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Organic waste-borne ZnS nanoparticles: the forgotten ones

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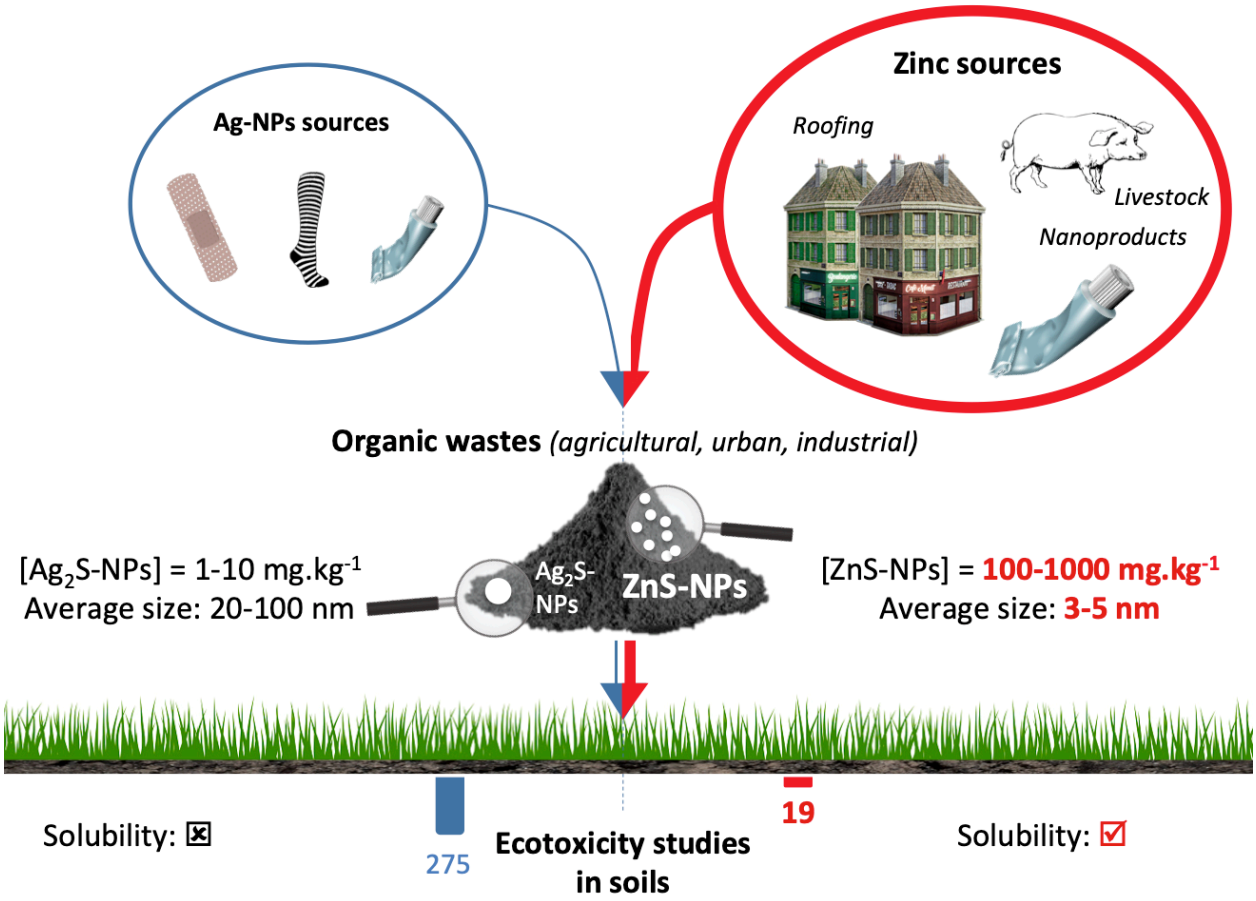
Highlights:

- Considerably more ZnS-NPs are released into the environment than most commercial NPs
- The fate of incidental ZnS-NPs formed in organic waste has been completely overlooked
- ZnS-NPs that form in organic waste are small and exhibit unique structural properties
- The reactivity and ecotoxicity of ZnS-NPs may be enhanced due to their small size

Keywords:

Incidental ZnS nanoparticles; organic wastes, environmental release, ecotoxicity



The market boom in nanotechnology has led to unprecedented and well justified scientific interest in the risks posed by the release of manufactured nanoparticles (NPs) into the environment. This interest is reflected in the funding of a large number of modeling and experimental studies. The latter are mainly physico-chemical and ecotoxicity investigations that were initially performed in simplified systems, but are becoming increasingly complex and realistic.

