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▶ **To cite this version:**

Alice Pradel, Charlotte Catrouillet, Julien Gigault. The environmental fate of nanoplastics: What we know and what we need to know about aggregation. NanoImpact, 2023, 29, pp.100453. 10.1016/j.impact.2023.100453 . insu-03962181

HAL Id: insu-03962181

https://insu.hal.science/insu-03962181

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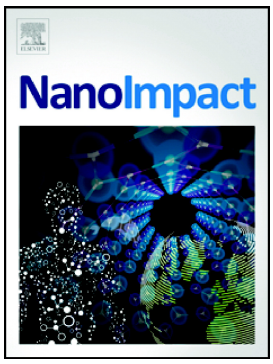

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PII: S2452-0748(23)00004-6

DOI: https://doi.org/10.1016/j.impact.2023.100453

Reference: IMPACT 100453

To appear in: *NANOIMPACT*

Received date: 20 October 2022

Revised date: 17 January 2023

Accepted date: 20 January 2023

Please cite this article as: A. Pradel, C. Catrouillet and J. Gigault, The environmental fate of nanoplastics: What we know and what we need to know about aggregation, *NANOIMPACT* (2023), https://doi.org/10.1016/j.impact.2023.100453

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The environmental fate of nanoplastics: What we know and what we need to know about aggregation

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Abstract

The presence of nanoplastics in the environment has been proven. There is now an urgent need to determine how nanoplastics react in the environment and to assess the risks they may pose. Here, we examine nanoplastic homo- and heteroaggregation, with a focus on environmentally relevant nanoplastic particle models. We made a systematic analysis of experimental studies, and ranked the environmental relevance of 377 different solution chemistries, and 163 different nanoplastic particle models. Since polymer latex spheres are not environmentally relevant (due to their monodisperse size, spherical shape, and smooth surface), their aggregation behavior in natural conditions is not transferable to nanoplastics. A few recent studies suggest that nanoplastic particle models that more closely mimic incidentally produced nanoplastics follow different homoaggregation pathways than latex sphere particle models. However, heteroaggregation of environmentally relevant nanoplastic particle models has seldom been studied. Despite this knowledge gap, the current evidence suggests that nanoplastics may be more sensitive to heteroaggregation than previously expected. We therefore provide an updated hypothesis about the likely environmental fate of nanoplastics. Our review demonstrates that it is essential to use environmentally relevant nanoplastic particle models, such as those produced with top-down methods, to avoid biased interpretations of the fate and impact of nanoplastics. Finally, it will be necessary to determine how the heteroaggregation kinetics of nanoplastics impact their settling rate to truly understand nanoplastics' fate and effect in the environment.

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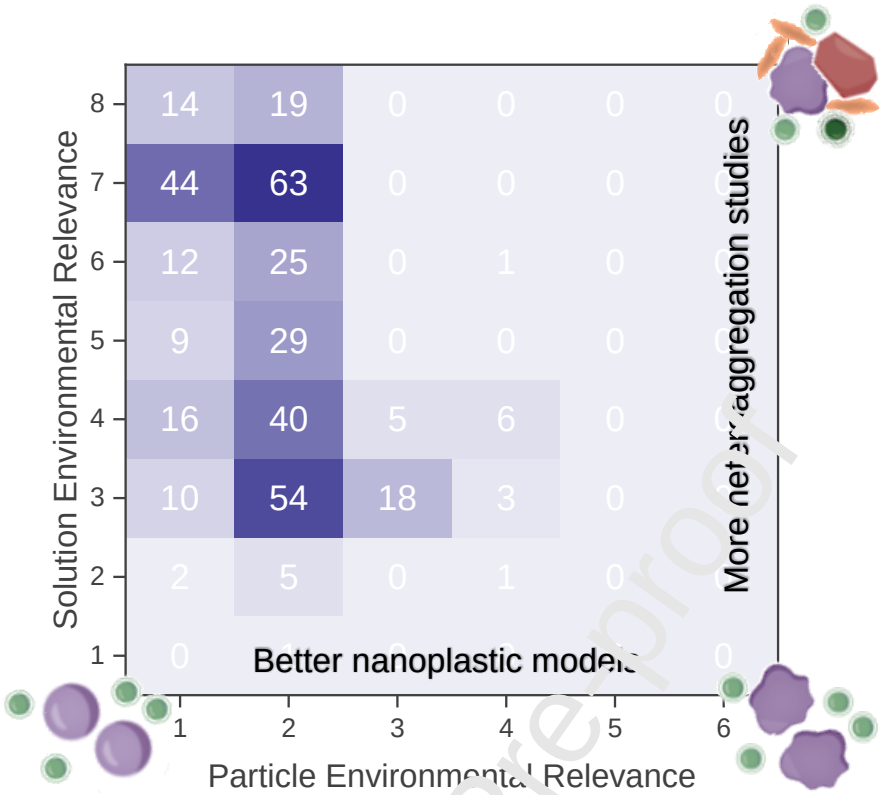
Graphical Abstract



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1. Introduction

Plastics have become an inherent component of the modern industrial world, bringing both significant societal benefits and widespread environmental contamination (Andrady and Neal, 2009). By 2015, plastics were the third most-produced material, with a production estimated at 8.3 billion metric tonnes (Geyer et al., 2017), roughly twice the mass of all animals on Earth (Elhacham et al., 2020). Plastic debris originates from mismanaged plastic waste and from the use and aging of plastic materials (e.g., textiles, tire wear, paint coatings, etc.), which incidentally release plastic particles (Mitrano and Wohlleben, 2020). As plastics degrade, they produce microplastics (1 µm to 5 mm) (Chamas et al., 2020; Efimova et al., 2018; Gewert et al., 2015; Song et al., 2020), and nanoplastics (<1 µm) (Dawson et al., 2018; Gigault et al., 2016; Lambert and Wagner, 2016; Mattsson et al., 2021). Consequently, all of the Earth's environmental compartments are contaminated by microplastics: including freshwater lakes (Eriksen et al., 2013), rivers (Lechner et al., 2014), sediments (Klein et al., 2015), soils (Zubris and Richards, 2005), seas, oceans close to anthropogenic activity (Thompson, 2004), and those that are more remote (Lusher et al., 2015), as well as some of the deepest ocean sediments (Peng et al., 2020), the atmosphere (Allen et al., 2019), and the biosphere (Provencher et al., 2019). Nanoplastics are present in soils (Wahl et al., 2021), freshwater (Li et al., 2022), seawater (Materić et al., 2022a; Ter Halle et al., 2017; Li et al., 2022), sea ice (Materić et al., 2022b), and snow (Materić et al., 2021). They are suspected to be present in many other environmental compartments also, but it is technically challenging to extract, characterize, and quantify plastic particles smaller than ~20 µm from environmental matrices (Ivleva, 2021).

As nanoplastics have only recently been discovered in the environment (Gigault et al., 2016; Ter Halle et al., 2017), and they are difficult to quantify in environmental matrices (Gigault et al., 2021), their effects on organisms and environmental processes is less clear than for microplastics. The colloidal properties of nanoplastics (Brownian motion and high surface reactivity) make them prone to aggregation (Gigault et al., 2021). They are also prone to leach additives and move through physiological barriers (Allan et al., 2022; Paul et al., 2020) more quickly than larger plastic particles, which can increase organisms' exposure to toxins, compared to the dangers of micro- and macroplastics that we knew about before. Consequently, the scientific community, the public, and policymakers expressed the urgent need to elucidate the environmental fate and impact of nanoplastics (Allan et al., 2020; GESAMP, 2015; SAPEA, 2019).

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In this study, we elucidate relevant points about the nanoplastics ecological crisis (Koelmans et al., 2017; Persson et al., 2022; Rockström et al., 2009):

i) what is known about the environmental fate of nanoplastics;
ii) what further needs to be known (including more research on aggregation mechanisms); and
iii) how to improve our understanding in a targeted way.

It is essential to assess the processes by which nanoplastics are transformed, transported, and accumulated in the environment, to assess their environmental fate. This study proposes up-to-date hypotheses of where nanoplastics are located, and where they accumulate in the environment based on a systematic review of nanoplastic homo- and heteroaggregation rates and processes. Aggregation (i.e., both homo- and heteroaggregation) is the focus of this study, because it is the primary process that dictates the transport of colloidal species in the environment. We focus on the behavior of environmentally relevant nanoplastic particle models. We interpret experiments through classical colloidal theory and compare them to studies of engineered nanomaterials. We also highlight a few knowledge gaps and identify strategic and efficient ways to move research forward.

2. Nanoplastic transport processes

2.1. The colloidal properties of nanoplastics

With decreasing size, particles transition away from motion dictated by gravitational forces (i.e., macro- to microparticle behavior) and towards motion dictated by Brownian motion and intermolecular forces (i.e., colloidal behavior) (Elimelech, 1998; Hiemenz and Rajagopalan, 1997). The transition to Brownian motion in water occurs when carbon-based particles are smaller than ~1 µm (Hiemenz and Rajagopalan, 1997). Given a favorable (attractive) balance of surface interactions and hydrodynamic forces, nanoplastics sorb onto particles and/or molecules. The increase in dimension caused by the sorption of such species onto nanoplastics can cause them take on a gravity-driven motion again, the same as larger particles. Therefore, the colloidal stability of nanoplastics (i.e., their capacity to remain dispersed) is the primary determinant of their environmental fate (Filella, 2007; IUPAC, 1997; Stumm and Morgan, 1996), and the focus of this review. The review focuses on nanoplastic stability in the hydrosphere, since water has been identified as one of the major transport pathways of plastic debris (Brahney et al., 2021). Atmospheric transport processes will not be investigated here, because there are not yet many studies on this topic and since atmospheric plastics are

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likely to re-enter the hydrosphere through precipitation (Allen et al., 2022, 2019; Bergmann et al., 2019; Wik and Dave, 2009).

2.2. *Physicochemical properties of environmental compartments*

The stability of colloids is sensitive to the interplay between the properties of the dispersed phase (colloid) and the continuous phase (fluid) (Buffle et al., 1998; Filella, 2007; Hiemenz and Rajagopalan, 1997; Stumm and Morgan, 1996). It is therefore practical to categorize the environment into different compartments, defined by common physicochemical properties, to predict the fate of nanoplastics. Key parameters to consider are the composition, concentration, shape, and size of colloids and the ionic composition, pH, temperature, and velocity gradients of fluids (Baalousha, 2017; Hotze et al., 2010; Peijnenburg et al., 2015). In the aqueous environment, nanoplastics are more likely to encounter naturally occurring species in concentrations ranging from μg L^{-1} to mg L^{-1} (Table 1) (Benner, 2002; Fraters et al., 2017; Libes, 2009; Stumm and Morgan, 1996), rather than other nanoplastics, since current and anticipated nanoplastic concentrations are currently in the range of pg L^{-1} to μg L^{-1} (Lenz et al., 2016; Li et al., 2022; Materić et al., 2022). Therefore, the stability of nanoplastics is mainly affected by the size and composition of natural species and the concentration and valence of electrolytes. In contaminated environments, anthropogenic species such as pesticides and pharmaceuticals can also interact with nanoplastics to modify their environmental fate and their toxicity (Velzeboer et al., 2014, Zarfl and Matthies, 2010).

