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Engineered nanomaterials in terrestrial systems: Interactions with co-existing contaminants and trophic transfer

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Abstract

Engineered nanomaterials (ENMs) are being introduced to soils and can interact with co-existing contaminants. The impacts of ENMs/co-contaminant exposure on plants are highly variable. Interactions of carbon- or metal-based ENMs with pollutants often result in a decreased co-contaminant toxicity, but are species- and exposure-scenario dependent. Moreover, current research suggests that it is possible for ENMs to be transferred through the food chain. This work presents an overview of the current efforts that have been made to understand the role of ENMs in the fate of other chemicals in terrestrial environments and the impacts on higher trophic levels.

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Engineered nanomaterials, Co-contaminants, Trophic transfer, Terrestrial food chain.

Introduction

Engineered nanomaterials (ENMs) come into contact with other chemicals present in the environment, including organic, inorganic and metal-based compounds. For instance, ENMs may interact with other nanomaterials (NMs), natural organic matter (NOM) [1,2] fertilizers, conventional pesticides, pharmaceutical/personal care products (PPCP) and persistent organic contaminants [3]. These abiotic interactions can lead to fate and exposure scenarios for biota that differ from the ENM or pollutant alone. A range of classical toxicant interactions such as additive, antagonist, or synergistic effects may enhance or diminish activity, subsequently increasing or decreasing bioavailability, accumulation and toxicity. Although the impact of these nanomaterial/co-contaminant effects on aquatic organisms has been studied, limited information exists for terrestrial plants [4]. Another topic in need of investigation is the trophic transfer and accumulation of ENMs within human and ecological food chains [5]. This review presents the efforts that have recently been made to understand the interaction of ENMs with other chemicals and the impacts on consumers of higher trophic levels.

ENMs and co-existing contaminants

Carbonaceous ENMs and other pollutants

The influence of carbon-based ENMs on other contaminants has been investigated in plants [6], including edible crops [7], but studies are limited. Previously, we described that the effect of C_{60} on the uptake of degradation products from dichlorodiphenyltrichloroethane (DDT) is species-dependent [8,9]. Liang et al. [10] demonstrates that the interactions between C_{60} and other contaminants (Cd, Cu and Pb metals in their study) varies not only by species, but within cultivars. In rice, C_{60} at 600 mg kg^{-1} either increased or decreased the amount of Cd in all tissues of cultivar 9311 and roots of LY8, but had no significant impact on Cd content of YB nor Nip rice (*Oryza sativa*). Also, C_{60} decreased Cu within rice 9311, but had no effect on Pb in the same cultivar. Overall, the interactions between C_{60} and other pollutants yield different effects that vary by co-exposure conditions.

Besides fullerenes, carbon nanotubes (CNTs) have also been investigated as components in mixtures of concern. Hamdi et al. [11] grew lettuce (*Lactuca sativa L.*) in vermiculite with non-functionalized or amino-functionalized multi-walled carbon nanotubes (MWCNTs) at 1000 mg L^{-1} and then irrigated with chlordane and dichlorodiphenyltrichloroethane (DDE) at 100 ng L^{-1}. A lesser co-contaminant interaction was observed for amino-functionalized MWCNTs, which reduced pesticide uptake by 57% and 23% in roots and shoots, respectively; the non-functionalized MWCNTs decreased tissue levels by 88% and 78%, respectively.

MWCNT reduced the toxicity of a range of organic and inorganic contaminants in sediments that had previously inhibited garden cress (*Lepidium sativum*) seed germination and root growth. Importantly, this effect was both dose- and size-dependent. Adding 1% MWCNTs (20–40 nm) to the sediment reduced germination toxicity by 60%, but at 5%, the alleviation was only 40%. Moreover, MWCNTs of <10 nm had a significant impact (24%) in reducing root growth inhibition, whereas MWCNTs of

20–40 nm had no effect [12]. Wang et al. [13] showed that the bioaccumulation of phenanthrene (Phen) and Phen derivatives in corn decreased with the carbon nanotube presence (CNTs). Interestingly, the authors showed that carbon-based nanomaterial uptake was occurring through the secondary roots, but that the Casparian strip was preventing translocation to the shoots. This is important because while the analysis of pollutants is routinely done, it is still challenging to observe and measure C-based NMs within tissues, which is fundamental to understand the mechanisms of co-contaminant interactions.