Silver nanoparticles (Ag-NPs) are strong biocides, and in the last 15 years, have been among the most widely studied and publicized NPs. These studies have shown that the main pathway by which Ag-NPs enter the environment is via sewage sludge spread as fertilizer on agricultural soils. Concentrations of Ag-NPs in sewage sludge typically range between 1 and 10 mg/kg. Bare Ag-NPs can have toxic effects on a variety of organisms, particularly when soluble Ag is released. However, it is acknowledged that Ag-NPs in the environment are mostly transformed into poorly soluble and less toxic Ag_2S (Courtois et al. 2019; Levard et al. 2013). Considering the low concentrations of Ag-NPs released in all environmental sinks and the rapid transformation of Ag-NPs into chemically stable Ag_2S, the actual environmental risk seems to be much lower than suspected 15 years ago.

Meanwhile, another class of nanomaterials formed unintentionally in organic wastes (Kim et al., 2014; Le Bars et al., 2018) has been vastly overlooked. Zinc sulfide nanoparticles (ZnS-NPs) are released in quantities that are several orders of magnitudes higher than those of Ag-NPs and other manufactured nanoparticles.

Zinc (Zn) is the fourth most abundant metal in use today, with 12 million tons produced in 2020 alone (International Lead and Zinc Study Group: https://ilzsg.org/static/statistics.aspx). Sources of Zn in sewage sludge include (i) runoff from Zn roofs, which can account for up to 50% of the Zn runoff load in urban areas (Thévenot et al., 2007 ; Gromaire et al., 2002), and (ii) the use of Zn as a pigment, catalyst, UV filter, luminescent, semiconductor (and many others) in electronics, paints, and care products (https://ilzsg.org/static/enduses.aspx). Furthermore, Zn is a ubiquitous supplement added to livestock feed to prevent disease and promote growth (Romeo et al. 2014; maximum authorized levels of trace elements in animal feeds are regulated in the European Union according to the Commission Regulation (EC) 1334/2003). Most of the added Zn is not taken up by the animals and livestock wastes (manure, slurries) are consequently rich in Zn (Romeo et al., 2014). Cropped soils are the most common destination of (agricultural) livestock waste and (urban) sewage sludge. Our calculations suggest that the Zn released into the environment every year by spreading on the soil corresponds to no less than 4.5% of annual Zn production. This overwhelming figure means about 553 000 t may enter the water-soil-plant compartments every year.

Zn in livestock waste and sewage sludge is mostly found in the form of ZnS-NPs. For instance, 54% of the total Zn present in a wide range of organic wastes sampled from full-scale treatment plants were shown to consist of ZnS-NPs (Le Bars et al., 2018). Extrapolation suggests that about 440 000 t/year of ZnS-NPs are released into the environment every year, i.e. 3 orders of magnitude more than the amount of Ag-NPs produced every year (400 t). If on the one hand, bulk ZnS has a very low solubility product constant (2×10^{-25}), the small diameter of ZnS-NPs in organic wastes (3–5 nm) gives them unique structural properties such as lattice strain, surface defects that may affect their solubility, surface reactivity and toxicity in the environment (Gilbert et al., 2004). Paradoxically, only a few studies have addressed the fate and toxicity of ZnS-NPs in the environment (Le Bars et al., 2022). In addition, most of these studies considered particle sizes > 10 nm, which are not representative of the ZnS-NPs that form in organic wastes (Voegelin et al., 2011).