Natural species have historically been classified based on size, as either solutes (<1 nm and in thermodynamic equilibrium with the solvent), colloids (1 nm to 1 μm), or particles (>1 μm) (Buffle, 1992; Lead and Wilkinson, 2007; Stumm and Morgan, 1996). However, operational definitions have been adopted and consider molecules that pass through 0.45 μm or 0.22 μm filters as "dissolved". This definition is problematic since this size cut-off randomly splits the colloidal fraction into the dissolved and particulate fractions. Since the literature reviewed does not distinguish particulate, colloidal and truly dissolved species, we chose to remain coherent with the terminology used in the reviewed articles. Therefore, we define dissolved species as electrolytes and molecules smaller than 0.22 or 0.45 μm. Particulate species are defined as solid species with defined geometrical dimensions and a high molar mass (approximately > 10^6 g mol^{-1}). This broadened definition includes species smaller than 0.22 μm (e.g., engineered nanomaterial).

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A range of processes can lead to the aggregation of colloids in environmental systems. The probability of aggregation occurring can be predicted by the classical DLVO (Derjaguin Landau Verwey Overbeek) theory of colloidal stability and its extended version (XDLVO), which model surface interaction energies. The DLVO theory states that colloidal particles can aggregate when the repulsive electrostatic force is less strong than the attractive van der Waals force (Derjaguin and Landau, 1941; Verwey et al., 1948). Repulsive electrostatic force originates from the overlapping of the electronic double layer surrounding particles of equal charge. The global (i.e., average) surface charge of incidental nanoplastics is negative (El Hadri et al., 2020; Blancho et al., 2022).

The charge of particles is pH-dependent if it originates from hydrolyzable surface functional groups, such as carboxylic acids. As pH nears the point zero of charge, the absolute zeta potential decreases, causing a decrease in electrostatic repulsion (Israelachvili, 2015; Stumm and Morgan, 1996). Increasing ionic strength (IS) also screens the electrostatic repulsion between particles of equal charge, thereby reducing their stability. The XDLVO incorporates other interactions, such as hydrophobic (Lewis Acid-Base) interactions which originate from the fact that water molecules form intramolecular hydrogen bonds with other water molecules and with hydrophilic surfaces (e.g., carboxylic acids and phenols). Hydrophobic nanoplastics tend to be less stable in water, and their surface tend to seek other hydrophobic species. However, not all aggregation processes are covered by the DLVO theory. For example, multivalent counterions (i.e., ions with an opposite charge than the particle) can also attract two oppositely charged surfaces and cause ion-specific interactions with surfaces (Labbez et al., 2009). As will be discussed below, the surface roughness of particles and surfaces and steric interactions are not entirely integrated in XDLVO models.

Table 1 presents typical concentrations of major chemical elements in surface water for five generic types of rivers, which were grouped to reflect a diversity of geologies, soil types, land use and climates (Hammes et al., 2013), as well as two soil pore water types (Fraters et al., 2017), and seawater (Benner, 2002; Libes, 2009). As illustrated in Figure 1A and B, due to electrostatic repulsion, nanoplastics with a given electronegativity and hydrophobicity are more stable in fresh water types with low IS and with many monovalent ions (e.g., Rivers 1&2 in Table 1) compared to brackish water (e.g., River 6 in Table 1) or seawater (Table 1).

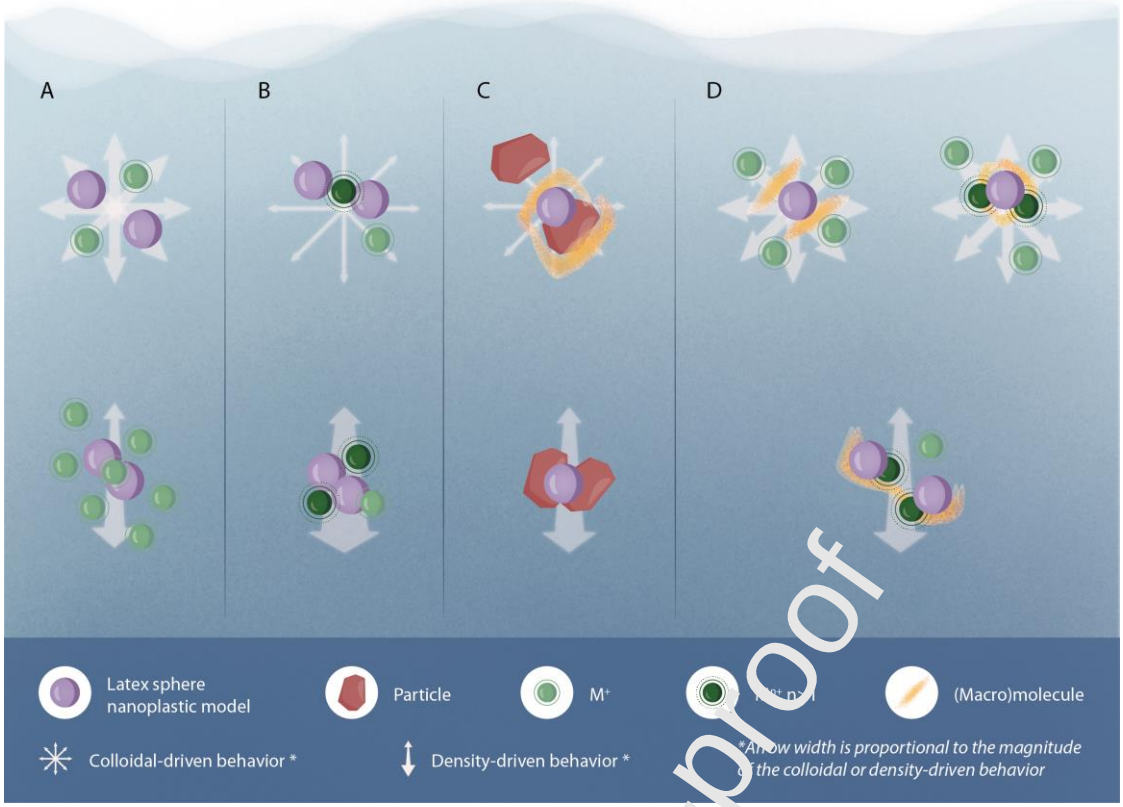

Figure 1: Nanoplastic aggregation pathways investigated in the literature. A) Homo-aggregation caused by electrostatic screening at high ionic strength. B) Enhanced homo-aggregation due to electrostatic screening and cation bridging by multivalent cations C) Hetero-aggregation of nanoplastics with particulate species (bottom) and reduced hetero-aggregation in the addition of (macro)molecules (top) D) Destabilization by high molecular weight (macro)molecules bridging nanoplastics (bottom), stabilization by (macro)molecule at high IS dominated by monovalent salts (top left) and stabilization with a complete coating of (macro)molecules in the presence of divalent cations (top right)

The effect of (macro)molecules on nanoplastic stability depends on the nature of the (macro)molecules and their concentration, as well as the type and concentration of electrolytes (Buffle et al., 1998; Yu et al., 2018). While natural organic matter generally has an overall negative charge, some humic substances and proteins contain positively charged sections (Buffle et al., 1998; .Z. Dong et al., 2020; Dubin et al., 1994; X. Li et al., 2021b; Wheeler et al., 2021). On one hand, negatively charged molecules entirely sorbed onto a nanoplastic particle, can stabilize it against aggregation by electrostatic and steric repulsion (i.e., the reduction of entropy and increase in osmotic repulsion as two layers of molecules overlap) (Napper, 1977; Fritz et al., 2002) (Figure 1D, top). This layer of sorbed materials, called an eco-corona, is formed spontaneously as nanoplastics enter the environment (Wheeler et al., 2021). It lends nanoplastics new properties (i.e., size, shape, surface charge & composition), which can modify its surface interactions and toxicity (Kihara et al., 2020; Paul et al., 2020). On the other hand, macromolecules can destabilize nanoplastics when their sorption reduces their diffusion coefficient and increases their gravity-driven behavior (Buffle et al., 1998; Enfrin et al., 2019). This

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occurs particularly when (macro)molecules form bridges between two particles (Fritz et al., 2002) (Figure 1D, bottom). These processes will cause nanoplastics to remain dispersed in water types that contain high dissolved organic carbon (DOC) content and low alkalinity, such as in Rivers 2 and 3 (Table 1). However, this stabilization depends on the geographic and seasonal variability of organic matter concentrations (Stumm, 2003), as well as the chemical properties of the organic matter (Buffle et al., 1998).

Finally, particulate species (whether organic, mineral or a mixture of both) can act as surfaces onto which nanoplastics can be attracted and attached in a process called heteroaggregation (Figure 1C). As is the case for engineered nanomaterials, heteroaggregation destabilizes nanoplastics and can accelerate their settling (Li et al., 2016; Quik et al., 2014). Yet despite the importance of particles in the environment, measurement of particle concentrations in natural water is not standard practice and is sometimes only assessed indirectly, for example with measurements of turbidity or dry weight.