Zhao et al. [14] were able to quantify and track carbonaceous nanomaterials inside several plant species (corn, soybean, rice, and *Arabidopsis thaliana*) with ^{14}C-radiolabeled MWCNTs. From a 2.25 mg L^{-1} hydroponic exposure, ^{14}C-MWCNTs amounts ranged from 0.53 in maize shoots to 76.6 mg kg^{-1} inside soybean roots. Importantly, the amount of *in planta* MWCNTs was altered when co-exposed with small polar aromatic organic molecules (nitrobenzene, chlorophenol and derivatives). In *A. thaliana*, 2,4-dichlorophenol reduced the translocation of MWCNTs to stems and leaves, while 1,4-dinitrobenzene had the highest effect inhibiting the root uptake of MWCNTs.

The interaction of ENMs with emerging contaminants has gained attention. Deng et al. [15] found that the amount of carbamazepine in collard greens (*Brassica oleracea*) was decreased by MWCNTs co-exposure under hydroponic and soil conditions (100 μg L^{-1} of the drug and MWCNTs at 50 mg L^{-1} or 500 mg kg^{-1}). The authors reported that carboxylated-carbon nanotubes reduced accumulation of the pharmaceutical in the roots to a greater extent than the non-functionalized tubes (53% vs 29% reduction), but promoted contaminant translocation within the plant.

It is clear that carbon-based nanomaterials often reduce the bioavailability of co-existing organic contaminants in soil (often through direct sorption to the high surface area sorbent), although species- and contaminant-specific interactions are evident.

Metal-based ENMs and other pollutants

Similar to carbon-based nanomaterials, the co-exposure of other ENMs and pollutants often results in decreased co-contaminant toxicity [16–18]. For example, TiO_2 reduces the toxicity caused by the antibiotic tetracycline (TC) in *A. thaliana* [19] and in rice [20]. Also in rice, TiO_2 and CeO_2 nanoparticles (NPs) reduced the toxicity of 2 mg L^{-1} Cu^{2+}. Co-exposure to 100 mg L^{-1} humic acid —resembling natural organic matter (NOM)— and TiO_2 NPs (1000 mg L^{-1}) completely alleviated Cu^{2+} induced toxicity as measured by root length [21]. Tannic acid (TA) has also been investigated by simulating NOM co-exposure with ENMs. Tannic acid at 60 mg L^{-1} reduced the nutrient deficient toxicity caused by Nd_2O_3 NPs at 100 mg L^{-1} in pumpkin (*Cucurbita maxima*) and decreased the accumulation of Nd in the roots [22]. In wheat (*Triticum aestivum*), root growth inhibition by the heavy metals Cd and Cr was mitigated in the presence of magnetite NPs [23]. Similarly ZnO NPs alleviated oxidative stress in the leguminous tree *Leucaena leucocephala* caused by Cd^{+} and Pb^{+} [24]. In Chinese cabbage (*Brassica pekinensis*), Ni/Fe NPs diminished the mobility and phytotoxicity of the flame retardant decabromodiphenyl ether (BDE-209) [25].

It is important to note that ENMs may transform as they age in the environment, which can alter their behavior and interactions with co-contaminants [26]. Antagonistic effects are often observed, where the combined effect of the contaminants is less toxic than what would result from each individually. However, the presence of a pollutant can also promote the uptake of metals sourced from the ENM. Higher levels of Ag from Ag NPs were detected in *A. thaliana* when the plants were co-exposed to the pesticide imazethapyr (IM); specifically, a 1.4-fold increase was noted in the roots and 78% more silver was present in shoots. Interestingly, the (R)-enantiomer of the pesticide resulted in greater Ag^{+} release and reactive oxygen species (ROS) production when compared to the (S)-enantiomer or to a racemic mixture [27]. Although TiO_2 NP decreased Cd toxicity in rice, the heavy metal enhanced the uptake of Ti [28]. Similarly, in soybean CeO_2 NPs reduced the translocation of Cd by 70%, but Cd enhanced Ce availability. The rare earth element concentration in shoots was increased by 60%, with a 40% reduction observed in the roots [29].

Comparable to carbon nanomaterials, the impact of metal ENMs/co-contaminant exposure is complex. Both the primary and secondary analyte affect each other differently across species, changing their availability and toxicity.

ENMs co-exposed to other ENMs

Co-contaminant interactions between multiple nanoparticles have only been studied to a limited extent. Pagano et al. [30] exposed zucchini to binary combinations of NP CeO_2, La_2O_3, CuO, ZnO and cadmium sulfide quantum dots (CdS QDs) and reported a broader range of co-contaminant interactions. For example, combining CeO_2 and La_2O_3 NPs resulted in >50% decrease in La within plant tissues, while Cu uptake more than doubled when co-exposed with La_2O_3. Importantly, a range of molecular endpoints in this study demonstrated consistent differences in plant response upon co-exposure to binary combinations when compared to single analyte exposure (Figure 1). Understanding the mechanisms responsible for observed