS can reduce the uptake of the ENPs by phytoplankton species (and thus ENPs cellular transformations). The exudates secreted by *S. obliquus* reduced cellular uptake of the eco-coronated amine and carboxyl functionalized CdSe/ZnS QDs inducing aggregation and altering the surface charge of the QDs (Chakraborty et al., 2021). The EPS of *C. pyrenoidosa* reduced the amount of the internalized anatase and rutile TiO₂NPs (Gao et al., 2021). The EPS from green alga *Scenedesmus* sp. formed corona on cemented tungsten carbide cobalt (WC-Co) NPs and CoNPs and decreased the toxicity of these ENPs on *Daphnia magna* (Ekvall et al., 2021). Bound EPS have shown a barrier effect on the toxicity of AgNPs nanoparticles relative to the released Ag (I) ions. However, they did not exhibit a distinct effect on the silver accumulation by AgNPs and Ag (I) in *C. vulgaris* (Zheng et al., 2019). Nevertheless, both soluble and bound EPS have been shown to modify the attachments of the ENPs to the phytoplankton cells. This alteration occurs through modification of the steric and electrostatic interactions between the ENPs and the cells (Natarajan et al., 2021). Similarly, the intact cells of *C. pyrenoidosa* with EPS was characterized with greater adsorption of both citrate and PVP coated AgNPs in comparison with cells with removed EPS (Zhou et al., 2016). Interestingly, the importance of the EPS thickness on cells of *C. reinhardtii* in AgNPs internalization have been demonstrated (Yan et al., 2021). The presence of EPS on the *C. pyrenoidosa* cell surface promoted the heteroaggregation between anatase and rutile TiO₂NPs with primary size of 25 nm, and algal cells. The amount of the TiO₂NPs accumulated on cell surface was higher in comparison to the algal cells with removed EPS

(Gao et al., 2021). Moreover, the EPS from *Chlorella* sp. increased the sedimentation of TiO₂NPs in mixture with polystyrene NPs thus contributing to the reduction of the number of ENPs interacting with the organism and consequently reducing the biouptake the TiO₂NPs (Natarajan et al., 2023). The presence of soluble and bound EPS induced heteroaggregation by forming EPS-NPs aggregates with cells of cyanobacterium *Microcystis aeruginosa* (Yang et al., 2018). To the best of our knowledge, no study has reported the role of the phytoplankton secretions in the cellular transformations of metal-containing ENPs, including processes like cellular dissolution, sulfidation, redox transformations exist.

7 Conclusions and research gaps

An examination of the current state of the research highlights that different constituents of the phytoplankton secretions play an important, yet incompletely understood, role in shaping the behavior of metal-containing ENPs in aquatic environment. These secretions interact with and adsorb on the ENPs, forming a biomolecular corona and altering their behavior. The formation of biomolecular corona on ENPs involves hydrodynamic, electrodynamic, electrostatic, steric, and bridging interactions as previously comprehensively reviewed for eco-corona formed by NOM on the ENPs (Pulido-Reyes et al., 2017). In most cases the adsorbed secretions, in particularly the EPS have been shown to stabilize the ENPs. As for the other components of the NOM, the adsorption and effect on the colloidal stability are dependent on the i) chemical composition, primary surface coating, surface charge, surface area and hydrophobicity; ii) chemical composition of the secretions, molecular weight and aromaticity, isomeric nature, which in turn are dependent on the phytoplankton species, algal growth stage and environmental parameters. The current body of literature primarily focusses on the interactions between TiO₂NPs or ZnONPs, and EPS isolated from green algae, diatoms and cyanobacteria. There is a limited amount of literature concerning the influence of exometabolites on the stability of the ENPs, despite their presumably important role in the phycosphere. Further attention and research are warranted in this area to better understand their impact.

Some discrepancy in the information exists concerning the role of the phytoplankton secretions in the ENPs dissolution, showcasing both decrease and increase in the dissolution rates. Limited studies have explored the role of phytoplankton secretions in other transformation processes, such as sulfidation. Further deep investigations are essential to understand how phytoplankton secretions contribute to both the dissolution and sulfidation of ENPs within aquatic environment.

Most of the up-to-date knowledge largely stems from the experiments involving whole EPS, isolated polysaccharides, or proteins from specific phytoplankton species and model compounds. As a result, the role of some EPS components, including nucleic acids, lipids, uronic acid, and inorganic compounds, all part of the phytoplankton secretome, remains unexplored, despite their likely influence on the stability, dissolution and transformation of metal-containing ENPs. In addition, major secretome components such as thiols and amino acids exist within concentrations ranging from ng L^{-1} to $\mu\text{g L}^{-1}$ in surface water. Their significance in modulating the aforementioned processes in the presence of the EPS or humic-like components of NOM (typically present in few mg L^{-1}) still requires a conclusive demonstration.

Phytoplankton secretions serve mediators in the synthesis of metal-containing nanoparticles from the dissolved ions. Nevertheless, the majority these studies are conducted within biotechnology context using high metal concentration than those found in the aquatic environment. Thus their contribution to the metal reduction in the natural environment is to be explored. In addition, the role of the EPS and exometabolites released by algae, as well as the importance of reductive mechanism for ENPs formation from metal ions, its environmental significance for the ENP biogeochemistry is to be further explored. It is currently unclear if the phytoplankton could be considered as a “source” of ENPs in metal contaminated environment and what will be the environmental relevance in the nanoparticle production. Further studies are, thus, necessary to understand the underlying mechanisms and their contribution in natural environment, where ENPs are present in quite low concentrations is still to demonstrate.

Exposure of phytoplankton species to ENPs leads to changes in the concentration and composition of secreted biomolecules. These alterations might act as a detoxification response and defensive pathway. To deepen our understanding it is crucial to explore the underlying regulatory mechanisms, encompassing changes in exometabolomics of phytoplankton due to ENP exposure.

In conclusion, the lack of understanding on the influence of the phytoplankton secretions on the destiny of the ENPs is a major

knowledge gap in the aquatic nanoscience. Considering the feedback of aquatic organisms and the control they exert in shaping the fate (and impact) of ENPs in the aquatic environment is necessary for: i) better understanding of drivers of environmental transformations of ENPs and their mechanisms and ii) reduction of the uncertainties and the improved assessment of the effect of the ENPs on the phytoplankton cells, given that the chemical conditions and ENPs stability will be strongly affected by these secretions in the microenvironment surrounding phytoplankton cells in comparison with bulk waters.

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