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*Table 1: Typical chemical characteristics of river water (Hammes et al., 2013), soil pore water (Fraters et al., 2017) and seawater (Benner, 2002; Stumm and Morgan, 1996). Ion concentration and ionic strength (IS) are in mmol L^{-1}, and dissolved organic carbon (DOC) concentration is in mg L^{-1} (*surface $^{+}$deep ocean). IS was calculated as* $\frac{1}{2}\sum_{i=1}^{n} z_i^2 n_i$

Type of water body	River water 1	River water 2	River water 3	River water 4	River water 5	River water 6	Soil pore water	Soil pore water	Seawater
Geology, climate and land use	Acidic rocks and moraine deposits. Alpine and Nordic regions. Pasture and grazing.	Acidic to neutral bedrocks and moraines. Pasture and grazing	Crystalline rocks. Agriculture	Calcareous rocks. Arid regions. Forestry and grazing.	Calcareous rocks and loess deposits. Agriculture.	Calcareous rocks and siliceous glacio-fluvial deposits. Some regions with high agricultural activity	Loess soil. Temperate maritime region. Pasture.	Loess soil. Temperate maritime region. Agricultural crops.	
Water characteristics	Low IS, DOC and alkalinity.	Low IS and alkalinity. Relatively high DOC concentrations.	Moderate alkalinity and IS. High concentrations of monovalent ions and DOC.	Higher Mg^{2+}, Ca^{2+} and HCO_3^- concentrations compared to Na^+ and K^+. Low DOC concentrations.	High alkalinity and IS.	High alkalinity, IS and SO_4^{2-} content.			High salinity. High concentration of multivalent ions. Low DOC concentrations
pH	7.31 ± 0.85	6.50 ± 0.78	7.11 ± 0.62	8.00 ± 0.48	7.98 ± 0.39	7.88 ± 0.40	7.46	8.42	7.7 to 8.3
[HCO_3^-]	0.109 ± 0.084	0.231 ± 0.142	1.16 ± 1.15	2.45 ± 1.46	4.00 ± 1.59	5.10 ± 2.69	-	-	2.33
[Cl^-]	0.020 ± 0.013	0.062 ± 0.091	0.362 ± 0.347	0.113 ± 0.111	0.542 ± 0.370	3.86 ± 12.3	0.477	0.382	546
[SO_4^{2-}]	0.021 ± 0.020	0.026 ± 0.021	0.154 ± 0.148	0.201 ± 0.291	0.543 ± 0.714	1.90 ± 3.30	0.189	0.221 to 0.546	28.25
[NO_3^-]	0.002 ± 0.004	0.004 ± 0.009	0.116 ± 0.163	0.040 ± 0.065	0.219 ± 0.221	0.332 ± 0.293	3.24	0.10 to 3.97	-
[K^+]	0.005 ± 0.005	0.012 ± 0.006	0.061 ± 0.048	0.022 ± 0.014	0.067 ± 0.038	0.237 ± 0.397	0.013	0.011 to 0.018	10.2
[Na^+]	0.040 ± 0.018	0.094 ± 0.074	0.389 ± 0.337	0.156 ± 0.145	0.515 ± 0.364	4.16 ± 15.81	0.561	0.244 to 0.309	468
[Mg^{2+}]	0.015 ± 0.013	0.041 ± 0.024	0.201 ± 0.151	0.316 ± 0.276	0.589 ± 0.428	1.31 ± 1.45	0.091	0.066 to 0.286	53.1
[Ca^{2+}]	0.050 ± 0.046	0.088 ± 0.057	0.573 ± 0.55	1.17 ± 0.71	2.09 ± 0.91	3.17 ± 2.14	1.63	1.45 to 3.57	10.3
DOC	1.84 ± 2.64	12.48 ± 9.79	11.05 ± 10.84	1.75 ± 1.99	4.6 ± 3.96	8.6 ± 6.5	4.8	4.4	0.7 to 1.0* 0.4 to 0.5$^+$
IS	0.25	0.43	2.3	3.16	6.47	16.5	6.8	4 to 10	≈700

2.3. Approaches to assess nanoplastic fate

Thorough assessment of the environmental fate of nanoplastics requires three complementary approaches:

i) Undertaking experiments that model the transport of nanoplastics in environmental systems; this approach can identify and quantify the processes that control the environmental fate of nanoplastics (Hendren et al., 2015).
ii) Numerically modeling the behavior of nanoplastics by combining the rates and probabilities obtained experimentally with estimates of nanoplastic concentrations; numerical simulations can either predict the environmental fate of nanoplastics (Besseling et al., 2017) or model all possible scenarios to determine the key processes controlling the fate of nanoplastics (Clavier et al., 2019).
iii) Quantifying and characterizing nanoplastics in environmental samples; this field data can be used to assess the validity of experimental and numerical studies.

These approaches have been used successfully to study natural, engineered, and incidental particles (Hochella et al., 2019). However, not all approaches are feasible for nanoplastics. For instance, characterization and quantification of nanoplastics in environmental samples is challenging because both nanoplastics and natural organic matter (NOM) are carbon-based, and NOM is orders of magnitude more abundant than nanoplastics (c.f.: Table 1). While most methods cannot quantify nanoplastics in environmental matrices due to the presence of NOM (Gigault et al., 2021; Ivleva, 2021), recent analytical developments have enabled such quantification (Materić et al., 2022a; Li et al., 2022).

Therefore, experimental approaches are currently the dominant way of investigating the environmental fate of nanoplastics. Indeed, 82 out of the 84 studies reported here were experimental studies. Of the two remaining studies, one characterized nanoplastics in the environment and the other modeled nanoplastic interaction with a peptide. For the first field study, polyethylene, polystyrene and polyvinyl chloride nanoplastics were extracted from contaminated soil. This study showed that the nanoplastics formed heteroaggregates with naturally occurring species, but did not quantify nanoplastics (Wahl et al., 2021). The numerical modeling study showed that oligoalanine, a small model peptide, can undergo conformational changes (denaturation) when it aggregates with low molecular weight PE and polyamide (Nylon) particles (Hollóczki, 2021). The insights obtained from field samples and numerical models concur with the experimental

observations described below. However, more evidence from these approaches would be beneficial to develop a complete understanding of nanoplastic fate. The following section first highlights the major trends in how experiments were designed, then describes the main findings of the experimental studies.

3. Lessons learned from experiments with nanoplastic particle models

As when studying other nanomaterials in the environment (Dale et al., 2015; Hammes et al., 2013), two complementary types of experimental designs are used for nanoplastics: 1) those that aim to gain insight into aggregation mechanisms by incrementally modifying certain parameters of the particle (e.g., size, type of function) or the matrix (e.g., cations, anions, pH); and 2) those aim to mimic the fate of nanoplastics by selecting environmentally representative nanoplastic particle models and natural matrices (e.g., natural river water, seawater).

On one hand, mechanistic studies identify conditions that cause aggregation, and provide explanations for more environmentally relevant studies. On the other hand, experiments performed with environmentally realistic conditions can be extrapolated to true environmental conditions and can validate mechanistic studies. To bridge the gap between these two types of experimental designs and to better identity where more knowledge is needed, we mapped the environmental relevance of the experiments performed, based on the proposed Framework for Relevance and Methods Evaluation (FRAME) (Surette et al., 2021).

3.1. Environmental relevance of nanoplastic particle models and solution chemistries

To assess the nature of the evidence gathered, we reviewed the 82 experimental studies, which assessed the environmental relevance of 163 particles and 377 solution chemistries (i.e., different electrolytes, dissolved and particulate species, without accounting for the different concentrations and pH). The environmental relevance was mapped in a two-dimensional matrix that included one score for the particles' environmental relevance and one score for the solution's environmental relevance. The number of experiments performed with a specific combination of these scores was reported in the matrix (Figure 2 and detailed in Tables 2 and 3).

The more diverse the mixture of species in a solution, the better it mimics the real environment. This forms the basis of our environmental relevance score. The criteria used to develop the score are primarily a function of the electrolyte composition. The presence of each (macro)molecule or particle adds one point to the score of environmental relevance (Table 2). Artificial water is defined as a mixtures of several electrolytes which mimic natural water. Biological growth media, which are used to culture organisms (e.g., cells, algae etc.) are considered to be artificial water, since they contain a mixture of several electrolytes. In some cases they contain organic molecules, such as vitamins. However, these are present in low concentrations, so the score remained 5, unless (macro)molecules or particles were added. Finally, natural water has a score of 7. Since most natural water types were filtered before being used, the score of environmental relevance was also increased to 8 when (macro)molecules and/or particles were added. While this ranking does not precisely measure increases in environmental relevance, it allows a rapid assessment of the types of experiments performed.

Table 2: Details of parameters used for the solution environmental relevance scores

Solution Environmental Relevance Score	Solution Properties
1	DI water only
2	DI water, with (macro)molecules and/or particulate species
3	One electrolyte only (e.g., just NaCl)
4	One electrolyte with (macro)molecules and/or particulate species
5	Artificial water only
6	Artificial water with (macro)molecules and/or particulate species
7	Natural water only
8	Natural water with added (macro)molecules and/or particulate species

The environmental relevance scores for nanoplastic particle models (Figure 2 and Table 3) were based on our understanding of the processes that generate incidental (i.e., secondary) nanoplastics in the environment. Primary nanoplastics (e.g. intentionally produced in the medical or agricultural sectors) were excluded, since their total mass in the environment is expected to be negligible compared to the incidentally released nanoplastics (Gigault et al., 2021). Nanoplastic particle models are either synthesized with bottom-up or top-down methods.

The bottom-up approach uses molecular components as starting material and links them with chemical reactions to form nanostructures. Lower scores were given to particle models produced from bottom-up synthesis methods for two reasons. First, these methods use surfactants and/or additives which are not expected in incidental

nanoplastics. The presence of surfactants and additives in the solution reduces the affinity of nanoplastics for other surfaces by masking surface charges and/or causing steric repulsion (Fan et al., 2015; Jódar-Reyes et al., 2006; Romero-Cano et al., 2001). Therefore, this modifies aggregation behavior in experiments and leads to erroneous hypotheses about the environmental fate of nanoplastics. Second, the most common bottom-up synthesis method, emulsion-polymerization, generates smooth, spherical particles with monodisperse sizes, called latex spheres. However, incidental nanoplastics are expected to have rough surfaces, to be non-spherical and polydisperse since they originate from a variety of primary materials and are generated by a variety of processes (e.g., photo-degradation or mechanical fragmentation).

Concerning particles produced from bottom-up methods, some studies use latex spheres grafted with chemical moieties such as carboxylate, amine, and sulfonate. We name latex spheres according to their composition, the functional group that they contain, and their charge. For example, PSL-COOH(-) is a negatively charged polystyrene latex sphere with carboxylic acid (COOH) functional groups on its surface. Each surface functional group has specific ionization and complexation constants. This generates a specific surface charge depending on the solution composition (mainly its pH, IS and the presence of ions that can form complexes). Therefore, the surface functionalization of nanoplastics governs the environmental relevance of studies.

- Particles produced from bottom-up processes that have sulfonate (SO_3) and amine (NO_2) surface-functionalization were given a score of 1. Additionally, a score of 1 is given to latex spheres that are stabilized by sulfate (SO_4) ions (e.g., sodium dodecyl sulfate), although the distinction between SO_3 and SO_4 is not always clearly indicated. Sulfur is not representative of nanoplastics since it is not a component of plastic polymers, nor is it generated during mechanical abrasion, photo-oxidation or hydrolysis of plastics (Mattsson et al., 2015). Nitrogen is a component of a few polymers (e.g., polyurethane, polyamide, acrylonitrile and acrylonitrile butadiene styrene) (Geyer et al., 2017; International Organization for Standardization, 2013). However, amine functional groups are often grafted in high surface concentrations onto polymer latex spheres compared to concentrations expected in environmental nanoplastics (Molecular Probes, 2004), which warrants giving them a low score of environmental relevance.
- Nanoplastic particle models synthesized without surface functionalization (NF for non-functionalized) or with carboxylic functional groups have a score of 2,

since nanoplastics generated from mechanical degradation retain their original polymer chemistry and those formed by photo-oxidation (and to a lesser extent digestion, and hydrolysis) have carboxylic functional groups (Gewert et al., 2015; Rowenczyk et al., 2020).

