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Impact of organic nano-vesicles in soil: The case of sodium dodecyl sulphate/didodecyl dimethylammonium bromide

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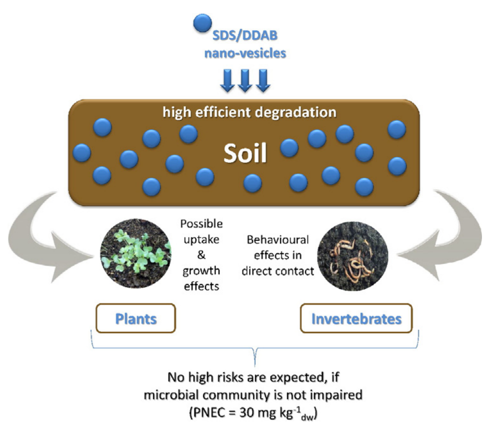
HIGHLIGHTS

- Invertebrates revealed to be sensitive to nano-SDS/DDAB, when in immediate contact
- Plants were not particularly sensitive to SDS/DDAB, except *B. oleracea*.
- The low toxicity is likely due to the high degradation of nano-vesicles in the soil.

GRAPHICAL ABSTRACT



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ABSTRACT

Aiming at contributing new insights into the effects of nanomaterials (NMs) in the terrestrial ecosystem, this study evaluated the impacts of organic nano-vesicles of sodium dodecyl sulphate/didodecyl dimethylammonium bromide (SDS/DDAB) on the emergence and growth of plant seeds, and on the avoidance and reproduction of soil invertebrates. For this purpose several ecotoxicological assays were performed with different test species (terrestrial plants: *Zea mays*, *Avena sativa*, *Brassica oleracea* and *Lycopersicon esculentum*; soil invertebrates: *Eisenia andrei* and *Folsomia candida*). A wide range of SDS/DDAB concentrations were tested, following standard protocols, and using the standard OECD soil as a test substrate (5% of organic matter). The aqueous suspensions of SDS/DDAB, used to spike the soils, were characterised by light scattering techniques for hydrodynamic size of the vesicles, aggregation index, polydispersity index, zeta potential and surface charge. The SDS/DDAB concentrations in the test soil were analysed by HPLC-UV at the end of the assays. Invertebrate species were revealed to be sensitive to nano-SDS/DDAB upon immediate exposure to freshly spiked soils. However, the degradation of SDS/DDAB nano-vesicles in the soil with time prevented the occurrence of significant reproduction effects on soil

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Reproduction
Avoidance
PNEC value

invertebrates. Plants were not particularly sensitive to SDS/DDAB, except *B. oleracea* (at concentrations above 375 mg $kg^{-1}{}_{dw}$). The results gathered in this study allowed a preliminary determination of a risk limit to nano-SDS/DDAB. The low toxicity of SDS/DDAB nano-vesicles could be explained by its high and fast degradation in the soil. The soil microbial community could have an important role in the fate of this NM, thus it is of remarkable importance to improve this risk limit by taking into account specific data addressing this community.

1. Introduction

Nanotechnology is an emerging and rapidly growing field of technology where some of the most prominent developments and innovations are occurring. Such advances will have tremendous impacts on the manufacturing of new materials with applications on the electronics, medicine, cosmetics and textile industries, food safety and environmental remediation within other areas (Hood, 2004; Doyle, 2006). The growing and widespread use of nanomaterials (NMs) foresees its release into all the environmental compartments with adverse consequences in human health and ecosystems. So, different studies have been conducted in this area to characterise the toxicity/ecotoxicity of NMs, as well as their fate in the environment (Sun et al., 2013; Kunhikrishnan et al., 2015; Vandhana et al., 2015). However, the knowledge in this area is still limited, because there are numerous NMs being produced each year (Science Policy Section, 2004; Roco, 2011), with different chemical compositions, sizes, surface properties, and chemical functionalizations, among others. Such different properties are expected to differently influence their fate and mechanisms of toxicity (Boverhof and David, 2010), making it even more difficult to preview the toxicity/ecotoxicity of a particular NM based on the available data for their bulk material or for similar NMs. To fill these knowledge gaps, and in order to gain meaningful insights into the risk assessment of NMs, it is essential to generate more data, especially for soils, in order to protect this environmental compartment already deeply impacted by several other contaminants. This can be done through the definition of risk limits, based on ecotoxicological data, before meaningful environmental concentrations are attained, resulting from a non-controlled use of NMs. Soils are essential to the sustainability of ecosystems, and to human survival and needs (O'Halloran, 2006). However, soil degradation is deeply constraining its regular functions and services (Swartjes et al., 2008).

