Natural Nanoparticles, Anthropogenic Nanoparticles, Where Is the Frontier?

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Nanoparticles are important components of the Earth biogeochemical system. However, in the Anthropocene, the human activities disturbed their natural cycle and increased their abundance by (i) affecting their emissions and releases; (ii) altering the environmental processes involving nanoparticles; and (iii) introducing anthropogenic nanoparticles (ANPs). Intentionally or unintentionally released, the occurrence of the anthropogenic nanoparticles in the environment is continuously rising. Both natural and anthropogenic nanoparticles are recognized as important carriers for trace elements and organic micropollutants and key modifiers of their transport, speciation, bioavailability, and effects in the environment. Nevertheless, currently they are considered separately, despite the necessity of more integrated, broader, and non-sectorial perspective taking together particles of different origins and various processes likely to generate and involve them. The present paper provides a perspective on the environmental processes involving anthropogenic and natural nanoparticles (NNPs) and discusses the role of human activities in nanoparticle cycling, as well as the necessity to bridge the divide between the NNPs and ANPs. The discussion will be supported by the examples of our own research to ask, if there is still a frontier between NNPs and ANPs?

Keywords: nanoparticle biogeochemical cycle, pollution, nanoparticle sources, fate, toxicity, Anthropocene

INTRODUCTION

Nano-sized particles,1 naturally present in the Earth, move through different compartments (biosphere, lithosphere, atmosphere, and hydrosphere) within global biogeochemical cycle. They play an important, but not fully understood, role in the dynamics of the overall Earth system. However, human activities disturbed the cycle of natural nanoparticles (NNPs) by (i) affecting their emissions and releases; (ii) altering the environmental processes involving nanoparticles; and (iii) introducing anthropogenic nanoparticles (ANPs). Both incidentally released nanoparticles (INPs)2

1Although still a question of debate, nano-sized particles definition used in the present paper involve any object (organic, inorganic, or organometallic) of nanometric size (or sub-micrometric size), which can be in dispersed form in a fluid (Faucher et al., 2019; IUPAC, 2019) and the small dimensions confer them peculiar physical and chemical properties that differ from larger objects made of the same material(s) (Maurice and Hochella, 2008). Natural nanoparticle describes a sub-set of the colloidal phase.

2Incidental nanoparticles are produced as a result of any form of direct or indirect anthropogenic activity or process.
and engineered nanoparticles (ENPs) form the pool of the ANPs. It is estimated that 1000s of Tg of NNPs, 1–10 Tg of INPs and less than 1 Tg of ENPs from different natural and anthropogenic sources co-exist and move annually between the Earth compartments (Hochella et al., 2019). Despite their small proportion of the total nano-sized particle mass, the amount of ENPs in the environmental compartments continues to increase with ever growing use of nano-enabled materials (Keller and Lazareva, 2014). ENPs were recently considered within the frame of global anthropogenic cycling of elements, concluding that for elements such Ag, Al, Ce, Co, Cu, Fe, Ni, and Zn, ENPs had a minor impact on their cycling, whereas SiO$_2$ ENPs represented 3–25% of mined Si (Janković and Plata, 2019). However, such integrated Earth system approach has emerged only recently; NNPs and ANPs are thus in most cases considered separately. Only few examples can be found in the literature providing a comprehensive comparison of the behavior of NNPs and ENPs (Baalousha et al., 2011; Wagner et al., 2014; Sigmund et al., 2018). Therefore, broader and integrated approach toward fate and impact of nano-sized particles in the environment would be useful for better understanding Earth systems biogeochemical dynamics. This requires considering nano-sized particles of different origins together with the various processes likely to generate and involve them.