- Particles produced by bottom-up methods and that were aged in a way that mimics environmental aging processes (e.g., UV-irradiation) have a score of 3.

The top-down approach starts with large objects and reduces their dimensions (generally with physical methods) to achieve nanoscale materials (Cao and Wang, 2004). The environmental relevance scores of nanoplastic particle models increases when they are produced from top-down methods since those methods mimic environmental degradation processes. Nanoplastic particle models generated with top-down processes from pre-production plastics or un-aged plastic objects have a score of 4. Nanoplastic particle models generated with top-down methods using plastics found in the environment have a score of 5, since they are formed by environmental degradation and transformation processes. The highest score, 6, was given to nanoplastics extracted from the environment.

Table 3: Details of parameters used for the particle environmental relevance scores

Particle Environmental Relevance Score	Particle Properties
1	Bottom-Up, NH_2 or SO_3
2	Bottom-Up, non-functionalized (NF) or COOH
3	Bottom-Up particles aged
4	Top-Down from pristine plastic
5	Top-Down from environmental plastic
6	Environmental nanoplastic

Using this classification, Figure 2 reveals that :

- There is a consistent lack of environmentally relevant nanoplastic particle models: 91% of the experiments used non-aged nanoplastic particle models produced by bottom-up processes (particle environmental relevance scores of 1 and 2).
- Particles produced with bottom-up processes (scores 1 and 2) have been studied in a range of solution chemistries, to understand mechanisms and also to mimic environmental conditions.

- Only 6% of nanoplastic particle models produced from bottom-up methods were aged (score 3). 3% of studies used nanoplastic particle models produced with top-down methods and un-aged plastics (score 4).
- No experiment was performed with particle models produced with top-down methods from environmental plastic (score 5). Nor were experiments performed with real nanoplastics (score 6) since these cannot yet be extracted from environmental matrices for experimental investigation.

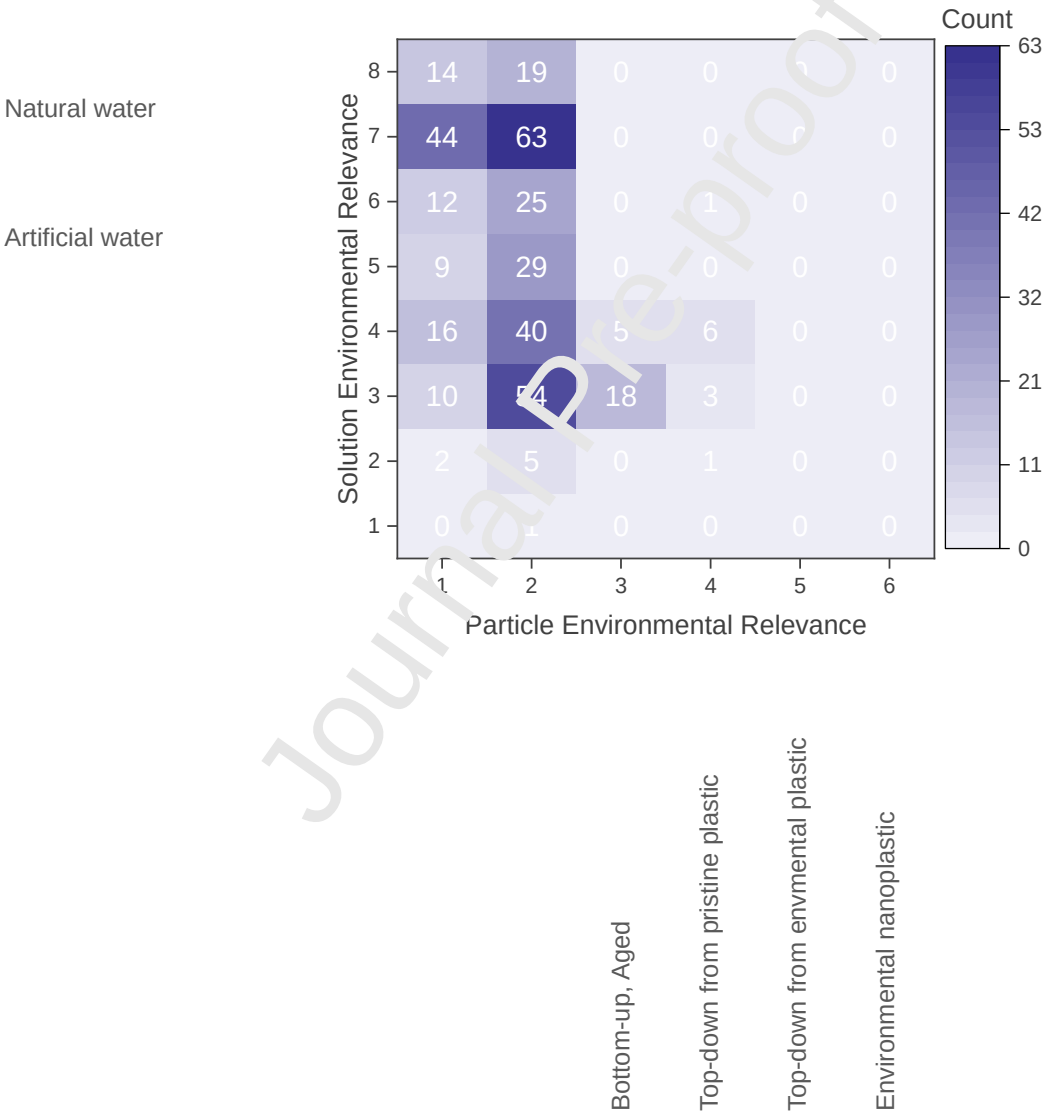

Figure 2: Two-dimensional matrix illustrating the number of times aggregation data was obtained from a given combination of particle environmental relevance score and solution environmental relevance score.

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The chemical composition of the nanoplastic dispersions is not environmentally relevant because 83% of the polymer latex spheres dispersions contained surfactants (80% of the nanoplastic dispersions). Furthermore, the composition of the nanoplastic particle models does not reflect the composition of plastic debris. As illustrated in Figure 3, 94% of nanoplastic particle models are composed of PS, and only 6% of plastic waste is composed of PS. Conversely, less than 2% of nanoplastic particle models were composed of either polypropylene (PP) or polyethylene (PE), although these polymers compose about half of the plastic waste generated (Geyer et al., 2017) and are the dominant types of plastic polymer found in the environment (Schwarz et al., 2019).

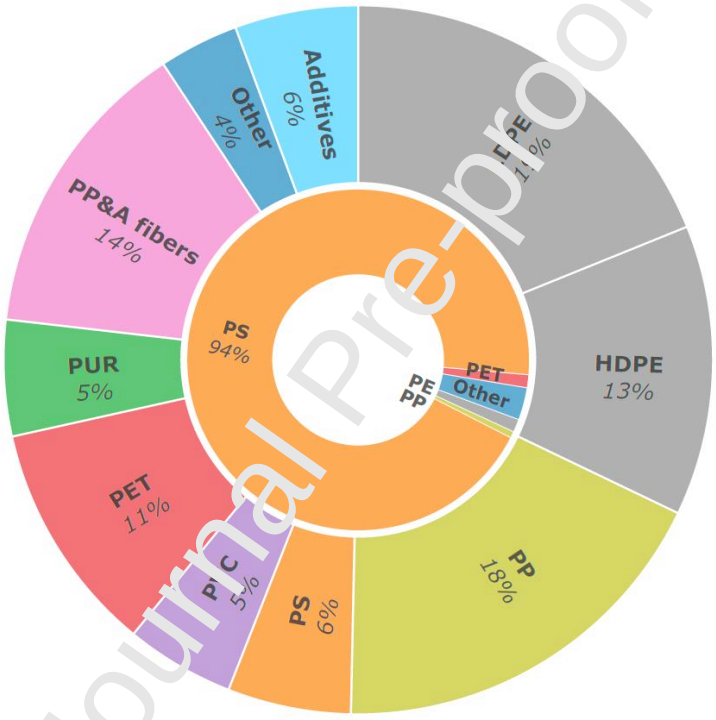

Figure 3: Distribution of the composition of nanoplastic particle models used in the reviewed studies (inner circle, with PET = 1% , PE = 1%, PP = 1% and Others = 3%) and of plastic waste composition in 2015 according to Geyer et al (2017) *(outer circle).*

55% of latex spheres used in the literature were functionalized. Carboxylic and amine functional groups were the most common (24% and 26%, respectively). Four studies artificially aged PSL particles by photo-oxidation to increase their environmental relevance (Liu et al., 2019; Y. Mao et al., 2020; Wang et al., 2020; Xu et al., 2021). While these particles were increasingly hydrophilic and had a rougher surface, compared to the original PSL, they generally remained spherical (Figures 4a and Figure 4b).

Six nanoplastic particle models were produced using top-down methods: two nanoplastic particle models were produced from laser ablation of un-aged PET and PS (Magrì et al.,

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2018; Yu et al., 2019), while four fragmental nanoplastic particle models were produced from mechanical abrasion of un-aged polymers (Astner et al., 2020; S. Dong et al., 2020; Pradel et al., 2021; Venel et al., 2021). Astner et al. (2020) produced fragmental nanoplastic particle models from a biodegradable agricultural mulch composed of polybutyrate adipate-co-terephthalate (PBAT). Dong et al. (2020) studied fragmental PET, whereas Venel et al. (2021) and Pradel et al. (2021) studied fragmental PS particles, using the same method as El Hadri et al. (2020).

Since top-down methods are less controlled than emulsion-polymerization, the morphology of the particles is more heterogenous than that of latex spheres. This is illustrated in Figure 4, which shows high polydispersity in sizes and the irregular shapes and surface roughness of the fragmental PS nanoplastics (Fig. 4c), compared to aged (Fig. 4b) and non-aged PSL (Fig. 4a). PBAT nanoplastic particle models have a surface roughness of 12 nm, which is significantly higher than PSL's surface roughness of 1 nm (Astner et al., 2020). This roughness can increase the surface area onto which dissolved species can sorb, thereby modifying the sensitivity of particles to dissolved species. Furthermore, top-down processes do not permit a controlled surface chemistry. This explains the small but significant differences in zeta potential and stability of fragmental PS nanoplastics produced using the same method (El Hadri et al., 2020; Pradel et al., 2021). So nanoplastic particle models produced from top-down processes must be characterized in depth to gain thorough understanding of what particle properties (e.g., charge, roughness, hydrophobicity) control their behavior. Furthermore, modeling the surface interaction energies of particles that are non-spherical and have rough surfaces, requires the use of the surface element integration (SEI) method (Huang et al., 2010; Vold, 1954). So far, to the best of our knowledge, the SEI method is only applicable to the van der Waals and electrostatic forces (classical DLVO) and does not integrate hydrophobic forces (XDLVO).

