



## Nanoplastic in a porous media: improbable transportation or realistic deposition?

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### Introduction

Nanoplastics (NPs) are defined as colloids that originate from the unintentional degradation of plastic. They have recently been detected in the North Atlantic Ocean and are characterized by a continuum in sizes ranging from 1nm to 1 $\mu$ m, associated to asymmetrical shapes and Brownian motion (Gigault et al., 2018). Since these particles could pose specific ecological and health risks, it appears crucial to describe their global environmental fate. In the life-cycle of a plastic debris, the terrestrial compartment is the main source and water is the main vector, so NP transport in soils must be elucidated. Up to now, the large majority of published results concerning the ecotoxicological impact of NPs as well as their environmental behavior in controlled conditions (porous systems, bulk etc.) use engineered plastic nanomaterials, called polystyrene latex (PSL) spheres. These are spherical and monodisperse size standards containing surfactants, properties that are significantly different from those of environmental NPs. In our study, we tackle such approach by describing the fate of different nano-sized polystyrene (PS) particles in a porous media in unfavorable deposition conditions (repulsion between media and particle). We compared 3 NPs mimicking more or less closely environmental NPs: commercially-available PSL spheres, soap and metal-free PSL spheres and an environmentally-relevant NP model. The parameters discriminating each of these particles are their average hydrodynamic diameters (200 to 530nm), surface properties (varying density of carboxylate functional groups), composition (presence or absence of additives) and shape (spherical or asymmetrical). Our results show that the asymmetrical, fractal-like shape of NPs are significantly more deposited in the porous media and undergo size changes. This is likely to affect their stability further along their journey.

### Materials and methods

Transport in a porous media was modeled in lab-scale packed-bed columns, using a liquid chromatography system (Äkta™ Pure, GE Healthcare). The porous media was composed of Fontainebleau sand, dry-packed into a borosilicate column, with an average porosity of 0.41 $\pm$ 0.13. The eluent (mobile phase) was composed of NaCl at 5 mmol L<sup>-1</sup> with pH fixed at 6.5 using NaOH and HCl. The sand was washed with at least 14 pore volumes (PVs) of deionized water and 22 PVs of the eluent. Tracer tests were done with NaCl or KBr. The NP solutions (dispersed phase) were injected for 6 PVs at a fixed rate of 1.57 10<sup>-5</sup> m s<sup>-1</sup> and a concentration of C<sub>0</sub>=5 10<sup>-3</sup> g L<sup>-1</sup>. Carboxylated PSL spheres of 200nm (PSL COOH 200) were purchased from Polysciences. Two model NPs are made of clean, additive-free “primary” (-P) PS: soap and metal-free carboxylated PS spheres of 530nm (PS COOH 530-P) produced by IPREM, Pau, and a model NPs (NP 350-P) formulated from mechanically crushed PS pellets by Cordouan Technologies, Pessac (preparations protected by pending patent).

Table 1: Properties of the nanoplastics studied

Nanoplastic name	Composition	Diameter (nm)	Shape
PSL COOH 200	Polystyrene + additives	200	Spherical
PS COOH 530-P	Primary polystyrene	530	Spherical
NP 350-P	Primary polystyrene	350	Asymmetrical

NP concentration eluted from the porous media was determined by the UV-Vis spectrophotometer paired to the chromatography system ( $\lambda$ =226nm). Breakthrough curves (BTCs) were obtained by plotting the outflowing concentration of NPs normalized by the initial concentration (C<sub>0</sub>) as a function of PVs eluted. Hydrodynamic diameters (d<sub>H</sub>) of NPs were determined by Dynamic Light Scattering (Vasco-Flex, Cordouan Technologies). The clean bed filtration model of colloid filtration theory (CFT) and the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory were used to analyse hydrodynamic processes and surface energetics (Petosa et al., 2010).

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## Results and Discussion

The BTCs in Fig. 1 show that the standard NPs are less deposited in the porous media compared to the model NPs. The mass balances (MBs), defined as the ratios of eluted to injected masses, are of 95% for *PSL COOH 200*, 40% for *PS COOH 530-P* and 25% for *NP 350-P* (Fig. 1). Average hydrodynamic diameters ( $d_{zH}$ ) of spherical NPs do not change significantly after flowing through the porous media: +6% for *PSL COOH 200* and -2% for *PS COOH 530-P*, whereas the  $d_{zH}$  of *NP 350-P* decreases by 20%.

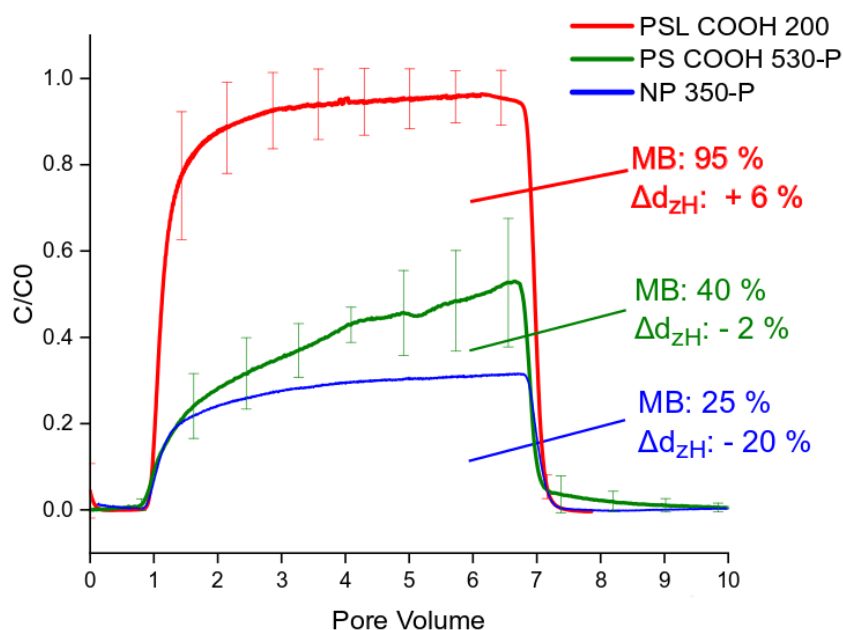


Figure 1: Breakthrough curves, mass balances and changes in hydrodynamic diameter ( $\Delta d_{zH}$ ) of NPs injected for 6 PVs at  $C_0 = 5 \cdot 10^{-3} \text{ g L}^{-1}$ , in  $5 \text{ mmol L}^{-1} \text{ NaCl}$ , pH 6.5 ( $n=1$  or 2).

The PS spheres' deposition rate is positively correlated to NP  $d_{zH}$  and negatively correlated to NP particle concentration, in agreement with the scientific literature. However, the *NP 350-P* have an intermediate  $d_{zH}$  and particular concentration, but are more deposited in the porous media than the spheres. So, asymmetrical shapes have a larger positive impact on the deposition rate than size and particle concentration. This may be due to the fact that a greater number of atoms are exposed to the collector (sand), increasing secondary energetic minimum adsorption. Asymmetrical shapes may have more affinity for the rough collector surfaces, compared to spheres.

## Conclusion

Our results show that *NP-P* are significantly more deposited in the porous media compared to the well-established standards in "nanoplastics" environmental investigation. Furthermore, *NP 350-P* undergo changes in size, unlike the PSL spheres. This suggests to reconsider the existing data on the environmental behavior of NPs in porous media since engineered plastic nanomaterials have limited to no environmental relevance. Also, NPs were reversibly deposited in the secondary energetic minimum, so they are likely to become remobilised. Changes in size and remobilization are processes that will influence NP stability as they travel from source to sink.

## Références

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