**NANOPARTICLE CYCLING IN THE ENVIRONMENT**

Natural nanoparticles are generated in different environmental compartments by various physical, chemical, and biological processes (Figure 1), such as (bio)chemical weathering of minerals, photo-oxidation, redox and precipitation reactions, (bio)mineralization, physical fragmentation, gas-solid nucleation in the atmosphere, etc. (Sharma et al., 2015). ANPs generation is a result of human-related activity or processes (e.g., combustion), due to the life cycle of products containing nanoparticles or accidental releases. Examples of such sources inherent for human activities include: (i) dust generation by various activities; typically mining, tillage, and demolition/construction. Atmospheric transport then constitutes a vector of long-distance transport (Jun et al., 2016); (ii) atmospheric release and nucleation (Lee et al., 2019); (iii) release of treated and untreated waste water (Brar et al., 2010); and (iv) storage in an insufficiently confined area or spreading of sludge from sewage treatment plants (Meier et al., 2016). Natural processes could also be responsible for the generation of the ANPs from different materials. For example, weathering of plastics could result in a formation of micro- and nano-plastics in waters and marine organisms (Ganesh Kumar et al., 2020; Kögel et al., 2020).

Independently on their origin, the nano-sized particles interact with different abiotic and biotic components, via various interconnected processes leading to their transformation in the environmental compartments. Processes such as aggregation, sedimentation, biological accumulation, biomagnification, dissolution, chemical and physical alterations, etc., are common for both NNPs and ANPs (Baalousha et al., 2011; Wagner et al., 2014; Sigmund et al., 2018). The nano-sized particles, regardless of their origin, participate in the same bio-physicochemical processes (Figure 1), which ultimate will determine their fate and impacts (Garner et al., 2017, 2018). The fate and behavior of bare ENPs was similar to their natural counterparts with the same composition (Garner and Keller, 2014; Wagner et al., 2014; Sigmund et al., 2018). Human activities also affect these processes by changing the surrounding physical and/or chemical conditions that govern them.

These processes depend on the multiple factors that can be grouped in three main categories intrinsic to: (i) nano-sized particles, including particle physicochemical speciation, size, shape, surface functionalization, etc.; (ii) environmental variables, including pH, water hardness, and alkalinity, presence and concentrations of different ligands from natural and anthropogenic origins, which may influence chemical and physicochemical speciation; and (iii) biological systems, including habitat, feeding pattern, etc. Abundant information on the environmental implications of ENPs can be found in recent review papers (Lead et al., 2018; Joonas et al., 2019; Mortimer and Holden, 2019; Kögel et al., 2020; Slaveykova et al., 2020).

It is out of the scope to provide a detailed overview on the fate and impact of the nano-sized materials in the environment. Hence, we make a parallel in some key properties and processes to consider toward bridging the gap between NNPs and ANPs.

**TOWARD BRIDGING THE GAP BETWEEN NNPS AND ANPS**

Whatever their origin, nano-sized particles are characterized by a greater fraction of atoms at the surface, which determine their enhanced surface energy and reactivity (Hochella et al., 2019). Purposely-made ENPs have controlled chemical composition, size, and properties. They therefore have less polydisperse character and some properties are enhanced as compared with NNPs. For example, due to their controlled surface structure and smaller sizes TiO$_2$ ENPs have catalytic and redox properties that natural ones do not present (Chin et al., 2011). In addition, the presence of persistent engineered coatings on the ENPs gives them properties which differ from the core material in terms of dissolution, stability and effects. Similarly to NNPs, the surface of ANPs is modified in the environmental and living systems, through the adsorption and desorption of organic and inorganic compounds of natural or anthropogenic origin. Such alterations can affect surface properties of nano-sized particles, hence their interactions with trace elements, organic micropollutants, colloids, surfaces, and biota (Wagner et al., 2014; Wang et al., 2015). Therefore, the pure synthetic identity of ENPs could also be questioned given their interactions with different naturally occurring compounds. The existence of “purely natural” NNPs is a source of interrogation insofar as the whole of the biosphere concerned by the processes of genesis and by materials/compounds qualified as natural are...
possibly affected by human activities. It would therefore be useful to consider that “altered” nano-sized particles involve both anthropogenic and natural components and thus would have more complex environmental fate and impact. Hereafter, we provide shortly two examples considering the interactions of the ANPs with naturally occurred compounds and of the NNPs with inorganic and organic pollutants.