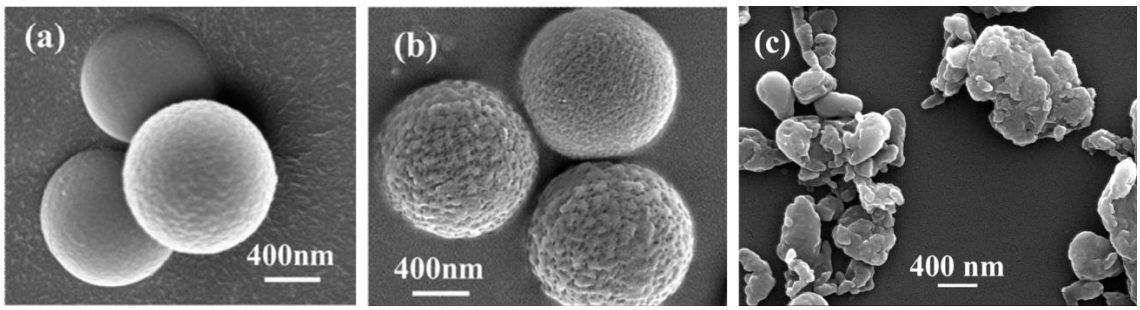

Figure 4: SEM images of a) non-aged PSL-NF(-), b) PSL-NF(-) that were aged by UV-irradiation and c) fragmental nanoplastic particle models produced from mechanical abrasion of pre-production PS pellets

using the method of El Hadri et al. (2020) *Figures 4a and 4b were re-used with permission from Mao et al.* (2020.)

So far, all the nanoplastics produced by top-down processes used clean, new plastic objects. On the contrary, nanoplastics in the environment are produced from aged plastics objects, and therefore have different properties (e.g., leached additives, oxidized surface, etc.). A recent method developed by Blancho et al. (2021) to extract nanoplastics from the weathered surface of marine plastic debris is a promising method to generate environmentally relevant nanoplastic particle models. However, one of the important difficulties of extracting nanoplastics from environmental matrices is the process of removing the NOM coating without disturbing the nanoplastic chemistry (Treilles et al., 2020).

3.2. Rapid aggregation of nanoplastic particle models produced with top-down methods

PSL have been used for decades to investigate colloidal processes and develop classical colloidal theory. Unsurprisingly, the conclusions drawn from mechanistic studies of nanoplastic aggregation are largely in agreement with classical colloidal theory. These aggregation mechanisms have been reviewed extensively for PSL (Alimi et al., 2018) and for engineered nanomaterials (Baalousha, 2017) and therefore will only be briefly described here. To quantify particles' susceptibility to aggregation, studies often determine the critical coagulation concentration (CCC), which is the minimal concentration of a salt required to provoke the maximum aggregation rate of particles. Conversely, the attachment efficiency of particles, which is the aggregation rate normalized by the maximum aggregation rate in a specific solution chemistry, is useful a useful metric to use in numerical models (Grolimund et al., 2001). Although homoaggregation is less environmentally relevant than heteroaggregation, determining the CCC for homoaggregation of nanoplastic particle models is useful to compare their sensitivity to the solution chemistry (e.g., ionic composition, IS, and pH).

Due to their high surface electronegativity, latex spheres are stable up to hundreds of mmol L^{-1} of monovalent ions in the pH range of natural water types (5 to 8), in agreement with the DLVO theory of colloidal stability. At pH 5, PSL-NF(-) have a CCC of 311 mmol L^{-1} NaCl, which is typical for CCC values of bottom-up particle models (X. Li et al., 2021b). As the pH increases, particles are increasingly negatively charged, which increases electrostatic repulsion and therefore, increases the CCC. PSL-NF(-) have a

CCC of 450 mmol L^{-1} and 591 mmol L^{-1} NaCl at pH 6 (Liu et al., 2019) and 7.5 (Y. Mao et al., 2020), respectively. Also, as PSL-NF(-) were increasingly photo-oxidized (environmental relevance score of 3), their electronegativity increased and their hydrophobicity decreased. This increased their stability in monovalent salts, as predicted by DLVO theory (Liu et al., 2019; Y. Mao et al., 2020; Xu et al., 2021). However, surfactants can cause PSL to remain stable when the electrical double layer (EDL) at the particle' surface is entirely screened (e.g., > 1000 mmol L^{-1} monovalent electrolytes) (González-Fernández et al., 2019; Y. Mao et al., 2020; Yu et al., 2019).

Multivalent ions strongly destabilized nanoplastics with opposite charge. A few mmol L^{-1} of multivalent cations can effectively destabilize negatively charged polymer latex spheres, even if they are non-functionalized (NF) (X. Li et al., 2020, 2021b; Liu et al., 2019; Y. Mao et al., 2020; Wang et al., 2021, 2020). In $CaCl_2$, $BaCl_2$, and $MgCl_2$, PSL-NF(-) had CCCs ranging from ≈ 30 to 40 mmol L^{-1} at pH 6, and ≈ 60 to 70 mmol L^{-1} at pH 7.5 (Liu et al. 2019; Mao et al. (2020). In trivalent cations, destabilization is even stronger with a CCC that is one order of magnitude lower than with divalent ions (Y. Mao et al., 2020). However, as will be explained below, if the speciation of cations is not measured, the actual concentration of electrolytes (especially trivalent cations) is often overestimated, which introduces some error in the determination of the CCC. Divalent or trivalent ions can bridge particles of opposite charge by forming surface complexes. For example, as the surface oxidation of UV-aged PSL-NF(-) increased, their stability in $CaCl_2$ decreased. This shows that Ca(II) was more likely to create bridges because of the increase in carboxylic functional groups produced by oxidation (Liu et al., 2019).

Nanoplastic particle models produced by top-down methods are globally less stable than polymer latex spheres in both monovalent and divalent electrolytes. For example, the CCC of fragmental PET particles was 54 and 55 mmol L^{-1} NaCl and KCl, respectively and 2 mmol L^{-1} for both $CaCl_2$ and $MgCl_2$, which is consistently one order of magnitude lower than for PSL-NF(-) (S. Dong et al., 2020). This reduced stability can be attributed to several differences in particle properties:

i) The absence of surfactants in the more environmentally relevant particle models decreases stability. For example, after removing surfactants from PSL-NF(-), the CCC of 140 mmol L^{-1} NaCl at pH 6 (Singh et al., 2019), whereas PSL-NF(-)with surfactants had a CCC of 591 and 310 mmol L^{-1} NaCl at pH 7.5 and 7.4, respectively (Y. Mao et al., 2020; Yu et al., 2019).

ii) Mechanical abrasion processes used to produce fragmental nanoplastic particle models generate lower surface charge than functionalized nanoplastic particle models (El Hadri et al., 2020). This lower electronegativity reduces electrostatic repulsion and makes them more prone to aggregate. Astner et al. (2020) noticed aggregation of fragmental PBAT nanoplastic particle models with slight agitation in deionized water. This could be attributed to the particles' relatively low zeta potential (-22 ± 3.6 mV) (Astner et al., 2020). However, Magrì et al. (2018) noted that PET produced from laser ablation were stable in monovalent salts (CCC = 700 mmol L^{-1} NaCl). This is explained by the fact that laser ablation can provoke photochemical interactions that mimic environmental photo-degradation (Zafiropoulos et al., 2000). This generates carboxylic functional groups which increase the electronegativity of the particles (-36 mV).

iii) Particles that have nonspherical and irregular shapes are suspected to have lower stability. Veclin et al. (2022) found that surfactant-free PSL with varying degrees of electronegativity, hydrophobicity and surface roughness are significantly more stable in synthetic seawater than fragmental PS particles. This showed that shape had a greater influence on homoaggregation compared to charge or hydrophobicity. However, in other experiments it is often difficult to separate the effects of surfactants, charge and shape. For example, laser-ablated PS were systematically less stable than PSL-NF(-), PSL-COOH(-) and PSL-NH_2(-) containing surfactants, in NaCl and $CaCl_2$ (Yu et al., 2019). Similarly, Pradel et al. (2021) observed that PSL-COOH (-) with surfactants did not aggregate even at 770 mmol L^{-1} NaCl (at pH 5, 6.5 and 8), whereas fragmental PS nanoplastics had a CCC of 59 and 67 mmol L^{-1} NaCl at pH 6.5 and 8, respectively. Interestingly, fragmental PET particles had similar CCC values to fragmental PS particles: 54 and 110 mmol L^{-1} NaCl at pH 6 and 10, respectively (S. Dong et al., 2020).

So, the CCC of 2 mmol L^{-1} for both $CaCl_2$ and $MgCl_2$ for fragmental PET particles suggests that in freshwater, nanoplastics are expected to aggregate rapidly in more alkaline conditions (e.g., river water types 5 and 6). The highest aggregation rate is expected in seawater, due to the combination of high IS (≈ 0.7 mol L^{-1}), a high concentration of multivalent ions (e.g., Mg^{2+}), and a low NOM content (Table 1). However, the behavior of environmentally relevant nanoplastic particle models in artificial water types (environmental relevance score of 5 and 6) has barely been studied.

Only one study of laser-ablated PET showed that, similar to polymer latex spheres, PET rapidly aggregated in a biological growth medium containing multivalent ions (Magrì et al., 2018). However, it is unclear whether all top-down particle models follow the same trend. For example, in $CaCl_2$ fragmental PET aggregates less as the pH increases (CCC = 2.1, 4.5 and 5.6 mmol L^{-1} $CaCl_2$ at pH 6, 8 and 10, respectively) despite having carboxyl and hydroxyl surface groups which can be deprotonated and could bridge with Ca^{2+}. This is contrary to what is observed with polymer latex spheres, and shows that we need more evidence on the aggregation of environmentally relevant nanoplastic particle models, especially in artificial water types.

3.3. What about elemental speciation?

When performing aggregation experiments, it is imperative to consider the speciation of elements in solution, since ions can form different aqueous complexes as a function of solution pH and ionic composition. This complexation modifies IS and the reactivity and solubility of the species, which in turn modifies aggregation. When ions form covalent bonds, the overall charge of the newly formed aqueous complex is lower than that of the free ions, which reduces the solution's ionic strength. As an example, the IS of an electrolyte composed of Na_2SO_4 is calculated as

$$IS = 0.5\left([Na^+] + [SO_4{}^{2-}] \times 2^2 + [NaSO_4] + [HSO_4{}^-] + [OH^-] + [H^+]\right) \quad (1)$$

whereas without considering ion speciation, the ionic strength is calculated as

$$IS = 0.5\left([Na^+] + [SO_4{}^{2-}] \times 2^2\right) \quad (2)$$

Comparing Equations 1 and 2 shows that forgetting to account for aqueous complexes overestimates IS. Furthermore, the presence of HSO_4^- shows that the solution pH is an essential parameter of speciation.