Catanionic vesicles are supra-molecular structures that can be formed spontaneously by mixing suitable amounts of commercial cationic (e.g., DDAB — didodecyl dimethylammonium bromide) and anionic (e.g., SDS — sodium dodecyl sulphate) surfactants (Zhao et al., 2013). In recent decades, synthetic catanionic surfactant vesicles have received great attention due to their almost spontaneous formation, stability, apparently low cytotoxicity and inexpensive raw materials (Marques et al., 1998; Jiang et al., 2012; Zhao et al., 2013). Thus, several potential applications in biomedicine (drug and biomolecule delivery), biophysics, pharmacology (vaccine production), and cosmetics (carrier substances for skin penetration) (Aiello et al., 2010; Jiang et al., 2012; Zhao et al., 2013; Barbetta et al., 2014) are being forecasted. Such applications rely on the ability of the vesicles to entrap chemicals in their lumen, releasing them in a controlled manner. A further interesting aspect of these vesicles is the possible control of their size and charge through adjustments in the mixing ratio of the two surfactants (Jiang et al., 2012). Nevertheless, some studies also arouse concerns about these vesicles. DDAB-rich catanionic vesicles proved to be cytotoxic to red blood cells (Zhao et al., 2013); SDS-CTAB (sodium dodecyl sulphate/hexadecyltrimethylammonium bromide) were cytotoxic to 3T6 (stabilized murine fibroblasts) and HeLa cells by triggering lipid peroxidation, DNA damage and activation of the apoptotic pathway (Aiello et al., 2010). Russo et al. (2013) also showed the toxicity of SDS/DDAB to HEK-293 cells, and concluded that these catanionic vesicles were more toxic than the SDS/CTAB vesicles, and that the toxicity was mainly caused by the DDAB surfactant.

The ecotoxic effects of SDS/DDAB nano-vesicles were also recorded by Lopes et al. (2012) and by Pereira et al. (2011) in the marine bacterium *Vibrio fischeri*, as well as by Galindo et al. (2013) to basidiomycete fungi. In this context, and considering the possible widespread use of these vesicles, it is important to pursue the evaluation of their cytotoxicity as well as their toxicity to the biota of receptor environmental compartments, where they are expected to occur. In fact, the same trend was recorded for other widely used surfactants that were found in surface waters, sediments and sludge-amended soils (e.g., Ying, 2006). Thus, considering that US (Clean Water Act, 40 CFR Part 503) and European policies (Directive 86/278/EEC) suggest the increasing use of sewage sludge for agricultural soil fertilization, it is of remarkable importance to evaluate the risks of these organic nano-vesicles to soil-dwelling organisms and plants.

Accordingly, this work aimed at assessing the effects of the organic nano-vesicles of sodium dodecyl sulphate/didodecyl dimethylammonium bromide (nano-SDS/DDAB) on soil invertebrates and terrestrial plants by performing a set of standard ecotoxicological tests. Additionally, the gathered data was used to derive a deterministic risk limit for this organic NM.

2. Material and methods

2.1. SDS/DDAB nano-vesicle preparation and characterisation of the suspensions

SDS/DDAB nano-vesicles were prepared as follows: a 55 mM surfactant stock solution (sodium dodecylsulfate + didodecyldimethyl-didodecyldimethylammonium bromide) with a mole fraction of sodium dodecylsulfate corresponding to 0.71 ((X_{SDS}) C_{SDS} / (C_{SDS} + C_{DDAB})) (C refers to concentration in mol L^{-1}, while X means

Table 1
DLS data for the characterization of SDS/DDBA nano-vesicle suspensions with different concentrations, at pH 6 and 20 °C.

Concentration of the SDS/DDBA suspension (mg mL^{-1})	Angle	Average size	Polydispersion Index (PDI)	Mode	Aggregation index (AI)	Zeta potential
20	12.8	313.93	0.31	496.03	4.48	−101
	173	57.27	0.26	74.75		
2.5	12.8	345.60	0.19	448.90	4.49	−82.5
	173	62.92	0.25	65.54		
0.63	12.8	290.0	0.30	457.40	3.39	–
	173	66.12	0.23	68.70		
0.08	12.8	180.50	0.26	277.10	1.15	–
	173	83.81	0.26	88.82		