**Interaction of ANPs With Naturally Occurring Compounds**

Interaction of ANPs with various naturally occurring compounds (e.g., humic acid, extracellular polymeric substances, peptides) results in a formation of eco-corona and gives them new surface properties (Louie et al., 2016; Pulido-Reyes et al., 2017). This new “environmental identity” has a great influence on their fate by affecting their dissolution, aggregation/agglomeration, stability in the water column (Gigault et al., 2012; Wang et al., 2015; Louie et al., 2016), deposition to mineral surfaces (Louie et al., 2016), attachment to biological surfaces and bioavailability (von Moos et al., 2014; Louie et al., 2016), and toxicity (Ivask et al., 2014; von Moos and Slaveykova, 2014). For example, natural organic matter was shown to reduce the toxicity of metallic nanoparticles to many organisms (Wang et al., 2016).

Similarly, in biological environment, ANPs interact with various biomolecules (e.g., proteins, peptides, DNA, RNA, lipids, etc.) and earn a new “biological identity” determining nanoparticle fate and effects within living organisms.
example, the antioxidant enzyme catalase formed a corona around AgNPs, and the released Ag together with AgNPs inhibited its enzymatic activity. However, AgNP—superoxide dismutase complex formation only slightly affected the protein conformation and had no impact on the enzymatic activity or AgNP dissolution (Liu et al., 2020). It is currently accepted that the formed bio-corona represents “what the cell sees” (Walczyk et al., 2010). Hence, it plays a critical role in modulation of the biological reactivity and nano-sized particle induced responses in living organisms, which may be significantly distinct from the expected one exclusively driven by the primary ENPs synthetic identity.

**Interaction of NNPs With Inorganic and Organic Pollutants**

Due to their small size and large specific surface area, NNPs play a key role in the transport, speciation, and bioavailability, and thus the ultimate impact of trace elements (Slaveykova and Wilkinson, 2005; Wilkinson and Lead, 2007; El Hadri et al., 2016), and organic micropollutants (Sigmund et al., 2018). NNPs possess a near infinite array of possible compositions and sizes and include principally oxides and oxyhydroxides of iron, manganese, and aluminum and aluminosilicates; humic-like substances, various biopolymers synthesized and released by living organisms involving various proteins, nucleic acids, and polysaccharides (Wilkinson and Lead, 2007; Hartland et al., 2011). Clear size dependence in a preferential binding of trace metals on NNPs was observed (Worms et al., 2010a,b). Following the adsorption of different inorganic and organic contaminants, the NNPs will acquire a new “anthropogenic identity,” which will have an important consequence for the pollutant availability and biological outcomes. For example, in the aquatic environment, NNPs reduce the bioavailability of the trace metals to various organisms, including bacteria, fungus, phytoplankton, daphnia, and fish, in direct proportion to the free metal ion concentrations (Slaveykova and Wilkinson, 2005). NNPs could therefore play the role of Trojan horses for their associated pollutants and increase the trace metals bioavailability to filter feeders (e.g., clams, mussels, and oysters) (Luoma and Rainbow, 2005). Similarly, the adsorption of metallic pollutants on ENPs could result in their surface modification, which could change their properties and the way they interact with biota (Naasz et al., 2018; Li et al., 2020).

Overall, despite the existing differences between NNPs and ANPs, similar properties and processes control their fate and effects in the environment. Therefore, process-oriented knowledge has a potential to lead to sound progress in the understanding the nano-sized particles dynamics in the multifaceted Earth (sub-) systems, and feedbacks with human activity.

**DATA AVAILABILITY STATEMENT**

Publicly available datasets were analyzed in this study. Requests to access the data can be directed to gaetane.lespes@univ-pau.fr.

**AUTHOR CONTRIBUTIONS**

GL and VS took part in conceptualization, manuscript writing, and editing. SF drew the figure and took part in the manuscript writing. All authors read and agreed to the published version of the manuscript.

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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