Environmental Science & Technology

Viewpoint

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100 Nanometers: A Potentially Inappropriate Threshold for Environmental and Ecological Effects of Nanoparticles

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Nanoparticles (NPs) are typically defined as materials with dimension(s) between 1 and 100 nm. The static value of 100 nm as the benchmark for "nano" or "not nano" was proposed and implemented before nanoecotoxicological studies were conducted; consequently, this benchmark does not reflect the complexity of ecological interactions with NPs. Many studies have demonstrated size-dependent physicochemical properties and environmental impacts for NPs.[1−4] Although not explicit in the literature, data suggest that the potential of threshold sizes exist regardless of proximity to 100 nm, and NP sizes larger than threshold sizes may have the similar potential ecological risks as bulk particles.[1−4]

Threshold sizes of NP physicochemical properties likely exist and can be determined by measures of surface area (S), optics, thermodynamics, magnetism properties, or catalytic activity. For example, the curve of S versus diameter of multiwall carbon nanotubes (MWCNTs) breaks into size-sensitive versus insensitive ranges. In the highly size-sensitive range, S decreases dramatically as the diameter increases from 9 to 28 nm. In the insensitive range, S remains relatively constant across diameter from 28 to 70 nm,[1] suggesting about 28 nm as a threshold size (Figure 1). Similarly, the threshold sizes of S and the solubility product (K_{sp}) were measured at 15 nm for ZnO-NPs.[2] The different threshold sizes of S for MWCNTs and ZnO-NPs demonstrate that thresholds can vary with composition and shape. The threshold sizes of bandgap energy for quantum dots (CdS-NPs, CdSe-NPs, and PbSe-NPs), melting temperature for In-NPs and Sn-NPs, and transition temperature for various NPs ($MnFe_2O_4$-NPs, $MgFe_2O_4$Mn-NPs, $BiFeO_3$-NPs, and $PbTiO_3$-NPs), were measured at 6−8 nm, 15 nm, and 20−30 nm, respectively.[3] The existence of different threshold sizes is likely attributable to changes in excess surface energy and crystallography of NPs as size decreases.[3]

The existence of threshold sizes of NP physicochemical properties suggests the possible existence of critical sizes for environmental impacts and the likelihood that these sizes will differ from 100 nm. Limited information about size-dependent NP environmental impacts has been reported, largely due to a lack of studies testing carefully controlled NPs across a broad size range or of NP aggregation, dissolution or coating acquisition in environmental matrices impacting size-specific effects. However, information such as particle dissolution, contaminant adsorption, and suspension stability can be used to establish the threshold size ranges for NPs, respectively. For instance, the curve of ZnO-NP dissolution with size separates into two stages, with a threshold at 15 nm.[2] Antibiotic and tannic acid adsorption decreased with increasing MWCNT diameter, with a threshold at 28 nm (Figure 1).[1,4] Dissolution of ZnO-NP and adsorption onto MWCNTs were controlled by and were consistent with the K_{sp} and S of the materials, respectively. This suggests that if NP environmental impacts are controlled by physicochemical properties, such relationships may exhibit similar threshold sizes. The threshold size of MWCNTs dispersibility by 500 mg/L tannic acid was 43 nm, different from that in simple media, demonstrating that threshold sizes are subject to environmental influences.[1] For more complex biological effects such as accumulation and toxicity, NPs may exhibit size-specific mechanisms for transformation, reactive oxygen species production, dissolution, translocation, and uptake behavior. However, an in vitro cytotoxicity study of Au-NPs showed no threshold size from 3 to 45 nm.[5] Therefore, further carefully designed research is merited.

Clearly, the existence of threshold sizes of NPs for environmental impacts is important. If threshold sizes do not exist, the mechanisms that limit NP size-specific effects should still be investigated. Interactions in environmental media such as hetero- or homoagglomeration, adsorption of natural organic matter and contaminants, and NP dissolution may minimize

Received: January 22, 2014
Published: February 27, 2014

   dx.doi.org/10.1021/es500365k | Environ. Sci. Technol. 2014, 48, 3098−3099

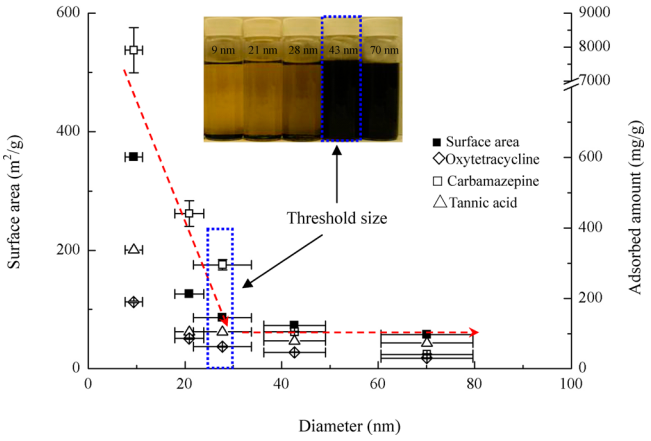

Figure 1. Surface area, adsorption capacity of oxytetracycline, carbamazepine, and tannic acid, and dispersion capacity versus out diameter of MWCNTs. Data and picture are adapted with permission from refs 1 and 4 copyright (2008, 2009) American Chemical Society. Data points represent mean and error bars the standard deviation values ($n \geq 2$).

these impacts even if threshold sizes might exist under carefully controlled laboratory conditions. If threshold sizes of nano-environmental impacts do exist, questions that need to be addressed are the following: (1) What are the NP metrology methods for accurately determining the threshold size? (2) To what extent does the threshold size change as a function of environmental factors, aging and agglomeration? (3) What is the relationship between threshold size and material composition? Although none of these questions have been studied, some guidance can be suggested to focus future work. It is relatively simple to measure threshold sizes of NP physicochemical properties; however, it is more difficult and time-consuming to make threshold determinations for their environmental impacts. Quantitative structure−activity relationships (QSAR) have clear advantages in predicting NP properties and behavior[3] and might be useful for determining threshold sizes for environmental impacts. Additionally, NP surface modification changes threshold sizes of physicochemical properties and will likely do so for environmental impacts as well. Preliminary data from Dr. White's laboratory suggests that Ag-NP accumulation by plants and earthworms changes significantly as a function of both functionalization and size.

The possible existence of the NP threshold sizes could dramatically influence our perspective on nanoparticle use, as well as our understanding of fate and effects. If threshold sizes do not exist, NP size can be selected according to application, and resulting environmental health and safety investigations can proceed under current guidelines. However, if threshold sizes of NP environmental impacts exist, these NPs may have enhanced or decreased effects that would not be predicted by larger NPs even though the larger particles are smaller than 100 nm. The likelihood of significant environmental risk could be minimized by the proper selection of NP sizes and/or functionalization during development if NPs below a certain threshold have substantially increased ecotoxicological effects. Additional studies are needed to assess the potential for threshold sizes for environmental impacts and to assess if NPs larger than the threshold sizes have different impacts than bulk particles of the same composition. These results may challenge the current definition of <100 nm for NPs and necessitate modifications to standard methods for NP environmental impacts and associated risk models.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was in part supported by NSFC (21077089, 40903036, 41328003, and 41173084) and USDA AFRI grant 2011-67006-30181. We very much thank Dr. Elijah Petersen for his helpful input about the potential for threshold ecotoxicological effects with nanoparticles.

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