The pioneering work of Banfield's group on biofilms helped understand the formation and properties of ZnS-NPs in organic wastes (e.g. Labrenz et al., 2000). A few recent studies point out that ZnS-NPs undergo (bio)chemical transformations after composting or stockpiling of organic waste (Lombi et al. 2012, Le Bars et al. 2018). Only one study assessed the fate of organic waste-borne ZnS-NPs in soil, reporting complete transformation of ZnS in a clayey soil within 6 months, followed by rapid immobilization of released Zn due to sorption by the soil matrix (Formentini et al., 2017). Similarly, studies of the fate of manufactured CdSe/ZnS core-shell quantum dots (3-14 nm, i.e., almost the same size as organic waste-borne ZnS-NPs) also suggest partial or total dissolution of the nano-ZnS shell in soil solution (Faucheur et al. 2018) or at the mineral/biofilm interface within hours (Desmau et al., 2020). Although synthetic ZnS-NP (3-5 nm) were shown to dissolve much more slowly in a sandy soil than in a clayey soil, the released Zn was more freely available in the sandy soil, and consequently potentially more toxic for soil organisms (Le Bars et al. 2022).

Despite the potentially high reactivity of ZnS-NPs, to the best of our knowledge, their ecotoxicity to soil ecosystems for example has only been investigated in 19 studies, as opposed to ZnO-NPs and Ag-NPs, each of which has been the subject of more than more than 250 studies. No study on ZnS-NPs ecotoxicity has been performed in a realistic agricultural soil environment with organic waste born ZnS-NPs. Among the 19 studies, in the nine most relevant ones (of which only one included organic waste), ZnS-NPs were synthetized (or obtained by sulfidation of ZnO-NPs), added to the soil (sometimes artificial

soil) system in pot experiments or in synthetic soil porewater, and the toxicity for model organisms (plants or soil organisms) was tested over a maximum period of a few weeks (Adele et al. 2018, Oleszczuk et al. 2019, Song et al. 2019, Starnes et al. 2019, Bao et al. 2020, Biruntha et al. 2020, Adele et al. 2021, Chen et al. 2021, Imperiale et al. 2022). Generally, these studies showed that ZnS-NPs could be toxic for plants, earthworms, nematodes, arthropods, fungi, and bacteria. The toxic concentration varied among the studies as it depends on the target organism and the environment. For example, the mortality and reproduction of the soil springtail *Folsomia candida* was affected by exposure as low as 2.5 mg.kg-1 in soil (Oleszczuk et al. 2019) whereas no toxic effect was found against the earthworm *Eisenia fetida* at 400 $mg.kg^{-1}$ in an artificial soil (Bao et al. 2020). Moreover, all the studies except three were performed using ZnS-NPs > 20 nm in size, that is, bigger than the ZnS-NPs found in organic wastes, even though the ecotoxicity of NPs is known to be highly dependent on the size of the nanoparticle (Lowry et al. 2012, Spurgeon et al. 2020). What is more, it is not clear whether ZnS-NPs are more or less toxic than ZnO-NPs and Zn^{2+}, and whether longer exposure (i.e. more than few weeks) to ZnS-NPs alters toxicity. Extrapolating these results to more realistic conditions is risky because the small number of studies cannot account for the large number of variables that affect ecotoxicity. Indeed, the ecotoxicity of NPs depends on interactions between the nanoparticle and its environment (e.g. solubility, aggregation). In turn, this interaction depends on the quantity and quality of organic matter, pH, ionic strength, chemical composition of soil solution, and the presence of colloids, among others (Lowry et al. 2012, Libralato et al. 2017, Spurgeon et al. 2020). A comprehensive range of experiments would be needed to assess the effect of exposure to organic waste-borne ZnS-NPs and associated hazards on a wider range of targeted organisms and of soil properties that may determine NP ecotoxicity.

We are convinced that the fate and ecotoxicity of ZnS-NPs formed in organic wastes deserve more attention in both modeling (currently not assessed, Avadi et al. 2022) and experimental studies, particularly in water-soil-plant systems, like other anthropogenic NPs such as Ag, ZnO, TiO_2, CeO_2, or carbon nanotubes. This is of utmost importance given the ever-increasing production of waste that calls on scientists, politicians, and civil society to transform waste into resources, while closing material loops in circular economies as a way to achieve sustainable development.

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Declaration of competing interest

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.

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