Trivalent cations tend to precipitate as hydroxides at intermediate and high pHs (Brown and Ekberg, 2016). Therefore, aggregation of PSL-NF(-) in these solutions is more likely caused by heteroaggregation rather than homoaggregation. Mao et al. (2020) performed experiments at pH 7.5 with Al concentrations ranging from 0.25 to 10 mmol L^{-1} and Fe(III) concentrations from 0.1 to 10 mmol L^{-1}. We performed geochemical modeling of these experimental conditions using PHREEQC software and sit database, and without considering the potential Al and Fe complexation onto PSL. This predicted that >95% and 100% of Al(III) and Fe(III) are present in solid form due to precipitation. Similarly, Fe(III) is present in a solid form in 0.01 and 1 mmol L^{-1} $FeCl_3$ at pH 5.4 (data from Cai et al., 2018).

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Geochemical speciation models provide information about solids or complexes that can form in different environments if they contain the equilibrium constants of all complexes and solids considered. For example, Singh et al. (2019) calculated that Hg(II) occurred mainly in the Hg(0) form at pH 6, whereas using an updated database (Lian et al., 2020), we calculated that Hg(II) is mainly in the $HgCl_2$ and HgOHCl forms. Also, Ramirez Arenas et al. (2020) calculated that Fe(III) mostly occurred as $Fe(OH)_2^+$ at pH 8.2. However, by including precipitation as a possible process in the models, we calculated that Fe(III) is mainly present in solid form.

3.4. Heteroaggregation must be further investigated

When nanoplastics are incidentally generated from a plastic object and released into the environment, they are most likely to encounter naturally occurring species. In the case where they are released in the technosphere (e.g., landfills or wastewater treatment plants) they will encounter anthropogenic species, such as contaminants or sludge. However, literature shows that nanoplastic aggregation is most often investigated without the addition of (macro)molecules or particles (64% of the experimental conditions reported). A quarter of the experimental conditions contained (macro)molecules, while only 7% contained particulate species and 3% contained both (macro)molecules and particulate species. In solutions with added (macro)molecules and/or particles, figure 5 shows that environmental (macro)molecules are most studied (31%), followed by biological (macro)molecules (30%) and anthropogenic (macro)molecules (16%). Environmental and anthropogenic particles were studied in 16 and 7% of these solutions, respectively. The shortage of heteroaggregation studies is particularly notable for environmentally relevant nanoplastic particle models (scores 4 and 5). Particulate species are present in all ecosystems and abundant in terrestrial ecosystems, so their impact on nanoplastic aggregation must be better understood.

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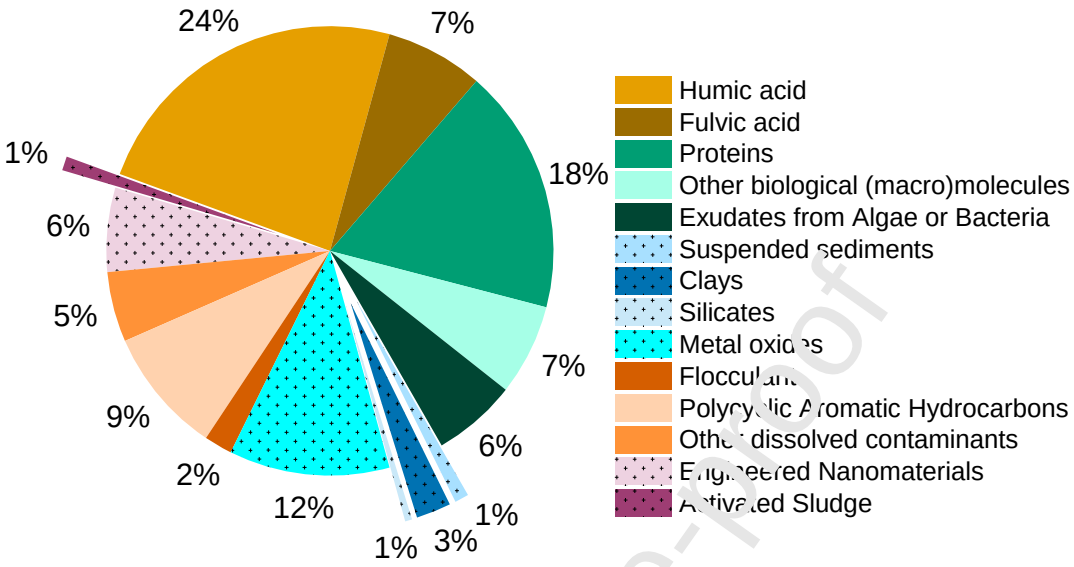

Figure 5: Frequency at which different types of natural and anthropogenic species were studied in experiments that contain natural or anthropogenic model materials.

Nanoplastics heteroaggregate with mineral species of opposite charge due to attractive electrostatic forces. Yu et al. (2021) compared the heteroaggregation rates of PSL with various surface functionalizations (NF(-), COOH(-) and NH_2(+)), with either hematite (positively charged) or kaolinite (negatively charged). As expected, hematite and kaolinite strongly heteroaggregated with nanoplastics of opposite charge, in both NaCl and in $CaCl_2$. In the pH range of natural water, PSL-COOH(-) only aggregated with the positively charged magnetite, goethite, and Al_2O_3 minerals, but did not aggregate with negatively charged kaolinite, montmorillonite, MnO_2 and SiO_2 (Zhang et al., 2020).

Nanoplastics also heteroaggregate with particles of equal but lower surface charge. Singh et al. (2019) noted that PSL-NF(-) heteroaggregated with bentonite (montmorillonite) clay which had a lower negative charge (Singh et al., 2019). This heteroaggregation can also be due to the presence of some positively charged edges on the bentonite clay, and to the hydrophobic nature of bentonite (Worrall, 1968). PSL-NF(-) were also found to sorb onto slightly negatively charged (-7 mV) flocs of biologically active sludge from a wastewater treatment plant, through van der Waals attraction and hydrophobic interactions (H. Li et al., 2020). Interestingly a more environmentally

relevant nanoplastic particle model (fragmental PBAT, score 4) strongly heteroaggregates with vermiculite even in the absence of electrolytes (Astner et al., 2020).

With the addition of (macro)molecules, heteroaggregation processes are less easy to predict, but generally point to increased stability. Suspended sediments, which are natural mixtures of organic and mineral species extracted from a river bottom, significantly heteroaggregated with PSL-SO_4(-) and induced settling in 50 to 500 mmol L^{-1} NaCl. The addition of 10 mg L^{-1} humic acid (HA) decreased the heteroaggregation rate due to steric repulsion (Li et al., 2019). Even the addition of low concentrations of HA (1 mgC L^{-1}, which is lower than the dissolved organic carbon content of rivers in Table 1) reduced heteroaggregation rates between negatively charged PSL and positive hematite, in up to 300 mmol L^{-1} NaCl (Yu et al., 2021). Similar behavior was observed for multi walled carbon nanotubes, since 0.5 mg L^{-1} HA inhibited their heteroaggregation with hematite nanoparticles in 100 mmol L^{-1} NaCl (Huynh et al., 2012).

Overall, current evidence suggests most natural rivers have NOM concentrations that can effectively slow down heteroaggregation, at least in monovalent salts (i.e., >1mgC L^{-1} in Table 1). However, in soil pore water and in freshwater bodies that contain high concentrations of suspended sediments and low concentrations of HA (e.g., after high intensity rainfall events, in agricultural watersheds with exposed soils), nanoplastics could quickly heteroaggregate with naturally occurring particles (Praetorius et al., 2012). In terrestrial ecosystems, nanoplastics are expected to be closely associated with wastewater treatment for biosolids, for example, which can lead to important co-transport of nanoplastics with biosolids, in sludge-amended soils (Keller et al., 2019). The recently developed suspended particulate matter models could be used to provide environmentally-relevant rates of heteroaggregation (Walch et al., 2022).

Interactions between nanoplastics, dissolved and particulate matter have not been investigated with divalent or multivalent cations, although these cations can have strong destabilizing effects even in the presence of environmental or biological (macro)molecules (c.f.: following section). Furthermore, these conclusions are drawn from nanoplastic particle models with low environmental relevance (score 1 or 2). The absence of heteroaggregation studies using environmentally relevant nanoplastic particle models leads to uncertainty about true heteroaggregation and settling rates.

3.5. (Macro)molecules can either stabilize or destabilize nanoplastics

Since the stabilizing effect of (macro)molecules against heteroaggregation has seldom been investigated, we can gain insight by investigating the stabilizing effect of (macro)molecules against homoaggregation. In monovalent electrolytes, (macro)molecules have a stabilizing effect on nanoplastics due to electrostatic repulsion and, when sorbed onto particles, due to steric repulsion (Liu et al., 2019; Y. Mao et al., 2020; Singh et al., 2019). Various types of organic macromolecules effectively increased the stability of 10 mg L^{-1} PSL-NF(-) in 500 mmol L-1 NaCl at pH 6 (Liu et al., 2020). The stabilizing effect was most pronounced for HA, followed by bovine serum albumin (BSA), a protein which is abundant in blood plasma, extracellular polymeric substances, and sodium alginate (SA). Stabilization was attributed to steric repulsion, as supported by the measurement of the eco-corona thickness by XPS, while differences in stability were attributed to the conformation of the different macromolecules. Interestingly, extracellular polymeric substances, which contain a mixture of proteins and polysaccharides, have a stabilizing effect intermediate between BSA and the polysaccharide SA (Liu et al., 2020). Similar trends in stability were observed for more environmentally relevant nanoplastic particle models. Fragments of PS particles were more effectively stabilized by HA than SA (Pradel et al., 2021). The addition of fetal bovine serum, which contains a mixture of biological molecules (e.g., hormones, lipids, sugars, etc.), increased the CCC of laser-ablated PET from 700 to over 4 000 mmol L^{-1} NaCl (Magrì et al., 2018).

In the presence of divalent counterions, macromolecules either stabilized or destabilized nanoplastic particle models, depending on the relative concentration of divalent counterions, macromolecules and nanoplastics, the surface functional groups of the nanoplastics, and the macromolecule chemical and physical properties. For example, in 20 mmol L^{-1} $CaCl_2$ at pH 6, the homoaggregation rate of 10 mg L^{-1} PSL-NF(-) alone was lower than with (macro)molecules. Then, homoaggregation rate was higher in 1 and 2 mgC L^{-1} of BSA and HA compared to 5 mgC L^{-1} (Liu et al., 2020). This was due to bridging at low concentrations of (macro)molecules, and by a more complete coverage of particle surface at higher (macro)molecule concentration which increases steric repulsion. Similarly, at pH 7.4, 1 mgC L^{-1} HA increased aggregation of 10 mg L^{-1} PSL-NF(-) and larger concentrations (5 and 10 mgC L^{-1}) reduced aggregation in $CaCl_2$ (Yu et al., 2019).

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For more environmentally relevant particles, 1 mg L^{-1} HA was enough to increase stability of 10 mg L^{-1} fragmental PET in both NaCl (Figure 6b) and $CaCl_2$ at pH 6. This suggests that even in rivers with higher IS and hardness (3, 4 and 5), and in soil porewater, low concentrations of NOM can increase nanoplastic stability. However, whether these molecules effectively reduce heteroaggregation rates remains to be verified.

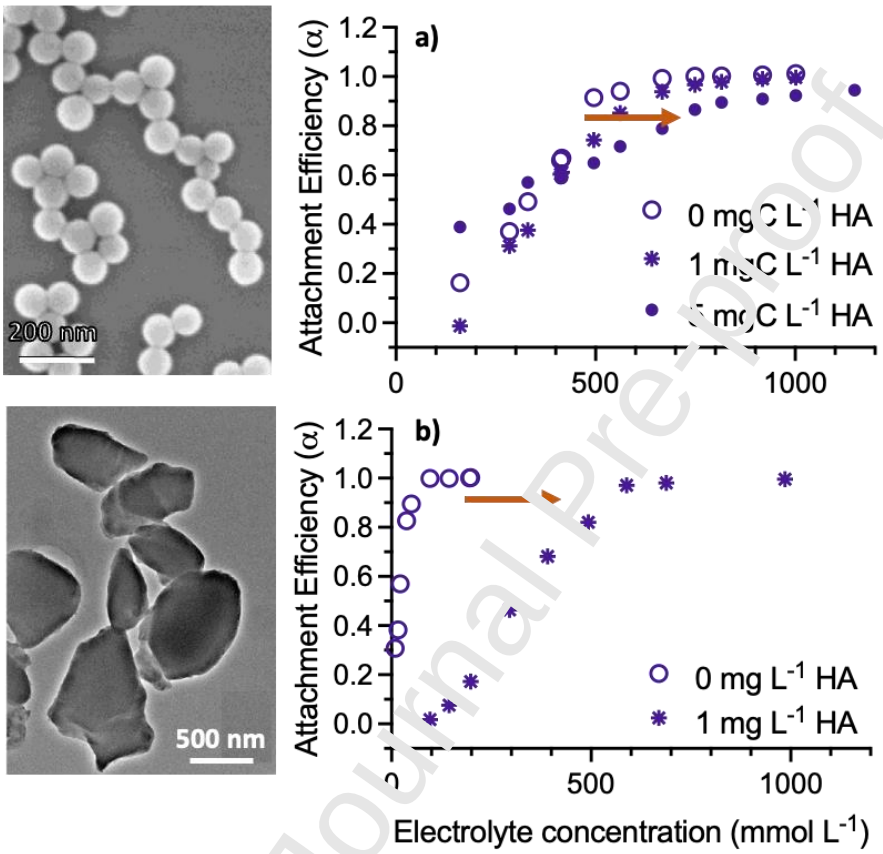

Figure 6: The effect of humic acid (HA) on attachment efficiencies of PSL-NF(-) (top) and fragmental PET (bottom) as a function of NaCl concentration. The arrows indicate increased stability. (Reproduced with permission from Yu et al. (2019) and S. Dong et al., (2020))

A couple of considerations should be kept in mind about the stabilizing effect of (macro)molecules. First, it is essential to reason in terms of particle number and surface area to compare studies. Collision rates are particle-number-dependent and (macro)molecule's sorption capacity is surface area-dependent. For nanoplastic particle models produced from top-down processes, a rigorous analysis of size distribution using several complementary techniques is essential to convert the mass of particles to the number and surface area of particles (Baalousha and Lead, 2012; Caputo et al., 2021). Second, while studying a range of (macro)molecule concentrations provides insight into

mechanisms, ultimately, mass concentrations of naturally occurring species that are lower or equal to nanoplastic mass concentrations has little environmental relevance. Indeed, bridging two nanoplastics by an organic (macro)molecule is an unlikely event, except at the surface of an aging plastic object. Finally, the eco-corona should also be tightly adsorbed onto the particle surface for steric repulsion to be effective in the environment, since other naturally occurring species (e.g., ligands, metal oxides, etc.) can compete for these (macro)molecules. Modeling steric repulsion provided by the eco-corona with the XDLVO theory is complicated by the fact that the solubility of molecules and the thickness of the coating must be known, but are difficult to determine for natural molecules in environmental systems (Fritz et al., 2002; Napper, D.H., 1977). Indeed, as nanoplastics travel through different compartments (e.g., rivers, estuaries, ingestion by organisms, biofilms) their eco-corona evolves, thereby modifying their chemical identity and their environmental fate (Wheeler et al., 2021).

3.6. Nanoplastic aggregation in natural water types

Studying nanoplastic aggregation and settling in natural water types is essential to validate the mechanisms investigated in simpler solutions and to confirm our hypothesis about the environmental fate of nanoplastics. 37% of the experiments used natural water types (with environmental relevance scores of 7 and 8). Most (65%) of the studies were done with freshwater (mostly lakes, rivers, and aquifers, with only a few studies of rainwater and wastewater) and 35% of natural water samples came from seas and oceans (Figure 7). However, all of the experiments involved non-aged polymer latex spheres as the nanoplastic particle model (scores of 1 and 2).

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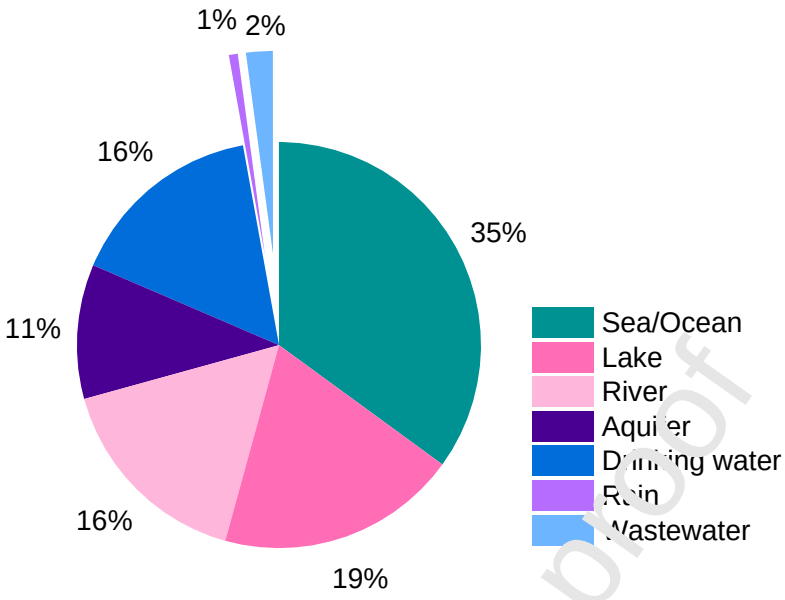

Figure 7: Relative proportion of different types of water in which nanoplastic particle models were studied.

While negatively charged PSL aggregate rapidly in seawater (Grassi et al., 2020; Manfra et al., 2017; Tallec et al., 2019), their aggregation in freshwater is very dependent on the IS, on the concentrations of divalent cations, and of environmental and biological (macro)molecules (X. Li et al., 2021a, Wang et al., 2021). Indeed, Manfra et al. (2017) observed rapid aggregation of PSL COOH(-) in Mediterranean seawater, which had a high organic carbon concentration (13 mg L^{-1}) despite having been filtered at 0.45 µm. Other studies found that extracellular polymeric substances, decreased the aggregation rate of both PSL-NF(-) (Summers et al., 2018) and PSL-COOH(-) (Grassi et al., 2020) in seawater. Interestingly, PLS-NH_2(+) was often stable in seawater (Della Torre et al., 2014; Tallec et al., 2019). This stresses the fact that using nanoplastic particle models that are not environmentally relevant can lead to incorrect conclusions about their environmental fate.

In the presence of CeO_2 nanoparticles, negatively charged PSL aggregated rapidly in seawater. In freshwater they were generally more stable: no heteroaggregation was observed in river water, while some heteroaggregation was observed in lake water that had a low pH (5.35) and groundwater that had a very high IS (712 mmol L^{-1}) (X. Li et al., 2020). In another study, PSL-NF(-) was more stable against homoaggregation in groundwater than in river water. While the IS of the groundwater was approximately

double the IS of the river water, the organic carbon concentration was almost double in the groundwater (3.33 mg L^{-1} *vs.* 1.90 mg L^{-1} in the river), which provided a stabilizing effect (Singh et al., 2019). Therefore, nanoplastics are expected to have longer residence times in freshwater types that are near neutral, and have a high NOM content, and a low water hardness (e.g., rivers 1, 2 and 3).

4. What we know about nanoplastic aggregation and what we need to know

We use the evidence gathered, to propose some hypotheses about nanoplastic aggregation pathways and their subsequent environmental fates. These are shown in Figure 8. Some uncertainty is caused by current knowledge gaps and illustrated with question marks. Homoaggregation has been shaded to illustrate that it has a low probability of occurring in the environment due to low nanoplastic concentrations (parts A and B, Fig. 8). However, studying homoaggregation in the presence of (macro)molecules has shown that the homoaggregation rate of nanoplastics is highly sensitive to the nature and concentration of dissolved species (part D, Fig. 8). While it has been shown that (macro)molecules, such as HA, can effectively stabilize these particles in simple solution chemistries, the effect of (macro)molecules on heteroaggregation in artificial and natural water types must be investigated. There are very few studies of heteroaggregation, and only one study with environmentally relevant nanoplastic particle models. Despite this, current evidence suggests that particulate species strongly heteroaggregate with nanoplastics and may accelerate the settling rate (part C, Fig. 8).

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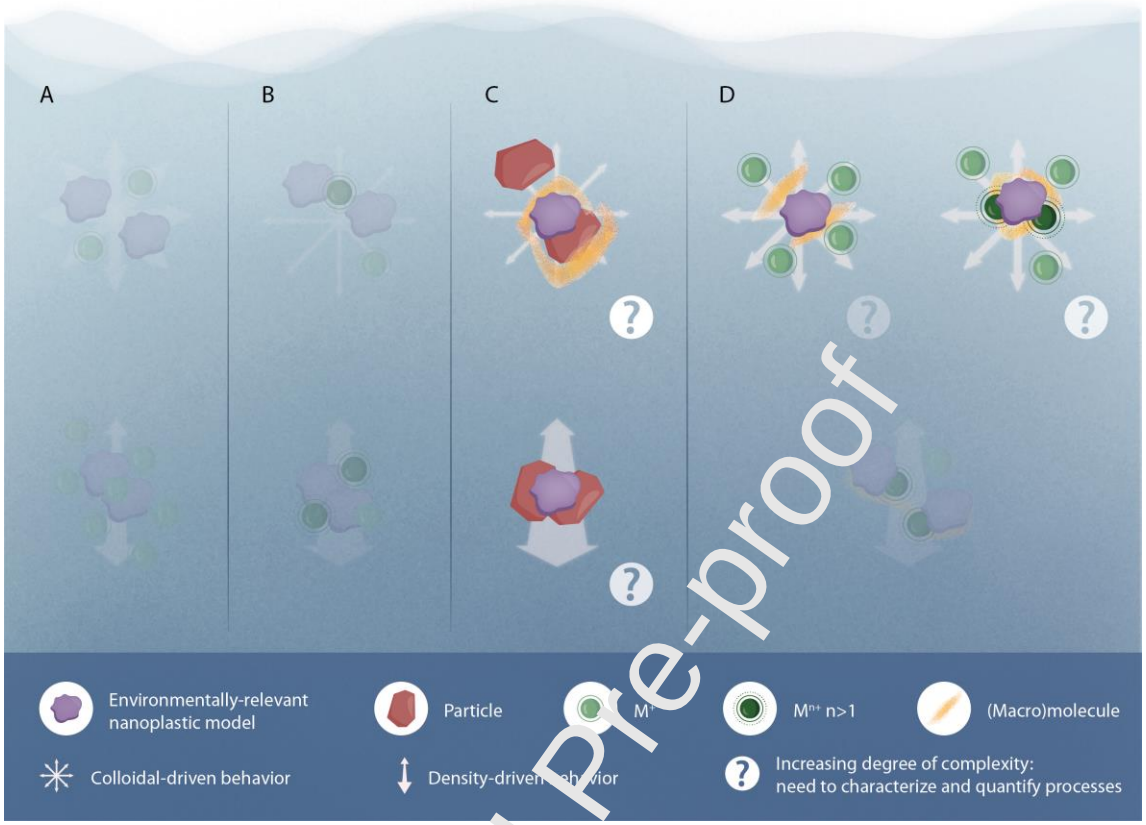

Figure 8: Nanoplastics homoaggregation is not likely to occur in A) monovalent and B) divalent electrolytes. Investigating homoaggregation is only relevant to characterize environmentally relevant nanoplastic particle models and understand the effect of naturally occurring species. C) The effect of particles on nanoplastic aggregation must be investigated in more depth, especially in the presence of (macro)molecules. D) Bridging of nanoplastics is a an unlikely event (bottom). It remains to be understood the extent to which nanoplastics can be stabilized by an eco-corona in the presence of monovalent cations (top left) and divalent cations (top right).

To gain a full picture of the environmental fate of nanoplastics, we suggest focusing on environmentally relevant nanoplastics, instead of exploring all particle properties. Nanoplastic particle models produced from pre-production plastics or un-aged plastic objects (environmental relevance score 4) are more sensitive to aggregation than commonly used polymer latex spheres (scores 1 to 3). To understand whether nanoplastics that are released from weathered plastic debris are also more sensitive to aggregation would require nanoplastic particle models produced with top-down methods from environmental plastics (score of 5). Methods to generate these nanoplastic particle models are being developed and provide hope for a better quantification of aggregation rates (Blancho et al., 2021; Villacorta et al., 2022).

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Important insight can be gained by comparing the aggregation and settling rates of nanoplastics with those of natural colloids with similar physicochemical properties. For example, the body of knowledge about the environmental fate of engineered or natural carbon particles (e.g., graphene or carbon black, respectively) can inform us about the fate of nanoplastics (Sigmund et al., 2018). To develop a better understanding of aggregation processes requires a detailed characterization of the dissolved, colloidal, and particulate species present. Studies should move beyond considering filtration as a method that creates homogenous solutions and dispersions, and instead characterize the speciation of ionic species and the molecular weight, surface potential, and polydispersity of colloids.

A relationship between the nanoplastic heteroaggregation state and settling rates needs to be established to quantify nanoplastic flux to sediments (Waldschläger et al., 2022; Zhang et al., 2021). Indeed, the speed at which aggregates settle is highly dependent on aggregate porosity and fractal dimension (Johnson et al., 1996). Without agitation, some aggregates can remain stable in a water column for a certain time (Rowenczyk et al., 2021; Wegner et al., 2012). With turbulence, shear stress breaks aggregates, thereby resuspending them (Adler, 1979; Chen et al., 2018; Summers et al., 2018). Therefore, investigating nanoplastic aggregation in dynamic systems can reveal insights about natural settling rates.

Developing the XDLVO model by incorporating the effects of surface roughness, nonspherical shape, and steric stabilization by macromolecules will help to advance the study of homo- and heteroaggregation. The XDLVO model is limited to van der Waals, electrostatic and hydrophobic interactions for smooth and spherical particles. Interactions between nonspherical and/or rough particles does not integrate hydrophobic or steric interactions. Coupling chemical interactions (e.g., surface complexation) with the XLDVO physical interactions would greatly improve our ability to predict particle aggregation in natural water.

Finally, the development of numerical models underpinned by high-quality experimental research is a promising way to assess the fate of nanoplastics in the environment (Besseling et al., 2017; C. Li et al., 2021; Lins et al., 2022; Wang et al., 2021). The experimental designs and the metrics used (e.g., collision rate and attachment efficiency) should be discussed with modelers to make sure results can be used in their models. Experimental studies should report the experimental and analytical conditions used

according to the suggested guidelines (Kokalj et al., 2021) to facilitate comparison of results.

Our review of homoaggregation studies shows that nanoplastic particle models that are more environmentally relevant have higher attachment efficiencies. This is also expected to be the case for heteroaggregation. This has important implications since numerical simulations of the transport of nanoplastics are sensitive to attachment efficiencies. For example, a study that modeled the transport and retention of micro- and nanoplastic heteroaggregates in a river showed that increasing the attachment efficiency above 0.01 significantly reduced the retention of plastic particles smaller than 4 μm in a riverbed (Besseling et al., 2017). In parallel to these experimental and modeling efforts, overcoming the analytical challenges to quantify nanoplastics in environmental matrices will be essential to verify our hypothesis about the environmental fate of nanoplastics (Ivleva, 2021).

5. Method

All original research articles that were present in the Web of Science search engine on August 16th 2021 and containing the words nanoplastic(s) and stability, or nanoplastic(s) and aggregation, or nanoplastic(s) and agglomeration in either the article's title, abstract or keywords were collected.

This resulted in 87 articles, of which 3 were excluded. Two of them were excluded because they did not actually investigate the aggregation of nanoplastics, while one pertained to the aggregation at the interface between plant leaves and air. Of the remaining 84 articles, only two were not experimental studies. Within the 82 experimental studies a total of 163 different particle types were studied (Alimi et al., 2021; Astner et al., 2020; Bergami et al., 2019; Cai et al., 2018; Canesi et al., 2016; Chakraborty et al., 2021; Chen et al., 2018, 2020; Cunha et al., 2020; de Oliveira et al., 2020; Della Torre et al., 2014; S. Dong et al., 2020; Dong et al., 2019a, 2019b; Z. Dong et al., 2020; Eliso et al., 2020; Fadare et al., 2019; Frankel et al., 2020; Ganguly and Ariya, 2019; González-Fernández et al., 2019; Grassi et al., 2020; Khoshnamvand et al., 2021; Kihara et al., 2019; C. Li et al., 2021; H. Li et al., 2020; X. Li et al., 2021a, 2021b, 2020; Li et al., 2019; Z. Li et al., 2020; Ling Liu et al., 2021; Liu et al., 2016, 2020, 2019; Liuqingqing Liu et al., 2021; Q. Liu et al., 2021; Magrì et al., 2018; Manfra et al., 2017; Y. Mao et al., 2020; Mekaru, 2020; Mishra et al., 2019; Murano et al., 2021; Nolte

et al., 2017; Okshevsky et al., 2020; Oriekhova and Stoll, 2018; Pradel et al., 2021; Ramirez Arenas et al., 2020; Ramirez et al., 2019; Reynolds et al., 2019; Ripken et al., 2020; Rowenczyk et al., 2021; Saavedra et al., 2019; Schampera et al., 2021; Sendra et al., 2020, 2019; Seoane et al., 2019; Shiu et al., 2020a, 2020b; Shupe et al., 2021; Silva et al., 2020; Singh et al., 2021, 2019; Song et al., 2019; Summers et al., 2018; H. Sun et al., 2020; X.-D. Sun et al., 2020; Tallec et al., 2019; Trevisan et al., 2019; Vaz et al., 2021; Venel et al., 2021; Wang et al., 2021, 2020; Wegner et al., 2012; Wu et al., 2021, 2019; Xu et al., 2021; Yu et al., 2021, 2019; Zhang et al., 2019, 2018, 2020; Zheng et al., 2021). A few of the particles could come from the same provider and have the same properties but it was impossible to verify if they came from the same batches, therefore they were all considered to be distinct. These particles were dispersed in a total of at least 377 different solution chemistries. A solution chemistry corresponds to a given combination of dissolved and particulate species but does not take into account all of the pH values or the varying concentrations .

The primary focus of most of the articles was aggregation and sedimentation processes (48% particles and 70% solution chemistries); followed by studies of (eco)toxicity, (35% particles and 21% solutions); transport and deposition (9% particles and 5% solutions); and interaction with biogeochemical processes (8% particles and 4% solution chemistries). A summary of the 82 articles studied is presented in the supplementary information.

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Acknowledgements

This work was supported by the French Ministry of Higher Education and Research, the French ANR through the program PLASTI-SCARE and the French Brittany Council through MONANO (SAD-Attractivité). Thank you to Mandy Ducy from Agence IMPAKT Scientifik Inc. for the illustrations. Thank you to Christa Bedwin for editing our work.

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Credit author statement

Alice Pradel: Conceptualization, Formal analysis, Methodology, Writing- Original draft preparation. **Charlotte Catrouillet.**: Writing- Reviewing and Editing. **Julien Gigault**: Conceptualization, Writing- Reviewing and Editing, Supervision Funding acquisition

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Highlights

- What is known about nanoplastics' environmental fate, and what needs to be known;
- A systematic review of nanoplastic aggregation rates and processes.
- Up-to-date hypotheses of where nanoplastics are accumulated in the environment
- Determine how nanoplastics' aggregation state impacts their settling rate.
- Nanoplastics models needed for the interpretations of nanoplastics' fate and impact.

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